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SUJET:

Une Nouvelle Approche au Traitement Théorique des Vibrations d'une Molécule Triatomique et de leurs Couplages. Application à CO_2 et CO_2^+

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Motto:

Căci unde-ajunge nu-i hotar
Nici ochi spre a cunoaşte

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Part I

Literature Overview

Chapter 1

Introduction

The electronic spectra of free radicals are often severely complicated by strong interactions between the electronic and nuclear degrees of freedom. These effects are of considerable interest, and have been the subject of a number of theoretical studies, but unfortunately the complexity frequently leads to ambiguities of analysis. The use of lasers to excite single vibronic levels fluorescence has recently provided a means of circumventing many of the problems of assignment of such spectra, particularly when the laser frequency can be tuned over a number of excited levels.

The excited states of neutral and free radicals of triatomic molecules are of great interest in astrophysics, in the study of the interstellar gas, dust clouds, nebulae and even in the chromospheres of cold stars. Because of the high vacuum existing usually in the interstellar medium, such excited states and free radicals can can have a long life time, and the spectral analysis can give informations about the environment and dynamics of the molecules. At the same time, some species and excited states can be observed only in interstellar medium, due to the particular conditions existing there. Moreover, in the dynamics of the Earth atmosphere, as well as in the interaction with ionizing radiation and cosmic rays, the triatomic molecules play a key role.

Triatomic molecules are widely used in the laser industry. From the standpoint of potential applications, the carbon dioxide laser unquestionably ranks first. It is capable of continously generating as high power as 10 kW at a relatively high efficiency (up to 40 carbon dioxide, molecular nitrogen, and diverse additives, such as water molecules. The active transitions occur between vibrational states of the molecule, and a good knowledge of the interactions involving these states is required.

Taking into account all degrees of freedom on the molecule in the adiabatic approximation, the energy of the molecule is the sum of three independent terms.

The first term $E_e = U_m(\vec{r})$, gives the value of the effective potential energy, corresponding to the energy of the electron subsystem of the molecule in the mth quantum state, the *electronic energy.*

The second term, E_v is the energy of vibrations in the molecule, the *vibrational energy.* The vibrational energy ω_v, depends on the electron configuration of the molecule, and it is important to note that *the potential energy* for the vibrational mouvement is in fact the electronic energy.

Finally, the third term, E_r is due to the rotation of the molecule, the *rotational energy.*

The order of magnitude of the three energy terms can be compared by using Heisenberg's uncertainty relations [1]. Assuming typical values, the electronic energy, is of order of magnitude $E_e \simeq 2\text{eV}$. The vibrational energy for weakly excited vibrations ($v \sim 1$) is $E_v \simeq E_e\sqrt{\frac{m_e}{M}} \simeq 10^{-2}\text{eV}$, where m_e is the electronic mass, and M is the molecular mass. The rotational energy of the molecule for weakly excited states ($J \sim 1$) is $E_r \sim E_e\frac{m_e}{M} \sim 10^{-4}\text{eV}$. The estimates obtained by taking into account all the degrees of freedom indicate that $\Delta E_e \gg \Delta E_v \gg \Delta E_r$.

The *ab initio* techniques are able to determine the shape of the electronic energy as function of the internal coordinates, necessary for the study of molecular problems of structure,

stability, calculation of harmonic vibrational frequencies [2]. However, widespread quantitative applications have only become practically possible in recent times, primarily because of explosive developments in computer hardware and associated achievements in the design of efficient mathematical algorithms. A complete specification of the molecular geometry requires not only a description of internal bond lengths and angles, but also of conformation. The computation required to map a conformational profile completely, may be significant for large molecules. There is ample incentive to use a simpler approach. Errors in calculated vibrational frequencies arise both from inherent inaccuracies of differentiation techniques required in the evaluation of the matrix of force constants, and from uncertainties in the selection of the equilibrum geometry.

For a triatomic molecule, the three different vibrational oscillations are called *vibrational modes*. In the *symmetric stretch mode*, the external atoms oscillate along the axis of the molecule, by simultaneously departing and approaching the central atom in between. In the *asymmetrical stretching mode*, the external atoms also move along the axis of the molecule, but both in one direction relative to the central atom itself moving to the other side (the projection on the linear axis of the molecule). In the *bending mode*, all three atoms of the molecule undergo vibrational oscillations by moving perpendicularly to the molecular axis. The frequencies of the symmetric stretching, bending and asymmetric stretching are denoted by ν_1, ν_2, and ν_3, respectively.

The form of the vibration Hamiltonian is a direct consequence of the coordinates and coordinate axis of the system chosen to describe the configuration of the molecule at any instant. Three parameters are necessary to describe the shape of a triatomic molecule, i.e. the *instantaneous values of the two bond lengths* r_{12} and r_{23},and the *instantaneous value of the angle between the two bonds*, α.

From the point of view of the intramolecular force field, a particularly appropriate set of three parameters consists of the deviations Δr_{12}, Δr_{23} and $\Delta\alpha$ of these quantities from the same reference values. These parameters are called the *generalised (true valence) coordinates* [3, 4]. The coordinates are very useful for the potential energy force constants, but the corresponding kinetic energy has a more complex expression and can not be solved analytically.

However it is customary to use as coordinates three rectilinear displacements of the molecule from the equilibrium, called the *linearised valence coordinates* [3, 4]. In the limit of small amplitudes, these coordinates become the true valence coordinates. For the molecules that can be treated in the standard approach, the equilibrium configuration corresponds to a well defined minimum of the nuclear potential energy function (i.e. all vibrations have small amplitude). The nuclear potential energy function is harmonic in the Cartesian displacement coordinates near the vicinity of the minimum. This allows the standard perturbation treatment to proceed.

When the amplitude of the bending vibration become large, but the stretches of the bond lengths are small, the *curvilinear coordinates* can be used. This treatment leads to a Hamiltonian which can be applied equally well to both linear and bent triatomic molecules [5, 6, 7], as opposite of the two separate formalisms used in the standard approach for the linear or nonlinear molecules [3, 4, 8, 9].

The *normal coordinates* are defined as a linear combination of the mass weighted Cartesian displacements and are similar to the linearized valence coordinates. The kinetic energy is diagonal with a unit metric tensor and the potential energy is harmonic in the vicinity of the minimum.

The historical development of the ro-vibronic Hamiltonian of triatomic molecules can be considered to have occured in three main stages. Initially, the nuclear motion of the molecules was described using the rotor-harmonic oscillator approximation, making extensive use of the perturbation theory. This approach is described in detail by Wilson, Decius and Cross [10], and by Nielsen [11]. It is an essential part of this "standard" treatment that all of the vibrational motions are assumed to be of small amplitude. Two separate vibration formalisms are commonly used for the triatomic molecules, depending on whether the molecule under consideration is linear or nonlinear [3, 4, 8, 9]. The main difference arise when treating the bending vibrations of small

amplitude for the triatomic molecules.

Following the observation and analysis of the electronic spectrum of the NH_2 free radical by Dressler and Ramsay [12], it was realised, particularly by Dixon [13], that the bending vibrational motion was of large amplitude. Subsequently Hougen, Bunker and Johns [5] realised that it was also necessary to consider the variation with the bending angle of the associated reduced mass, the bending "g - value". This greatly improved the description of the vibration - rotation motion which could be described using a single large amplitude vibrational coordinate. The *rigid bender model* of HBJ contains a key idea, which is the definition of a large amplitude reference configuration. In the rigid bender model the coupling between large amplitude bending and small amplitude stretching is completely neglected. An improved description is obtained with the *semirigid bender* Hamiltonian, proposed by Bunker and Landsberg [14]. In this method the bond lengths are allowed to stretch as the molecule bends, mimicking the motion along the minimum of the potential energy surface for symmetric stretching and bending. This approach has been widely used in vibronic calculations by Jungen and Merer [15] and their collaborators, and by Duxbury and Dixon [16]. The effective rotation-bending Hamiltonian for *the nonrigid bender* approach is obtained by using the rigid bender Hamiltonian as the zeroth order solution and by treating the effects of the neglected terms in the HBJ Hamiltonian by perturbation theory using a contact transformation, [17, 6] . Because the perturbation theory is used to treat the effects of the small amplitude vibrations, the effects of resonances between states involving different amounts of excitation of these vibrations are not allowed for [18].

A major new line of approach was begun by Carter and Handy [19], and by Tennyson and Sutcliffe [20], who developed general methods of solving the full three dimensional vibration-rotation problem using an instantaneous axis system. To some extent these developments have become possible because of the increases power of the supercomputers necessary to solve these equations.

The small amplitude stretching vibrations are treated in the normal coordinate formalism as separate harmonic oscillators, with eventually anharmonic terms considered [5, 6, 18]. In some variational methods, the matrix of the stretching Hamiltonian is set up in a basis of Morse oscillator product functions (symmetrized for an AB_2 molecule, and unsymmetrical for a ABC molecule), and is diagonalized using Householder's method [7, 21].

In considering the ro-vibronic structure of open shell molecules, the primary effects of the bending of the nuclear framework are to lift the degeneracy of the electronic states with non-zero values of the electronic angular momentum, for example Π states with $\Lambda = 1$ and Δ states with $\Lambda = 2$. This is ussualy referred to as *Renner-Teller* effect (RT), and describes the coupling of the electronic orbital motion with the nuclear motion round the axis of a linear molecule, with the definition of the linear, extended to include molecules that become linear as a result of vibration. The effect is not just a spectroscopic curiosity because, included within this wider definition, are familiar molecules such as NO_2 and SO_2, where some of the complexity of their spectra is a direct result of the Renner-Teller coupling. The development of the theory of this type of system parallels that of the vibration-rotation problem described previously. Renner's classic paper [22] based on an idea of E. Teller's appears in 1934, with a detailed analysis of the coupling in a degenerate Π electronic state, was made within the framework of the harmonic oscillator rigid-rotor expansion. Almost 25 years passed before the first example was reported, in the spectrum of NH_2 molecule [12, 23]. This was a type that Renner has not considered: NH_2 is a nonlinear molecule and the interpretation of the spectrum required an extension of his concepts. This was done by Pople and Longuet Higgins [24, 25]. This model has been extended to include the spin-coupling and the vibrational anharmonicity and to take into account the rotation and the spin uncoupling [26, 27, 28, 29]. An example following Renner's ideas more closely, was latter found during the study of the ground state of the linear molecule NCO [30].

An Electron Spin Resonance (ESR) study on Renner effect in the $^2\Pi$ ground state of NCO by Carrington et all [31] attributed the observed anomaly in the orbital g-factor of some ro-spin-

vibronic levels partly to the presence of the vibronic interaction in the $^2\Pi$ electronic ground state with the excited electronic states, i.e., *Herzberg-Teller* (HT) interaction. The Herzberg-Teller interaction is due to a nontotally symmetric vibration which gives rise to forbidden components in an electronic transition [32]. A suitable vibration mixes a vibronic state of the Π ground state with vibronic states of excited Σ^+, Σ^- and Δ electronic states, if the former and latter vibronic states have the same symmetry and differ only one quantum in the bending vibration. The HT interaction is introduced by means of a parameter g_K, [33, 34, 35, 15], which is related to other observable quantities.

The *Fermi resonance* arises when two energy levels lie close together and the symmetry requirements are met. The Fermi resonance is due to a mutual interaction between energy levels attributable to anharmonic terms in the potential energy expression. Fermi originally proposed such an interaction to explain certain anomalies in the spectrum of CO_2 involving (100) and (020) vibrational energy levels [36]. The treatment of Fermi is valid in detail for linear triatomic molecules in nondegenerate electronic states (Σ states), between states in the form $(v_1 + 1\, v_2\, v_3)$ and $(v_1\, v_2 + 2\, v_3)$. Hougen [37] generalized the treatment for linear triatomic molecules in degenerate electronic states (Π, Δ, Φ states). In general, the Fermi resonances cause severe complications in electronically degenerate states subject of Renner-Teller effect - a good example is the $A^2\Pi_u - X^2\Pi_g$ system of BO_2 [38].

As was mentioned above, in many triatomic molecules only the bending motion is of large amplitude, but the coupling between the bending and stretching motion, whilst weak, can often lead to complicated vibrational resonances. The aim of this thesis is to develop an approach which, while accounting in detail for the large amplitude bending motion, and the anharmonic resonances, preserves the relative simplicity of the semirigid bender method.

The reduction in computer time associated with this analytical development of the new Hamiltonian would allow the resultant Hamiltonian to be used as core part of another more extensive calculations, such the motion of a Rydberg electron coupled to a polyatomic frame.

The method which has been developed for this purpose, the "Stretch-Bender" (SB), relies on modelling the stretching displacements relative to the semirigid bender framework. The nuclear displacements from the reference frame to the instantaneous axis frame should be of small amplitude, and hence the size of the basis of stretching functions should be minimised. The implementation has so far been restricted to symmetric AB_2 molecules, even if the model have been developed at the level of the rigid bender formalism for unsymmetric ABC molecules.

The development of the stretch-bender method follow the usual route, firstly considering the treatment of a non-degenerate electronic state and then considering the extension to include the electronic angular momentum coupling (RT effect) which occurs in a degenerate electronic state, along with the interaction between stretching and bending vibrations (FR).

Chapter 2

Theoretical Overview on the Bending and Stretching Models and their Interactions

2.1 Coordinates and Axis

The geometry of a triatomic molecule in the molecule fixed coordinate system and the Cartesian coordinates corresponding to it, is given in (Fig.2.1).

2.1.1 Generalized (Free Valence) Coordinates

We define the generalized valence-force displacements coordinates (see Fig.2.1), following [3, 4, 5, 6, 39]:

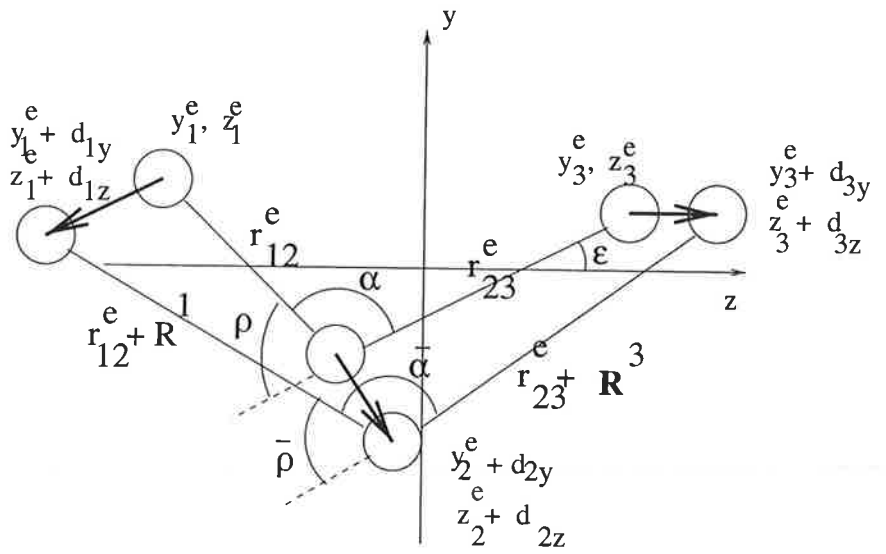

Figure 2.1: The definitions of the angles $\bar{\rho}, \rho$, and ε used for the triatomic molecule and the molecule -fixed coordinate system, which is chosen so that the x, y, and z axes form a right-handed axis system. The open circles are the positions of the nuclei in the reference configuration ; the shaded circles are the actual positions of the nuclei

- The bond-stretching coordinates $\mathbf{R}^1$ and $\mathbf{R}^3$ represent the instantaneous changes in the internuclear distances:

$$\begin{aligned} \mathbf{R}^1 &= r_{12} - r_{12}^e \\ \mathbf{R}^3 &= r_{23} - r_{23}^e \end{aligned} \tag{2.1}$$

The instantaneous changes in the bond lengths may be expressed in terms of the Cartesian coordinates of the displaced nuclei for a bent molecule as:

$$\begin{aligned} \mathbf{R}^1 &= \left\{[-r_{12}^e\cos(\rho-\varepsilon)+(d_{1z}-d_{2z})]^2+[r_{12}^e\sin(\rho-\varepsilon)+(d_{1y}-d_{2y})]^2\right\}^{\frac{1}{2}} - r_{12}^e \\ \mathbf{R}^3 &= \left\{[-r_{23}^e\cos\varepsilon+(d_{3z}-d_{2z})]^2+[r_{23}^e\sin\varepsilon+(d_{3y}-d_{2y})]^2\right\}^{\frac{1}{2}} - r_{23}^e \end{aligned} \tag{2.2}$$

For a linear molecule the generalized coordinates and the Cartesian coordinates are related by the eq. (2.2), with the condition $\rho = \varepsilon = 0$.

- The angle-deformation coordinate $\mathbf{R}^2$ is defined as the actual change in the valence angle of the triatomic molecule:

$$\mathbf{R}^2 = \bar{\alpha} - \alpha_e = \rho_e - \bar{\rho} \tag{2.3}$$

The instantaneous angle may be expressed in terms of the Cartesian coordinates for a bent molecule:

$$\tan\left(\alpha + \mathbf{R}^2\right) = \frac{A}{B} \tag{2.4}$$

where:

$$\begin{aligned} A &= [r_{12}^e\sin(\rho-\varepsilon)+(d_{1y}-d_{2y})]\,[r_{23}^e\cos\varepsilon+(d_{3z}-d_{2z})] \\ &\quad +[r_{12}^e\cos(\rho-\varepsilon)+(d_{2z}-d_{1z})]\,[r_{23}^e\sin\varepsilon+(d_{3y}-d_{2y})] \\ B &= [r_{12}^e\sin(\rho-\varepsilon)+(d_{1y}-d_{2y})]\,[r_{23}^e\sin\varepsilon+(d_{3y}-d_{2y})] \\ &\quad -[r_{12}^e\cos(\rho-\varepsilon)+(d_{2z}-d_{1z})]\,[r_{23}^e\cos\varepsilon+(d_{3z}-d_{2z})] \end{aligned}$$

In the case of the linear molecule, the orientation in space of the $\mathbf{R}^2$ coordinate is defined by the projections $\mathbf{R}_x^2$, $\mathbf{R}_y^2$ of the $\mathbf{R}^2$ in the xz and yz planes of the Cartesian coordinate system. The $\mathbf{R}_y^2$ is defined by the eq. (2.4) with the condition $\rho = \varepsilon = 0$ and $\mathbf{R}_x^2$ by an equation similar with (2.4), in which we replace d_{iy} by d_{ix} $(i = \overline{1,3})$.

Obs. *1* The equations (2.2) and (2.4) are more general than the equations [3, eq.(3a)-(3c)].

Obs. *2* The relations (2.2) and (2.4) are quite general and involve no approximations.

Obs. *3* In Pliva's treatment [3], the angle ε is chosen as $\varepsilon = \frac{\rho}{2}$, for the bent molecule.

In equations (2.1) and (2.3) the quantities r_{12} , r_{23} and $\bar{\alpha}$ are the instantaneous values of the two bond lengths and the bond angle, respectively. At the minimum of the potential energy function, the molecular geometry corresponds to the values $r_{12} = r_{12}^e$, $r_{23} = r_{23}^e$ and $\bar{\alpha} = \alpha_e$. The angle $\bar{\rho}$ is defined by the relation: $\bar{\rho} = \pi - \bar{\alpha}$. By definition, $0 \leq \bar{\alpha} \leq \pi$. Consequently, the bounds of $\bar{\rho}$ are $0 \leq \bar{\rho} \leq \pi$ and $\mathbf{R}^2$ must be in the interval $\rho_e - \pi \leq \mathbf{R}^2 \leq \rho_e$.

2.1.2 Linearized Valence-Force Coordinates

The linearized coordinates can be defined for small displacements from equilibrium. Following [3, 4], for small displacements it is possible to expand eq. (2.2) and (2.4) in power series in the displacement coordinates. If only linear terms are retained, the relations between the instantaneous bond lengths and instantaneous angle, and the Cartesian displacement coordinates follows:

$$\begin{aligned} q_0^1 &= (d_{1y} - d_{2y})\sin(\rho - \varepsilon) - (d_{1z} - d_{2z})\cos(\rho - \varepsilon) \\ q_0^3 &= (d_{3y} - d_{2y})\sin\varepsilon + (d_{3z} - d_{2z})\cos\varepsilon \\ \gamma^0 &= -\frac{1}{r_{23}^e}(d_{2y} - d_{3y})\cos\varepsilon + \frac{1}{r_{12}^e}(d_{2y} - d_{1y})\cos(\rho - \varepsilon) \\ &- \frac{1}{r_{12}^e}(d_{2z} - d_{1z})\sin(\rho - \varepsilon) - \frac{1}{r_{23}^e}(d_{2z} - d_{3z})\sin\varepsilon \end{aligned} \tag{2.5}$$

For a linear molecule the eq. (2.5) can be applied by taking into account the condition $\rho = \varepsilon = 0$. The angular coordinate γ^0 is defined by the projections γ_x^0 and γ_y^0 of the γ^0 in the xz and yz planes of the Cartesian coordinate system in the case of a linear molecule. The γ_y^0 is defined by the last equation of (2.5) and γ_x^0 by an similar equation with (2.5) in which d_{1y} is replaced by d_{1x} and $i = \overline{1,3}$. q_0^1 and q_0^3 represent projections of the true general valence-force coordinates, $\mathbf{R}^1$ and $\mathbf{R}^3$, in the directions of the undisplaced bonds. From the relations (2.5) and the Eckart conditions [40, 5], the relations between the Cartesian displacement coordinates and the linearized valence-force coordinates are found for the linear molecules in [4, eq.(5)-(6)], and for the bent molecules in [3, eq.(5)]. On substituting these relations in (2.2) and (2.5) and by expanding in series, the relations between the general and linearized valence-force coordinates are obtained in [3, eq.(6)-(9)] for the bent molecules, and in [4, eq.(8a)-(9b)] for the linear ones.

2.1.3 Curvilinear Coordinates

The curvilinear coordinates [5, 6, 7] are able to describe triatomic molecules for which only the bond stretches are small amplitude vibrations and the bending motion can be a large amplitude vibration.

For a triatomic molecule with a large amplitude bend we cannot choose the vibrational coordinates as in the standard approach (i.e. as displacements from a rigid structure as in (§2.1.2)) since then all three vibrational coordinates would describe large amplitude motions and the diagonalization of the Hamiltonian would become unmanageable.

The curvilinear coordinates minimize the coupling between the large amplitude and small amplitude vibration. The stretching coordinates measure the instantaneous displacement from a variable reference configuration with fixed bond lengths r_{12}^e and r_{23}^e and bond angle α. They are defined in the eq. (2.1) and (2.2) accordingly with the Fig.2.1. The third vibrational coordinate is chosen as: $\rho = \pi - \alpha$.

It is almost, but not quite, equal to the instantaneous value ρ of the bond angle supplement. The ρ coordinate defines the reference configuration that "follows" the large amplitude motion and is not an internal coordinate in that it has no simple definition in terms of the bond lengths and bond angle.

The reference configuration is chosen so that in the molecule fixed axis system:

- the nuclear center of mass is at the origin
- all nuclei are in the yz plane
- the bond lengths are fixed at the values r_{12}^e and r_{23}^e (taken to be the values corresponding to the potential energy minimum in all three coordinates)

- the z-axis makes an angle ε with r_{23}^e (Fig.2.1).

The ε value is chosen by requiring that the angular momentum of the reference configuration vanish in the molecule-fixed axis system, i.e.,

$$\sum_i m_1 \vec{a}_i(\rho) \times \left(\frac{d\vec{a}_i}{d\rho}\right) = 0 \tag{2.6}$$

where $\vec{a}_i(\rho)$ represent the reference configuration from which the small-amplitude displacement vectors $\vec{d}_i$ are measured. The equations for $\vec{a}_i(\rho)$ are done in [5, eq.(2)] or [6, eq.(2.3)]. From the eq.(2.6) we find that:

$$\frac{d\varepsilon}{d\rho} = \frac{u_1 + u_{13}\cos\rho}{u_1 + u_3 + 2u_{13}\cos\rho} \tag{2.7}$$

with

$$\begin{aligned} u_1 &= m_1 (m_2 + m_3) (r_{12}^e)^2 \\ u_3 &= m_3 (m_2 + m_1) (r_{23}^e)^2 \\ u_{13} &= m_1 m_3 (r_{12}^e) (r_{23}^e) \end{aligned} \tag{2.8}$$

which represent the terms introduced by [5]. The displacements $\vec{d}_i$ are subject to the following constraint equations:

- the center of mass condition
- the Eckart conditions [40]
- the Sayvetz condition [41] which defines the ρ angle and the relation between ρ and $\bar{\rho}$ (instantaneous coordinate), [6, eq.(3.13)]

Because the potential energy is expressed in terms of the $\mathbf{R}_2$ generalized coordinate, which is function of $\bar{\rho}$, from (2.3), we have to express $\bar{\rho}$ in terms of ρ in order to obtain V as a function of $\mathbf{R}_1$, $\mathbf{R}_2$, ρ. The equation between $\bar{\rho}$ and ρ, expanded as a power series in $\mathbf{R}_1$ and $\mathbf{R}_2$ is:

$$\bar{\rho} = \rho - \sum_i A_i \mathbf{R}_i + \ldots \tag{2.9}$$

with the summation over $i = 1, 3$

$$A_i = -\frac{(u_i + u_{13}\cos\rho)\sin\rho}{r_{i2}^e (v + u_{13}\sin^2\rho)} \tag{2.10}$$

$$v = u_{13}\left(\frac{u_1 u_3}{u_{13}^2} - 1\right) = m\, m_2 r_{12}^e r_{23}^e \quad \text{and } m = m_1 + m_2 + m_3$$

Two symmetrized linearized internal stretching coordinates are defined by:

$$\vec{S} = \begin{pmatrix} S_1 \\ S_3 \end{pmatrix} = \mathbf{U}\,\mathbf{B}\,\vec{\mathbf{d}} \tag{2.11}$$

where:

- $\vec{\mathbf{d}}$ is a nine element vector containing $d_{i\alpha}$
- $\mathbf{B}$ matrix is given by :

$$\mathbf{B} = \begin{pmatrix} 0 & \sin(\rho-\varepsilon) & -\cos(\rho-\varepsilon) & 0 & -\sin(\rho-\varepsilon) & \cos(\rho-\varepsilon) & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sin\varepsilon & -\cos\varepsilon & 0 & \sin\varepsilon & \cos\varepsilon \end{pmatrix} \tag{2.12}$$

- the **U** matrix is depending on the molecule:
  - for a symmetrical AB_2 molecule:

$$\mathbf{U} = \sqrt{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \tag{2.13}$$

  - for a unsymmetrical ABC molecule **U** is a unit matrix.

We can write:

$$\vec{d} = \hat{\mathbf{A}}\, \mathbf{U}\, \vec{S} \tag{2.14}$$

where the **A** matrix (whose elements are functions of ρ) for a general triatomic molecule is given in [7, Table1] :

$$\mathbf{A} = \begin{pmatrix} 0 & 0 \\ m_2(m_2+m_3)\sin(\rho-\varepsilon)D^{-1} & m_2 m_3 \cos\rho \sin(\rho-\varepsilon)D^{-1} \\ -m_2(m_2+m_3)\cos(\rho-\varepsilon)D^{-1} & -m_2 m_3 \cos\rho\cos(\rho-\varepsilon)D^{-1} \\ 0 & 0 \\ -m_1(m_2+m_3)\sin(\rho-\varepsilon)D^{-1} & -m_1 m_3 \cos\rho \sin(\rho-\varepsilon)D^{-1} \\ -m_1 m_3 \cos\rho \sin\varepsilon D^{-1} & -m_3(m_1+m_2)\cos\varepsilon D^{-1} \\ m_1(m_2+m_3)\cos(\rho-\varepsilon)D^{-1} & m_1 m_3 \cos\rho\cos(\rho-\varepsilon)D^{-1} \\ -m_1 m_3 \cos\rho\cos\varepsilon D^{-1} & -m_3(m_1+m_2)\cos\varepsilon D^{-1} \\ 0 & 0 \\ m_1 m_2 \cos\rho \sin\varepsilon D^{-1} & m_2(m_1+m_2)\sin\varepsilon D^{-1} \\ m_1 m_2 \cos\rho\cos\varepsilon D^{-1} & m_2(m_1+m_2)\cos\varepsilon D^{-1} \end{pmatrix} \tag{2.15}$$

with $D = m_2\,(m_1+m_2+m_3) + m_1\, m_3\, \sin^2\rho$.

2.1.4 Normal Coordinates

The normal coordinates are defined as linear combination of the mass-weighted Cartesian displacement coordinates:

$$d_{i\alpha} = m_i^{-\frac{1}{2}} \sum_s l_{i\alpha,s}(\rho)\, Q_s \tag{2.16}$$

where: the summation is over $s = \overline{1,3}$
$i = 1, 2, 3$
$\alpha = x\,, y\,, z$

The potential energy can be expressed in normal coordinates and becomes a sum of terms, each involving only one coordinate. The kinetic energy expressed in normal coordinates is also a similar sum of terms. Hence, the Hamiltonian is separable in normal coordinates.

The properties for the $\hat{l} = (l_{i\alpha,s})$ matrix are discussed in [8, eq.(11)-(14)] and [6, eq.(4.21) and Table IV,V]. It is possible to use the equations from (§2.1.2) in order to construct the kinetic energy in the traditional GF matrix formalism [10], if we write them in the form:

$$m_1^{-\frac{1}{2}}\, d_{i\alpha} = \sum_s l_{i\alpha,s}\, Q_s \tag{2.17}$$

where $Q_s = q_0^1, q_0^3, \gamma^0 \quad ; \quad \alpha = x, y, z$. The $\hat{l}$ matrix from (2.16) can be chosen as orthogonal $\hat{l}^+ \hat{l} = \hat{I}$ where $\hat{l}^+$ is the transpose of $\hat{l}$ and $\hat{I}$ is the unit matrix. $\hat{l}$ is the matrix of the eigenvectors of $\hat{M}^{-\frac{1}{2}} \hat{V} \hat{M}^{-\frac{1}{2}}$.

$$\hat{l}^+ \hat{M}^{-\frac{1}{2}} \hat{V} \hat{M}^{-\frac{1}{2}} \hat{l} = \hat{\Lambda} \tag{2.18}$$

where:

- $\hat{V} = (u_{i\alpha,k\beta}) = \left(\frac{\partial^2 V}{\partial d_{i\alpha}\, d_{k\beta}}\right)_e$ is the potential energy matrix
- $\hat{M}^{-\frac{1}{2}} = \left(m_i^{-\frac{1}{2}} \delta_{i\alpha,k\beta}\right)$ is the diagonal matrix of the square root of the masses
- $\hat{\Lambda}$ is the diagonal eigenvalue matrix.

As pointed out by Hougen *et al* [5], the traditional GF matrix formalism (WDC) with the bending coordinate removed can be applied for the curvilinear coordinate case, by using the coordinates S_1 and S_3 to perform a GF calculus.

The normal coordinate-ordinates are defined by [6] as:

$$\vec{\mathbf{Q}} = \begin{pmatrix} Q_1 \\ Q_3 \end{pmatrix} = \hat{\mathbf{L}}^{-1} \vec{S} \tag{2.19}$$

where the 2x2 $\hat{\mathbf{L}}$ matrix is obtained from the eigenvalue equation:

$$\hat{\mathbf{L}}^{-1} \hat{\mathbf{G}} \hat{\mathbf{F}} \mathbf{L} = \Lambda \tag{2.20}$$

$\hat{\mathbf{L}}$ is normalized so that:

$$\hat{\mathbf{L}} \hat{\mathbf{L}}^+ = \hat{\mathbf{G}} \tag{2.21}$$

The $\hat{\mathbf{G}}$ and $\hat{\mathbf{F}}$ matrix in the $\vec{S}$ coordinate-ordinates are [42]

- for a symmetrical AB_2 molecule:

$$\hat{\mathbf{G}} = \begin{pmatrix} \frac{m_2 + m_1 \sin^2 \frac{\rho}{2}}{m_1 m_2} & 0 \\ 0 & \frac{m_2 + m_1 \cos^2 \frac{\rho}{2}}{m_1 m_2} \end{pmatrix} \qquad \hat{\mathbf{F}} = \begin{pmatrix} F_{11} + F_{13} & 0 \\ 0 & F_{11} - F_{13} \end{pmatrix} \tag{2.22}$$

- for a nonsymmetrical ABC molecule:

$$\hat{\mathbf{G}} = \begin{pmatrix} \frac{1}{m_1} + \frac{1}{m_2} & -\frac{1}{m_2} \cos\rho \\ -\frac{1}{m_2} \cos\rho & \frac{1}{m_2} + \frac{1}{m_3} \end{pmatrix} \qquad \hat{\mathbf{F}} = \begin{pmatrix} F_{11} & F_{13} \\ F_{13} & F_{33} \end{pmatrix} \tag{2.23}$$

The $\hat{l}$ matrix can be computed from [43]:

$$\hat{l} = \hat{\mathbf{M}}^{-\frac{1}{2}} \hat{\mathbf{B}}^+ \hat{\mathbf{U}}^+ (\hat{\mathbf{L}}^{-1})^+ \tag{2.24}$$

2.2 Perturbational Approach for the Vibration Energies of the Molecules

Of most interest are the vibration levels where the vibration energies are small. Nielsen [11] has derived the relationships correct through second-order of approximation, relating the vibrational energies and rotational constants to the cubic and quartic terms in the potential energy, expressed in normal coordinate space.

The coordinates used for this approach have been defined in eq. (2.16) , (2.17) . In order to deal only with the vibrational coordinate-ordinates, the following constraints are used:

1. the nuclear center of mass remains at the origin (it was neglected the difference between the center of mass of the molecule and that of the nuclei).

2. the x,y,z axes of the reference system coincide with the principal axes of inertia when the nuclei are in their equilibrium positions.

3. the Eckart conditions (in the zeroth order of approximation the internal angular momentum of the molecule shall be zero).

With these constraints we will minimize the expression:

$$\int \dots \int \bar{\Phi}(T + V - E)\, \Phi\, dV_1 dV_2 \dots dV_r \tag{2.25}$$

where

- ϕ is the total wavefunction
- T is the kinetic energy
- V is the potential energy

The eq.(2.25) is subject to the normalization condition:

$$\int \dots \int \bar{\Psi}\, \Psi d\theta\, d\chi\, d\varphi \prod_s dQ_s \prod_{\alpha j} d\alpha_j = 1 \tag{2.26}$$

where

- $\Psi = \mu^{-\frac{1}{4}} \sin^{\frac{1}{2}} \theta\, \Phi$ is due to a change of the volume element
- $\theta\,, \chi\,, \varphi$ are the Euler angles
- Q_s are the normal coordinates
- α_j are the Cartesian coordinates of the electrons
- μ is the inverse of the determinant of the 3x3 inertia momentum tensor

The minimization process does not lead finally to an exact solution: but if we consider as small certain terms in it, and neglect them at the present, we may effect a partial separation of variables by adopting for $\Psi^{(0)}$ the following function:

$$\Psi^{(0)} = \Phi(\alpha_j\,, \sigma_j\,; r_{mn})\, R(\theta_s\,, \theta\,, \chi\,, \varphi) \tag{2.27}$$

where

- $\Phi(\alpha_j\,, \sigma_j\,; r_{mn})$ is the electronic wavefunction depending on the α_j Cartesian coordinates and σ_j spin of the electrons.
- r_{mn} is the distance between two atomic nuclei and enter as parameter in the electronic wavefunction.
- $R(Q_s\,, \theta\,, \chi\,, \varphi)$ is the vibrational wavefunction which depends on the normal coordinates and the Euler angles.

After averaging the cross terms over the electronic coordinates, the vibrational Schrödinger equation is:

$$\left\{\frac{1}{2}\mu^{\frac{1}{4}}\left[\sum_{\alpha\beta}(J_\alpha - p_\alpha)\,\mu_{\alpha\beta}\,\mu^{-\frac{1}{2}}\,(J_\beta - p_\beta)\,\mu^{\frac{1}{4}}\right.\right.$$
$$\left.\left. + \sum_{s} p_s\,\mu^{-\frac{1}{2}}\,p_s\,\mu^{\frac{1}{4}}\right] + U_e(r_{mn}) - E\right\} R(Q_s\,,\theta\,,\chi\,,\varphi) = 0 \tag{2.28}$$

where

- J_α is the total angular momentum, expressed classically as $J_\alpha = \left(\frac{\partial T}{\partial \omega_\alpha}\right)$
  - $\alpha = x\,, y\,, z$
  - ω_α is the α component of the angular velocity vector of the molecule fixed axes system in the laboratory fixed axes system.
  - $\beta = x\,, y\,, z$ and $\alpha \neq \beta$
- p_α is the component of the internal angular momentum of the nuclei directed along α axis:

$$p_\alpha = \sum_{s}\sum_{s'} \zeta^{(\alpha)}_{s,s'}\,Q_{s'}\,p_s \tag{2.29}$$

- $\zeta^{(\alpha)}_{s,s'}$ is the Coriolis coupling factor:

$$\zeta^{(\alpha)}_{s,s'} = \sum_{i}\left(l_{i\beta\,,s'}\;l_{i\gamma\,,s} - l_{i\beta\,,s}\;l_{i\gamma\,,s'}\right) \tag{2.30}$$

  - $\alpha = x\,, y\,, z,\ \beta = x\,, y\,, z,\ \gamma = x\,, y\,, z$
  - $\alpha \neq \beta \neq \gamma$
- $p_s = -i\hbar\frac{\partial}{\partial Q_s}$
- $\mu_{\alpha\beta}$ are the inverse elements of the 3x3 inertial tensor,

$$\mu_{\alpha\beta} = (I_{\alpha\beta})^{-1} \tag{2.31}$$

- $U_e(r_{mn})$ are the electronic energies which depend upon the internuclear distances as parameters.

The electronic energies define the potential energy function which determines the manner in which the atomic nuclei may vibrate when they are free to move. Since the energy values $U_e(r_{mn})$ cannot readily be determined, they are replaced by another function $U_e(Q_s)$, which approximates the actual function very closely, particularly in the region where, in a classical sense, the atoms spend most of their time.

Of most interest are the vibration levels where the vibration energies are small. Since in such instances the amplitudes are small, we can replace the actual potential energy surface by a power series expansion about the equilibrium values. Such a function has the disadvantage that it contains more independent constants than can be determined from the experimental data. In such cases simplifying assumptions must be made which will supply additional relations between these constants:

- The assumption of the *valence forces* supposes the forces between the atomic nuclei to be directed along the valence bonds and between the valence arms.

- The assumption of the *central forces*, but less successful.

These assumptions may be introduced at the end, since they simply impose definite relationships between the generalized force constants k_{ij}.

In order to express $U_e(r_{mn})$ in terms of the Q_s coordinates, i.e. $U_e(Q_s)$, the displacement coordinates Δr_{mn} are expressed in terms of the coordinates $d_{i\alpha}$. The $d_{i\alpha}$ coordinates are expressed as function of the normal coordinates using eq. (2.16).

For the quadratic portion of the potential energy we have:

$$U_0 = \frac{1}{2}\sum_s \lambda_s Q_s^2 \tag{2.32}$$

where $\lambda_s = (2\pi c\omega_s)^2$. In eq. (2.32), ω_s is expressed in cm^{-1}.

The cubic and quartic terms in the potential energy expansion, when expressed in the coordinates Q_s will be:

$$\begin{aligned} U_1 &= hc \sum_{s,s',s''} k_{s,s',s''}\, Q_s\, Q_{s'}\, Q_{s''} \\ U_2 &= hc \sum_{s,s',s'',s'''} k_{s,s',s''}\, Q_s\, Q_{s'}\, Q_{s''}\, Q_{s'''} \end{aligned} \tag{2.33}$$

where $s \le s' \le s'' \le s'''$. The potential energy constants $k_{ss's''}$ and $k_{ss's''s'''}$ are expressed in cm^{-1}. The equation (2.28) does not adapt itself to an exact solution. It becomes necessary to replace it by its expansion in order of magnitude and obtain an approximate solution by using the methods of the perturbation theory. The expansion is made on the basis that the displacement coordinates $d_{i\alpha}$ and therefore the normal coordinates Q_s are small when compared with the equilibrium values of the nuclear coordinates.

The Hamiltonian will be:

$$H = H^{(0)} + H^{(1)} + H^{(2)} \tag{2.34}$$

where:

$$\begin{aligned} H(0) &= \frac{1}{2}\sum_s \left[p_s^2 + \lambda Q_S^2\right] + \frac{1}{2}\sum_\alpha \frac{P_\alpha}{I_{\alpha\alpha}} \\ H(1) &= T^{(1)} + U_1 \\ H(2) &= T^{(2)} + U_2 \end{aligned} \tag{2.35}$$

with $\alpha = x, y, z$. $T^{(1)}$ and $T^{(2)}$ are the terms from the kinetic energy arising when μ, $\mu_{\alpha\beta}$ are expanded in Q_s basis [11].

The solution of the zeroth order problem:

$$\left(H^{(0)} - E^{(0)}\right)\Psi^{(0)} = 0 \tag{2.36}$$

is separable into the vibrational coordinates Q_s and the rotational coordinates θ, χ, φ if one adopts for $\Psi^{(0)}$ a function:

$$\Psi^{(0)}(Q_s, \theta, \chi, \varphi) = \prod_s \chi_s(Q_s)\, R(\theta, \chi)\, e^{iM\varphi} \tag{2.37}$$

The separation of the variables leads to a set of differential equations of the following kind for the vibrational problem, one for each vibration frequency ω_s:

$$\left[\frac{1}{2}p_s^2 + \lambda_s Q_s^2 - E_s\right]\chi_s(Q_s) = 0 \tag{2.38}$$

If the frequency ω_s is nondegenerate, the eq.(2.38) is the equation for the *linear* harmonic oscillator, if ω_s has two vibrational coordinates associated with it, eq. (2.38) becomes the

equation for the *two - dimensionally isotropic* oscillator. When there are three coordinates required to describe a vibration frequency ω_s, eq. (2.38) becomes the equation for the *three dimensional oscillator* [44].

The contributions to the energy due to $H^{(1)}$ and $H^{(2)}$ may be evaluated by the usual methods of the perturbation theory but, because of the large number of terms in $H^{(1)}$ and $H^{(2)}$, this is a formidable undertaking, especially since the zero order energies may be degenerate. This suggests the effectiveness of transforming H by a contact transformation $\hat{\mathbf{T}}H\hat{\mathbf{T}}^{-1}$ into $(H^{(0)})' + \lambda(H^{(1)})' + \lambda^2(H^{(2)})' + \ldots$, so that to the second order of approximation $(H^{(1)})'$ will contain only the degenerate Coriolis terms. The evaluation of the second-order energies is thus, in principle, reduced to a first order perturbation calculation.

The transformation function is $\mathbf{T}(\lambda) = e^{i\lambda S}$, which, to second order of approximation is equal to [45]:

$$\mathbf{T} = 1 + i\lambda S - \left(\frac{\lambda^2}{2}\right) S^2 - \left(i\frac{\lambda^3}{6}\right) S^3 + \ldots \tag{2.39}$$

To second order of approximation the transformed Hamiltonian will become:

$$H' = (H^{(0)})' + \lambda(H^{(1)})' + \lambda^2(H^{(2)})' + \ldots \tag{2.40}$$

where:

- $(H^{(0)})' = H^{(0)}$
- $(H^{(1)})' = H^{(1)} - i\left[H^{(0)}\,S - S\,H^{(0)}\right]$
- $(H^{(2)})' = H^{(2)} + \frac{i}{2}\left[S\left(H^{(1)} + (H^{(1)})'\right) - \left(H^{(1)} + (H^{(1)})'\right) S\right]$

The portion of $H^{(1)}$, that we wish to remove, consists of terms each of which is a function of the normal coordinates Q_s (or the conjugate momenta p_s) multiplied by a coefficient which either is a constant or a function of the angular momentum operator J_α. The basis transformation functions S which remove from the first-order transformed Hamiltonian the type of the terms occurring in $H^{(1)}$ are given in [44, Table.II]. In the case of resonance between frequencies (i.e. $2\omega_s \simeq \omega_{s'}$, the term $hc\,k_{sss'}\,Q_s^2\,Q_{s'}$) the usual methods of the perturbation theory fail and such terms in the first order Hamiltonian which are instrumental in setting up resonance must also be retained as part of $(H^{(1)})'$. When the zero, first and second order contributions to the vibration energy are combined, one obtain for the vibration energy [11, eq.(IV.19)], in the absence of the resonance:

$$\begin{aligned}\frac{E_{vib}}{hc} &= \frac{E_0}{hc} + \sum_s \omega_s \left(V_s + \frac{g_s}{2}\right) \\ &+ \sum_{ss'} \chi_{ss'} \left(V_s + \frac{g_s}{2}\right)\left(V_{s'} + \frac{g_{s'}}{2}\right) + \sum_{tt'} \chi_{l_t l_{t'}}\, l_t\, l_{t'}\end{aligned} \tag{2.41}$$

where

- g_s is a weight factor equal to 1, 2 or 3, respectively as ω_s is one, two or threefold degenerate
- $\chi_{ss'}$ and $\chi_{l_t l_{t'}}$ are the anharmonic constants (corresponding to $\omega_e\,\chi_e$ in diatomic molecules)
- V_s and l_t are the quantum numbers associated with the two or three dimensional harmonic oscillator:

$$\frac{1}{hc}\,H_v^{harm}\,\chi_{s,l} = \left(V_s + \frac{g_s}{2}\right)\omega\,\chi_{s,l} \tag{2.42}$$

The relations between the anharmonic constants of (2.41) and the force field constants given by the potential

$$V_s = \frac{1}{2}\sum_i k_{ij}\,Q_i^2 + \frac{1}{6}\sum_{i,j,k} k_{ijk}\,Q_i\,Q_j\,Q_k + \frac{1}{24}\sum_{i,j,k,l} k_{ijkl}\,Q_i\,Q_j\,Q_k\,Q_l \tag{2.43}$$

are [46, eq.(17)-(20)]:

$$\begin{aligned}
\chi_{ss} &= \frac{1}{4}\left[6k_{ssss} - 15\left(\frac{k_{sss}^2}{\omega_s}\right) - \sum_{s'}\left(\frac{k_{sss'}^2}{\omega_{s'}}\right)\cdot\frac{8\omega_s^2 - 3\omega_{s'}^2}{4\omega_s^2 - \omega_{s'}^2}\right] \\
\chi_{ss'} &= \frac{1}{2}\left\{k_{sss's'} - 6\left(\frac{k_{sss}k_{ss's'}}{\omega_s}\right) - 4k_{sss'}^2\left(\frac{\omega_s}{4\omega_s^2 - \omega_{s'}^2}\right) - \sum_{s''}\left(\frac{k_{sss''}k_{s''s's'}}{\omega_{s''}}\right)\right. \\
&\quad - \sum_{s''}\left(\frac{k_{ss's''}^2}{2(g_s + g_{s'} - 2)!}\right)\omega_{s''} \\
&\quad \times \left[\frac{\omega_{s''}^2 - \omega_{s'} - \omega_{s'}^2}{(\omega_s + \omega_{s'} + \omega_{s''})(\omega_s + \omega_{s'} - \omega_{s''})(\omega_s - \omega_{s'} + \omega_{s''})(\omega_s - \omega_{s'} - \omega_{s''})}\right] \\
&\quad + \left.\frac{2}{g_s g_{s'}}\sum_\alpha\sum_{\sigma\sigma'}\left(\zeta_{s\sigma,s'\sigma'}^{(\alpha)}\right)^2 B_e^{(\alpha\alpha)}\left(\frac{\omega_{s'}}{\omega_s}\right)\right\} \\
\chi_{l_t l_t} &= -\frac{1}{4}\left[2k_{tttt} + \sum_{s'} k_{tts'}^2\frac{\omega_{s'}}{4\omega_t^2 - \omega_{s'}^2}\right] \\
\chi_{l_t l_{t'}} &= \frac{1}{2}\sum_{s''}\left(k_{tt's''}^2\right)\left[\frac{\omega_t\,\omega_{t'}\,\omega_{s''}}{(\omega_t + \omega_{t'} + \omega_{s''})(\omega_t + \omega_{t'} - \omega_{s''})(\omega_t - \omega_{t'} + \omega_{s''})(\omega_t - \omega_{t'} - \omega_{s''})}\right] \\
&\quad + \sum\frac{1}{2}\left(B_e^{\alpha\alpha}\right)\left(\zeta_{t_1,t_1'}^{(\alpha)}\,\zeta_{t_2,t_2'}^{(\alpha)} - \zeta_{t_1,t_2'}^{(\alpha)}\,\zeta_{t_2,t_1'}^{(\alpha)}\right)
\end{aligned} \tag{2.44}$$

where $\alpha = x, y, z$. The sum over σ indicates a sum over the components of a degenerate vibration and the index t takes on those values of s corresponding to doubly degenerate vibrations. $B_e^{(\alpha\alpha)}$ is the rotational constant for equilibrium. The relations between the cubic and quartic force constants in (2.43) and (2.44) are given by [46, eq.(3)].

2.3 Bending Vibrations

2.3.1 Harmonic Oscillator

For the small amplitude bending vibrations we have two different treatment, depending if the molecule is bent or linear.

Bent Molecules

For a bent molecule the Hamiltonian corresponding to the bending motion is the harmonic oscillator:

$$H_b^0 = \frac{1}{2\mu_2}P_2^2 + \frac{1}{2}k_{22}\,Q_2^2 \tag{2.45}$$

where μ_2 is the "bending" mass, $P_2 = -i\hbar\frac{\partial}{\partial Q_2}$ and k_{22} is the force harmonic constant for the bending vibration. The eigenvalue for the eq. (2.45) is:

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{2.46}$$

In this case the eigenfunction is:

$$\chi_n(\xi_2) = \frac{1}{\sqrt{2^n n!\sqrt{\pi}\,\alpha}} H_n(\xi_2)\, e^{-\frac{\xi^2}{2}} \tag{2.47}$$

with $H_n(\xi)$ - Hermite polynomials and ξ_2 connected with the coordinate Q_2 through:

$$\xi_2 = \alpha Q_2 \quad \text{with} \quad \alpha = \sqrt{\tfrac{\mu_2\omega_2}{\hbar}} \tag{2.48}$$

The volume element for $\chi_n(\xi)$ is: $dV = dQ_2$ and the parity is $(-1)^n$.

Linear Molecules

In the case of a linear molecule the bending vibration has an elliptical motion. In a Cartesian coordinate system there are two bending coordinates, q_x and q_y, which correspond to two orthogonal vibrational motions at right angles. The elliptical motion of the respective atoms result in vibrational angular momenta directed along the z axis (the axis of the linear molecule). It is advantageous to convert to the cylindrical polar coordinates system [44], by taking into account the combinations, because of the symmetry of the molecule:

$$q_\pm = q_x + iq_y = qe^{\pm i\varphi} \tag{2.49}$$

where q is the linear displacement from the equilibrium (which correspond to the general displacement coordinate ρ) and φ to the vibrational angular coordinate (the third Euler angle).

The Hamiltonian for the twofold isotopic oscillator in polar coordinates can be written in the form,

$$H^{harm} = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial q^2} + \frac{1}{4q^2}\right) - \frac{\hbar^2}{2\mu q^2}\frac{\partial^2}{\partial\varphi^2} + \frac{1}{2}kq^2 \tag{2.50}$$

where

- $P_q = -i\hbar\frac{\partial}{\partial q}$ is the kinetic momentum corresponding to the linear displacement coordinate
- $P_\varphi = -i\hbar\frac{\partial}{\partial\varphi}$ is the vibrational angular momentum
- $\mu = \frac{m_2 m_1}{2(m_2+2m_1)}$ for a symmetrical molecule.

The wavefunction for the eq.(2.50) is then [47, 33]:

$$\chi_{v,l}(q,\varphi) = (-1)^{\frac{v-l}{2}}\sqrt{\frac{\left[\frac{1}{2}(v+l)\right]!}{2\pi\left[\frac{1}{2}(v-l)\right]!}}\, q^{\frac{1}{2}}\, x^{\frac{l}{2}}\, qe^{-\frac{x}{2}}\, L^l_{\frac{v-l}{2}}(x)e^{il\varphi} \tag{2.51}$$

In the eq.(2.51) the vibrational quantum numbers are v (for the energy) and l (for the angular momentum). The variable x is related to the coordinate q by:

$$x = \frac{\mu\omega}{\hbar}\, q^2 \tag{2.52}$$

and $L^l_{\frac{v-l}{2}}(x)$ is an associate Laguerre polynomial, defined as in [49, 50, 51].

Obs. In the literature there are sometimes other definitions for the associate Laguerre polynomials, as in [47] or in [33, 44, 52].

The matrix elements between the harmonic oscillator vibrational functions (2.51) are [33, 53, 54]:

$$\begin{aligned}
\langle v\pm 1, l+1|q_+|vl\rangle &= \sqrt{\frac{\hbar}{2\mu\omega}}\sqrt{(v+1)\pm(l+1)} \\
\langle v\pm 1, l-1|q_-|vl\rangle &= \sqrt{\frac{\hbar}{2\mu\omega}}\sqrt{(v+1)\mp(l-1)}
\end{aligned} \tag{2.53}$$

2.3.2 Large Amplitude Bending Models

In many triatomic molecules only the bending vibration is of large amplitude, and the rectilinear displacement coordinates are inappropriate for large amplitude of the bending vibrations, because no single rectilinear coordinate can describe large changes in the bending angle without simultaneously introducing large change in one or both bond distances.

To derive the vibration Hamiltonian for a triatomic molecule, the curvilinear coordinates described in (§2.1.3) are used.

Rigid Bender Model

In the rigid bender model, the two bond length of the reference configuration do not vary with ρ [5].

The kinetic rotation-bending energy can be derived as in [10, 5]:

$$T_{rb} = \frac{1}{2}\mu^{\frac{1}{4}} \sum_{\alpha,\beta} (J_\alpha - p_\alpha)\ \mu_{\alpha\beta}\, \mu^{-\frac{1}{2}}\ (J_\beta - p_\beta)\ \mu^{\frac{1}{4}} \tag{2.54}$$

where $J_\alpha\,, p_\alpha\,, \mu_{\alpha,\beta}$ are defined below in the eq.(2.28), and $\alpha = x, y, z$. The moment of inertia matrix have been enlarged as a 4x4 matrix, including the bending coordinate too. The volume element corresponding to the form of T given in eq. (2.54) is:

$$dV = \sin\theta d\theta d\chi d\varphi d\rho \tag{2.55}$$

where θ, χ, φ are the Euler angles and ρ is the bending angle.

The zeroth-order kinetic energy is obtained by setting $Q_1 = Q_3 = 0$ in the μ matrix (which then becomes the μ^0 matrix) and by ignoring the vibrational angular momenta p_α. The replacement of μ by μ^0 is analogous to the similar approximation made in the normal treatment. This can be done because Q_1 and Q_3 are always of small amplitude. This result is obtained when remove the ρ from the vibrational problem. In the normal formalism Q_1 and Q_3 are not of small amplitude when the displacement of the bending angle from equilibrium is large.

The zeroth-order rotation-bending Hamiltonian is :

$$H^0_{rb} = \frac{1}{2}(\mu^0)^{\frac{1}{4}} \sum_{\alpha,\beta} J_\alpha\, \mu^0_{\alpha\beta}\, (\mu^0)^{-\frac{1}{2}}\, J_\beta\, (\mu^0)^{\frac{1}{4}} + V_0(\rho) \tag{2.56}$$

Since the elements of the μ^0 matrix depend on ρ, they do not commute with J_ρ. The matrix elements of $\mu^0_{\alpha\beta}$ are analytic functions of ρ and are described in [5, eq.(37)]. The eq.(2.56) can be simplified and will be [5, eq.(35)]:

$$H^0_{rb} = H^0_b(\rho) + H^{(z)}_r + H^{(x,y)}_r \tag{2.57}$$

where the terms are:

- $H^0_b(\rho)$ is the bending Hamiltonian, obtained by [5] with the form:

$$H^0_b(\rho) = \frac{1}{2}\mu^0_{\rho\rho}\, J^2_\rho + \frac{1}{2}\left[J_\rho, \mu^0_{\rho\rho}\right]\, J_\rho + \frac{1}{2}(\mu^0)^{\frac{1}{4}}\ \left[J_\rho, \mu^0_{\rho\rho}(\mu^0)^{-\frac{1}{2}}\ \left[J_\rho\,, (\mu^0)^{\frac{1}{4}}\right]\right] + V_0(\rho) \tag{2.58}$$

- $H^{(z)}_r$ represents the rotation around the z axis (the axis of the linear molecule):

$$H^{(z)}_r = \frac{1}{2}\mu^0_{zz}\, J^2_z \tag{2.59}$$

- $H^{(x,y)}_r$ represents the rotation around the x,y axis:

$$H^{(x,y)}_r = \frac{1}{2}\mu^0_{xx}\, J^2_x + \frac{1}{2}\mu^0_{yy}\, J^2_y + \frac{1}{2}\mu^0_{yz}\, [J_y J_z + J_z J_y] \tag{2.60}$$

The H^0_{rb} section corresponding to the degenerate angular momentum of the linear molecule is, from (2.57, 2.59,2.60):

$$H^{gr.ampl.} = H^0_b(\rho) + H^{(z)}_{rot} \tag{2.61}$$

If we make a change of the wavefunction from the old one, $\psi_b(\rho\,\varphi)$ to a new one, $\Phi_b(\rho\varphi)$:

$$\psi_b(\rho\,\varphi) = \left(\mu^0_{\rho\rho}\right)^{-\frac{1}{2}} \Phi_b(\rho\varphi) \tag{2.62}$$

there is a change of the volume element from $d\rho d\varphi$ to $\left(\mu^0_{\rho\rho}\right)^{-1} d\rho d\varphi$ and the linear derivative from (2.58) is removed. The bending Hamiltonian becomes [5]:

$$H^0_b = \frac{1}{2}\left\{\mu^0_{\rho\rho}\, J^2_\rho - \underbrace{(\mu^0)^{\frac{1}{4}}\left(\mu^0_{\rho\rho}\right)^{-\frac{1}{2}}\left[J_\rho, \left[J_\rho\,, (\mu^0)^{-\frac{1}{4}}\left(\mu^0_{\rho\rho}\right)^{\frac{1}{2}}\right]\right]}_{f_1(\rho)}\right\} + V_0(\rho) \tag{2.63}$$

The numerical integration is performed using the Numerov-Cooley technique of integration in two directions (in and out) with a matching procedure. [55, 5, 57, 14].

Obs. For high quantum numbers, the integration of Milne's equation instead of the Schrödinger equation may be a better method [56].

For small angles $f_1(\rho)$ has the behavior:

$$\lim_{\rho\to 0}\left[\hbar^2\mu^0_{\rho\rho}\, f_1(\rho)\right] = -\frac{1}{4\rho^2} \tag{2.64}$$

Taking into account the eq.(2.64) together with the condition that $V_0(\rho) = \frac{1}{2}k_2\rho^2$, in the linear limit, the eq.(2.61) reduces to the equation of the two-dimensional isotopic harmonic oscillator bending vibration in a linear triatomic molecule (eq. (2.50)).

The rigid bender Hamiltonian was used by Hougen et all. [5] in studies of vibrational levels (i.e. $J = 0$) of HCN and DCN and by Bunker and Stone [57] in studies of rotation-vibration levels for HCN, DCN, H_2O, D_2O, and HDO. The rigid bender model is easily generalized to molecules with more that three nuclei and such generalized models have been used by Stone [58] to describe the bending motion of fulminic acid HCNO and isocyanate HNCO, by Houle and Rao [59] and Kręglewski [60] to describe the inversion motion in excited electronic states of formaldehyde H_2CO. In the initial stages of the work on NH_3 by Papousek [61, 62] a rigid bender model was used too.

Semirigid Bender Model

The semirigid bender Hamiltonian is written in the same form as the rigid bender model one, eq.(2.61). The μ tensor elements are obtained essentially as for the rigid bender model, but the bond length are allowed to depend on ρ in such a way that the molecule follows the valley in the potential function along the coordinate ρ. For a triatomic molecule this means that the quantities u_1, u_3 and u_{13} (eq. 2.8) are functions of ρ (since the bond lengths r^e_{12} and r^e_{23} now are varying with ρ). $\varepsilon(\rho)$ from $\vec{a}_i(\rho)$ is computed so that the eq. (2.6) is fulfilled and the eq.(2.7) is replaced by:

$$\frac{d\varepsilon}{d\rho} = \frac{u_1 + u_{13}\cos\rho + m_1 m_3(r_{23}r'_{12} - r_{12}r'_{23})\sin\rho}{u_1 + u_3 + 2u_{13}\cos\rho} \tag{2.65}$$

where r_{ij} is a ρ dependent bond length and $r'_{ij} = \frac{dr_{ij}}{d\rho}$. The eq.(2.65) can be numerically integrated to yield ε as a function of ρ. For symmetrical molecules $\varepsilon = \frac{\rho}{2}$. In the semirigid

bender the equations for $I^0_{\alpha\beta}$ ($\alpha,\beta = x,y,z$) from [5, eq.(37)] are still valid (when u_1, u_3 and u_{13} are allowed to vary with ρ)., but $I^0_{\rho\rho}$ is replaced by:

$$I^0_{\rho\rho} = \sum_{i=1}^{3} m_i \left[\left(\frac{da_{ix}}{d\rho}\right)^2 + \left(\frac{da_{iy}}{d\rho}\right)^2 + \left(\frac{da_{iz}}{d\rho}\right)^2 \right] \tag{2.66}$$

where $a_{i\alpha}$ are given in [5, eq.(2)] and r^e_{ij} are allowed to vary with ρ.

The variation of the bond lengths is introduced to model the difference $(\mu^{eff}_{\alpha\beta} - \mu^0_{\alpha\beta})$. Usually, the bond lengths are expanded as power series in ρ with coefficients that are determined by fitting to experiment.

The semirigid bender model for triatomic molecules has been used for H_2O by Bunker and Landsberg [14] and the generalized versions of it have been used for $HCNO$ in [63], for C_3O_2 by Bunker [64], for $HCN - HNC$ isomerization by Ross and Bunker [65], for H_2CO by Jensen and Bunker [66, 67] and for H_2NNC by Jensen [6].

Nonrigid Bender Model

In the nonrigid bender model the Hamiltonian is derived correct to order of magnitude k^2T_v, where k is the Born-Oppenheimer expansion coefficient $k = (\frac{m_e}{m})^{\frac{1}{4}}$, m_e and m being the electronic and nuclear masses respectively, and T_v is a typical small amplitude vibrational energy [68, 6]. In the model a perturbation calculation is used to reduce the complete Hamiltonian to an effective rotation-bending Hamiltonian within each small amplitude stretching state. This procedure used by [6] closely follows the method used in the standard treatment [68], where an effective rotational Hamiltonian is obtained for each vibrational state.

The quantum mechanical kinetic energy operator, similar with eq. (2.54), but containing a stretching part too [6, eq.(4.1)], is expanded to order of magnitude k^2T_v and can be rearranged into [6, eq.(4.42),(4.49)]:

$$\begin{aligned}
T &= \frac{1}{2}\sum_{\alpha\beta}\mu^0_{\alpha\beta}\,J_\alpha\,J_\beta + \frac{1}{2}\sum_s P_s^2 - \sum_{\alpha\beta}\mu^0_{\alpha\beta}\,p_\alpha\,J_\beta - \frac{1}{2}\sum_{\alpha\beta\delta\varepsilon}\sum_r \mu^0_{\alpha\delta}\,a^{\delta\varepsilon}_r\,\mu^0_{\varepsilon\beta}\,Q_r\,J_\alpha\,J_\beta \\
&+ \frac{1}{2}\left[J_\rho\,,\mu^0_{\rho\rho}\right]J_\rho + \frac{1}{2}\sum_{\alpha\beta}\mu^0_{\alpha\beta}\,p_\alpha\,p_\beta + \frac{3}{8}\sum_{\alpha\beta\delta\varepsilon\eta\theta}\sum_{rs}\mu^0_{\alpha\delta}\,a^{\delta\varepsilon}_r\,\mu^0_{\varepsilon\eta}\,a^{\eta\theta}_r\,\mu^0_{\theta\beta}\,Q_r\,Q_s\,J_\alpha\,J_\beta \\
&+ U_0(\rho) + \frac{1}{2}(\mu^0)^{\frac{1}{4}}\left[J_\rho\,,\mu^0_{\rho\rho}(\mu^0)^{-\frac{1}{2}}\left[J_\rho\,,(\mu^0)^{\frac{1}{4}}\right]\right] \\
&- \left\{\frac{1}{2}\sum_r \mu^0_{\rho\rho}\,a^{\rho\rho}_r\,\mu^0_{\rho\rho}Q_r - \frac{3}{8}\sum_{\delta\varepsilon}\sum_{rs}\mu^0_{\rho\rho}\,a^{\rho\delta}_r\,\mu^0_{\delta\varepsilon}\,a^{\varepsilon\rho}_s\,\mu^0_{\rho\rho}\,Q_r\,Q_s\right\} \\
&\times (\mu^0)^{\frac{1}{4}}\left[J_\rho\,,(\mu^0)^{-\frac{1}{2}}\left[J_\rho\,,(\mu^0)^{\frac{1}{4}}\right]\right]
\end{aligned} \tag{2.67}$$

(summation over $\alpha\beta\delta\varepsilon\eta\theta = x,y,z,\rho$ and $rs = 1\,,3$). Here $U_0(\rho)$ consist of the part of the stretching kinetic energy $\frac{1}{2}\mu^{\frac{1}{4}}\sum_s\left[P_r\,,\mu^{-\frac{1}{2}}\left[P_r\,,\mu^{\frac{1}{4}}\right]\right]$ having the order of magnitude k^2T_v [17, eq.(5)-(6)], [6, eq.(4.44)]. The expansion of $\mu_{\alpha\beta}$ in power series as function of Q_s is [6, 8]:

$$\begin{aligned}
\mu_{\alpha\beta} &= \mu^0_{\alpha\beta} - \sum_{\delta\varepsilon=xyz\rho}\sum_{s=1,3}\mu^0_{\alpha\delta}\,a^{\delta\varepsilon}_s\,\mu^0_{\varepsilon\beta}\,Q_s \\
&+ \frac{3}{4}\sum_{\delta\varepsilon\eta\theta=xyz\rho}\sum_{ss'=1,3}\mu^0_{\alpha\delta}\,a^{\delta\varepsilon}_s\,\mu^0_{\varepsilon\eta}a^{\eta\theta}_s\,\mu^0_{\theta\beta}\,Q_s\,Q_{s'}
\end{aligned} \tag{2.68}$$

The potential energy, expanded to order of magnitude k^2T_v is [6]:

$$\begin{aligned}
V &= V_0(\rho) + \sum_r \Phi_r\,Q_r + \frac{1}{2}\sum_{rs}\Phi_{rs}\,Q_r\,Q_s + \frac{1}{6}\sum_{rst}\Phi_{rst}\,Q_r\,Q_s\,Q_t \\
&+ \frac{1}{24}\sum_{rstu}\Phi_{rstu}\,Q_r\,Q_s\,Q_t\,Q_u
\end{aligned} \tag{2.69}$$

where the Φ tensor elements are given by [6, eq.(3.37)-(3.40)].

In order to obtain the effective rotation-bending Hamiltonian for each stretching state, a Van Vleck transformation [69, 70, 71] of the Hamiltonian given by the eq.(2.67) and (2.69) is done. This procedure can be viewed as an *averaging* of H over small amplitude coordinates Q_1 and Q_3 in a particular (v_1, v_3) state. The resulting Hamiltonian, which still contains all ρ-dependent functions and J_α operators explicitly, describes only the rotation-bending states superimposed on the (v_1, v_3) state.

By using the perturbational theory with zeroth order stretching wavefunctions for the terms such as: $[\langle v_1, v_3|H|v_1', v_3'\rangle]^n$, with $n \geq 1$ and by discarding terms of order of magnitude $k^3 T_v$ or smaller, the effective Hamiltonian has the form:

$$\begin{aligned} H_{rb}^{eff} &= \frac{1}{2}{\sum_{\alpha\beta}}' \mu_{\alpha\beta}^{eff} J_\alpha J_\beta + \frac{1}{2}\mu_{\rho\rho}^{eff}\,\Omega + \frac{1}{2}\mu_{\rho\rho}^{co} J_\rho^2 + \frac{1}{4}{\sum_{\alpha\beta}}'{\sum_{\delta\varepsilon}}' \tau_{\alpha\beta\delta\varepsilon} J_\alpha J_\beta J_\delta J_\varepsilon \\ &+ \frac{1}{4}{\sum_{\alpha\beta}}' \tau_{\alpha\beta\rho\rho}\left(J_\alpha J_\beta \Omega + \Omega J_\alpha J_\beta\right) + \frac{1}{4}\tau_{\rho\rho\rho\rho}\,\Omega^2 + \frac{1}{2}\left[J_\rho\,,\mu_{\rho\rho}^0\right] J_\rho \\ &+ \frac{1}{2}(\mu^0)^{\frac{1}{4}}\left[J_\rho\,,\mu_{\rho\rho}^0\right]\left[J_0\,,(\mu^0)^{\frac{1}{4}}\right] + V_{eff}(\rho) \end{aligned} \tag{2.70}$$

where

$$\begin{aligned} \Omega &= J_\rho^2 + \hbar^2 g(\rho) \\ g(\rho) &= \frac{1}{\hbar^2}(\mu^0)^{\frac{1}{4}}\left[J_\rho\,,(\mu^0)^{-\frac{1}{2}}\left[J_\rho\,,(\mu^0)^{\frac{1}{4}}\right]\right] \end{aligned} \tag{2.71}$$

and the summation is over $\alpha\beta\varepsilon = x, y, z, \rho$. A prime ($\sum'$ indicates that the term with $\alpha = \beta = \rho$ (or $\delta = \varepsilon = \rho$) is excluded from the sum.

The μ^{eff} tensor elements are given by [6, eq.(5.25)-(5.27)]. The $\mu_{\rho\rho}^{cor}$, given by [6, eq.(5.28)], appears only for the unsymmetrical ABC molecule, for which $\zeta_{13}^{(\rho)}$ is nonvanishing. The $\tau_{\alpha\beta\delta\varepsilon}$ functions are given by [6, eq.(5.16)].

Since $\mu_{\alpha\beta}^0$, $a_r^{\alpha\beta}$ and $\zeta_{13}^{(\alpha)}$ are functions of ρ, they do not commute with J_ρ. However, the extra terms arising from this noncommutation are found to be of order of magnitude $k^3 T_v$ or smaller and they are consequently neglected. As a result of this, the Hamiltonian is not Hermitian.

An improvement of the NRB1 Hamiltonian described previously, in that allowance for the dependence of the energy denominators on v_2 and K_a (rotational number) is done in the NRB2 Hamiltonian [72, 73, 74].

The nonrigid bender model has been used in studies of H_2O [17, 75], CH_2 [76, 77, 78, 79], CNC^+ and C_3 [80]. For H_2O and CH_2 least squares fits to experimental data for the ground electronic states have been performed, yielding the equilibrium bond length together with a number of force constants (for CH_2, which has a $^3B_1$ electronic ground state, the fine and hyperfine splitting have to be suppressed before the fit could carried out).

Other Types of Bending Models

- The large amplitude Hamiltonian of Freed and Lombardi [81] is given directly in terms of the true instantaneous internal valence coordinates $r_1\,, r_2\,, \rho$, whereas that of HBJ [5] uses as a reference coordinate system in which the Eckart conditions are applied in a different way. Consequently there is not a direct equivalence between the Hamiltonian of FL and HBJ.

  Barrow, Dixon and Duxbury [82] derived a new Hamiltonian for a symmetrical molecule, by starting from FL Hamiltonian and by assuming that the frequency of the stretching vibrations are high compared to the bending vibration. In that case the leading term in

FL's stretch-bending interaction $\mathcal{H}_3$ may be taken to second order, giving a contribution to the zeroth order bending Hamiltonian $\mathcal{H}^{(0)}_{bend}$, with a kinetic operator which is almost identical to $\mathcal{H}^{(1)}_{bend}$.

The kinetic operator in this Hamiltonian can be simplified by a change of variable $\psi(\rho) = \sin^{-\frac{1}{2}}\rho\,\chi(\rho)$, or $\sin^{\frac{1}{2}}\rho\,\mathcal{H}^{(2)}_{bend}\sin^{-\frac{1}{2}}\rho$. The volume element becomes after this transformation: $dV = d\rho d\rho$ and $\mathcal{H}^{(2)}_{bend}$ appropriate to the wavefunction $\chi(\rho)$ will be:

$$\begin{aligned}\frac{\mathcal{H}^{(2)}_{bend}}{hc} &= -g^{(2)}(\rho)\frac{\partial^2}{\partial\rho^2} - \frac{\partial^2}{\partial\rho^2}g^{(2)}(\rho) - g^{(2)}(\rho)\left(1+\frac{\cos^2\rho}{2\sin^2\rho}\right)\\ &\quad -A(\rho)\frac{\partial^2}{\partial\varphi^2} + V_{eff}(v_1, v_3, \rho)\end{aligned} \tag{2.72}$$

where

$$g^{(2)}(\rho) = \frac{\hbar^2}{2hcr_0^2}\times\frac{(m_1+2m_2)}{m_1\left[m_2+m_1(1-\cos\rho)\right]} \tag{2.73}$$

This Hamiltonian commutes with the operator for the z-axis angular momentum, and $-A(\rho)\frac{\partial^2}{\partial\varphi^2}$ can be replaced by $A(\rho)K^2$ in eq. (2.72). The $g^{(2)}(\rho)$ expression is equivalent with $\left(I^0_{\rho\rho}\right)^{-1}$ from [5, ec.(37)] and (§2.3.2). The second-order Hamiltonian of (2.72) is essentially equivalent to the zeroth-order bending z-axis rotation Hamiltonian of HBJ (eq. (2.58) and (2.61)). The difference arise from the omission of negligible higher-order terms in both cases. It should be noted that Fred and Lombadri [81] carried out the second-order transformation to the z-axis rotation which is equivalent to the change from the instantaneous coordinates to HBJ's particular choice, but neglected to do so for the bending vibration.

This model has been used to analyze the vibronic and spin-orbit coupling between the $\tilde{A}\,^3\Lambda_1$, $\tilde{X}\,^2B_1$ states of PH_2 and in studies of CS_2 molecule [82].

- As it was pointed out in [74], the results obtained with the nonrigid bender Hamiltonian for the comparatively rigid H_2O molecule imply that the perturbed harmonic oscillator approach used to describe the vibrations is very often not satisfactory. This is why are developed variational approaches, in which the matrix representation of the rotation-vibration Hamiltonian is diagonalized in a truncated set of basis functions without the use of the perturbation theory. Such approach are reviewed in the paper by Carter and Handy [83]. The variational methods have been developed mainly in two different forms:
  - Whitehead and Handy [84] use the "standard" untransformed Watson-type Hamiltonian [68] and diagonalize it using harmonic oscillator basis functions. A disadvantage is that in the standard approach, linear and nonlinear molecules have different Hamiltonians. Both of these Hamiltonians have convergence problems when they are used to calculate the energy levels of a quasilinear molecule [85], i.e., a molecule that has a relatively low barrier to linearity, so that it is neither truly linear nor truly bent.
  - Sutcliffe and co-workers [86] construct a Hamiltonian expressed in terms of geometrically defined coordinate.

On the basis of Sutcliffe's ideas two methods have been developed:

- Tennyson and Sutcliffe construct a Hamiltonian expressed in terms of geometrically defined coordinates most appropriate for describing the interaction between a diatomic molecule and a third particle, e.g., a Van der Waals complex [86]. A very

large number of basis functions are generally necessary in order to obtain converged energies for usual triatomic molecules with atom-atom bonds, because the coordinates used are those of an atom-diatom system.

- Carter and Handy [83] express the Hamiltonian in terms of two bond lengths and a bond angle. The method uses coordinates that reflect better the physical behavior of ABC molecules that can be viewed as performing stretching of the $A-B$ and $B-C$ bonds and angle bending.

- A variational method for calculating the rotation-vibration energies of a triatomic molecule directly from the nuclear potential energy function (MORBID) was developed by Jensen [7, 87, 88]. The bending Hamiltonian is the non-rigid bender model Hamiltonian (§2.3.2) , and for the stretching functions a Morse oscillator is used. The eigenvalues of this Hamiltonian are obtained variationally, i.e. through direct matrix diagonalization without the use of the perturbation theory as in (§2.3.2). As vibrational basis functions, numerically integrated bending functions obtained as in [6], combined with Morse oscillator stretching functions are used. Converged energies can be obtained with a relatively small basis set.

  The lowest X^3B_1 vibrational energy for the methylene radical CH_2 have been calculated with the MORBID program, and compared with the variational, Carter and Handy JGEOS program [83] and NRB2 [72, 73, 74] results.

2.4 Renner-Teller Effect

If the nuclei are strictly in a linear configuration their charges do not perturb the motion of the electrons round the linear axis in any way, but as soon as they assume a nonlinear configuration, their charges set up an electrostatic dipole field which disturbs the circular motion of the electrons and tends to couple it to the instantaneous configuration of the nuclei. For a degenerate electronic state, the two states now cannot be at the same energy for a given nonlinear nuclear configuration, and the degeneracy is lifted. This implies that there are strictly two electronic potential functions, which are in contact at the linear configuration and which start to diverge as the molecule bends.

2.4.1 Small Amplitude treatment of Renner-Teller Effect

The electronic energies of the two states (evaluated in fixed nuclear configuration) may behave in one of the three ways from (Fig.2.2).

The coordinate system used is illustrated in (Fig.2.3).

If the size of the dipole produced by the nuclei is μ, an electron, whose distance from is r, experiences a potential:

$$V'(r\,,\nu-\varphi)=\frac{\mu(\rho)}{r^2}\cos(\nu-\varphi)+\text{ higher terms in }\ \cos(\nu-\varphi) \tag{2.74}$$

ρ is the amplitude of the bending motion displacement from the linear configuration.

The interaction between the nuclear and the electronic motions must involve all the electrons: the Hamiltonian for the interaction is therefore derived by averaging the energy of each electron over the range of all its coordinates, except $(\nu-\varphi)$, and summing over the various electrons.

In setting up the Schrödinger equation for the vibronic energy levels of the components of a degenerate electronic state, it is convenient to define the Hamiltonian as a sum of the four terms:

$$H_{el}(\rho=0)+H_b+H_{rot}^{(z)}+H'_{el} \tag{2.75}$$

where:

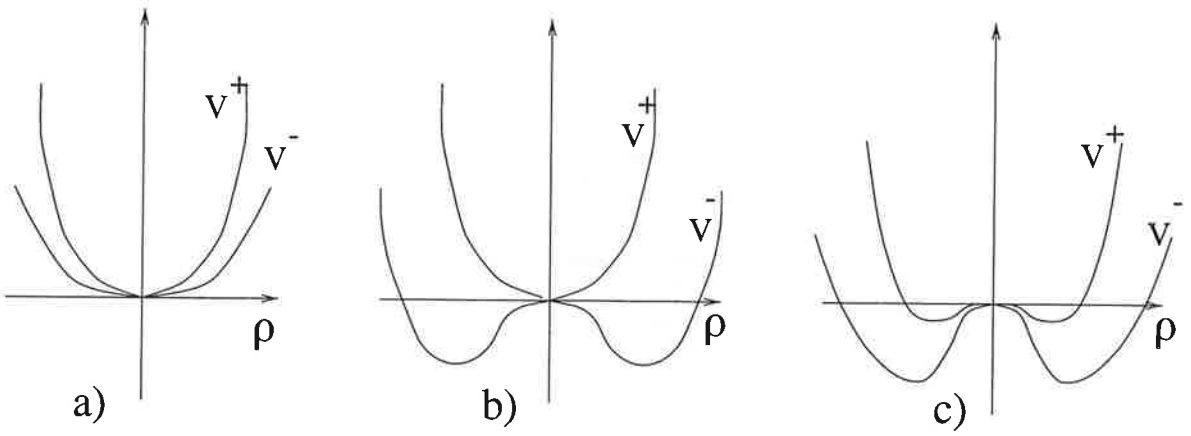

Figure 2.2: The electronic energies of the two states diverge from one another as the angle of bending increases. The abcissa denotes the extent of the deformation. Cases: **a)** both states are linear at equilibrum; **b)** upper state linear and lower bent at equilibrum; **c)** both states bent at equilibrum

- $H_{el}(\rho = 0)$ is the fixed-nuclei Hamiltonian for the linear molecule, those eigenvalue $E_{el}(\rho = 0)$ is the energy at the linear configuration.
- H_b is the radial part of the Hamiltonian for the kinetic energy corresponding to the bending motion (defined is section §2.3).
- $H_{rot}^{(z)}$ is the angular part of the Hamiltonian, defined in eq. (2.59). with J_z^2 replaced by $(J_z - L_z)^2$ to give the vibrational angular momentum [89, 90].
- The operator $H'_{el} = H'_{el}(\rho) - H_{el}(\rho = 0)$ represent the additional interaction between nuclei and electrons that arise when the nuclei move into a nonlinear configuration. It depends on all the electronic and nuclear coordinates, but only the electronic coordinate $(\nu - \varphi)$ and the bending amplitude ρ need appear explicitly, since the Born-Oppenheimer approximation allows one to average over the other electronic coordinates.

From (2.74), it can be simplified to:

$$H'_{el} = V_0(\rho) + j_1\rho\cos(\nu - \varphi) + j_2\rho^2\cos 2(\nu - \varphi) + \ldots \tag{2.76}$$

In the previous equation $V_0(\rho)$ is the potential function for the bending motion and the other terms are coupling terms. The parameter j_n, with $n \geq 1$ arise from the averaging over the radial wavefunctions of the various electrons.

The potential function and the coupling terms occur together in (2.76) and can be separated into potential and coupling terms in two different ways, corresponding to the linear and the bent molecule limits. The Schrödinger equation may be written as:

$$\left[H_b + H_{rot}^{(z)} + V_0(\rho) + V(\nu - \varphi\,,\rho) - E\right]\psi(\nu\,,\varphi\,,\rho) = 0 \tag{2.77}$$

where $V(\nu - \varphi\,,\rho)$ consists of those terms in $\cos n(\nu - \varphi)$, $n \geq 1$ from the eq.(2.76) which have matrix elements *within* the particular degenerate electronic state ($E_{el}(\rho = 0)$ has been included in $V_0(\rho)$).

The eigenvalue of L_z in (2.77) does not vanish in a degenerate electronic state, but take the two values $\pm\Lambda$ (in units of $\hbar$); therefore in zeroth order, the eq.(2.77) represent *two* different differential equations and they are coupled by the Renner-Teller perturbation $V(\nu - \varphi\,,\rho)$. $\psi(\nu\,,\varphi\,,\rho)$ is considered as a superposition of two functions, one of each component of the electronic state:

$$\psi(\nu\,,\varphi\,,\rho) = \begin{pmatrix} \psi^+(\nu\,,\varphi\,,\rho) \\ \psi^-(\nu\,,\varphi\,,\rho) \end{pmatrix} \tag{2.78}$$

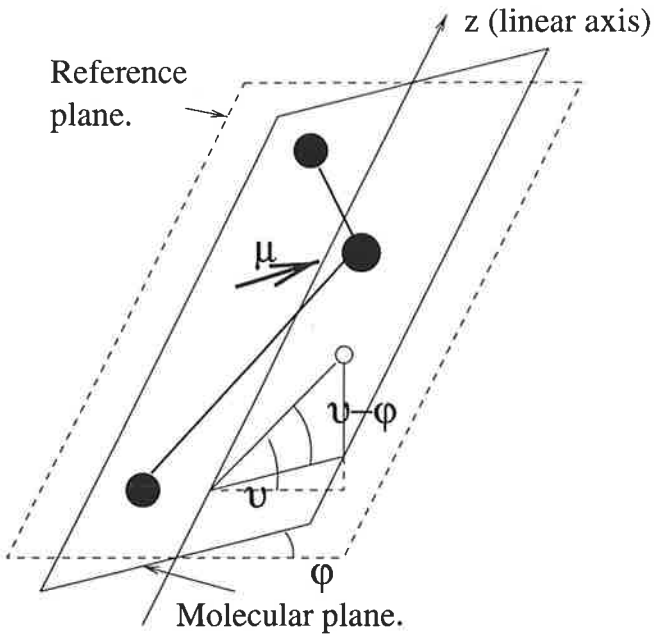

Figure 2.3: Coordinate system used to describe the Renner-Teller effect. The angle φ is the angle of the molecular plane to a reference plane, ν is is the azimuth angle between an electron and the reference plane.

where the two functions $\psi^{\pm}(\nu\,,\varphi\,,\rho)$ are each products of an electronic and a vibrational part,

$$\psi^{\pm}(\nu\,,\varphi\,,\rho) = \psi^{\pm}_{el}(\nu-\varphi)\,\frac{e^{iK\varphi}}{\sqrt{2\pi}}\,\Phi^{\pm}_{v,K}(\rho) \tag{2.79}$$

In eq.(2.79), K is the quantum number for the vibronic angular momentum, i.e., the eigenvalue of J_z. The eq.(2.77) is multiplied by $\frac{1}{\sqrt{2\pi}}\,e^{-iK\varphi}\,\left(\psi^{-}_{el}\right)^{\star}$, and integrated over ν and φ. The result is a differential equation in the single variable ρ, which involves the two vibrational functions $\Phi^{+}_{v,K}(\rho)$ and $\Phi^{-}_{v,K}(\rho)$. A similar differential equation is obtained by premultiplying by $\frac{1}{\sqrt{2\pi}}\,e^{-iK\varphi}\,\left(\psi^{+}_{el}\right)^{\star}$, and integrating. The eq.(2.77) becomes a system of two coupled differential equations,

$$\begin{pmatrix} H_b + U^{-}_{K}(\rho) - E & H_K(\rho) \\ H_K(\rho) & H_b + U^{+}_{K}(\rho) - E \end{pmatrix} \begin{pmatrix} \Phi^{-}_{v,K}(\rho) \\ \Phi^{+}_{v,K}(\rho) \end{pmatrix} = 0 \tag{2.80}$$

The form of the coupling function $H_K(\rho)$ and the effective potential functions $U^{\pm}_{K}(\rho)$ depend on the choice of the functions in the eq.(2.79). The two logical choices for the eq. (2.79) are the limits of the strictly linear or the strongly bent molecule, where the forms of the vibrational wavefunctions are well known [47, 91]. There is, however, one big advantage to the linear molecule formalism, which is that the vibrational angular quantum number l (i.e. the eigenvalue of $(J_z - L_z)$ in units of $\hbar$) is contained as an additional "good" quantum number in the basis functions.

Linear Molecules in Electronic Π States

The "linear molecule" choice of the basis functions for the eq.(2.79) is:

$$|\Lambda\,,v\,,l\rangle = \frac{1}{2\pi}\,e^{i\Lambda\nu}\,e^{il\varphi}\,\Phi_{v,l}(\rho) \tag{2.81}$$

where the first two terms are the angular factors equivalent to treating the electron and the nuclear motions as independent circular motions round the axis, and the third term is a radial vibrational factor. The quantum number l is connected with K and Λ by the relation:

$$l = K - \Lambda \tag{2.82}$$

With this choice, the potential and coupling functions of the eq.(2.80) are:

$$\begin{aligned} U_K^{\pm}(\rho) &= V_0(\rho) + \mu_{zz}^0 (K \pm \Lambda)^2 \\ H_K(\rho) &= \frac{1}{2} j_{2\Lambda} \rho^{2\Lambda} + \dots \end{aligned} \tag{2.83}$$

where :

- $V_0(\rho)$ is the *mean* of the two purely electronic potential functions
- $H_K(\rho)$ is *half* their splitting, which is entirely an electronic effect.

The significance of the two functions $U_K^{\pm}(\rho)$ is that the Hamiltonians $\left[H_b + U_K^{\pm}(\rho)\right]$ are those which are needs to calculate the vibrational basis functions for a particular value of the "good" quantum number K.

The potential energy $V_0(\rho)$ is taken as a simple quadratic, so the Hamiltonian $\left[H_0 + U_K^{\pm}(\rho)\right]$ becomes that of the two-dimensional harmonic oscillator, with the radial functions of (2.51) and (2.52). Since L_z has two eigenvalues $\pm\Lambda$ in a degenerate electronic state, the values of l required for the basis functions must be $l = K \pm \Lambda$, from (2.82). The matrix elements of the cylindrical polar coordinates $q_{\pm}$ defined in (2.49), are given in eq.(2.53). The matrix elements of $q_{\pm}^2$ are obtained by matrix multiplication from eq.(2.53):

$$\begin{aligned} \langle v+2, l \pm 2 | q_{\pm}^2 | v, l \rangle &= \left(\frac{\hbar}{2\,\mu\omega}\right) \sqrt{(v \pm l + 2)(v \pm l + 4)} \\ \langle v, l \pm 2 | q_{\pm}^2 | v, l \rangle &= \left(\frac{\hbar}{\mu\omega}\right) \sqrt{(v \mp l)(v \pm l + 2)} \\ \langle v-2, l \pm 2 | q_{\pm}^2 | v, l \rangle &= \left(\frac{\hbar}{2\,\mu\omega}\right) \sqrt{(v \mp l)(v \mp l + 2)} \end{aligned} \tag{2.84}$$

The electrostatic splitting $H_K(\rho)$ is truncated after the first term which is equivalent to picking out from the eq.(2.83) only the term $j_{2\Lambda}\, \rho^{2\Lambda} \cos 2\Lambda(\nu - \varphi)$, which gives matrix elements within a state of given $|\Lambda|$ value.

In a calculation of the vibronic energies, a separate matrix must be set up for each value of $|K|$ [1].

The first step is to add the matrix of the perturbation $\frac{1}{2} j_2\, \rho^2$ (for a Π state) to the diagonal matrix of the harmonic oscillator basis energies.

In harmonic approximation the result is an infinite tridiagonal matrix, infinite because the value of v is unlimited, and tridiagonal because from the eq.(2.84), the perturbation has matrix elements $\Delta v = 0\,, \pm 2$ only. Each element of the matrix is actually a 2x2 block since the electronic quantum numbers $\pm\Lambda$ must be taken with each value of v.

The sums and differences of the basis functions are considered. In the simplest case, where $K = 0$, this has the effect of factorizing the matrix into two submatrices, since each 2x2 block is symmetric about both diagonals; the Renner-Teller perturbation no longer couples the sum and the difference functions together. The nonvanishing elements are [33]:

$$\frac{1}{2} \left[\langle 1\,, v\,, l = -1| \pm \langle -1\,, v\,, l = 1|\right] V \left[|1\,, v\,, l = -1\rangle \pm |-1\,, v\,, l = 1\rangle\right]$$

[1] K, Λ and l are signed quantities. However states with the same value of $|K|$ have the same energy, so that the sign of K can usually be ignored: the signs of Λ and l must still be kept in the calculation of the matrix elements.

$$= \pm\frac{1}{2}\varepsilon\tilde{\omega}(v+1)$$

(2.85)

$$\frac{1}{2}\left[\langle 1\,,v+2\,,l=-1|\pm\langle -1\,,v+2\,,l=1|\right]V\left[|1\,,v\,,l=-1\rangle\pm|-1\,,v\,,l=1\rangle\right]$$
$$= \pm\frac{1}{4}\varepsilon\tilde{\omega}\sqrt{(v+1)(v+3)}$$

In eq.(2.85), ε is Renner's parameter ($\varepsilon = \frac{j_2}{k}$, with k the harmonic force constant $k = \mu\omega^2$), and $\tilde{\omega}$ is the harmonic frequency in cm^{-1}.

The elements in eq.(2.85) are exactly the same as those of different perturbation:

$$V'(q) = \pm\frac{1}{2}j_2\,q^2 = \pm\frac{1}{4}j_2\,(q_+\,q_- + q_-\,q_+) \tag{2.86}$$

acting on the bending vibration of a molecule with $\Lambda = 0$ those potential energy function is $V_0(\rho)$, as in eq.(2.83). The energy levels expression then follow the harmonic oscillator formulas, for the purely electronic potential,

$$V^{\pm}(\rho) = \frac{1}{2}(k \pm j_2)\,\rho^2 \tag{2.87}$$

and are given exactly by:

$$E_{v,K=0} = \omega\sqrt{1\pm\frac{j_2}{k}}(v+1) = \omega(v+1)\sqrt{1\pm\varepsilon} \tag{2.88}$$

For $K = 0$, therefore, the vibronic coupling between the component electronic states vanishes, and the energy levels correspond to the purely electronic potentials. This is true whatever the shape of the electronic potential is; the reason is that the Renner-Teller interaction for $K = 0$ couples basis functions differing only in the sign of l (corresponding to the degenerate basis levels), so that it can always be made electronically diagonal by taking sums and differences of the basis functions. In experimental determinations of the Born-Oppenheimer (i.e. purely electronic) potential functions from the observed spectra it is usual to use data from $K = 0$ levels, since these contain no vibronic coupling effects.

For $K \neq 0$, the vibronic coupling between the component electronic states does not vanish when sums and differences of the basis functions are taken, because the 2x2 block is not always symmetric. Small vibronic coupling elements remain in the off-diagonal positions of the outer 2x2 blocks, which act *between* the component electronic states. Renner ignored these, since they are off-diagonal in v.

The diagonal elements of the transformed 2x2 blocks for $K \neq 0$ are *not quite* the same as those of the perturbation from the eq.(2.86) so that the eq.(2.88) does not quite hold, through it becomes a good approximation when v is large. Renner used second order perturbation theory to treat the diagonal elements of the outer 2x2 blocks, which are of the type $\Delta v = \pm 2$; the energy level expression are [33]:

$$E_{\substack{K\neq 0\\ v,K<v+1}} = \omega(v+1)\left(1-\frac{1}{8}\varepsilon^2\right)\pm\frac{1}{2}\varepsilon\omega\sqrt{(v+1)^2-K^2} \tag{2.89}$$

The difference between the matrix elements of $V' = \pm j_2\,q^2$ and those of $V = \frac{1}{2}j_2\,(q_+^2+q_-^2)$, (which cause eq.(2.88) and (2.89) not to be the same) are named "reordering" elements, since they represent vibronic coupling *within* a Renner-Teller component state. The elements acting *between* the components can be considered "coupling" elements. The reordering elements are [33]:

$$H_{v,v}^{\mp\mp\,(reord.)} = \pm\frac{1}{2}\frac{\varepsilon\omega}{\sqrt{1\mp\varepsilon}}\left[(v+1)-\sqrt{(v+1)^2-K^2}\right]$$

$$H_{v,v+2}^{\mp\mp\,(reord.)} = \pm\frac{1}{8}\frac{\varepsilon\omega}{\sqrt{1\mp\varepsilon}}\left[\sqrt{(v+K+1)(v-K-3)}\mp\sqrt{(v+K+1)(v+K+3)}\right.$$
$$\left.\mp\sqrt{(v-K+1)(v-K+3)}-(1\mp 2)\sqrt{(v-K+1)(v+K+3)}\right] \quad (2.90)$$

where $\mp$ refers to the lower/upper Renner-Teller component. Similarly, the coupling elements, which Renner ignored, become [33]:

$$H_{v,v+2}^{\mp\mp\,(coupl.)} = \frac{1}{8}\varepsilon\omega\left[\sqrt{(v+K+1)(v-K+3)}\pm\sqrt{(v+K+1)(v+K+3)}\right.$$
$$\left.\mp\sqrt{(v-K+1)(v-K+3)}-\sqrt{(v-K+1)(v+K+3}\right] \quad (2.91)$$

In the limit where $v \gg K$, the reordering elements vanish, and the coupling elements become [33]:

$$H_{v,v+2}^{\mp\pm\,(coupl.)} = \pm\frac{1}{4}\varepsilon\omega K \quad (2.92)$$

The eq.(2.92) is a special case of a rule that holds for any shape of the Born-Oppenheimer (i.e. purely electronic) potential functions: the interactions between the Renner-Teller components are always approximately proportional to K. This means essentially that the Renner-Teller coupling can always be considered as a Coriolis effect, or, in other words, an angular momentum coupling of Λ with the rotation of the nuclei round the axis of the linear molecule.

An unexpected difficulty for K /=0 occurs in the lowest level of each K value. It can understood with reference to the left hand of the Fig.2.4, as follows [2].

In a $^1\Pi$ electronic state, the first $l = 0$ basis level must go with the electronic function $|\Lambda = +1\rangle$ (the eq.(2.82)) to form a vibronic level with $K = +1$, but it cannot be coupled by the Renner-Teller perturbation to a level *at the same energy* with $\Lambda = -1$ and $l = 2$, because no such level exists. The energy of the resulting vibronic "unique" level, which is the lowest with $K = 1$, is unchanged from that of its basis level in the first order; to second order, for any K value,

$$E_{v,K=v+1}^{unique} = \omega(v+1) - \frac{1}{8}\varepsilon^2\omega K(K+1) \quad (2.93)$$

The wavefunction for a "unique" level is *not* a linear combination of $|+\Lambda\rangle$ and $|-\Lambda\rangle$ factors, so that a "unique" level is the only level of each K value where the orbital angular momentum $\langle L_z\rangle$ is not "quenched" and the spin-orbit coupling and the orbital magnetic moment attain their maximum values; only "unique" levels will have a first order orbital Zeeman effect, for the other levels of each K, the Renner-Teller effect lifts the orbital degeneracy. The energy of a "unique" level, to first order, is the same as that of the basis level $v = K - \Lambda$ given by the Hamiltonian $H_b + V_0(\rho)$, corresponding to the mean of the two Born-Oppenheimer potential curves; it strictly does not "belong" to either of the Born-Oppenheimer potential curves, and represent the largest breakdown of the Born-Oppenheimer approximation produced by the Renner-Teller effect in a linear molecule.

[2] It is the customary to label the vibronic states according to the angular momentum representations for the point groups $C_{\infty v}$ or $D_{\infty h}$, i.e., Σ, Π, Δ, ... , for $K = 0, 1, 2, \ldots$, since K, the eigenvalue of J_z, is the only "good" projection quantum number [92]. Note how both Σ^+ and Σ^- vibronic levels occur for $K = 0$; this is because the sum and difference vibronic functions
$\frac{1}{\sqrt{2}}(|\Lambda, v, l = -\Lambda\rangle \pm |-\Lambda, v, l = +\Lambda\rangle)$
have definite transformation properties under the symmetry operation σ_v for the reflection in any plane containing the linear molecule [93]. The representations Σ^+ and Σ^- correlate directly with the representations for the Born-Oppenheimer component states classified according to C_s or C_{2v} symmetry for the non-linear molecule [92, 94]. For the $^2\Pi$ states, bracketed letters show the type of spin coupling, clasified according to the Hund's coupling cases [48, 93], and subscript fractions give the value of the projection quantum number $P = K + \Sigma$ (cf. Ω in diatomic molecules [93]); subscripts r and i indicate regular and inverted spin multiplet states.

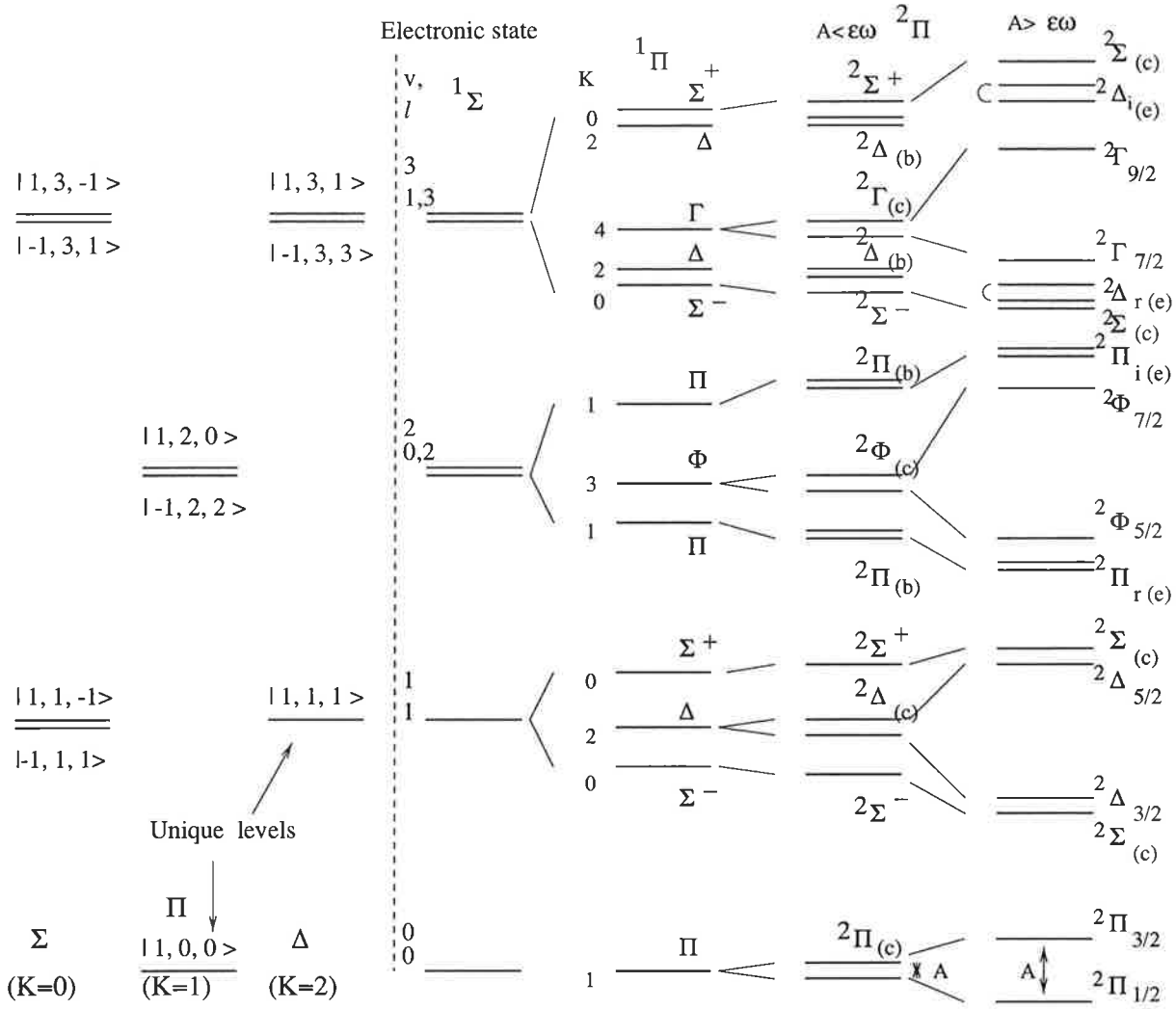

Figure 2.4: Vibronic energy levels of linear molecules in $^1\Sigma$, $^1\Pi$ and $^2\Pi$ electronic states for $v^{lin} \leq 3$ [33]. Left side of the figure shows the levels in a linear molecule, in absence of Renner-Teller effect. The levels are labeled as $|\Lambda v l\rangle$ [24]

Most of the known examples of the Renner-Teller effect occur in molecules with unpaired electron spins, where the energy level patterns are considerably modified by the spin-orbit coupling (see Fig.2.4).

Vibronic energy level expression for $^2\Pi$ states were derived by Pople [26]. Pople's treatment was extended to the $^2\Delta$ states by Merer and Travis [95].

Pople's results for the $^2\Pi$ states are easily derived by including the spin orbit operator:

$$H_{s.o} = A\, L_z\, S_z \tag{2.94}$$

as a second perturbation in addition to $H_K(\rho)$ from the eq.(2.83).

The right hand side of the Fig.(2.4) show the levels of a $^2\Pi$ state, for the cases where the spin-orbit coupling constant A is smaller or larger than the vibronic energy $\varepsilon\omega$. The diagrams correspond approximately to the $X^2{}''\Pi$ states of NCO [96] and NCS [97] respectively [33]. Good examples occur in the spectra of N_3 [98] and NCO or CCN [95] and in CNC [99].

The theory of the rotational fine structure in $^2\Pi$ and $^3\Pi$ states and of the spin-uncoupling effect when the spin-orbit coupling is large compared to $\varepsilon\omega$ has been given by Hougen [28, 100,

101]. Good examples occur in BO_2 [38] and NCO [33]. Example of the $^3\Pi$ states are found in NCN and CCO [102].

The Herzberg-Teller interaction give rise to forbidden components in an electronic transition [32], due to a nontotally symmetric vibration which couple states forbidden by the Franck-Condon principle [48, 103]. A special case of the Herzberg-Teller interaction occur in linear molecules where the "active" nontotally symmetric vibration is the bending vibration, and the mechanism of the interaction is the Renner-Teller coupling.

The principal term causing this effect is $j_1 \rho \cos(\nu - \varphi)$ in eq. (2.76), which has matrix elements of the type $\Delta\Lambda = \pm 1$, $\Delta l = \pm 1$, and $\Delta v = \pm 1$ that follow directly from the eq. (2.53). When two interacting states are close in energy, and are observed in transitions from a third state, the interaction is forced to induce vibrationally forbidden $\Delta v = \pm 1$ bands in the bending vibration in each of the two transitions, and small perturbations occur. A satisfying simple model has been given by Bolman and Brown [104], and a new term $g_K|K|$, due to the Herzberg-Teller interaction has been introduced by Bolman *et al.* [96]. This new term has been derived by Brown [34] in a second order perturbation treatment by means of the projection operator technique. Aarts [35] extended the theory by taking into account simultaneously Renner-Teller, Herzberg-Teller and spin-orbit interactions by means of a Van Vleck transformation of the Hamiltonian. Good results occur in NCS (excited electronic states $A\,^2\Pi^+$ and $B\,^2\Sigma^+$) [105], HNC^+ ($X\,^2\Pi$ and $A\,^2\Sigma^+$ states) [106], NCO ($\tilde{A}\,^2\Sigma^+$ and $\tilde{X}\,^2\Pi$ states) [96] , N_2O^+ [107, 108], NCN ($\tilde{A}^3\Pi$ state) [102, 109], and CO_2^+ [110].

Most recently, Brown and Jorgensen [111] have returned to Renner's original formulation of the problem and showed how the Renner Hamiltonian can be developed in a rigorous and natural way, that is particularly useful for fitting to experimental data.

In this formalism, the Renner operator can be written [111, 112]:

$$\begin{aligned} \mathbf{H} &= H_\sigma + H' = H_\sigma + \frac{1}{2}\varepsilon\omega\, q^2 \begin{Bmatrix} 0 & 1 \\ 1 & 0 \end{Bmatrix} \\ &= H_\sigma + \frac{1}{2}\varepsilon\,\lambda\,\rho^2\,\sigma_z \end{aligned} \tag{2.95}$$

where

- H_σ is the harmonic oscillator term ($H_\sigma = T_\sigma + \frac{1}{2}\omega q^2$ in the usual notation with q a dimensionless coordinate)
- $\varepsilon = \frac{\lambda_+ - \lambda_-}{\lambda_+ + \lambda_-}$ is the Renner parameter
- $\lambda_\pm$ are the quadratic force constants

The force constant, λ is chosen to make the second terms as small as possible ($2\lambda = \lambda_+ + \lambda_-$) and the matrix ($\sigma_z$) implies that the matrix elements of H' are between the vibronic functions belonging to different electronic states. In this formalism a harmonic basis set is used.

Several groups [113, 111, 112] have considered the effects of purely bending anharmonicities, which can be written as,

$$H_{anh} = g_4\, q^4 + \hat{g}_4\, q^4\, \sigma_z + g_K\, J_z\, \sigma_y \tag{2.96}$$

Frye and Sears [112] are used this formalism to fit the experimental data of the $^2\Pi$ electronic state in CO_2^+.

Bent and Quasi-linear Molecules

The electronic states of these molecules are nondegenerate since the bent molecule does not possess cylindrical symmetry. However, it is always possible for a bent molecule to become linear by vibration (or "quasi-linear") if its bending vibration energy is high enough. If two

electronic states of the bent molecule correlate with a single degenerate electronic state of the linear molecule, they form a Renner-Teller pair. The effects of it in the spectrum appear mainly in the form of strong vibronic interactions in levels near the energy at which the molecule become linear.

The two purely electronic potential curves are assumed initially to be coincident, and characterized by an equilibrium angle ρ_m, and a bending frequency ω; the electrostatic splitting, $V_{2\Lambda}(\rho)$ is introduced.

At energies far below the barrier to linearity, the linear molecule bending vibration corresponds to the nondegenerate bending vibration of the bent molecule plus the rotation around the a inertial axis (corresponding to Oz in the linear molecule).

In the Schrödinger equation (2.77), the electrostatic term dominates, and H^z_{rot} acts as a perturbation rather than the other way round. It is possible, as Dixon [33, 97, 114] to derive directly the coupled equations, by starting from the Born-Oppenheimer approximation and introducing a rotational-electronic Coriolis interaction. This illustrates another way of thinking of the Renner-Teller effect, in which an angular motion of the electrons in a bent molecule becomes progressively uncoupled from the nuclear frame as the molecule rotates faster around the a axis.

In general the Renner-Teller effect implies any degree of coupling between the electrons and the nuclear frame that falls "between" the limiting cases of zero coupling (in the strictly linear molecule) and rigid coupling (in the strongly bent molecule).

Instead of use the "linear molecule" choice of basis functions (2.81) in the eq.(2.79), the "bent molecule" factors, the angular part of which are defined in the eq.(2.97) are used:

$$\begin{aligned}\Psi^{\pm}_{el}(\nu-\varphi)\frac{e^{iK\varphi}}{\sqrt{2\pi}} &= \frac{1}{\sqrt{8\pi^2}}\left[e^{i\Lambda\nu}\,e^{il\varphi} \pm e^{-i\Lambda\nu}\,e^{-il\varphi}\right] \\ &= \frac{1}{\sqrt{2\pi}}e^{iK\varphi}\,\frac{1}{\sqrt{4\pi}}\left[e^{i\Lambda(\nu-\varphi)} \pm e^{-i\Lambda(\nu-\varphi)}\right] \end{aligned} \tag{2.97}$$

The factors for the eq.(2.97) describe the electronic angular motion as coupled rigidly to the instantaneous plane of the bent molecule. The electronic factors in the previous equations have definite transformation properties under the operation of the reflection in the molecular plane (which reverses the sense of the angle $\nu-\varphi$), so that they can be classified according to the representations of the point groups C_s or C_{2v}.

When the functions from the eq.(2.97) are used, the potential and coupling functions of the eq.(2.80) are,

$$\begin{aligned} U^{\pm}_K(\rho) &= V^{\pm}(\rho) + \mu^0_{zz}(K^2+\Lambda^2) \\ H_K(\rho) &= -2\,A(\rho)\,K\,\Lambda \end{aligned} \tag{2.98}$$

where the Born-Oppenheimer potentials are still given by:

$$V^{\pm}(\rho) = V_0(\rho) \pm \frac{1}{2}j_{2\Lambda}(\rho) \pm \ldots \tag{2.99}$$

In eq.(2.98), $A(\rho) = \mu^0_{zz}$ is the rotational constant corresponding to the a inertial axis.

With (2.98) and (2.99), the equation (2.80) becomes,

$$\begin{pmatrix} \omega^+(v^+ + \frac{1}{2})\delta_{vv'} + (v^+)'|A(\rho)|v^+\rangle(K+\Lambda)^2 & -2\langle(v^+)'|A(\rho)|v^-\rangle K\Lambda \\ -2\langle(v^+)'|A(\rho)|v^+\rangle K\Lambda - E_{v,K}\delta_{vv'} & \\ -2\langle v^-|A(\rho)|v^+\rangle K\Lambda & \omega^-(v^- + \frac{1}{2})\delta_{vv'} + (v^-)'|A(\rho)|v^-\rangle(K-\Lambda)^2 \\ & +2\langle(v^-)'|A(\rho)|v^-\rangle K\Lambda - E_{v,K}\delta_{vv'} \end{pmatrix} \tag{2.100}$$

where, as before,

- $\pm$ refers to the upper or lower Renner-Teller component, respectively

- the vibrational functions $|v\rangle$ are those for the one-dimensional harmonic oscillator
- K remains the vibronic angular momentum, corresponding to J_z.

The vibrational functions are labeled by the quantum number v^{bent} for the bent molecule. The functions $|v\rangle$ do not depend on the l or K, as in the case of the bidimensional oscillator. The symbol l is used as an eigenvalue of $(J_z - L_z)$, which in a bent molecule represent the nuclear rotation around the Oz axis.

In eq.(2.100) the terms in $K\Lambda$ are the exact analogs of the reordering and coupling elements-defined in the eq.(2.90-2.91). The reordering elements are diagonal in the new basis (2.97), while the coupling elements connect levels in the two electronic components. Neglecting local interactions, second order perturbation theory gives the vibronic energy level expressions [97, 33],

$$E_{v,K} = V^{\pm}(\rho_m) + A^{\pm}\Lambda^2 + \omega^{\pm}(v + \frac{1}{2}) + A^{\pm}\left[1 \pm \frac{4A^{\pm}\Lambda^2}{V^{+}(\rho_m) - V^{-}(\rho_m)}\right] K^2 \qquad (2.101)$$

The corresponding expression for $\Lambda = 0$ is the familiar:

$$E_{v,K} = V(\rho_m) + \omega(v + \frac{1}{2}) + A\,K^2 \qquad (2.102)$$

From the eq.(2.101) it can be seen that the Renner-Teller coupling affects the bent molecule levels in two ways:

- First a term $A\Lambda^2$ is added to the energy of each component
- Second, the effective rotational constant A is modified. The second effect should be taken into account when A rotational constant is used to calculate the molecular structure; since the K^2 dependence of the rotational energy is unaffected, it is essentially a large contribution to the inertial defect resulting from the electronic motion [115]

A more striking consequence of the second order Renner-Teller coupling is the appearance of transitions forbidden by the electric dipole selection rules. These will occur if the optical transitions from a third electronic state is allowed to one of the Renner-Teller components, but is forbidden to the other.

The mixing of the electronic wavefunctions is, to first order, proportional to K; the induced intensity in the forbidden transition should increase as K^2.

An example of these has been found by Jungen,Malm and Merer [116, 117, 118], who observed the electronically forbidden ${}^1A_2 - \tilde{X}^1\Sigma_g^+$ transition of CS_2, near 3400 Å.

The same results must be obtained for the vibronic energy levels whether one integrate the coupled equations (2.80) in the form of the eq.(2.83) or in the form of the eq.(2.98), sinces the choice of the basis set in immaterial. The two forms serve to illustrate the *two aspects* of the Renner-Teller effect, which may be considered as an *electrostatic perturbation on the linear molecule* or a *Coriolis perturbation on the bent molecule.* [33, 15].

In the matrix (2.100), the interacting basis levels always occur in pairs (since each vibrational level contain all the values of the rotational quantum number l), so that there are no "unique" levels in the bent molecule. "Unique" levels still exist, but their character is diluted over several levels near the barrier to linearity.

The vibronic pattern alters as the vibrational energy becomes greater than the potential barrier to linearity. The energy level pattern for a quasi-linear molecule with $\Lambda = 0$ were first described by Dixon [119]. An interesting point which Dixon discovered is that the successive vibrational intervals in a bending progression *pass through a minimum at the potential barrier* as in Fig.(2.5). Bellow the barrier, the energy roughly follow the bent molecule formula from eq.(2.102) with l substituted for K; above the barrier the levels form alternating groups with

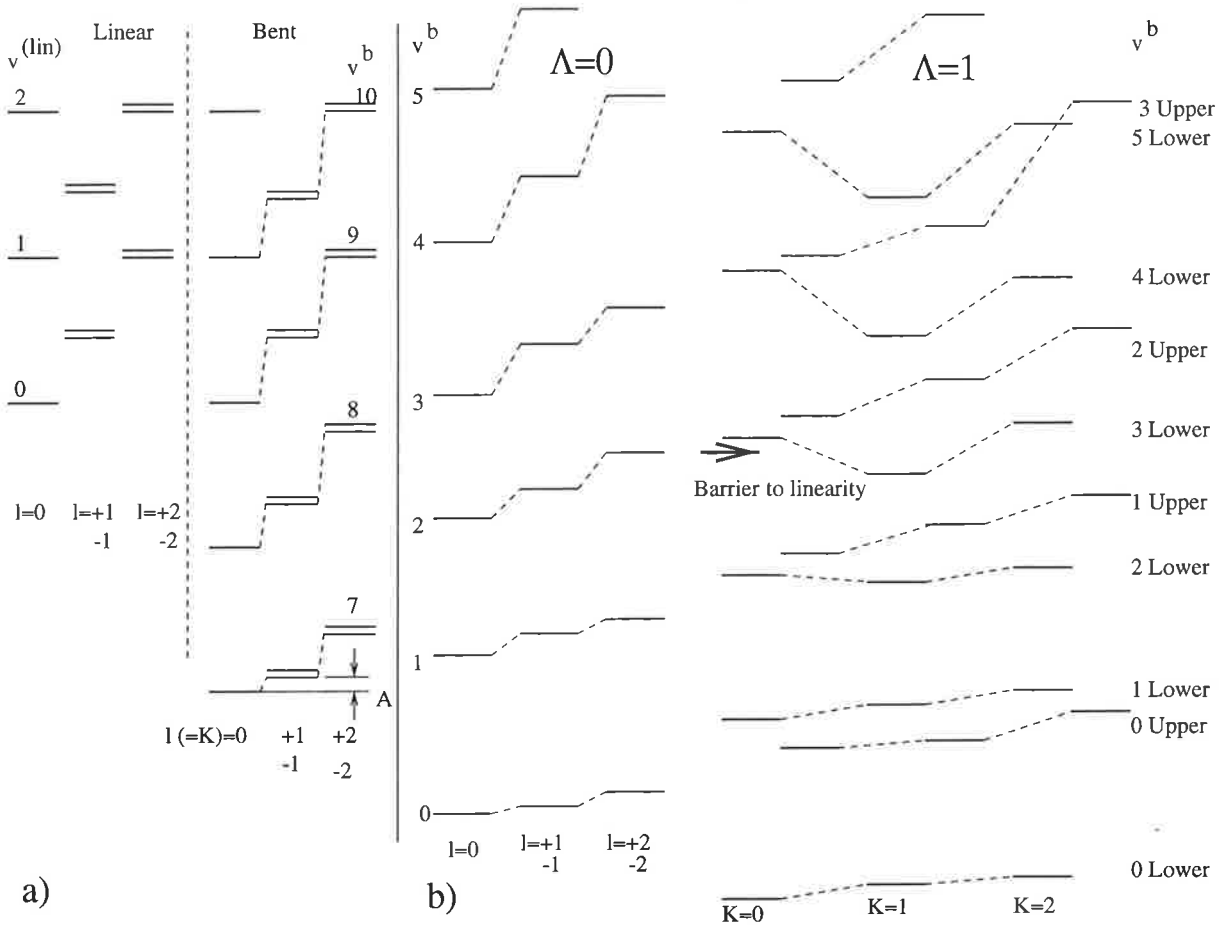

Figure 2.5: **a)** Schematic bending vibrational levels of linear and bent molecules in Σ electronic states, drawn such that the potential minimum for the linear molecule lies at the same energy as the barier to linearity of the bent molecule [15]; **b)** Vibronic energy levels of quasi-linear molecules in $^1\Sigma$ and $^1\Pi$ electronic states. The barrier to linearity is assumed to lie near the level $v^{bent} = 2$ [33] .

either even or odd values of l, as in a linear molecule. The changeover reflects the different ways in which the quantum numbers v and l are related in the two limits: for any value of l, bent molecule levels occur for all values of v^{bent}, but the linear molecule levels only occur for every second value of v^{lin}, where $v^{lin} \geq |l|$. This leads to the equation:

$$v^{lin} = 2v^{bent} + |l| \tag{2.103}$$

Consider now two vibrational progressions whose l values differ by two. Following the same argument as was used before eq.(2.93) it is found that there is always one more level with the lower of the two l values, up to any given energy above the barrier. This extra level is the analog of a "unique" level, and its accommodation in the level structure of the quasi-linear molecule requires that the levels be crowded more closely at the barrier, producing the observed minimum in a graph of the vibrational spacing against energy. The depth of this "dip" depends on l, and it is largest for $l = 0$. It disappears altogether in the limit of very large momentum, because the nuclei are then effectively held away from the linear configuration by centrifugal forces, and the presence or absence of a potential barrier is irrelevant for their motion.

The situation becomes much more complicated for $\Lambda \neq 0$. The coupling term $H_K(\rho)$ from (2.80) always has the effect of pushing the levels of a given K value to the approximate positions that the levels with $l = K \pm \Lambda$ would occupy in a molecule with $\Lambda = 0$ vibrating in the Born-

Oppenheimer potentials $V^{\pm}(\rho) = V_0(\rho) \pm j_{2\Lambda}\rho^{2\Lambda}$ .... Essentially, to obtain the $K = 0, 1, 2 \ldots$ levels of the upper or lower $^1\Pi$ electronic state Renner-Teller component, on transfers the $l = 1, 2, 3 \ldots$ or $l = -1, 0, 1, \ldots$ levels, respectively.

For $K = 0$, this procedure is exactly correct, because the vibronic coupling vanish. Since the $U_K^{\pm}(\rho)$ functions become the same as those of levels in Σ electronic states with $l = \Lambda$, it is possible to determine Λ in a quasi-linear molecule provided the $K = 0$ levels can be observed beyond the barrier.

Dixon [119] used this method to show that the $\tilde{A}^2A_1$ state of PH_2 [120] correlates with a Π electronic state of a linear molecule, and it has since been applied to the isoelectronic H_2S^+ ion [121], and to the $\tilde{A}^1A''$ state of HCCl [122] where $\Lambda = 2$.

The recipe for constructing $\Lambda = 1$ levels from $\Lambda = 0$ levels leads to an unexpected rearrangement of the $K \neq 0$ levels near the barrier to linearity. This is apparent in the pattern of $K = 1$ levels belonging to the *lower* Renner-Teller component in Fig.2.5. These *fall behind* the $K = 0$ levels with the same value of v^{bent} as the barrier is approached, and in terms of the bent molecule on would say that the apparent rotational constant $A = E^-_{v,K=1} - E^-_{v,K=0}$ becomes *negative*. This is not so surprising in terms of the linear molecule, because the lowest vibronic level has $K = 1$ in a Π electronic state. The effect provides probably the strongest experimental evidence for the presence of the Renner-Teller coupling in a non-linear molecule, because it can be seen directly in the spectrum as a reordering of the asymmetric top K-structure near the barrier to linearity.

It can happen that the potential minimum in the lower Renner-Teller component corresponds to a non-linear configuration while the molecule is linear (or very nearby so) in the upper component (see 2.2). The molecules NH_2 [12, 23], H_2O^+ [123], HCO [124], BH_2 [100], and NO_2 [125, 126] fall in this class. In all cases the lower state is the ground state and an optical transition to the upper component is observed in the visible region.

The vibronic levels of the upper component correspond to the upper halves of the patterns for each value of v^{lin} in Fig.(2.4) (the remainder, including the "unique" levels, becoming the ground state), and it can be seen from this figure that they are almost indistinguishable from those of a Σ electronic state.

Pople and Longuet-Higgins [24] proposed another way of establishing the presence of the Renner-Teller interaction, based on the effect of the reordering matrix elements for $K \neq 0$. The reordering elements describe the vibronic interaction *within* a Renner-Teller component and depend, not on the shape of the other component, but only on the *splitting parameter* $j_{2\Lambda}$. Ignoring the fact that the lower component has a very different potential function, and including a quartic term in the potential function for the upper component, the energy levels are [24, 33],

$$\begin{aligned} E^+_{v^{lin},K} &= \omega^+(v^{lin}+1) - \frac{1}{2}\varepsilon^+\omega^+\left[(v^{lin}+1) - \sqrt{(v^{lin}+1)^2 - K^2}\right] \\ &+ 3g_{22}\,(v^{lin}+1)^2 - g_{22}(K^2+1) \end{aligned} \tag{2.104}$$

In eq.(2.104) , ε^+ is defined as $\frac{j_2}{k^+}$ (where k^+ is the force constant for the upper component) so that $\varepsilon^+ = \frac{\varepsilon}{1+\varepsilon}$. Defining $\omega\sqrt{1+\varepsilon}$ in eq.(2.88), as ω^+, it follows that $\varepsilon^+\omega^+ = \frac{\varepsilon\omega}{\sqrt{1+\varepsilon}}$.

If the molecule is linear in the upper component, eq.(2.104) predicts that the reordering term should decrease with increasing v^{lin}. The predicted decrease of the vibronic reordering with v^{lin} is verified in HCO.

2.4.2 Large Amplitude treatment of the Renner-Teller Effect

Even in a nondegenerate electronic state, the region near the top of the barrier presents difficulties, because the vibrational potential function is highly anharmonic and the reduced mass changes during the vibration: any realistic treatment of the levels must be carried out numerically. Barrow, Dixon and Duxbury [82], Jungen and Merer [15] and Peric, Buenker and

Peyerimhof [127] extended the picture to include the effects of large amplitude bending motion and the complications associated with this. Finally, Carter and Handy [128] and their collaborators, principally Rosmus and Chambaud [129], extended their full three dimensional vibration-rotation Hamiltonian to include the interactions which occur in electronic states which are degenerate at linearity.

Three rather different approaches have been proposed, which use the variational calculations involving the diagonalization of the Hamiltonian matrix for the rotation and bending of a triatomic molecule in a given bending potential.

K-Basis Formalism

Dixon and Duxbury [82, 121, 130, 131] do not attempt to integrate the coupled equations (2.80) directly, but instead they use two "effective" potentials $V^{\pm}_{eff}(\rho)$ for the calculation of the large amplitude motion in the two components. These are obtained by diagonalizing at each ρ value the 2x2 matrix formed by the quantities $U^{\pm}_K$ and $H_K(\rho)$ from the eq.(2.98). This procedure amounts to taking for the wavefunctions the linear combinations from (2.97) for each value of ρ.

The resulting "effective" potentials are the same no matter whether the definitions shown in the eq.(2.83) or (2.98) are used for $U^{\pm}_K(\rho)$ and $H_K(\rho)$, so that they combine the characteristics of the Renner-Teller effect in both linear and bent molecules, and therefore accounts, in some average way, for the vibronic interaction in a quasi-linear molecule.

The potentials $V^{\pm}_{eff}(\rho)$, serve for the numerical evaluation of bending levels and wavefunctions in the two "effective" electronic components separately :

$$\begin{aligned} V^{\pm}_{eff}(\rho) &= \frac{1}{2}\left[V^{+}(\rho)+V^{-}(\rho)\right] + A(\rho)\left(K^2+\Lambda^2\right) \\ &\pm \sqrt{\frac{1}{4}\left[V^{+}(\rho)-V^{-}(\rho)\right]^2 + \left[2A(\rho)K\right]^2} \end{aligned} \tag{2.105}$$

The transformation giving $V^{\pm}_{eff}(\rho)$, [82, eq.(16)],is a contact transformation [82, 131]:

$$\begin{pmatrix} \cos\gamma(\rho) & \sin\gamma(\rho) \\ -\sin\gamma(\rho) & \cos\gamma(\rho) \end{pmatrix} (H_b + H_{ev}) \begin{pmatrix} \cos\gamma(\rho) & -\sin\gamma(\rho) \\ \sin\gamma(\rho) & \cos\gamma(\rho) \end{pmatrix} \tag{2.106}$$

equivalent to the use of rotationally adiabatic potential curves at each value of ρ. In the previous equation, the vibronic perturbation operator is [82]:

$$H_{ev} = \left[V^{+}(\rho)-V^{-}(\rho)\right]\cos 2\Lambda\rho \tag{2.107}$$

- H_b is the large amplitude Hamiltonian defined in (2.72-2.73)
- $\gamma(\rho)$ is a function of ρ, chosen to diagonalise all of H, except the nuclear kinetic operator $T(\rho)$. The functional dependence of $A(\rho)$ and $[V^{+}(\rho)-V^{-}(\rho)]$ with ρ then leads to $\gamma \to 0$, when ρ is large, and $\gamma \to \frac{\pi}{4}$ as $\rho \to 0$.

Additional vibronic interaction occurs for $K \neq 0$ because the transformation giving $V^{\pm}_{eff}(\rho)$ is a function of ρ and does not commute with the bending Hamiltonian H_b. This is then accounted for in a final step by setting up a perturbation energy matrix, with the elements :

$$\begin{aligned} H'_{ij} &= \langle \Phi^{+}_{i,k} | T(\rho)\gamma - \gamma T(\rho) | \Phi^{-}_{j,k} \rangle \\ &= \left(E^{+}_i - E^{-}_j\right)^{(0)} \langle \Phi^{+}_{i,k} | \gamma | \Phi^{-}_{j,k} \rangle - \langle \Phi^{+}_{i,k} | \gamma \left(V^{+}(\rho)-V^{-}(\rho)\right) | \Phi^{-}_{j,k} \rangle \end{aligned} \tag{2.108}$$

It should be noted that the choice of γ leads to a boundary condition for the upper state vibronic wavefunctions corresponding to $l \equiv |K+\Lambda|$ as $\rho \to 0$, and $l \equiv |K-\Lambda|$ for the lower state. This choice builds into the zero order problem the inversion of the part from the K structure of the

upper levels corresponding to the lower state, the presence of which may be interred from a correlation diagram between the levels of a linear and a bent state.

The method has been successfully applied to several molecules in instances where the bending levels are known up to the potential barrier: PH_2 [82, 119, 130, 132, 133, 134, 135, 136], CS_2 [82, 137, 138]. The authors point out, however, that their approach may describe levels above the barrier less successfully. The reason is a less flexible choice of the wavefunctions, due to only one transformation applied to the Hamiltonian, compared with two transformations, in the case of l - basis formalism described below. Extension of this model have been made by Duxbury and Dixon [16] and by Alijah and Duxbury [139] .

K-Basis Formalism Using Three-dimensional Bending and Stretching Potential Surface

The bent molecule "K basis" has recently been adopted by Jensen *et al.* [141]. The work is based on the MORBID Hamiltonian and computer program [7, 87, 88] for the variational calculation of the rotation-vibration energy levels of a triatomic molecule from the potential energy function.

The resulting 2x2 interaction matrix has the same form as in the previous section, with the kinetic energy operator from MORBID, and a $V^{\pm}_{eff}(\rho)$ similar with (2.105) is obtained. The ro-vibronic wavefunctions are linear combinations of the basis functions describing the bending and stretching motion. The symmetry of the rotation- spin basis functions are labeled as the irreductible representations of C_s and $C_{2v}$from [92], and the rotational basis functions have relative phases differing from those chosen by Hallin and Merer [140]. The $\tilde{a}^1A_1$ and $\tilde{b}^1B_1$ electronic states of CH_2 are analyzed in [141] compared with [142, 143, 144], and a range of hybrids in [145].

Other variational calculus using the full three-dimensional bending and stretching potential surface have been carried out by Carter, Handy and co-workers [19, 128, 129, 142] and by Tennyson and Sutcliffe [20] who developed general methods using an instantaneous axes system. More recently, Alijah, Hinze and Wolniewicz [146] developed an alternate method based on a hyperspherical harmonic expansion of the total wavefunction. This approach is completely general and allow all the nuclear displacements to be of large amplitude, but requires a rather complete knowledge of the entire potential energy surface of the electronic state being studied.

l-Basis Formalism

An attempt to overcome the difficulty from the K-basis (the effective potentials do not contain l as quantum number) have been made by Jungen and Merer [15, 147], who, following Renner, use a matrix approach and start out from the coupled equations shown in eq.(2.80) in their linear molecule form, with eq.(2.83). The approach differs from that of the Barrow, Dixon and Duxbury [82] in that, here the vibronic energy matrix is transformed rather than the Hamiltonian in order to minimize the coupling elements. Briefly, the method is the following. The coupled differential equations (2.80) can be set up as a matrix, whose eigenvalues are the required energy levels. The large amplitude radial functions $\Phi_{v,l}(\rho)$, corresponding to the Born-Oppenheimer potentials, can be obtained by treating them as belonging to a Σ electronic state; for particular K the values of l are chosen according to (2.82). For any chosen value of K, the vibrational basis functions are obtained by integrating the differential equations:

$$\left[H_b + \frac{1}{2}\hbar^2\mu^0_{zz}(\rho)\, l^2 - V^-(\rho) - E^-_{v,l}\right]\Phi^-_{v,l}(\rho) = 0 \tag{2.109}$$

The form of the basis functions near the linear configuration is obtained from an exact series solution of the wave equation (2.109). The differential equation to be solved can be expressed in the form [147, 5, 57]:

$$\left(\frac{\partial^2}{\partial\rho^2} - \frac{l^2 - \frac{1}{4}}{\rho^2} + p + q\rho^2 + r\rho^4\right)\Phi_{v,l}(\rho) = 0 \tag{2.110}$$

where p,q,r are the coefficients representing the potential function and the large amplitude mass correction. The $r(\rho)$ dependence of the bond length with the bending angle in the semirigid bender model have been taken as, [147]:

$$r(\rho) = r^0 + d_1 \tan^2\left(\frac{1}{2}\rho\right) + d_2\,\rho^2 \tag{2.111}$$

The potential function in (2.109) is chosen either in a linear molecule harmonic oscillator function plus a Lorentzian perturbation,

$$V(\rho) = \frac{1}{2}k\,\rho^2 + \frac{a}{b+\rho^2} + \text{correction terms} \tag{2.112}$$

where the correction terms may be needed to polish the shape of the potential [147], or the alternative form of Dixon *et. all* [121, 147],

$$V(\rho) = \frac{hf\left(\rho^2 - \rho_{min}^2\right)^2}{f\rho_{min}^4 + (8h - f\rho_{min}^2)\,\rho^2} \tag{2.113}$$

In eq.(2.113) h is the barrier to linearity for the Born-Oppenheimer component and f is the harmonic oscillator force constant for bending near the equilibrium angle ρ_{min}. The relationship between the sets of parameters in (2.112) and (2.113) is done in [147, eq.(3),(4)].

The integration of (2.109) must be performed twice, with l taking the values $K-\Lambda$ and $K+\Lambda$, respectively, according to (2.82). From (2.83), the elements of $\mathbf{H}$ matrix are those of the coupling function $H_K(\rho)$ between the vibrational basis functions, with the energies of the basis levels added to the diagonal:

$$\begin{aligned} H_{v,v'}^{\pm\pm} &= E_{v,l=K\pm\Lambda}^{-}\,\delta_{v,v'} + \langle\Phi_{v,K\pm\Lambda}^{-}(\rho)|H_K(\rho)|\Phi_{v,K\pm\Lambda}^{-}(\rho)\rangle \\ H_{v,v'}^{-+} &= H_{v',v}^{+-} = \langle\Phi_{v,K-\Lambda}^{-}(\rho)|H_K(\rho)|\Phi_{v',K+\Lambda}^{-}(\rho)\rangle \end{aligned} \tag{2.114}$$

The block structure of the $\mathbf{H}$ matrix is already apparent: there are two diagonal blocks, $\mathbf{H}^{++}$ and $\mathbf{H}^{--}$, which contain integrals over basis functions with the same l value, and two off-diagonal blocks $H^{+-} = (H^{-+})^{+}$ which contain only coupling elements.

For large amplitude vibrational motion the off-diagonal elements become very large and a direct diagonalization loses track of what the levels are. It is necessary to perform a matrix transformation of $\mathbf{H}$ which minimizes the coupling elements and at the same time allows each level to be given a set of definite labels.

The transformation performed in $\mathbf{H}$ is an orthogonal transformation [15]:

$$\mathbf{H}' = \mathbf{S}^{+}\,\mathbf{H}\,\mathbf{S} \tag{2.115}$$

$\mathbf{S}$ has the same block structure as $\mathbf{H}$ and is a generalization of Renner's original $\mathbf{S}$ transformation [15]. The $\mathbf{S}$ matrix transformation is analogous to the contact transformation used by Dixon and Duxbury [82]. The procedure for constructing the $\mathbf{S}$ matrix follows the method used by Lewis and Hougen [15, 148] to eliminate coordinate dependent coupling terms from a matrix formulation of a pair of coupled differential equations.

A phase angle $\alpha(\rho)$ is introduced such that an orthogonal transformation of the coupled equations, corresponding to a rotation through the angle $\alpha(\rho)$, removes the coupling for each value of ρ. To eliminate the coupling term from (2.83), the functions are defined:

$$\begin{aligned} \cos\alpha(\rho) &= \frac{\mathbf{H}_K(\rho)}{\sqrt{\Theta^2(\rho) + \mathbf{H}_K^2(\rho)}} \\ \sin\alpha(\rho) &= \frac{\Theta(\rho)}{\sqrt{\Theta^2(\rho) + \mathbf{H}_K^2(\rho)}} \end{aligned} \tag{2.116}$$

where:

- $$\Theta(\rho) = \sqrt{\left[\hbar^2\,\mu^0_{zz}(\rho) K\,\Lambda\right]^2 + \mathbf{H}_K(\rho)^2} - \hbar^2\,\mu^0_{zz}(\rho)\,K\,\Lambda \tag{2.117}$$

- S matrix is constructed by integrating over the vibrational basis functions:

$$\begin{aligned} \mathbf{S}^{\pm\pm}_{v,v'} &= \langle \Phi^-_{v,K\pm\Lambda}(\rho)|\cos\alpha(\rho)|\Phi^-_{v',K\pm\Lambda}(\rho)\rangle \\ -\mathbf{S}^{-+}_{v,v'} &= \mathbf{S}^{+-}_{v',v} = \langle \Phi^-_{v,K-\Lambda}(\rho)|\sin\alpha(\rho)|\Phi^-_{v',K+\Lambda}(\rho)\rangle \end{aligned} \tag{2.118}$$

The orthogonality of the basis functions is preserved in the construction of **S**, so that its rows are orthogonal, except for effects resulting from the incompleteness of the basis set. To allow from these **S** is subject to a symmetric orthogonalization [149],

$$\mathbf{S}^{orth} = \mathbf{B}^+\,\mathbf{d}^{-\frac{1}{2}}\,\mathbf{B}\,\mathbf{S} \tag{2.119}$$

where **B** is the matrix of eigenvectors ($\mathbf{SS}^+$) and **d** is the diagonal matrix of the eigenvalues of ($\mathbf{SS}^+$). More comments about the **S** matrix can be found in [15]. The generalized transformation (2.115), changes over smoothly from one limiting case to the other; in this way the elements of the vibronic energy matrix are minimized both above and below the barrier to linearity [33].

The largest breakdown of the Born-Oppenheimer approximation occurs, in this approach, near the barrier to linearity, because this is where the "unique" level lies, and the "unique" level is essentially the one responsible for the mismatch of the two limiting transformations; the generalized transformation dilute the character of the "unique" level over several vibrational levels in this region.

After the transformation (2.115), the diagonal blocks $(\mathbf{H}')^{++}$ and $(\mathbf{H}')^{--}$ have off-diagonal elements which represent vibronic coupling *within* each component state, corresponding to the process of turning an electronic Σ state into half a Π state for $\Lambda = 1$. The elements of the off-diagonal blocks represent vibronic coupling *between* the components, corresponding to the interactions between the halves of a Π state. From the comments after eq. (2.89) and (2.90 - 2.92), these elements are "reordering" and "coupling", respectively.

At this point the elements of $(\mathbf{H}')^{--}$ $(\mathbf{H}')^{+-}$ and $(\mathbf{H}')^{-+}$ have been minimized, but those of $(\mathbf{H}')^{++}$ still contain the large terms required to construct the upper state potential by adding the perturbation $\mathbf{H}_K(\rho)$ to the lower state potential. If these terms are removed, the coupling can be formulated more explicitly in terms of the two potentials.

Accordingly, the upper component basis function for $l = K + \Lambda$ are computed by integrating the equation :

$$\left[\mathbf{H}_b + \frac{1}{2}\mu^0_{zz}(\rho)\,(K+\Lambda)^2 + V^+(\rho) - E^+_{v,K+\Lambda}\right]\,\Phi^+_{v,K+\Lambda}(\rho) = 0 \tag{2.120}$$

and set up the overlap matrix **T**, defined as:

$$\begin{aligned} \mathbf{T}^{--}_{v,v'} &= \delta_{v,v'} \qquad ; \qquad \mathbf{T}^{+-}_{v,v'} = \mathbf{T}^{-+}_{v,v'} = 0 \\ \mathbf{T}^{++}_{v,v'} &= \langle \Phi^-_{v,l=K+\Lambda}(\rho)|\Phi^+_{v,l=K+\Lambda}(\rho)\rangle \end{aligned} \tag{2.121}$$

T is in block form, like **H** and **S**, and it is a unit matrix except for $\mathbf{T}^{++}$ block, which contains the overlap integrals required to transform $\mathbf{H}'$, where necessary, to the upper component basis.

The next step is to subtract from $(\mathbf{H}')^{++}$ those terms that build the upper component as a perturbation in the lower; only the (much smaller) reordering elements remain:

$$[\mathbf{H}'_{reord}]^{++}_{v,v'} = (\mathbf{H}')^{++}_{v,v'} - E^-_{v,l=K+\Lambda}\,\delta_{v,v'} - \langle \Phi^-_{v,l=K+\Lambda}(\rho)|2H_K(\rho)|\Phi^-_{v',l=K+\Lambda}(\rho)\rangle \tag{2.122}$$

Then $\mathbf{H}'$ in its modified form is transformed:

$$\mathbf{H}'' = \mathbf{T}^+\,\mathbf{H}'\,\mathbf{T} \tag{2.123}$$

Finally, the *exact* upper component energies, $E^{+}_{v,l=K+\Lambda}$, from (2.120), are added to $(\mathbf{H}'')^{++}$, and $\bar{\mathbf{H}}''$ is diagonalized to give the vibronic energies.

A key quantity in Renner-Teller effect is the expectation value $\langle L_z \rangle$ in a vibronic level. Its magnitude may be inferred directly from the extent to which the mixture of $|+\Lambda\rangle$ and $|-\Lambda\rangle$ functions is unbalanced. The quantity $\langle L_z \rangle$ tells up how freely in space the electronic orbital motion occurs, and is therefore a measure of the breakdown of the Born-Oppenheimer approximation.

In a bent molecule, the L_z operator has the expression [15]:

$$\langle {}^{e}A_1 | L_z | {}^{e}B_1 \rangle = \zeta_e^{(z)} \hbar = \hbar\Lambda \left[1 - \frac{g_K}{2A(\rho)\,\Lambda} \right] \tag{2.124}$$

with g_K introduced by Brown [34] to explain the effects of the admixture of Σ and Δ state character into the electronic Π state. The g_K element has the formula:

$$g_K = \frac{1}{2} A(\rho)\, \rho^2 \sum_{\eta'} (-1)^p \frac{|\langle \eta | j_1 | \eta' \rangle|^2}{(\Delta E)^2} \tag{2.125}$$

where $p = 0$ for $(\Lambda - 1)$ states and 1, for $(\Lambda + 1)$ states.

In levels above and below the barrier L_z is "quenched", and a small amount of orbital angular momentum, proportional to K, is build up only by the effect of the vibronic coupling elements. The orbital angular momentum reaches a maximum in the levels near the barrier, where for $K \neq 0$ the "unique" level lies, and the vibronic interaction is largest; its dependence with K will be small at this energy.

The quantity $\langle L_z \rangle$ is easy to calculate. $\mathbf{L}$ is transformed according to the expression:

$$\mathbf{L}''' = (\mathbf{S}\,\mathbf{T}\,\mathbf{U})^{+}\ \mathbf{L}\,\mathbf{S}\,\mathbf{T}\,\mathbf{U} \tag{2.126}$$

where the matrix $\mathbf{U}$ contains the eigenvectors of $\mathbf{H}''$, and the required quantities $\langle L_z \rangle$ are the diagonal elements of $\mathbf{L}'''$.

Gauyacq and Jungen [113] introduced two dimensionless parameters ε_1 and ε_2, related to the dipolar (Hertzberg-Teller) and quadrupolar (Renner-Teller) terms:

$$k\varepsilon_1 = -\frac{|\langle \eta | j_1 | \eta' \rangle|^2}{2\Delta E} \qquad\qquad k\varepsilon_2 = \langle \eta | j_2 | \eta \rangle \tag{2.127}$$

with

- $k = \frac{(k^{+}+k^{-})}{2(1+\varepsilon_1)}$
- $\Delta E = E(\Sigma^{+}) - E(\Pi)$ states.

The Renner parameter ε and g_K are expressed as functions of ε_1 and ε_2 as, [113]:

$$\varepsilon = \frac{k^{+}-k^{-}}{k^{+}+k^{-}} = \frac{\varepsilon_1+\varepsilon_2}{1+\varepsilon_1} \quad \text{and} \quad g_K = -\frac{\varepsilon_1 \omega_m^2}{2\Delta E(1+\varepsilon_1)} \tag{2.128}$$

with $\omega_m = \frac{\omega^{+}+\omega^{-}}{2}$ and according to the eq.(2.127), ε_1 has a sign opposite to that of the ΔE so that g_K is positive.

The method described in this section has been applied to the vibrational and K-type rotational structure in $A\,^2A_1 - X\,^2B_1$ transitions of NH_2 and H_2O^{+} [147], as well as for spin and rotational fine structure effects in the same molecules [150]. The electronic orbital momentum effects in the $\tilde{A}^1\Pi_u$ state of C_3 have been considered [151], and the anharmonic effects in the CO_2^{+} molecule [113]. A quantitative description of $\tilde{a}^1A_1$ and $\tilde{b}^1B_1$ states of the CH_2 [152], as well as the bending potential energy curves for N_2O^{+} and CO_2^{+} molecules have been discussed [153], based on this approach.

2.5 Stretching Vibrations

The small amplitude stretching vibrations are treated in the normal coordinate formalism (see §2.1.4) as separate harmonic oscillators, described by (2.38). This is the case of the rigid bender approach (see §2.3.2) and the perturbational approach for the vibration energies of the molecules (see §2.2). The eigenvalues of the stretching Hamiltonian are [5, 6, 18] :

$$E_{v_1,v_2} = hc \sum_{r=1,3} \omega_r(\rho_e) \left(v_r + \frac{1}{2}\right) \tag{2.129}$$

and are added to the bending potential, because of ρ dependence of $\omega_r(\rho_e)$. In the rigid bender model, the coupling between large amplitude bending and small amplitude stretching is completely neglected; this is an unsatisfactory approximation.

An improved description is obtained in the semi-rigid bender Hamiltonian, where anharmonic terms are considered [6, 18] :

$$E_{v_1,v_3} = hc \sum_{r=1,3} \omega_r(\rho) \left(v_r + \frac{1}{2}\right) + hc \sum_{r \geq s} \chi_{rs}(\rho) \left(v_r + \frac{g_r}{2}\right) \left(v_r + \frac{g_s}{2}\right) \tag{2.130}$$

and the g_i is the degeneracy of the vibration v_i. The functions $\omega_r(\rho)$, $\chi_{rs}(\rho)$ are usually modelled as power series in ρ; the coefficients in these series are determined by fitting to experiment. In the semirigid bender model one must be careful in interpreting the bond length and bond angles variations that come out of a semirigid bender fit [18]. From the eq. (2.130) , each (v_1, v_3) state will have slightly different effective bending potential functions within which the (slow) bending motion take place. This is a result of the stretch-bender anharmonicity interaction terms in the full potential energy expression. Probably the most interesting result of the semirigid bender fit is the variation of $V_{eff}(\rho)$ with the small amplitude quantum numbers v_r.

In the case of MORBID or RENNER Hamiltonians, where an interaction matrix is set-up, the basis stretching functions are eigenfunctions of the stretching Hamiltonian [6, 141],

$$\begin{aligned} H_{str} &= \frac{1}{2}\left[\frac{1}{m_1} + \frac{1}{m_2}\right] \hat{P}_1^2 + \frac{1}{2}\left[\frac{1}{m_3} + \frac{1}{m_2}\right] \hat{P}_3^2 \\ &- \frac{1}{m_2} \cos\rho_e^{(\mp)}\, \hat{P}_1\, \hat{P}_3 + V(\Delta r_{12}, \Delta r_{23}) \end{aligned} \tag{2.131}$$

when the molecule stretch with the bond angles fixed at the value $(\pi - \rho_e)$.

The matrix of H_{str} is set up in a basis of Morse oscillator product functions (symmetrized for an AB_2 molecule, and unsymmetrical for a ABC molecule), and is diagonalized using Householder's method [7, 21].

In the case of the non-rigid bender Hamiltonian, in order to perform the perturbation calculation, the zeroth order stretching Hamiltonian is defined as the harmonic oscillator [6, 17], by eq.(2.38), using the normal coordinates. Because the perturbation theory is used to treat the effects of the small amplitude vibrations, the effects of resonances between states involving different amounts of excitation of these vibrations are not allowed for. These effects have to be treated by performing a matrix diagonalization of the Hamiltonian *between the states in resonance* [18].

2.6 Fermi Interaction

If in eq.(2.44) the zeroth order frequency $\omega_{s''}$ lies close to ω_s and $\omega_{s'}$, the coefficient of the cubic term $k_{ss's''}$ blows up and the phenomenon is described as Fermi resonance, when $k_{ss's''} \neq 0$.

The Fermi resonance operator is diagonal in Σ and Λ, but, as the Fig.2.4 suggests, the levels forming a Fermi polyad will have different spin-orbit splittings and different contributions to the energy from vibronic coupling of the Renner-Teller effect [33].

2.6.1 Fermi Resonance in Linear Triatomic Molecules in Π Electronic States

The treatment of Fermi (valid for the Σ states), was extended for linear molecules in degenerate electronic states by Hougen [37], providing that the spin-orbit interaction and the Renner-Teller interaction are both small compared to the frequency of the bending vibration.

The potential energy function V, giving the total energy, can be expressed in the usual fashion:

$$V^{\pm}(q_2, Q_1, Q_3) = \frac{1}{2}\sum_{r=1,3} k_{rr}\, Q_r^2 + \frac{1}{2}\, k_{22}^{\pm}\, q_2^2 + \frac{1}{2} f_{122}^{\pm}\, q_2^2\, Q_1 + \ldots \tag{2.132}$$

Only the anharmonic term $f_{122} q_2^2 Q_1$ has been included in eq.(2.132), that one which leads to Fermi resonance between states of the type $(v_1 + 1\,, v_2\,, v_3)$ and $(v_1\,, v_2 + 2\,, v_3)$. The quantity $f_{122} Q_1$ can be thought of as the second term in a power series development in the variable Q_1 of the force constant for the bending vibration,

$$\begin{aligned} k(Q_1) &= k_{Q_1=0} + \left(\frac{\partial k}{\partial Q_1}\right)_{Q_1=0} Q_1 + \frac{1}{2}\left(\frac{\partial k^2}{\partial Q_1^2}\right)_{Q_1=0} Q_1^2 + \ldots \\ &= k_{22} + f_{122} Q_1 + \ldots \end{aligned} \tag{2.133}$$

In general $k_{22}^{+} \not= k_{22}^{-}$ and $f_{122}^{+} \not= f_{122}^{-}$. The inequality between the quantities $k_{22}^{\pm}$ leads to the Renner-Teller effect described in (§2.4), and characterized by the parameter ε from (2.128).

The basis set of wavefunctions $|v_1, v_2, v_3\,; \Lambda\,, l\,\Sigma\rangle$ are characterized by the vibrational quantum numbers v_1, v_2, v_3 and also by the quantum numbers Λ, l, Σ, which describe, respectively, the projection along the linear axis of the electronic orbital angular momentum, the vibrational angular momentum, and the electronic spin angular momentum.

The term of interest can be taken to be:

$$V_F = \frac{1}{2}\,(f^{+} + f^{-})\; Q_1\, q_2^2 + \frac{1}{2}\,(f^{+} - f^{-})\; Q_1\, q_2^2 \cdot 2\cos 2(\nu - \varphi) \tag{2.134}$$

with the definition of the angles from the Fig.(2.3). The electronic part of wavefunctions are those defined in eq.(2.81). If we use instead the symmetry functions of eq.(2.97), the expectation value of (2.134) is $f^{+}\, Q_1\, q_2^2$ for any symmetric state and is $f^{-}\, Q_1\, q_2^2$ for any antisymmetric state.

The quantity $\frac{1}{2}\,(f^{+} + f^{-})$ can be considered to represent the second term in power series expansion in the variable Q_1 of the average force constant of the bending vibration. The quantity $\frac{1}{2}\,(f^{+} - f^{-})$ can be considered to represent the second term in a power series expansion in the variable Q_1 of a quantity proportional to the Renner-Teller parameter ε.

The phases of the bidimensional oscillator used in the calculus are those of the eq.(2.51), and the matrix elements of V_F, arising from the harmonic oscillator $\langle Q_1 \rangle$ matrix elements and the eq.(2.53) are

$$\begin{aligned} \langle v_1+1, v_2, v_3; \Lambda, l, \Sigma | V_F | v_1, v_2+2, v_3; \Lambda, l, \Sigma\rangle &= W_1 \sqrt{(v_1+1)(v_2+2-l)(v_2+2+l)} \\ \langle v_1+1, v_2, v_3; \Lambda, l, \Sigma | V_F | v_1, v_2+2, v_3; \Lambda \mp 2, l \pm 2, \Sigma\rangle &= W_2 \sqrt{(v_1+1)(v_2+2+l)(v_2+4+l)} \\ \langle v_1+1, v_2, v_3; \Lambda, l, \Sigma | V_F | v_1, v_2, v_3; \Lambda, l, \Sigma\rangle &= 2W_1 \sqrt{v_1+1}\,(v_2+1) \\ \langle v_1+1, v_2, v_3; \Lambda, l, \Sigma | V_F | v_1, v_2, v_3; \Lambda \mp 2, l \pm 2, \Sigma\rangle &= 2W_2 \sqrt{(v_1+1)(v_2 \mp l)(v_2+2 \pm l)} \end{aligned} \tag{2.135}$$

where the Fermi parameters defined by Hougen [37] are,

$$\begin{aligned} W_1 &= \frac{1}{2}\,(f^{+} + f^{-}) \sqrt{\frac{\hbar}{m\omega_1}} \left(\frac{\hbar}{m\omega_2}\right) \\ W_2 &= \frac{1}{2}\,(f^{+} - f^{-}) \sqrt{\frac{\hbar}{m\omega_1}} \left(\frac{\hbar}{m\omega_2}\right) \end{aligned} \tag{2.136}$$

Obs. If the force constant and the vibration frequency are in cm^{-1}, the multiplication constant will be: $\sqrt{\frac{\tilde{\omega}_1}{2\tilde{f}_{11}}}\left(\frac{\tilde{\omega}_2}{2\tilde{f}_{22}}\right)$

In the case of a $^1\Pi$ state, for the (100) and (020) states, the energy matrix of interacting states is,

$$\begin{pmatrix} \Delta & (\sqrt{2}\,W_1+2\,W_2)\left(1-\frac{\varepsilon}{\sqrt{2}}\right) & (-\sqrt{2}\,W_1+2\,W_2)\left(1+\frac{\varepsilon}{\sqrt{2}}\right) \\ (\sqrt{2}\,W_1+2\,W_2)\left(1-\frac{\varepsilon}{\sqrt{2}}\right) & +s-C & 0 \\ (-\sqrt{2}\,W_1+2\,W_2)\left(1+\frac{\varepsilon}{\sqrt{2}}\right) & 0 & -s-C \end{pmatrix} \tag{2.137}$$

The matrix elements in (2.137) were computed using the vibronic wavefunctions obtained from a first order perturbation treatment of the Renner-Teller effect

$$\begin{array}{l} |100;10\rangle^{(1)} \\ \frac{1}{\sqrt{2}}\left(|020;10\rangle^{(1)}+|020;-12\rangle^{(1)}\right) \\ \frac{1}{\sqrt{2}}\left(-|020;10\rangle^{(1)}+|020;-12\rangle^{(1)}\right) \end{array} \tag{2.138}$$

and hence are correct only through terms linear in ε (and the results are valid when the parameter ε is small compared to unity).

The off-diagonal elements represent the Fermi interaction, and the diagonal elements represent the energy of the three states in the absence of the Fermi resonance. The zero of energy has been arbitrary chosen as the energy of the components of the unperturbed (020) vibrational state in the absence of any Renner-Teller interaction and of any anharmonic perturbation involving the bending vibration Fig.(2.6).

The relative position of the unperturbed (100) vibrational state is specified by the single parameter Δ. When the Renner-Teller effect is taken into account, from the eq.(2.89), the shift is:

$$\pm s-C=\pm\frac{1}{2}\varepsilon\omega_2\sqrt{(v_2+1)^2-K^2}-\frac{1}{8}\varepsilon^2\,\omega_2\,(v_2+1) \tag{2.139}$$

In the case of a $^2\Pi$ electronic state, the spin-orbit interaction is added to the previous discussion. The Fermi diad (100)-(020) of a $^2\Pi$ molecule breaks up into two groups of three states each, which can be considered separately; the states with $|P|=|\Lambda+l+\Sigma|=\frac{1}{2}$, and the states with $|P|=\frac{3}{2}$. Such a factorization of the energy matrix is possible since P is a good quantum number for the molecule in the absence of the rotation.

The wavefunctions for $|P|=\frac{1}{2}$, expressed by first-order wavefunctions $|\cdots\rangle^{(1)}$, are:

$$\begin{array}{l} |100;1,0,-\frac{1}{2}\rangle^{(1)} \\ \sin\beta|020;1,0,-\frac{1}{2}\rangle^{(1)}+\cos\beta|020;-1,2,-\frac{1}{2}\rangle^{(1)} \\ -\cos\beta|020;1,0,-\frac{1}{2}\rangle^{(1)}+\sin\beta|020;-1,2,-\frac{1}{2}\rangle^{(1)} \end{array} \tag{2.140}$$

and for $|P|=\frac{3}{2}$,

$$\begin{array}{l} |100;1,0,\frac{1}{2}\rangle^{(1)} \\ \cos\beta|020;1,0,\frac{1}{2}\rangle^{(1)}+\sin\beta|020;-1,2,\frac{1}{2}\rangle^{(1)} \\ -\sin\beta|020;1,0,\frac{1}{2}\rangle^{(1)}+\cos\beta|020;-1,2,\frac{1}{2}\rangle^{(1)} \end{array} \tag{2.141}$$

The elements of the interaction matrix for $|P|=\frac{1}{2}$ are,

$$\begin{array}{ll} H_{11}=\Delta-\frac{1}{2}A & H_{12}=H_{21}=2(W_1-\varepsilon W_2)\sin\beta+\sqrt{2}(2W_2-\varepsilon W_1)\cos\beta \\ H_{22}=+r+\frac{AKC}{2r}-C & H_{13}=H_{31}=-2(W_1-\varepsilon W_2)\cos\beta+\sqrt{2}(2W_2-\varepsilon W_1)\sin\beta \\ H_{33}=-r-\frac{AKC}{2r}-C & H_{23}=H_{32}=0 \end{array} \tag{2.142}$$

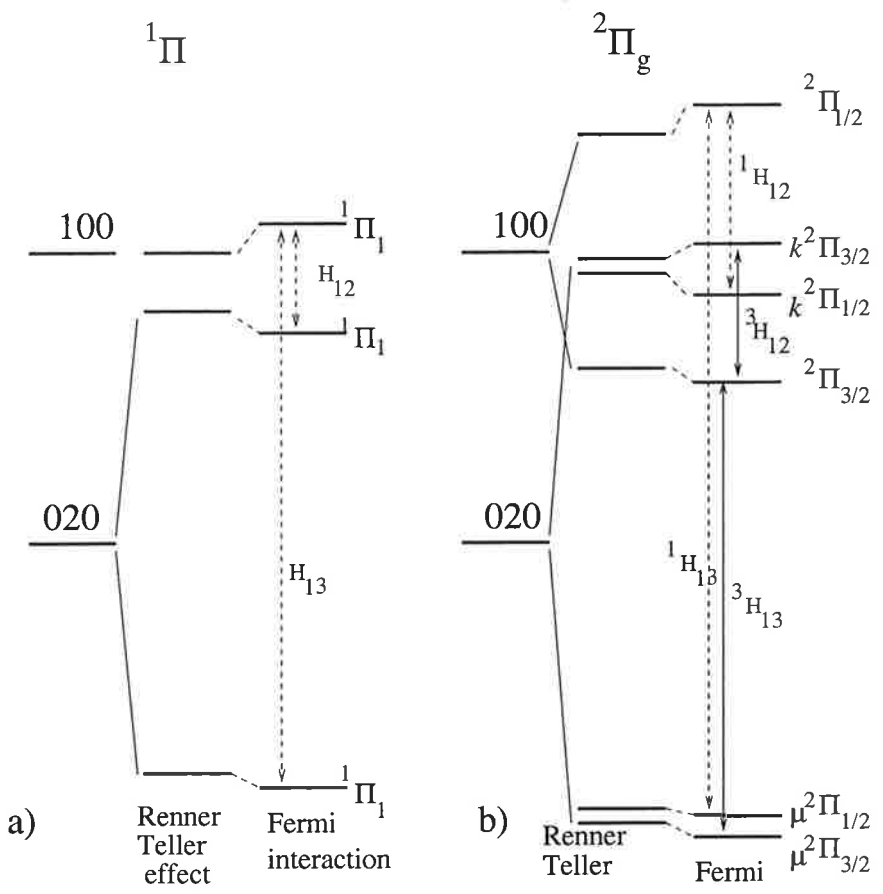

Figure 2.6: Energy level diagram of the 100 and 020 levels in the case of **a)** $^1\Pi$ and **b)** $^2\Pi_g$ [154] symmetry for a triatomic molecule. The levels are shown without Renner-Teller effect, with Renner-Teller effect and with Fermi interactions. The interactions matrix elements between states, as defined in (2.137) are equally shown.

and for $|P| = \frac{3}{2}$ the matrix elements are,

$$\begin{array}{ll} H_{11} = \Delta + \frac{1}{2}A & H_{12} = H_{21} = 2(W_1 - \varepsilon W_2)\cos\beta + \sqrt{2}(2W_2 - \varepsilon W_1)\sin\beta \\ H_{22} = +r - \frac{AKC}{2r} - C & H_{13} = H_{31} = -2(W_1 - \varepsilon W_2)\sin\beta + \sqrt{2}(2W_2 - \varepsilon W_1)\cos\beta \\ H_{33} = -r + \frac{AKC}{2r} - C & H_{23} = H_{32} = 0 \end{array} \quad (2.143)$$

The zeroth energy, and parameters Δ , W_1 , W_2 are defined as above (see 2.6). A is the spin-orbit coupling constant of the electronic $^2\Pi$ state. The other quantities occuring in (2.142) and (2.143) are defined by [37],

$$\begin{aligned} r\cos 2\beta &= \frac{1}{2}A \\ r\sin 2\beta &= \frac{1}{2}\varepsilon\,\omega_2\sqrt{(v_2+1)^2 - K^2} \\ C &= \frac{1}{8}\varepsilon^2\,\omega_2(v_2+1) \end{aligned} \quad (2.144)$$

The quantity r is takent to be positive, and $0 \leq \beta \leq \pi$.

Dixon, Field and Noble [154], introduce two new parameters, each associated purely with only one of the potentials V^+ or V^-:

$$W^{\pm} = f_{122}^{\pm}\sqrt{\frac{\hbar}{m\omega_1}}\left(\frac{\hbar}{m\omega_2\sqrt{1\pm\varepsilon}}\right) \quad (2.145)$$

Then Hougen's parameters are given by:

$$\begin{aligned} W_1 &= \frac{1}{2}\left[\sqrt{1+\varepsilon}W^+ + \sqrt{1-\varepsilon}W^-\right] \\ W_2 &= \frac{1}{2}\left[\sqrt{1+\varepsilon}W^+ - \sqrt{1-\varepsilon}W^-\right] \end{aligned} \tag{2.146}$$

The analysis done by [154] on (100) and (020) levels of the $^2\Pi_g$ ground state of BO_2, with results found by [46] for CO_2, suggest that the observed Fermi resonance parameters can be understood in terms of the transformation into rectilinear normal coordinates of a near harmonic bending contribution to the potential function expressed in curvilinear valence coordinates.

Duxbury and Jungen [152] in the case of $\tilde{a}^1A_1$ and $\tilde{b}^1B_1$ states of CH_2, and Larzilliere and Jungen [153] in the case of the $\tilde{X}\,^2\Pi_g$ state of CO_2^+ show that the semi-rigid bender model with a bond length dependence with angle like in the eq.(2.111) implies Fermi interaction constants of the correct order of magnitude despite the fact that it does not explicitly allow for stretching motion.

2.6.2 Standard Treatment for the Interaction Between Bending and Stretching Vibrations

The eq.(2.41) - (2.44) from the perturbational approach (section §2.2) can not be applied directly in the case when $\delta = \omega_{s''} - (\omega_s + \omega_{s'}) \to 0$, and the anharmonic corrections χ_{ss} can no longer be obtained by simple first-order treatment of a transformed Hamiltonian. The term in χ_{ss} containing $k_{s,s',s''}$ no longer appears. It is replaced by [11], [46, it is a sign error at eq.(27)]:

$$-\frac{k^2_{s,s',s''}}{8}\left[\frac{1}{\omega_s+\omega_{s'}+\omega_{s''}} + \frac{1}{\omega_s-\omega_{s'}+\omega_{s''}} - \frac{1}{\omega_s-\omega_{s'}-\omega_{s''}}\right] \tag{2.147}$$

The case where $\delta = \omega_{s''} - 2\omega_s \to 0$ is treated similarly. The term involving $k^2_{s,s',s''}$ in χ_{ss} is replaced by [46]:

$$-k^2_{s,s',s''}\left[\left(\frac{1}{2}\omega_{s''}\right)^2 + \frac{1}{8}\left(2\omega_s+\omega_{s''}\right)\right] \tag{2.148}$$

, the term in $\chi_{ss'}$, by:

$$-\frac{k^2_{ss's''}}{2}\,\frac{1}{2\omega_s+\omega_{s''}} \tag{2.149}$$

and the term in χ_{l_t,l_t} by:

$$\frac{1}{4}k^2_{sss''}\cdot\frac{1}{2\omega_s+\omega_{s''}} \tag{2.150}$$

The perturbed levels (through first order) are given by the solutions of a secular determinant, involving only the interacting levels [11, 46, 155],

$$\det\begin{bmatrix} (E_1^0-E) & H'_{12} & 0 & 0 & \dots \\ H'_{12} & (E_2^0-E) & 0 & 0 & \dots \\ 0 & H'_{23} & (E_3^0-E) & H'_{34} & \dots \end{bmatrix} = 0 \tag{2.151}$$

where the off-diagonal terms are given by $\langle state_1|H^{(1)}|state_2\rangle$, with $H^{(1)}$ from [37, eq.(4)], and are functions only of $k_{ss's''}$ and the vibrational quantum numbers.

2.7 Molecular Orbital Theory

The molecular orbital theory can predict the equilibrium values of a molecular geometry, as well as the electronic states involved in the electronic transitions [156, 157]. The theoretical calculus of the equilibrium geometry for a molecule involves systematically minimizing the total energy of the system with respect to all independent internal displacement of the molecule [158]. While the position of the absolute minimum for the total energy of the system is specified by the equilibrium geometry, the shape of the potential curve in this region is reflected in the various force constants characteristic of each of the normal modes of vibration of the system.

Force constants may be calculated by evaluating the total energy of the system at several points along a normal coordinate and fitting the values to a polynomial. A rigorous treatment of this type for polyatomic molecules was done in [158]. It is rather disturbing that the calculate force constants may be strongly dependent on the number and locations of the energy values employed in the curve fitting procedure [159, 160, 161]. The source of numerical inaccuracy is largely eliminated if the force method [162, 163] is used. This model involves only a single numerical differentiation of the energy because the force constants are evaluated from the force of the nuclei, i.e., from the first derivatives calculated analytically.

Another problem encountered with the SCF calculations is the choice of the geometry for which the energy derivatives should be calculated. It is preferable to use experimental geometries instead of calculated geometries [164], because the basis set dependence of the calculated force constants is much smaller [165] and better agreement with the experiment is achieved than with the force constants calculated from the optimum geometry. Experimentally, force constants are deduced from the vibrational frequency of the characteristic normal mode, as obtained form an analysis of the infrared or Raman absorption spectra of the molecule [11, 46].

In the case of the potential curves calculations, the Hartree-Fock approximation is especially poor on more remote regions of the energy hypersurfaces in which there is a tendency to the electron pair rupture, because the effect of the electron correlation is extraordinarily large in this case. This not lead to a correct dissociation limit i.e. to the atoms in the Hartree-Fock ground states. It is therefore necessary in the configuration-interaction (CI) method to assume also quadruply excited states and include all single and double excitations with respect to all configurations. The coupled-electron-pair-approach (CEPA) include those quadruple excitations. However other quadruple excitations that are necessary for the proper dissociation are not included in CEPA, and this is why CEPA tends to deviate from the experiment at large distances [159].

Before discussing the applications, it should be noted that the correspondence between the calculated and the experimental quantities need not be straightforward. Typically, the "observed" quantity results also from an assumed theoretical model, which need not be compatible with the assumptions involved in the *ab initio* calculations [166]. From example, the bond lengths are most usually determined from the dependence of the total energy on the positions of the nuclei, in the Born-Oppeheimer approximation. The interatomic distance corresponding to the lowest energy is not compatible with the experimental bond length because the later is not only due to the electronic energy, but it is also affected by the vibrational motion. Hence a rigorous comparison requires that a correction of the observed value for this effect be performed, i.e., the calculated equilibrium distances should be compared with the spectroscopic quantities r_e and not r_0 [159].

Another problem of a rigorous comparison of the *ab initio* results with the experiment is encountered with any observable which is determined by a polynomial fit to calculated points. Some molecular properties (mainly spectroscopic constants), depend on the fitting procedure rather strongly and if an inappropriate fit is used the discrepancies with the experiment which are found, may be erroneously assigned [46].

In an *ab initio* calculus, accurate predictions of the molecular properties are dependent on the basis functions used and correlations effects. It is important to note that the above dependence

is not always monotonic [167]. Since the *ab initio* self consistent-field (SCF) calculations were still rather costly to performed, Pople and co-workers developed in 1965 a new set of methods to provide approximations to these *ab initio* minimum-basis-set calculation which require only a fraction of the computational time that is necessary in the purely *ab initio* case [168]. These methods are the well known CNDO and INDO methods which are all-valence-electrons theories [169, 170, 171, 172]. Their purpose is to mimic the *ab initio* calculation [167], and contain a little semiempiricism through the use of the atomic data for the one-center coulomb integrals [169, 173], but is in the spirit of the atoms-in-molecules theory [174]. Because of their intent, CNDO like methods should be viewed as clever numerical approximations to the *ab initio* theories, is in fact a first order approximation of an *ab initio* calculus in an orthogonal basis of atomic orbitals [175]. The results of the CNDO/2 calculations on a number of AB_2 molecules are done in [169, 176]. Of particular interest are the two Renner molecules BH_2 and NH_2, for which the electronic energy functions as function of the bending angle is computed.

For the NH_2 molecule the equilibrium state of the upper state $^2A_1$ was calculated as bent with $\alpha = 145.1°$, even if early experimental work suggested that the upper state is linear [24].

In the last time a series of accurate *ab initio* calculations have been reported on higher order force constants of small polyatomic molecules [158].

2.8 Simultaneous Treatment of Bending and Stretching Vibrations and their Interactions

2.8.1 Matrix Formulation for Small Amplitude

Frye and Sears [112] used a small amplitude formalism to set up an interaction matrix which take into account the Renner-Teller effect, bending anharmonicities, as well as Fermi interaction, in order to fit the experimental data of the $^2\Pi_g$ electronic state in CO_2^+ molecule.

For the Renner-Teller interaction they use the Hamiltonian discussed at the eq.(2.95), with bending anharmonicities from the eq.(2.96). A harmonic basis set is used, bidimensional oscillator for the bending vibration and uni-dimensional harmonic oscillator for the symmetric stretching.

The matrix elements of H' from the eq.(2.95) in the harmonic basis $|\Lambda, v, K\rangle$, are done in [112, eq.(7)-(9)], and for the anharmonic elements H_{anh} in [112, eq.(14)-(20)]. Using the parameters W_1 and W_2 from the eq.(2.136), the Fermi operator is,

$$H_{FR} = W_1 q_1 q^2 + W_2 q_1 q^2 \sigma_z \tag{2.152}$$

with σ_z defined in (2.95), and q_1, q dimensionless harmonic coordinates, and the Fermi parameters such as W_1 and W_2 from the eq.(2.136) becomes:

$$W_1 = \frac{1}{2}(f^+_{122} + f^-_{122}) \qquad W_2 = \frac{1}{2}(f^+_{122} - f^-_{122}) \tag{2.153}$$

Other workers have attacked the eigenvalue problem for the Hamiltonian including H_{FR} , by introducing higher order perturbation theory terms [177, 154], or by direct diagonalization of a large matrix [178]. The matrix elements of H_{FR} are done in [112, eq.(24)-(27)]. The main advantage is the analytical calculus for all matrix elements, even if the size of the matrix becomes inconveniently large as v_2 increases.

The energies computed on the basis of a perturbation theory treatment of matrix elements of the Renner-Teller Hamiltonian (eq.(2.95)), followed by first order treatment of the anharmonic corrections (eq.(2.96)) [111], are found to be different from those calculated on the basis of an "exact" calculation involving diagonalization of a large matrix [112].

The derived Fermi resonance parameters for CO_2^+ molecule are close to those derived for BO_2 by Dixon *et all* [154]. This means that the bending motion is nearby exactly harmonic when true valence field coordinates are used.

2.8.2 Constants derived from Molecular Orbital Calculation

In a molecular orbital treatment of the electronic and nuclear states it is quite essential to take into account the coupling of electronic, electron-spin and ro-vibrational momenta, in order to explain the pattern of the ro-vibronic states. The three-dimensional adiabatic potential energy function (APEF) for the electronic states can be obtained from the highly correlated electronic wavefunctions and it can be computed the ro-vibronic energy levels of this species by considering full dimensionality anharmonicity, rotation-vibration, electronic angular momenta and spin coupling effects.

The electron correlation effects on the APEF's can be analyzed in terms of anharmonic force fields and the theoretical three-dimensional APEF's are empirically modified to reproduce the known vibronic band origins. In the computation of the ro-vibronic levels, the variational procedure of Carter and Handy [128] extended by the effects of electron spin are employed [129]. The APEF's have been expanded at their computed equilibrium geometries and the force field constants can be computed in different SCF approximations or by standard perturbation theory.

The electronic levels formula for electronically degenerate states [111] and the Fermi resonances are not considered at this stage. The variation of the bond length with the bending angle from the semi-rigid bender effective Hamiltonian [14, eq.(21)], can be computed form an inspection of the contour plot of the APEF projection, but the numerical accuracy of this value may be uncertain, because of the very small differences in the bond length entering into the fits. The Renner-Teller splitting parameter ε can be calculated from the corrected APEF's, in good agreement with the value derived form the experiment. The Fermi interaction W_1 and W_2 parameters can be computed from the potential constants in the appropriate units. The vibronic levels exhibiting anharmonic Fermi resonance agree to within about 10 cm^{-1} with the experiments, using the Carter-Handy Hamiltonian.

With this method the theoretical potential energy and the ro-vibronic spectrum of $X\,^2\Pi_g$ state of CO_2^+ have been analyzed [179, 180] and compared with the results previously obtained from the small and large effective bending Hamiltonians (§2.3).

Calculus concerning $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ electronic states of CH_2 are done by [142]. In [143, 181, 182] the Renner effect is not take into account. Some effects due to the angular momentum operators have been discussed in [183]. When compared with the RENNER effective Hamiltonian, some of the results derived from the variational calculus [143, 144] seems to be in error [141].

In the case of $X\,^3B_1$ ground state of CH_2 quasilinear molecule, the rotation-vibration energies were carried out by [79, 184].

A stretch-bender calculation of the effects of orbital angular momentum and vibrational vibrational resonances in the spectrum of CH_2 is done in [185].

Part II

The Symmetric Stretch - Bender Model

Chapter 3

The Symmetric Stretch - Bender Model

3.1 Instantaneous and Reference Configuration

3.1.1 Reference Configuration

Following the approach from [5, 6, 14], we consider the instantaneous displacement of the molecule from a symmetrical variable reference configuration with bond angle α. The coordinates used, in the present work, for the bending and stretching motion consists of two linearized coordinates S^s and S^a , corresponding to the two bond - stretching motion and one curvilinear coordinate α , which, for small S^s and S^a is nearby, but not exactly, equal to the instantaneous bending angle $\bar{\alpha}$. The angle α is equal to the instantaneous bending angle of a reference configuration for the molecule, whereas the angle $\bar{\alpha}$ is equal to the instantaneous bending angle of the molecule itself. The reference configuration is chosen to ensure that the bond stretching is of small amplitudes. Instead of α , the bending vibrational coordinate is chosen as ρ , because for $\rho \to 0$, the molecule will be linear: $\rho = \pi - \alpha$. The coordinate $\rho\,(0 \leq \rho \leq \pi)$ describes the large amplitude displacement.

The coordinate ρ defines the reference configuration that "follows" the large amplitude displacements. The definition of ρ has the advantage of yielding a kinetic energy operator with minimized coupling between over-all rotation, small amplitude vibration and large amplitude vibration [6].

The stretch-bender reference configuration is chosen so that in the molecule axis fixed system (Figure 3.1):

1. the nuclear center of mass is at the origin
2. all the nuclei lie in a plane making an angle φ with the xz plane
3. the bond length can vary with the angle $r^0(\rho)$, so that as the molecule bends the reference geometry follows the minimum on the energy surface:

$$r_i^0(\rho) = r_i^e + \mathcal{R}_i(\rho) \tag{3.1}$$

4. the xy plane bisects the bond angle α , so that the angular momentum of the reference configuration vanishes in the molecule fixed axis system (the Eckart condition of [5]).

The coordinates of the i-th nucleus (i=1,2,3) in the molecule fixed axis system can be written:

$$\vec{t_i} = \vec{a}_i(\rho) + \vec{d_i} \tag{3.2}$$

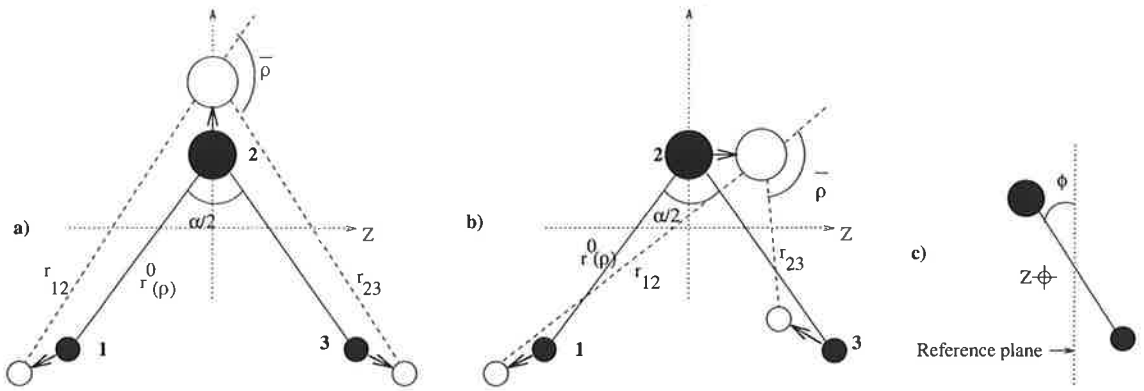

Figure 3.1: The definition of the molecule-fixed stretch-bender coordinate system and the displacement coordinates used for a triatomic molecule with a symmetrical equilibrum configuration. **a)** Symmetric stretching; **b)** Asymmetric stretching; **c)** Azimuthal angle φ. The displacements in figure are much greater than in reality.

,where $\vec{t}_i$, $\vec{a}_i(\rho)$ and $\vec{d}_i$ are three dimensional column vectors. The vector $\vec{a}_i(\rho)$ contains the three Cartesian coordinates (in the molecule fixed axis system) of the i-th nucleus in the reference configuration and $\vec{d}_i$ is a small amplitude displacement from this configuration.

Since we are considering a symmetrical reference configuration with variable bond lengths it is more convenient to introduce vectors $\vec{d}_i^s$ and $\vec{d}_i^a$, corresponding to the symmetric S^s and antisymmetric S^a vibrational coordinates, respectively. The $\vec{d}_i^s$ and $\vec{d}_i^a$, displacement are related with $\vec{d}_i$ by the condition: $\vec{d}_i = \vec{d}_i^s + \vec{d}_i^a$.

The components of the vectors $\vec{a}_i(\rho)$ in the molecule fixed axis system are given by (§A.1):

$$\begin{aligned}
a_{1x} &= -\frac{r_\rho}{p}\sin\theta\cos\varphi \\
a_{1y} &= \frac{r_\rho}{p}\sin\theta\sin\varphi \\
a_{1z} &= -r_\rho\cos\theta \\
a_{2x} &= \left(2\frac{m_1}{m_2}\right)\frac{r_\rho}{p}\sin\theta\cos\varphi \\
a_{2y} &= -\left(2\frac{m_1}{m_2}\right)\frac{r_\rho}{p}\sin\theta\sin\varphi \\
a_{2z} &= 0 \\
a_{3x} &= -\frac{r_\rho}{p}\sin\theta\cos\varphi \\
a_{3y} &= \frac{r_\rho}{p}\sin\theta\sin\varphi \\
a_{3z} &= r_\rho\cos\theta
\end{aligned} \tag{3.3}$$

where the two identical atoms have the masses m_1 and the central atom has the mass m_2. r_ρ is a shortcut to $r(\rho)$. p has the following formula:

$p = 1 + \frac{2m_1}{m_2}$.

In the previous equation and below were employed the shortcuts:

$$\theta = \tfrac{\rho}{2} \quad \text{and} \quad r_\rho = r^0 = r^0(\rho) \tag{3.4}$$

The $\vec{a}_i(\rho)$ values may be chosen so that the molecule fixed axis system is a principal axis system, but instead, it is chosen so that:

$$\sum_i m_i\vec{a}_i(\rho) \times \left(\frac{d\,\vec{a}_i(\rho)}{d\,\rho}\right) = 0 \tag{3.5}$$

The equation (3.3) requires that the angular momentum of the reference configuration vanish in the molecule fixed axis system (§A.2).

3.1.2 Displacements and Instantaneous Configuration

The vectors $\vec{d}_i$, i=1,2,3 have each three components and all nine components cannot be independent since they describe the small amplitude stretching vibration motions, corresponding to only two degree of freedom. They are subject to the following constrains:

1. the nuclear center of mass remains at the origin:

$$\sum_i m_i d_i = 0 \tag{3.6}$$

2. the Eckart conditions [40]

3. the Sayvetz condition :

$$\sum_i m_i \left(\frac{d\,\vec{a}_i(\rho)}{d\,\rho} \right) \vec{d}_i = 0 \tag{3.7}$$

Equation (3.7) means in essence that $\vec{d}_i$ and $\left(\frac{d\,\vec{a}_i(\rho)}{d\,\rho}\right)$ are "at right angles" - this ensure separation of bending and stretching.

Following the calculus of (§A.3) we find that the final relations between the displacements $\vec{d}_i$ and the stretching-bending coordinates:

$$\begin{aligned}
d_{1x} &= -\frac{1}{\sqrt{2}} (S^s + S^a) (\sin\theta - b\cos\theta) \cos\varphi \\
d_{1y} &= \frac{1}{\sqrt{2}} (S^s + S^a) (\sin\theta - b\cos\theta) \sin\varphi \\
d_{1z} &= -\frac{1}{\sqrt{2}} (S^s + S^a) (\cos\theta + b\sin\theta) \\
d_{2x} &= \left(2\frac{m_1}{m_2}\right) \frac{1}{\sqrt{2}} S^s (\sin\theta - b\cos\theta) \cos\varphi \\
d_{2y} &= -\left(2\frac{m_1}{m_2}\right) \frac{1}{\sqrt{2}} S^s (\sin\theta - b\cos\theta) \sin\varphi \\
d_{2z} &= \left(2\frac{m_1}{m_2}\right) \frac{1}{\sqrt{2}} \cdot S^a (\cos\theta + b\sin\theta) \\
d_{3x} &= -\frac{1}{\sqrt{2}} (S^s - S^a) (\sin\theta - b\cos\theta) \cos\varphi \\
d_{3y} &= \frac{1}{\sqrt{2}} (S^s - S^a) (\sin\theta - b\cos\theta) \sin\varphi \\
d_{3z} &= \frac{1}{\sqrt{2}} (S^s - S^a) (\cos\theta + b\sin\theta)
\end{aligned} \tag{3.8}$$

In eq. (3.8) and below the following notations were used:

$$b = \frac{2 \cdot r^{0\prime}}{r^0} \quad \text{and} \quad r_i^{0\prime} = r_i^{0\prime}(\rho) = \frac{\partial r_i^0(\rho)}{\partial \rho} = \frac{\partial \mathcal{R}_i(\rho)}{\partial \rho} = \mathcal{R}_i' \tag{3.9}$$

However, it must be born in mind that the reference bond length will always be a function of the bending of the reference configuration. When $r^{0\prime} = 0$, the equations for the antisymmetric and symmetric coordinate are identical to those derived by Jensen [6].

The instantaneous coordinates in terms of the reference geometry and the displacement coordinates are obtained by using the eq. (3.3) and (3.8):

$$\begin{aligned}
x_1 &= -\frac{r_\rho}{p}\sin\theta\cos\varphi - \frac{1}{\sqrt{2}}\left(S^s + S^a\right)\left(\sin\theta - b\cos\theta\right)\cos\varphi \\
y_1 &= \frac{r_\rho}{p}\sin\theta\sin\varphi + \frac{1}{\sqrt{2}}\left(S^s + S^a\right)\left(\sin\theta - b\cos\theta\right)\sin\varphi \\
z_1 &= -r_\rho\cos\theta - \frac{1}{\sqrt{2}}\left(S^s + S^a\right)\left(\cos\theta + b\sin\theta\right) \\
x_2 &= \left(2\frac{m_1}{m_2}\right)\left[\frac{r_\rho}{p}\sin\theta\cos\varphi + \frac{1}{\sqrt{2}}S^s\left(\sin\theta - b\cos\theta\right)\cos\varphi\right] \\
y_2 &= -\left(2\frac{m_1}{m_2}\right)\left[\frac{r_\rho}{p}\sin\theta\sin\varphi + \frac{1}{\sqrt{2}}S^s\left(\sin\theta - b\cos\theta\right)\sin\varphi\right] \\
z_2 &= \sqrt{2}\cdot S^a\cdot\frac{m_1}{m_2}\left(\cos\theta + b\sin\theta\right) \\
x_3 &= -\frac{r_\rho}{p}\sin\theta\cos\varphi - \frac{1}{\sqrt{2}}\left(S^s - S^a\right)\left(\sin\theta - b\cos\theta\right)\cos\varphi \\
y_3 &= \frac{r_\rho}{p}\sin\theta\sin\varphi + \frac{1}{\sqrt{2}}\left(S^s - S^a\right)\left(\sin\theta - b\cos\theta\right)\sin\varphi \\
z_3 &= r_\rho\cos\theta + \frac{1}{\sqrt{2}}\left(S^s - S^a\right)\left(\cos\theta + b\sin\theta\right)
\end{aligned} \tag{3.10}$$

The Sayvetz equation (3.7) vanishes identically for the antisymmetric displacements $\vec{d}_i^a$, as it is shown in (§A.3). This means that the relations between the displacements $\vec{d}_i^a$ and coordinates S^a has a degree of arbitrariness. The choice of the eq. (3.8) ensure that the Jacobian of the transformation, defined below (§3.2.2) is invariant in the case of a symmetric AB_2 and asymmetric ABC molecule, respectively.

In the case of the potential energy, we need to obtain an expansion in terms of the reference angle ρ , rather than the instantaneous angle, $\bar{\rho}$. The reference configuration will be defined below in (§3.3.1). The instantaneous bond angle may be written to the first order in terms of ρ as:

$$\bar{\rho}\left(\rho, S^s, S^a\right) \approx \rho + \left(\frac{\partial\bar{\rho}}{\partial S^s}\right)_{S^s=0} S^s + \left(\frac{\partial\bar{\rho}}{\partial S^a}\right)_{S^a=0} S^a \tag{3.11}$$

Since our reference configuration stretches as the molecule bends, the higher order terms are omitted because the difference between ρ and $\bar{\rho}$ is always small in our method (see the similar [6, eq. (3.14)]).

The first derivative of ρ relative to the symmetric and antisymmetric stretching displacements may be written as in (§A.4) and is based on the (Figure 3.2):

$$\frac{\partial\bar{\rho}}{\partial S^s} = -\frac{R_2\left(r^0,\rho\right)}{\sqrt{2}\,r^0} \quad \text{and} \quad \frac{\partial\bar{\rho}}{\partial S^a} = 0 \tag{3.12}$$

By analogy with ρ and $\bar{\rho}$ (the bending reference and respectively instantaneous bending coordinate), we have two stretching coordinates: the reference and the instantaneous one; S^i and $\bar{S}^i$, $i = s, a$. This is due to the ρ dependence of the bond length and therefore we have two bond lengths: the reference and the instantaneous one.

If we consider the curvilinear internal displacement coordinates for the stretching vibrations [6, eq.(3.1) and (3.3)] and our stretching coordinates, we are obtaining (§A.5):

$$\begin{aligned}
\Delta r_1 &= r_{12} - r_{12}^0(\rho) = \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s + R_5\left(r^0,\rho\right)S^a\right] \\
\Delta r_3 &= r_{23} - r_{23}^0(\rho) = \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s - R_5\left(r^0,\rho\right)S^a\right]
\end{aligned} \tag{3.13}$$

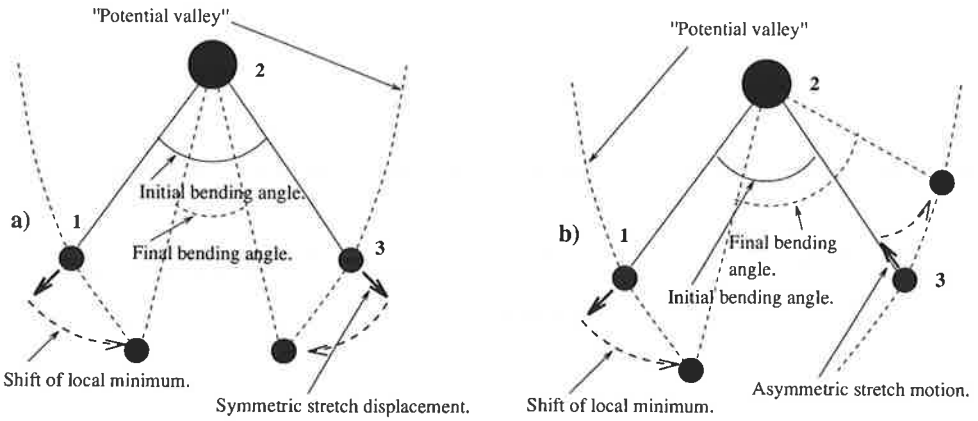

Figure 3.2: Interaction between stretching and bending motion in the case of: **a)** symmetric stretching and **b)** antisymmetric stretching. The displacements in figure are much greater than in reality.

Here Δr_1, Δr_3 are the displacements from the equilibrium position in the "potential valley", $r_{i2}(\rho)$, i=1,3.

Since our reference configuration bends as the molecule stretch, we need to obtain an expression in terms of the reference stretching coordinates S^s and S^a (§A.6), rather than the instantaneous stretching coordinates $\bar{S}^s$ and $\bar{S}^a$:

$$\begin{aligned} \bar{S}^s &= S^s + \left(\frac{\partial \bar{S}^s}{\partial \rho}\right)_{\bar{S}^s=S^s} (\rho - \rho_e) \\ \bar{S}^a &= S^a + \left(\frac{\partial \bar{S}^a}{\partial \rho}\right)_{\bar{S}^a=S^a} (\rho - \rho_e) \end{aligned} \tag{3.14}$$

The above formula is correct for small changes in the bending angle, when $d\rho = \rho - \rho_e$. The first derivative of the symmetric and antisymmetric coordinate to the ρ value may be written as (§A.6):

$$\left(\frac{\partial \bar{S}^s}{\partial \rho}\right) = \sqrt{2}\left(\frac{\mathcal{R}(\rho)'}{R_1(r^0,\rho)}\right)_0 = \sqrt{2}\left(\frac{r(\rho)'}{R_1(r^0,\rho)}\right)_0 \quad \text{and} \quad \left(\frac{\partial \bar{S}^a}{\partial \rho}\right) = 0 \tag{3.15}$$

There are some auxiliary functions, $R_i(r^0,\rho)$, $i = \overline{1,5}$, used for the conversion from the instantaneous to the reference frame. They are also used in the definitions of the contravariant $g^{\alpha\alpha}$ metric tensor analyzed below as well as to express the instantaneous bond length and their derivatives in terms of the reference coordinates:

$$\begin{aligned} R_1(r^0,\rho) &= \left(\cos^2\theta + p\sin^2\theta\right) - b\,(p-1)\sin\theta\cos\theta \\ R_2(r^0,\rho) &= -2\,(p-1)\sin\theta\cos\theta + 2b\left(p\cos^2\theta + \sin^2\theta\right) \\ R_3(r^0,\rho) &= \left(\cos^2\theta + p\sin^2\theta\right) - 2b\,(p-1)\sin\theta\cos\theta + b^2\left(p\cos^2\theta + \sin^2\theta\right) \\ &= R_1(r^0,\rho) + \left(\frac{r^{0\prime}}{r^0}\right) R_2(r^0,\rho) \\ R_4(r^0,\rho) &= \left(\sin^2\theta + p\cos^2\theta\right) \\ &\quad +2b\,(p-1)\sin\theta\cos\theta + b^2\left(\cos^2\theta + p\sin^2\theta\right) \\ R_5(r^0,\rho) &= \left(\sin^2\theta + p\cos^2\theta\right) + b\,(p-1)\sin\theta\cos\theta \end{aligned} \tag{3.16}$$

There are some aspects that must be emphasized:

1. In the case of the rigid-bender formalism, the $R_2(r^0, \rho)$ function became

$$R_2(r^0, \rho) \mid_{r'=0} = -2(p-1)\sin\theta\cos\theta \tag{3.17}$$

and express only the fix position of the center of mass when a symmetric stretch occur (in a symmetric stretch, the ρ angle increases), as in the literature [5, 6].

2. The derivative of the symmetric stretching coordinate in the rigid-limit vanish:

$$\left(\frac{\partial \bar{S}^s}{\partial \rho}\right) \mid_{r'=0} = 0$$

3. The eq. (3.11) and (3.14) together with eq. (3.12) and (3.15) can be easily understood by analyzing the (Figure 3.3), where there are shown the extreme cases: a bending motion (rigid-limit) followed by a stretch to arive in the potential valley and a stretch motion followed by a bending motion (rigid-limit).

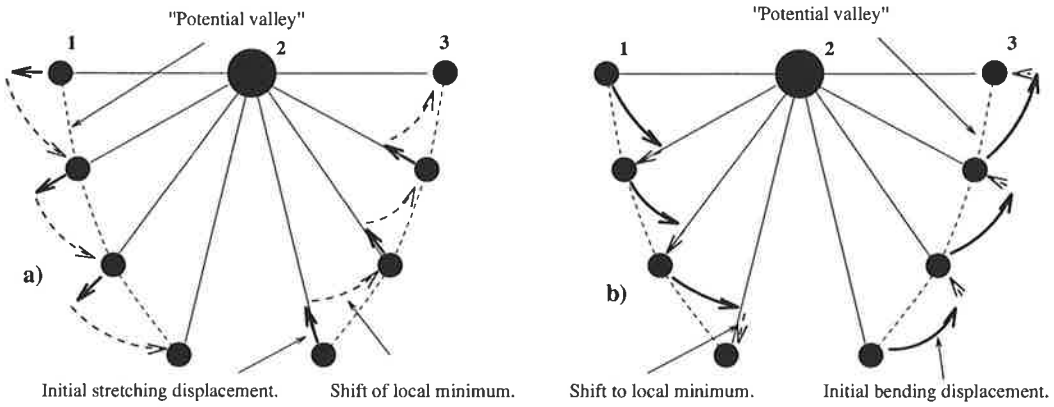

Figure 3.3: Changement of the instantaneous reference frame in the case of: **a)** stretching motion and **b)** bending motion. The displacements in figure are much greater than in reality.

3.1.3 Relations Between the Literature Coordinates and the Stretch - Bender coordinates

The curvilinear bending coordinate ρ, used here, is the same as in the case of [5, 6]. The eq. (3.11) for the case of the rigid-bender limit is equivalent to [6, eq. (3.14)] , or [5, eq.(50)].

The difference arises when we consider the case of the internal curvilinear displacement coordinates for the stretching vibrations and the linearized internal coordinates S^s and S^a.

If we consider [6, eq.(3.1) and eq.(3.3)] and the eq. (3.13) , we find the transformation between our internal coordinates and the generalized internal coordinates (§A.7), when ρ is not very different from ρ_e:

$$\Delta r_{i2} = \Delta r_i + \mathcal{R}_{i2}(\rho) \tag{3.18}$$

$$\begin{aligned} \Delta r_{i2} &= \frac{1}{\sqrt{2}}\left[R_1\left(r^0, \rho\right) S^s \pm R_5\left(r^0, \rho\right) S^a\right] + \mathcal{R}_{i2}(\rho) \\ &= \frac{1}{\sqrt{2}}\left[R_1\left(r^0, \rho\right) \bar{S}^s \pm R_5\left(r^0, \rho\right) \bar{S}^a\right] + \mathcal{R}_{i2}(\rho_e) \end{aligned} \tag{3.19}$$

where, for i=1 we consider "+" sign and for i=3 "-" sign, respectively.

In the rigid-bender limit, the Cartesian vibrational coordinates S^s and S^a are related to the coordinates S_1^{Jen} and S_3^{Jen} from [6, eq.(3.17)]. The later ones are used to define the A matrix [7, Table I] , [186, Table I] for a triatomic molecule (§A.8):

$$\begin{aligned} S^s &= \frac{1}{\sqrt{2}\,D}\left\{m_2\left[m_2+m_1\left(1+\cos\rho\right)\right]\right\}\left(S_1^{Jen}+S_3^{Jen}\right) \\ S^a &= \frac{1}{\sqrt{2}\,D}\left\{m_2\left[m_2+m_1\left(1-\cos\rho\right)\right]\right\}\left(S_1^{Jen}-S_3^{Jen}\right) \end{aligned} \tag{3.20}$$

where $D = m_2\left(2m_1+m_2\right)+m_1^2\sin^2\rho = m_2^2 p + m_1^2\sin^2\rho$

The coordinates S_1^{Jen} and S_3^{Jen} are related to the internal Cartesian vibrational coordinates S^s and S^a, by (§A.8):

$$\begin{aligned} S_1^{Jen} &= \frac{1}{\sqrt{2}}\left[R_3(r^0,\rho)|_{r'=0}\cdot S^s + R_4(r^0,\rho)|_{r'=0}\cdot S^a\right] \\ S_3^{Jen} &= \frac{1}{\sqrt{2}}\left[R_3(r^0,\rho)|_{r'=0}\cdot S^s - R_4(r^0,\rho)|_{r'=0}\cdot S^a\right] \end{aligned} \tag{3.21}$$

where from the eq. (3.16) we have:

$$\begin{aligned} R_3(r^0,\rho)|_{r'=0} &= \left[\frac{p+1}{2}-\frac{p-1}{2}\cos\rho\right] = \left[1+\frac{2m_1}{m_2}\sin^2\theta\right] \\ R_4(r^0,\rho)|_{r'=0} &= \left[\frac{p+1}{2}+\frac{p-1}{2}\cos\rho\right] = \left[p+\frac{2m_1}{m_2}\cos^2\theta\right] \end{aligned}$$

We will use the non-symmetric coordinates:

$$\begin{aligned} S_1 &= \frac{1}{\sqrt{2}}\left(S^s+S^a\right) \\ S_3 &= \frac{1}{\sqrt{2}}\left(S^s-S^a\right) \end{aligned} \tag{3.22}$$

and in this case the relation between them and the coordinates S_1^{Jen} and S_3^{Jen}, in the rigid-bender limit, are the following (§A.9):

$$\vec{S} = \hat{C}\cdot\vec{S}^{Jen} \tag{3.23}$$

with

$$\hat{C} = \begin{pmatrix} \frac{m_2(m_1+m_2)}{D} & \frac{m_1 m_2\cos\rho}{D} \\ \frac{m_1 m_2\cos\rho}{D} & \frac{m_2(m_1+m_2)}{D} \end{pmatrix}$$

and D defined in eq.(3.20).

If we use the equation [6, eq.(13)],[5, eq.(16)]

$$\vec{d} = \tilde{A}\cdot\vec{S} \tag{3.24}$$

our $\tilde{A}$ matrix, in the rigid-bender limit, is proportional to the $\hat{B}$ matrix of [5, Table I] or [6, Table 3], as shown in (§A.9). The choice of our stretching coordinates makes more difficult the use of the generalized moment of inertia [6, eq. (48)] and it will be easier the use of the metric tensor into the kinetic energy formalism.

It is interesting to analyze the behavior of our transformation formula in the case of small amplitude bending movement, it means when $\rho \to 0$. In this case the auxiliary functions will be, as it is shown in (§A.10):

$$\begin{aligned} R_1|_{\rho\to 0} &\approx 1+\left[p-1-2\left(p-1\right)\left(\frac{4d_r}{r_0}\right)\right]\cdot\frac{\rho^2}{4} \\ R_2|_{\rho\to 0} &\approx -\left[p-1-2p\left(\frac{4d_r}{r_0}\right)\right]\cdot\rho \end{aligned}$$

$$
\begin{aligned}
R_3|_{\rho\to 0} &\approx 1+\left[p-1-4\,(p-1)\left(\frac{4d_r}{r_0}\right)+4p\left(\frac{4d_r}{r_0}\right)^2\right]\cdot\frac{\rho^2}{4} \\
R_4|_{\rho\to 0} &\approx p-\left[p-1-4\,(p-1)\left(\frac{4d_r}{r_0}\right)+4\left(\frac{4d_r}{r_0}\right)^2\right]\cdot\frac{\rho^2}{4} \\
R_5|_{\rho\to 0} &\approx p-\left[p-1-2\,(p-1)\left(\frac{4d_r}{r_0}\right)\right]\cdot\frac{\rho^2}{4}
\end{aligned}
\tag{3.25}
$$

where we consider, from eq. (3.1), that $\mathcal{R}(\rho)=d_r\,\rho^2$. The eq. (3.20) become, as it is shown in (§A.11),

$$
\begin{aligned}
S^s &= \left[1-\left(\frac{p-1}{4}\right)\rho^2\right](S^s)^{Jen} \\
S^a &= \frac{1}{p}\left[1+\left(\frac{p-1}{4p}\right)\rho^2\right](S^a)^{Jen}
\end{aligned}
\tag{3.26}
$$

where

$$
\begin{aligned}
(S^s)^{Jen} &= \frac{1}{\sqrt{2}}\left(S_1^{Jen}+S_3^{Jen}\right) \\
(S^a)^{Jen} &= \frac{1}{\sqrt{2}}\left(S_1^{Jen}-S_3^{Jen}\right)
\end{aligned}
\tag{3.27}
$$

It can be seen from (3.26), that the antisymmetric stretching vibration is in our case p times lesser that in the usual case of [5, 6]. More than this, if we use the $(S^s)^{Jen}$ and $(S^a)^{Jen}$, we have from the eq.(3.19),(3.22) and (3.26) an approximate formula:

$$
\begin{aligned}
(S^s)^{Jen} &\simeq R_3\cdot S^s \\
(S^a)^{Jen} &\simeq R_4\cdot S^a
\end{aligned}
\tag{3.28}
$$

In the first approximation we have [7, eq. (23)]:

$$
S_1^{Jen}\simeq\Delta r_{12}\quad\text{and}\quad S_3^{Jen}\simeq\Delta r_{32} \tag{3.29}
$$

From eq.(3.13) and (3.19), in the rigid-bender limit, we find that:

$$
(S^s)^{Jen}=R_1\cdot S^s\quad\text{and}\quad(S^a)^{Jen}=R_5\cdot S^a \tag{3.30}
$$

The eq.(3.26),(3.28) and (3.30) are the same because, in the rigid-bender limit we have:
$R_1|_{r'=0}=R_3|_{r'=0}$ and $R_4|_{r'=0}=R_5|_{r'=0}$
with:
$(R_1)^{-1}\simeq 1-(p-1)\,\frac{\rho^2}{4}$ and $(R_5)^{-1}\simeq\frac{1}{p}\left[1+\frac{(p-1)}{p}\frac{\rho^2}{4}\right]$
There are some comments concerning the eq. (3.13), (3.14), (3.18), (3.19):

- If the stretching displacement from the stretch-bender reference configuration is assumed to be small [186], the reference bond length in the zeroth approximation is considered as constant during the stretching motion and in this case the eq. (3.13) become:

$$
\begin{aligned}
\Delta r_1^0 &= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s+R_5\left(r^0,\rho\right)S^a\right] \\
\Delta r_3^0 &= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s-R_5\left(r^0,\rho\right)S^a\right]
\end{aligned}
$$

- If we consider the reference stretching coordinates, the formula (3.19) can be changed by using the eq. (3.14) and will have the expression (§A.7):

$$
\begin{aligned}
\Delta r_{i2} &= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s+R_5\left(r^0,\rho\right)S^a\right]+\mathcal{R}_i(\rho) \\
&= \Delta r_1^0+\mathcal{R}_i\left(\rho\right)
\end{aligned}
$$

because: $\mathcal{R}(\rho)=\mathcal{R}(\rho_e)+\mathcal{R}'(\rho)\cdot(\rho-\rho_e)$, for ρ near ρ_e.

- We see that the generalized internal stretching coordinates can be expressed either in the instantaneous stretching coordinates for a reference bond angle (3.18), or in a reference stretching coordinates for an instantaneous bending angle (equations above).

- For $\rho \to 0$ we find ($R_1(r^0, \rho) \simeq 1$, $R_5(r^0, \rho) \simeq p$):
  $\Delta r_1^0 \simeq \frac{1}{\sqrt{2}}(S^s + p \cdot S^a)$ and $\Delta r_3^0 \simeq \frac{1}{\sqrt{2}}(S^s - p \cdot S^a)$

3.2 Kinetic Energy

3.2.1 Expression of the Classic and Quantum Hamiltonian

The classical kinetic energy is:

$$2T = \sum_i m_i (\dot{t}_i)^2 \tag{3.31}$$

where the instantaneous position vectors of the atoms were defined in eq. (3.2). In order to obtain the expression of the kinetic energy in curvilinear coordinates, we will change the classical kinetic energy from the Cartesian coordinates to $(\rho, \varphi, S^s, S^a)$. We are using the definitions of Podolski [187] rather than those of Wilson, Decius and Cross [10].

Expanding the eq. (3.31), we have,

$$2T = \sum_i m_i \left(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2\right) \tag{3.32}$$

When we change the coordinates to $(\rho, \varphi, S^s, S^a)$, we find (§B.1)

$$2T = \sum_{i,\alpha,\beta} m_i \, g_{\alpha\beta}^{[i]} \, \dot{u}_\alpha \dot{u}_\beta = \sum_{\alpha,\beta} g_{\alpha\beta} \, \dot{u}_\alpha \dot{u}_\beta \tag{3.33}$$

with $\vec{u} = (\rho, \varphi, S^s, S^a)$, curvilinear coordinates and:

$$\begin{aligned} g_{\alpha\beta} &= \sum_{k=1}^{n} m_k \, g_{\alpha\beta}^{[k]} \\ &= \sum_{k=1}^{n} m_k \left[\left(\frac{\partial x_k}{\partial u_\alpha}\right)\left(\frac{\partial x_k}{\partial u_\beta}\right) + \left(\frac{\partial y_k}{\partial u_\alpha}\right)\left(\frac{\partial y_k}{\partial u_\beta}\right) + \left(\frac{\partial z_k}{\partial u_\alpha}\right)\left(\frac{\partial z_k}{\partial u_\beta}\right) \right] \end{aligned} \tag{3.34}$$

Here $g_{\alpha\beta}^{[k]}$ is the metric tensor element for the i -th atom and $g_{\alpha\beta}$ is a pseudo - metric tensor (because is multiplied by the mass). The eq.(3.33) may be transformed (§B.2), giving the final classical kinetic energy:

$$2T = \sum_{\alpha\beta} g^{\alpha\beta} P_\alpha P_\beta \tag{3.35}$$

According to Podolski [187], the quantum kinetic energy operator connected with the eq.(3.35) is given by:

$$2T = \mu^{\frac{1}{4}} \sum_{\alpha\beta} P_\alpha \, \mu_{\alpha\beta} \, \mu^{-\frac{1}{2}} \, P_\beta \, \mu^{\frac{1}{4}} \tag{3.36}$$

where:

- $\mu = g^{-1}$, the inverse of the transformation Jacobian
- $\mu_{\alpha\beta} = g^{\alpha\beta}$, the elements of the contravariant metric tensor,
- $\alpha, \beta = \rho, \varphi, S^s, S^a$.

The quantum operators are:

$$P_\rho = -i\hbar\frac{\partial}{\partial\rho} \qquad P_\varphi = -i\hbar\frac{\partial}{\partial\varphi}$$
$$P_s = -i\hbar\frac{\partial}{\partial S^s} \qquad P_a = -i\hbar\frac{\partial}{\partial S^a} \tag{3.37}$$

The volume element for the kinetic energy operator eq. (3.36) is $dV = d\rho\, d\varphi\, dS^s\, dS^a$, according to [187]. In the kinetic energy operator we do not take into account the end-over-end rotation and even more, any rotational terms, as well as the Coriolis coupling terms. The eq. (3.36) analyses only the stretch-bending terms. The φ coordinate (the rotation around Oz axis) is taking into account because corresponds to the bending movement in the small-amplitude formalism of the bidimensional oscillator.

3.2.2 Elements of the Metric Tensor and the Kinetic Energy Terms

Before trying to find the terms of the kinetic energy, we must find the analytical expressions for the metric tensor elements. Using the formula (3.10) and (3.34) we obtain the metric tensor elements after an extensive algebraic calculus (§B.3):

$$\begin{aligned}
g_{\rho\rho} &= \frac{m_1 r^2}{2p}\left[(\cos\theta + b\sin\theta)^2 + p\,(\sin\theta - b\cos\theta)^2\right] + \frac{m_1 r}{\sqrt{2}}S^s\left[1 + b^2 - 2b'\right] \\
&\quad + \frac{m_1}{4}(S^s)^2\left\{p\left[(1-2b')\cos\theta + b\sin\theta\right]^2 + \left[(1-2b')\sin\theta - b\cos\theta\right]^2\right\} \\
&\quad + \frac{m_1 (S^a)^2}{4}\left\{p\left[(1-2b')\sin\theta - b\cos\theta\right]^2 + \left[(1-2b')\cos\theta + b\sin\theta\right]^2\right\} \\
g_{\rho\varphi} &= 0 \\
g_{\rho s} &= \frac{m_1 S^s}{2}\left\{p\left[(1-2b')\cos\theta + b\sin\theta\right](\sin\theta - b\cos\theta)\right. \\
&\quad \left. - \left[(1-2b')\sin\theta - b\cos\theta\right](\cos\theta + b\sin\theta)\right\} \\
g_{\rho a} &= \frac{m_1 S^a}{2}\left\{\left[(1-2b')\cos\theta + b\sin\theta\right](\sin\theta - b\cos\theta)\right. \\
&\quad \left. - p\left[(1-2b')\sin\theta - b\cos\theta\right](\cos\theta + b\sin\theta)\right\} \\
g_{\varphi\varphi} &= \frac{2m_1}{p}\left[r\sin\theta + \frac{p\,S^s}{\sqrt{2}}(\sin\theta - b\cos\theta)\right]^2 + m_1 (S^a)^2 (\sin\theta - b\cos\theta)^2 \\
g_{\varphi s} &= 0 \\
g_{\varphi a} &= 0 \\
g_{ss} &= m_1\left[p\,(\sin\theta - b\cos\theta)^2 + (\cos\theta + b\sin\theta)^2\right] \\
g_{sa} &= 0 \\
g_{aa} &= m_1\left[(\sin\theta - b\cos\theta)^2 + p\,(\cos\theta + b\sin\theta)^2\right]
\end{aligned} \tag{3.38}$$

Form the above formula we can observe that the φ coordinate do not couple with any other one and than the tensor elements vanish because of the symmetry requirements. The $g_{\alpha\beta}$ elements do not depend on φ because the vibration is symmetric to the rotation around Oz axis. More than this, the antisymmetric stretch coordinate arise only as a square value (exception in $g_{\rho a}$). This is quite normal because for a symmetrical molecule the bend and the symmetric stretch belong together, but the antisymmetric stretch is orthogonal to them.

The Jacobian of the transformation is (§B.3):

$$\begin{aligned}
g &= \frac{m_1^4 \cdot r^4}{p^2}\left\{\left[\sin\theta + \frac{pS^s}{\sqrt{2}r}(\sin\theta - b\cos\theta)\right]^2 + \frac{p}{2}\left(\frac{S^a}{r}\right)^2(\sin\theta - b\cos\theta)^2\right\} \\
&\quad \left\{\left[(\sin\theta - b\cos\theta)^2 + p\,(\cos\theta + b\sin\theta)^2\right]\right.
\end{aligned} \tag{3.39}$$

$$\left[(\cos\theta + b\sin\theta)^2 + p\,(\sin\theta - b\cos\theta)^2 + \frac{p}{\sqrt{2}}\frac{S^s}{r}\left(1 + b^2 - 2b'\right)\right]^2$$
$$+ \frac{p^2}{2}\left(\frac{S^a}{r}\right)^2\left(1 + b^2 - 2b'\right)^2\left[p\,(\sin\theta - b\cos\theta)^2 + (\cos\theta + b\sin\theta)^2\right]\Bigg\}$$

As in the above comment, the ρ and S^s coordinate belong together and S^a is at square. In fact the eq.(3.39) look very simple and "symmetric".When we analyze the $g_{\alpha\beta}$ elements, they are nearly "symmetric".

The contravariant elements of the metric tensor are presented in (§B.4). We can see that all the elements $g^{\alpha\varphi}$, with $\alpha \neq \varphi$ are 0.

We assume that if the reference configuration is close to that of the instantaneous configuration, the derivatives of the displacements may be evaluated in the "0" point, when $S^s = 0$ and $S^a = 0$, i.e. $\left(\frac{\partial f}{\partial \alpha}\right)_0 = \left(\frac{\partial f}{\partial \alpha}\right)_{S^s=S^a=0}$ where $\alpha = \rho, S^s, S^a$. In this case all the derivatives to antisymmetric coordinates (S^a), except the second derivative of g, will vanish. More than this, the following terms will vanish also(because of symmetry requirements): $g^{as}|_0 = g^{\rho a}|_0 = g^{\rho s}|_0 = 0$. Taking into account all the terms that must vanish (§B.5), the kinetic energy become [188]:

$$\begin{aligned}
T &= \frac{1}{2}g_0^{\rho\rho}P_\rho^2 + \frac{1}{2}\left[P_\rho, g_0^{\rho\rho}\right]P_\rho + \frac{1}{2}(g_0)^{-\frac{1}{4}}\left[P_\rho, g^{\rho\rho}(g_0)^{\frac{1}{2}}\left[P_\rho, (g_0)^{-\frac{1}{4}}\right]\right] \\
&+ \frac{1}{2}g_0^{\varphi\varphi}P_\varphi^2 \\
&+ \frac{1}{2}g_0^{ss}P_s^2 + \frac{1}{2}g_0^{aa}P_a^2 \\
&+ \frac{1}{2}(g_0)^{-\frac{1}{4}}g^{ss}\left[P_s, g^{\frac{1}{2}}\left[P_s, g^{-\frac{1}{4}}\right]\right]_0 + \frac{1}{2}(g_0)^{\frac{1}{4}}g^{aa}\left[P_a, \left[P_a, g^{-\frac{1}{4}}\right]\right]_0 \\
&+ \frac{1}{2}(g_0)^{\frac{1}{4}}\left[P_s, g^{s\rho}\right]_0\left[P_\rho, (g_0)^{-\frac{1}{4}}\right] + \frac{1}{2}(g_0)^{\frac{1}{4}}\left[P_a, g^{a\rho}\right]_0\left[P_\rho, (g_0)^{-\frac{1}{4}}\right]
\end{aligned} \tag{3.40}$$

where the commutator of two operators: $[F, G] = FG - GF$ and $[F, G]_0$ means that the values after the operations are in the reference system: $(FG - GF)_0$.

In the formula (3.40), the first row is the BL (and formally the HBJ) bending Hamiltonian, the second row is a rotational Hamiltonian around Oz axis (axis of linear molecule), the third row describe the stretching kinetic Hamiltonian, the fourth row incorporate some of the terms described in the U_0 term of Jensen [6] and Watson [8], and in the fifth row are terms specific to our model.

3.2.3 Comparison with Previous Formulas from Literature

In the case of the HBJ [5] large amplitude bending vibration approach, the Q_1 and Q_3 normal stretching coordinates were used, instead of our S^s and S^a coordinates. The same normal coordinates Q_1, Q_3 are used in BL [14] semirigid bender Hamiltonian as well as in Hoy and Bunker [17] and Jensen [6] non-rigid bender Hamiltonian. For this reasons, in all these papers $g_{11} = g_{33} = 1, g_{1\alpha} = g_{3\alpha} = 0$, where $\alpha = x, y, z, \rho$. This simplify the kinetic energy formula, but usually it is more difficult to use normal coordinates in numerical computing.

In the case of MORBID Hamiltonian [7], the stretching part is described in [7, eq.(15) and eq.(39)], as: $\frac{1}{2}\dot{S}\hat{G}^{-1}\dot{S}$ (classical energy), and the $\hat{G}$ matrix has the form [6, eq.(3.20)]

$$\hat{G} = \begin{pmatrix} \frac{R_3(r^0,\rho)}{m_1} & 0 \\ 0 & \frac{R_4(r^0,\rho)}{m_1} \end{pmatrix} \tag{3.41}$$

for a symmetric molecule. This will determine a term of stretching as:
$\frac{1}{2}\frac{m_1}{R_3(r^0,\rho)}\left[\left(\dot{S}^s\right)^{Jen}\right]^2 + \frac{1}{2}\frac{m_1}{R_4(r^0,\rho)}\left[\left(\dot{S}^a\right)^{Jen}\right]^2$

If we use the eq.(3.30) (with $r'(\rho) = 0$) , we will find that in our coordinates the term will be:

$$\frac{1}{2}m_1 R_3 \left(\dot{S}^s\right)^2 + \frac{1}{2}m_1 R_4 \left(\dot{S}^a\right)^2 \tag{3.42}$$

If we are comparing the relation (3.42) with (3.33) and (3.38), we will see that it is the same term as in our case, but $g_{as} = 0$ in the MORBID Hamiltonian.

In the HBJ formalism, the rigid-bender is used for the large amplitude bending vibration. The $g_{\rho\rho}$ and $g_{\varphi\varphi}$ from (3.38), in the rigid-bender limit, coincides with $I_{\rho\rho}$ and I_{zz}. The second and the last two lines in eq.(3.40) do not exist in the HBJ formalism. The last term of the first line from eq. (3.40) is different too, in our formalism we have $g_0^{\rho\rho}$ instead of $g^{\rho\rho}$.

The semirigid bender formalism of BL [14] is the same as the HBJ formalism, except that $g_{\rho\rho}$ and $g_{\varphi\varphi}$ from (3.38) are identical with $I_{\rho\rho}$ and I_{zz}. (however in [14], for the expression of $I_{\rho\rho}$ the terms in $r^{0'}$ were omitted).

In the case of the non-rigid bender Hamiltonian, of [17] or [6], the first, third and fourth lines of the eq.(3.40) have a similar formal behavior as in our model. We will emphasis the differences between the two approaches:

- in the non-rigid approach, the bond length is constant and therefore $r^{0'} = 0$, in the $\mu_{\alpha\beta}$ terms
- the fourth line of (3.40) is similar with the term: $\frac{1}{2}\mu^{\frac{1}{4}} \sum_r \left[P_r, \mu^{-\frac{1}{4}} \left[P_r, \mu^{\frac{1}{4}}\right]\right]$ of [17] or [6]. The difference between the two approaches arise from the last formula, where μ contains I_{xx}, I_{yy} terms, compared with our formalism.

In the initial stretch-bender approach [186], the derivatives have been evaluated after setting $S^s = 0$ and $S^a = 0$. This means that the metric tensor is in fact diagonal, $g_{\alpha\beta} = g_{\alpha\alpha}\delta_{\alpha\beta}$, and all the derivatives other than $\frac{\partial^n}{\partial\rho^n}$ vanishes. The last two lines of the eq.(3.40) do not exist in this formalism. The eq.(3.40) is correct to order of magnitude $k^2 T_v$, where:

- k is the Born-Oppenheimer expansion coefficient $k = (\frac{m_e}{m})^{\frac{1}{4}}$, where m_e and m are the electronic and nuclear mass, respectively.
- T_v is a typical small amplitude vibrational energy (evaluation in §B.6).

The kinetic energy order of magnitude is the same as for the non-rigid bender Hamiltonian [17, 6].

3.2.4 The Final Kinetic Hamiltonian in Reference Coordinates

We are expanding now the eq. (3.40) and changing the wavefunctions for the pure bending Hamiltonian, as in HBJ formalism [5]. We will expand some of the $\mu_{\alpha\beta} = g^{\alpha\beta}$ terms in the powers series of the reference coordinates (implicit S^s and S^a are small stretching vibrations).

The rotation bending Hamiltonian will be obtained from the eq.(3.40) as:

$$\begin{aligned} T_{rb} &= \frac{1}{2}g_0^{\rho\rho} \cdot P_\rho^2 + \frac{1}{2}\left[P_\rho, g_0^{\rho\rho}\right] P_\rho + \frac{1}{2}(g_0)^{-\frac{1}{4}} \left[P_\rho, g_0^{\rho\rho}(g_0)^{\frac{1}{2}} \left[P_\rho, g_0^{-\frac{1}{4}}\right]\right] \\ &+ \frac{1}{2}g_0^{\varphi\varphi} P_\varphi^2 \end{aligned} \tag{3.43}$$

We will consider the substitution [5]:

$$\Psi_b(\rho) = (g^{\rho\rho})^{-\frac{1}{2}} \cdot \Phi_b(\rho) \tag{3.44}$$

This substitution will remove the linear derivative terms and the eq.(3.43) become (§B.7):

$$T_{rb} = \frac{1}{2}g_0^{\rho\rho} \cdot P_\rho^2 + \frac{\hbar^2}{2} g^{\rho\rho} f_0(\rho) + \frac{1}{2}g_0^{\varphi\varphi} P_\varphi^2 \tag{3.45}$$

where:

$$f_0(\rho) = (g_0)^{-\frac{1}{4}} (g_0^{\rho\rho})^{-\frac{1}{2}} \frac{\partial^2}{\partial\rho^2} \left[(g_0)^{\frac{1}{4}} (g_0^{\rho\rho})^{\frac{1}{2}} \right]$$

$$f_0(\rho)|_{\rho\to 0} \simeq -\frac{1}{16} \left[\frac{1+\sin^2\left(\frac{\rho}{2}\right)}{\sin^2\left(\frac{\rho}{2}\right)} \right] \tag{3.46}$$

Near $\rho \simeq 0$ this correction term behaves like $\left(-\frac{1}{4\rho^2}\right)$ as given by [5] and it is the most important term for small bending angles. We recover the rigid-bender formalism of [5] by omitting all the derivatives in S^s and S^a and by taking r^0 as a constant. If r^0 is allowed to vary with the ρ angle, we will obtain the semirigid bender formalism of [14].

The substitution (3.44) is equivalent to the transformation $(g_0^{\rho\rho})^{\frac{1}{2}} H_{rb}^{kin} (g_0^{\rho\rho})^{-\frac{1}{2}}$. This transformation change the volume element $dV = d\rho\, d\varphi\, dS^s\, dS^a$ to $dV = (g_0^{\rho\rho})^{-1} d\rho\, d\varphi\, dS^s\, dS^a$.

Before discussing in more detail the last term in the first row of eq. (3.40), we must analyze the expansion of $\mu_{\alpha\beta}$ terms in (S^s) and (S^a) powers series. The expansion is similar to [8, eq.(31)] or [6, eq.(4.24)] as it can be seen in (§B.8):

$$\begin{aligned} \mu_{\alpha\beta}(\rho, S^s, S^a) &= \mu^0_{\alpha\beta} - \sum_r \sum_{\delta\gamma} \mu^0_{\alpha\delta} a_r^{\delta\gamma} \mu^0_{\gamma\beta} S^r \\ &+ \sum_{rt} \left[-\sum_{\delta\gamma} \mu^0_{\alpha\delta}\, a_{rt}^{\delta\gamma}\, \mu^0_{\gamma\beta} + \sum_{\delta\gamma\epsilon\eta} \mu^0_{\alpha\delta}\, a_r^{\delta\gamma} \mu^0_{\gamma\epsilon} a_t^{\epsilon\eta} \mu^0_{\eta\beta} \right] \cdot S^r\, S^t \end{aligned} \tag{3.47}$$

where:

$\mu^0_{\alpha\beta} = \mu_{\alpha\alpha}\delta_{\alpha\beta}$ $\quad a_r^{\alpha\beta} = \left(\frac{\partial g_{\alpha\beta}}{\partial S^r}\right)|_0$ $\quad a_{rt}^{\alpha\beta} = \left(\frac{\partial^2 g_{\alpha\beta}}{\partial S^r\, \partial S^t}\right)|_0$

The differences between the eq.(3.47) and the literature (term $a_{rs}^{\alpha\beta}$, a missing $\frac{3}{4}$) arise from the difference in our stretching coordinates. With this expansion, the last term in the first line of (3.40) become (§B.9):

$$\begin{aligned} \frac{1}{2}(g_0)^{-\frac{1}{4}} \left[P_\rho, g^{\rho\rho}(g_0)^{\frac{1}{2}} \left[P_\rho, (g_0)^{-\frac{1}{4}}\right]\right] &\simeq \frac{1}{2}(g_0)^{-\frac{1}{4}} \left[P_\rho, g_0^{\rho\rho}(g_0)^{\frac{1}{2}} \left[P_\rho, (g_0)^{-\frac{1}{4}}\right]\right] \\ &+ (g_0)^{-\frac{1}{4}} \left[P_\rho, (g_0)^{\frac{1}{2}} \left[P_\rho, (g_0)^{-\frac{1}{4}}\right]\right] \times \\ &\left(\sum_r f_1^r(\rho) S^r + \sum_{rt} f_2^{rt}(\rho) S^r S^t\right) \end{aligned} \tag{3.48}$$

where $f_1(\rho)^r$ and $f_2(\rho)^{rt}$ are functions of ρ, only. The last term in eq.(3.48) is similar to the last term in [6, eq. (4.42)].

The stretching term in the kinetic energy, from (3.40) is:

$$T_{str} = \frac{1}{2} g^{ss} \cdot P_s^2 + \frac{1}{2} g^{aa} \cdot P_a^2 \tag{3.49}$$

By taking into account the consideration from (§3.2.2) together with the eq. (3.45) and (3.48), the eq.(3.40) can be rearranged as it is shown in (§B.10):

$$\begin{aligned} T \simeq\ & T^0_{rb} + T_{str} \\ & + \frac{1}{2}(g_0)^{-\frac{1}{4}} g_0^{ss} \left[P_s, g^{\frac{1}{2}} \left[P_s, g^{-\frac{1}{4}}\right]\right]_0 + \frac{1}{2}(g_0)^{\frac{1}{4}} g_0^{aa} \left[P_a, \left[P_a, g^{-\frac{1}{4}}\right]\right]_0 \\ & - \frac{1}{2} g_0^{\rho\rho}(g_0)^{\frac{1}{4}} \left[P_\rho, (g_0)^{-\frac{1}{4}}\right] \left\{g_0^{ss}[P_s, g_{s\rho}]_0 + g_0^{aa}[P_a, g_{a\rho}]_0\right\} \\ & + \frac{1}{2}(g_0)^{-\frac{1}{4}} \left[P_\rho, (g_0)^{\frac{1}{2}} \left[P_\rho, (g_0)^{-\frac{1}{4}}\right]\right] (g_0^{\rho\rho})^2 \times \left\{-a_s^{\rho\rho} \cdot S^s \right. \\ & \left. + \left[-a_{ss}^{\rho\rho} + (a_s^{\rho s}\, g_0^{ss}\, a_s^{\rho s} + a_s^{\rho\rho}\, g_0^{\rho\rho}\, a_s^{\rho\rho})\right](S^s)^2 + \left[-a_{aa}^{\rho\rho} + a_a^{\rho a}\, g_0^{aa}\, a_a^{\rho a}\right](S^a)^2\right\} \end{aligned} \tag{3.50}$$

The second line of eq.(3.50) is similar with U_0 from [6, eq.(4.44)], as previously discussed. The second and the third lines can be incorporated in the bending kinetic energy because they are functions depending on ρ, only:

$$T_{rb} = T_{rb}^0 + (\text{row 2-3.50}) + (\text{row 3-3.50}) \tag{3.51}$$

The pseudo-potential term for the bending kinetic energy will be:

$$f(\rho) = f_0(\rho) + \left(\frac{\hbar^2}{2}\right)^{-1} (g_0^{\rho\rho})^{-1} [(\text{row 2-3.50}) + (\text{row 3-3.50})]$$

Near $\rho \approx 0$, the $f(\rho)$ terms behaves like $f_0(\rho)$ (§B.11).

The final kinetic energy term become:

$$\begin{aligned} T \simeq\ & T_{rb} + T_{str} \\ & + \frac{1}{2} (g_0)^{-\frac{1}{4}} \left[P_\rho\,, (g_0)^{\frac{1}{2}} \left[P_\rho\,, (g_0)^{-\frac{1}{4}}\right]\right] (g_0^{\rho\rho})^2 \times \{-a_s^{\rho\rho} \cdot S^s \\ & + [-a_{ss}^{\rho\rho} + (a_s^{\rho s}\, g_0^{ss}\, a_s^{\rho s} + a_s^{\rho\rho}\, g_0^{\rho\rho}\, a_s^{\rho\rho})] (S^s)^2 + [-a_{aa}^{\rho\rho} + a_a^{\rho a}\, g_0^{aa}\, a_a^{\rho a}] (S^a)^2 \Big\} \end{aligned} \tag{3.52}$$

3.3 Potential Energy

3.3.1 The Semi-Rigid Bender Approximation

In the semirigid bender approximation, we allow the bond length to vary with the bending angle in such a manner that the nuclei move along the valley of the potential function as the molecule bends.

We use the generalized internal coordinates, that are related to the internal displacement coordinates by the eq.(3.13). If we are considering the symmetry coordinates, Δr_s and Δr_a the relation will be:

$$\begin{aligned} \Delta r_s &= \frac{1}{\sqrt{2}} (\Delta r_{12} + \Delta r_{23}) = R_1 \left(r^0\,, \rho\right) S^s + \sqrt{2}\, \mathcal{R}(\rho) \\ \Delta r_a &= \frac{1}{\sqrt{2}} (\Delta r_{12} - \Delta r_{23}) = R_5 \left(r^0\,, \rho\right) S^a \end{aligned} \tag{3.53}$$

By analyzing the eq.(3.53) we find that the angle variation of the bond length along the valley of the potential function (case when $S^s = S^a = 0$, no stretching movements) is:

$$\Delta r_s|_{S^s=0} = \sqrt{2}\, \mathcal{R}(\rho) \quad \text{and} \quad \Delta r_a|_{S^a=0} = 0 \tag{3.54}$$

The potential corresponding to the stretching is the complete intramolecular potential function, expanded as a Taylor power series in the generalized internal coordinates.

We choose the ρ dependent bond lengths r_{ij} to be such that $\left(\frac{\partial V^{as}}{\partial \Delta r_{ij}}\right) = 0$ for each value of the bending angle ρ.

The potential energy expansion coefficients in the terms of an instantaneous configuration is truncated after the cubic term (§C.1), to *analyze only the terms connected with the bond length due to the bond angle*

$$\begin{aligned} V^{as}(\bar{\rho}, \Delta r_s, \Delta r_a) = & \frac{1}{2} (f_{11} + f_{13})\, \Delta r_s^2 + \frac{1}{2} (f_{11} - f_{13})\, \Delta r_a^2 \\ & + \sqrt{2} F_{122} \Delta r_s\, (\bar{\rho} - \rho_e)^2 + \mathcal{O}|_{n+m>4} (\rho^m \Delta r_s^n) \end{aligned} \tag{3.55}$$

By analyzing the eq.(3.55) we find that the angle variation of the bond length is given by [189]:

$$\mathcal{R}(\rho) = -\frac{F_{122} \cdot (\rho - \rho_e)^2}{f_{11} + f_{13}} \tag{3.56}$$

If we include the eq.(3.53) in the potential form (3.55), we will find the potential in curvilinear stretch-bender coordinates, in an instantaneous configuration (§C.2):

$$\begin{aligned} V^{as}(\bar{\rho}, \Delta r_s, \Delta r_a) &= \frac{1}{2}(f_{11} + f_{13})\, R_1^2(r^0, \rho)\, (S^s)^2 \\ &+ \frac{1}{2}(f_{11} - f_{13})\, R_5^2(r^0, \rho)\, (S^a)^2 + \mathcal{O}(\rho^4) \end{aligned} \tag{3.57}$$

There are some aspects that must be emphases concerning the above formula:

- The term corresponding to the Fermi interaction in the eq.(3.56) vanish in the stretch-bender approach (eq. (3.57)), expressed in an instantaneous configuration.
- The coordinate r_i^0 in the eq.(3.1) are effective bond lengths since they are averaged over the stretching part of the potential function. These bond lengths are slightly different from the effective bond lengths that occur in the rigid bender because of the separate treatment of the stretch-bender force constants in the semirigid bender. These bond lengths vary with the stretching vibrational state and with isotopic substitution [14].
- If we take into account all the terms in the generalized potential, not only those from the eq.(3.55) and if we are neglecting the quartic and upper terms, the variation of the bond length (3.56) do not change the expression for a linear molecule (§C.3), compared with the BL formalism [14].

It is important that all the terms in the kinetic and potential energy to have the same order of magnitude. The kinetic energy is assumed to have the order of magnitude k^2T_v (see §3.2.3). The derivation of $\mathcal{R}(\rho)$ formula (the ρ dependence of the bond length) is proceeded only in the first order kT_v of magnitude, because a term in the expansion (3.55), containing n powers of vibrational coordinates (bending, stretching) is assumed to have the order of magnitude $k^{n-2}T_v$, $n \geq 2$. This apparently mismatch is due to the algebraic problem (for a rigorous k^2T_v order of magnitude, we must solve an equation of third order (§C.3) and is important only for terms greater than $(\rho_e - \rho)^n$, $n \geq 3$.

3.3.2 Change from the Instantaneous Frame to Reference Frame

In order to do the change from the instantaneous frame to the reference frame, we need to transform all the functions, from those in terms of $\bar{\rho}$, to those expressed in terms of ρ. This transformation has been discussed in detail in (§3.1.2). It is important to appreciate that the angle ρ (defined by eq.(3.5)) for the purpose of simplifying the kinetic energy expression, is different from the geometrically defined angle $\bar{\rho}$ if the molecule is not in its reference configuration. We use ρ because is leads to a kinetic energy operator with minimized couplings between over-all vibration, large amplitude bending and small amplitude bond stretching. However, the *ab initio* potential energy is expressed in terms of the isotopically invariant quantity $\bar{\rho}$ (see next section) and we must express $\bar{\rho}$ in terms of ρ in order to obtain V as a function of $\mathbf{R}^1$, $\mathbf{R}^3$, ρ. The equation relating ρ and $\bar{\rho}$ is (3.11). For $S^s = 0$ and $S^a = 0$, this equation requires $\bar{\rho} = \rho$ as it should be for the molecule in the reference configuration.

The semirigid bender approach is present in $R_2(r^0, \rho)$ function, in (3.12) and express the change of the reference configuration when the molecule stretch.

In the semirigid bender approach, the bond length change when the bond angle change and this determine a changing of the stretching reference configuration in function of the bonding angle. We are using the stretch coordinate of the reference frame in order to simplify the potential energy expression in the instantaneous configuration (3.57). The $\mathcal{R}'(\rho) = r'(\rho)$ function, (3.15) is different from zero only in the semirigid approach and express the change of the reference configuration when the molecule bends.

3.3.3 The Potential Energy

The potential energy operator is initially written in terms of the instantaneous axis coordinates $(\bar{\rho}, r_{12}, r_{23})$, since in these coordinates it is most easily to be compared with surfaces derived from the *ab initio* electronic structure calculations.

$$\begin{aligned} V(\bar{\rho}, \Delta r_{12}, \Delta r_{23}) &= \frac{1}{2}\sum_{ij} f_{ij}\,\mathbf{R}^i\,\mathbf{R}^j + \sum_{i\le j\le k} F_{ijk}\mathbf{R}^i\,\mathbf{R}^j\,\mathbf{R}^k \\ &+ \sum_{i\le j\le k\le l} F_{ijkl}\mathbf{R}^i\,\mathbf{R}^j\,\mathbf{R}^k\,\mathbf{R}^l + \mathcal{O}\left((\mathbf{R})^5\right) \end{aligned} \tag{3.58}$$

where

$$\mathbf{R}^1 = \Delta r_{12} = r_{12} - r_{12}^e \quad \mathbf{R}^2 = \Delta\bar{\rho} = \bar{\rho} - \rho_e \quad \mathbf{R}^3 = \Delta r_{23} = r_{23} - r_{23}^e$$

and $r_{12}^e, r_{23}^e, \rho_e$ are the values at the minimum potential energy.

The parameters of the nuclear potential function in the Born -Oppenheimer approximation are isotopically independent, since $\mathbf{R}^i$ and $\Delta\bar{\rho}$ are geometrically defined coordinates [6]. The $F_{ij\ldots}$ terms are similar with those of [46]. In the potential, the series expansion is truncated after the quartic terms and is consequently correct to order of magnitude $k^2\,T_v$.

Using $\Delta\bar{\rho}$, we can rewrite eq.(3.58) for each value of $\bar{\rho}$ as series expansion in $\mathbf{R}^1$ and $\mathbf{R}^3$ with $\bar{\rho}$ -dependent expansion coefficients (§C.3),

$$V(\bar{\rho}, \Delta r_{12}, \Delta r_{23}) = V^b(\bar{\rho}) + V^{as}(\bar{\rho}, \Delta r_{12}, \Delta r_{23}) \tag{3.59}$$

The first term relates to bending and the second one to the stretching, as it can be seen:

$$V^b(\bar{\rho}) = V_0(\bar{\rho}) = F_{22}(\rho_e - \bar{\rho})^2 + F_{222}(\rho_e - \bar{\rho})^3 + F_{2222}(\rho_e - \bar{\rho})^4$$

$$\begin{aligned} V^{as}(\bar{\rho}, \Delta r_{12}, \Delta r_{23}) &= \sum_i \bar{F}_i(\rho)\mathbf{R}^i + \sum_{i\le j}\bar{F}_{ij}(\rho)\,\mathbf{R}^i\,\mathbf{R}^j \\ &+ \sum_{i\le j\le k}\bar{F}_{ijk}(\rho)\,\mathbf{R}^i\,\mathbf{R}^j\,\mathbf{R}^k + \sum_{i\le j\le k\le l}\bar{F}_{ijkl}(\rho)\,\mathbf{R}^i\,\mathbf{R}^j\,\mathbf{R}^k\,\mathbf{R}^l \end{aligned} \tag{3.60}$$

and the $\bar{F}_{ij\ldots}(\rho)$ terms are defined in (§C.3).

If $(\rho_e - \bar{\rho})$ is of large amplitude, that the power series representations for $V_0(\bar{\rho})$ and $\bar{F}_{ij\ldots}(\rho)$-tensor elements will be replaced by the explicit functions, although it may be difficult to express the $\bar{\rho}$ dependence of the $\bar{F}(\rho)$- tensor elements. We can, however, easily express $V_0(\bar{\rho})$. It should be noted that the functions $\bar{F}_{ij\ldots}(\rho)$ do not necessarily fulfill the equation $\left(\frac{\partial V}{\partial\bar{\rho}}\right)$, for $\bar{\rho} = 0$ (i.e. the potential energy function is not necessarily an even function of $\bar{\rho}$). This does not matter when the barrier to linearity is high so that the bending wavefunctions have a vanishing amplitude near linearity. When the barrier to linearity is low (or zero), the parameterization of V_0 and the $\bar{F}(\rho)$ tensor elements must be chosen as an even function of $\bar{\rho}$, by symmetry (it is no difference between $V(\bar{\rho})$ and $V(-\bar{\rho})$). It is, however, essential in the development of the stretch-bender theory that $V(\bar{\rho}, \Delta r_{12}, \Delta r_{23})$ can be expanded as a Taylor series expansion (with $\bar{\rho}$ dependent expansion coefficients) in the small amplitude $\mathbf{R}^1$ and $\mathbf{R}^3$ coordinates. This is because the harmonic oscillator model is used to treat the ν_1 and ν_3 vibrations.

Since we wish to express the potential energy surface in terms of a reference configuration, we will replace the eq. (3.59) by:

$$V(\Delta\rho, \Delta r_1, \Delta r_3) = V^b(\Delta\rho) + \hat{V}^{as}(\Delta\rho, \Delta r_1, \Delta r_3) \tag{3.61}$$

The change from the instantaneous to the reference frame is based on the transformation of all the functions from $\bar{\rho}, \Delta r_{12}, \Delta r_{23}$ to the $\rho, \Delta r_1, \Delta r_3$ dependence. For ρ this type of transformation has been discussed in eq. (3.11) and in [6]. For $\Delta r_1, \Delta r_3$, the transformation is done in eq. (3.13).

In our expansion (3.61) some of the terms above will be folded into the effective stretching force constants, whereas for the large amplitude bending part, we have chosen to keep the extra expansion terms. This means that some of the higher-order stretch-bend interactions will need to be included in the perturbation terms (which will be discussed later).

We initially consider the expansion of the stretching part of the potential function since we have separated $V(\rho, \Delta r_1, \Delta r_3)$ into a bending and a stretching part and since the latter vibrations are assumed to be of small amplitude, too.

The Stretching Potential

In the harmonic oscillator model we have assumed that the bond length obeys Hooke's law, with a potential which is almost harmonic , with a small anharmonic correction, too. Within this approximation we write the potential energy operator in the "potential valley" reference frame, by taking into account the semirigid bender approach, as:

$$V^{as}(\bar{\rho}, \Delta r_1, \Delta r_3) = \bar{F}_{11}(\rho)\left[\Delta r_1^2 + \Delta r_3^2\right] + \bar{F}_{13}(\rho) \cdot \Delta r_1 \cdot \Delta r_3 \tag{3.62}$$

The linear term in $\mathbf{R}^i$ in eq. (3.60) vanish in the zeroth order of the semirigid approach, because (§C.3):

$$(\Delta r_1)\,|_0 = r_i(\rho_0) - r_i^0 = -\frac{1}{2}\frac{\bar{F}_i(\rho)}{\bar{F}_{ii}(\rho)}$$

(similar to the eq. (3.56) and $\left(\frac{\partial V^{as}(\rho)}{\partial(\mathbf{R}^i)}\right)_0 = 0$).

As we are assuming that the stretching displacement from the reference stretch-bender frame is small, we can use the eq.(3.13) in order to expand the generalized stretching coordinates in function of the stretch coordinates introduced by our stretch-bender model. We can rewrite the eq.(3.62) by using these expansions, as:

$$\begin{aligned} V^{as}(\bar{\rho}\,\bar{S}^s, \bar{S}^a) &= \left[\bar{F}_{11}(\bar{\rho}) + \bar{F}_{13}(\bar{\rho})\right] R_1^2\left(r^0, \bar{\rho}\right)\left(\bar{S}^s\right)^2 \\ &+ \left[\bar{F}_{11}(\bar{\rho}) - \bar{F}_{13}(\bar{\rho})\right] R_5^2\left(r^0, \bar{\rho}\right)\left(\bar{S}^a\right)^2 \end{aligned} \tag{3.63}$$

The eq.(3.63) is similar to the eq.(3.57), but in this case the potential constants $\bar{F}_{ij}(\bar{\rho})$ are functions of $\bar{\rho}$ and not constant, as in (3.57). When we are changing to the stretching reference frame, we are obtaining some pure bending terms, which will be introduced in the bending potential part, as mention above.

In eq.(3.63) and below we will suppose in the first approximation that $\bar{F}_{ij}(\bar{\rho}) \approx F_{ij}(\rho)$, it means the instantaneous and the reference frames are enough close and the stretching amplitude is small relative to the reference stretch-bender frame.

We need to obtain an expression in terms of reference stretching coordinates, rather that the instantaneous ones. The instantaneous stretching coordinates, may be written to the first order in terms of the reference stretching coordinates, as in eq.(3.14). The potential energy in the instantaneous configuration can be related to that in the reference frame by:

$$V^{as}(\bar{\rho}, \bar{S}^s, \bar{S}^a) = V_0^{as}(\rho, S^s, S^a) + \sum_{i=s,a}\left(\frac{\partial V^{as}}{\partial \bar{S}^i}\right)_0\left(\frac{\partial \bar{S}^i}{\partial \rho}\right)_0(\rho - \rho_e) \tag{3.64}$$

Taking into account $\left(\frac{\partial \bar{S}^i}{\partial \rho}\right)$, i=a,s, from the eq.(3.15) and $V_0^{as}(\rho, S^s, S^a)$ from eq.(3.63), the potential $V^{as}(\bar{\rho}, \bar{S}^s, \bar{S}^a)$ become:

$$V^{as}(\bar{\rho}, \bar{S}^s, \bar{S}^a) = V_0^{as}(\rho, S^s, S^a) + \sqrt{2}\, f_{eff}^s(\rho)\,\frac{r'(\rho)}{R_1\left(r^0, \rho\right)}\,S^s\,(\rho - \rho_e) \tag{3.65}$$

with:

$$V_0^{as}(\rho, S^s, S^a) = \frac{1}{2} f_{eff}^s(\rho)\left(S^s\right)^2 + \frac{1}{2} f_{eff}^a(\rho)\left(S^a\right)^2 \tag{3.66}$$

$$f^s_{eff} = [f_{11}(\rho) + f_{13}(\rho)] \cdot \left(R_1\left(r^0, \rho\right)\right)^2$$
$$f^a_{eff} = [f_{11}(\rho) - f_{13}(\rho)] \cdot \left(R_5\left(r^0, \rho\right)\right)^2$$

$f_{11}(\rho)$ and $f_{13}(\rho)$ are the potential coefficients in the reference configuration.

If we consider the terms from eq.(3.66) near $\rho \to 0$, we have (with eq.(3.25)) the harmonic terms [189]:

$$f^s_{eff} = [f_{11} + f_{13}]_0 \tag{3.67}$$
$$f^a_{eff} = p^2 \cdot [f_{11} - f_{13}]_0 \qquad [\text{ cm}^{-1}/\text{Å}^2]$$

Apparent, in this reference system, the f^a_{eff} antisymmetric term enter with a greater weight (a facto of p^2) than in the true valence-force coordinate system as it is seen from above equation. But from the eq.(3.26) we see that $S^a \approx \frac{1}{p}(S^a)^{Jen}$ and in reality

$$f^a_{eff}(S^a)^2 \equiv (f_{11} - f_{13})_0 \left[(S^a)^{Jen}\right]^2$$

The covariants elements of the metric tensor (from eq.(3.38)) g_{ss} and g_{aa}, have simultaneously, near $\rho \to 0$, the values: $g_{ss} \approx m_1$ and $g_{aa} \approx m_1 \cdot p$

The Bending Potential

As it was expressed above, it is easy to model $V_0(\bar{\rho})$, the Born-Oppenheimer potential functions for the bending problem. It is important to write the expressions for the Born-Oppenheimer potential functions in such a way that the correlation between the parameters is minimized.

A general potential function can be chosen as a linear molecule harmonic oscillator function plus a Lorentzian perturbation [5, 14, 147],

$$V^b(\bar{\rho}) = \frac{1}{2} k \bar{\rho}^2 + \frac{a}{b + \bar{\rho}^2} + V^b_2(\bar{\rho}) \tag{3.68}$$

where the correction terms may be needed to polish the slope of the potential. But the parameters in eq. (3.68) become highly correlated when the molecule is strongly non - linear at equilibrium and it is better to use the alternative form [147]:

$$V^b(\bar{\rho}) = \frac{hf\left(\bar{\rho}^2 - \rho_e^2\right)^2}{f\rho_e^4 + (8h - f\rho_e^2)\bar{\rho}^2} + V^b_2(\bar{\rho}) \tag{3.69}$$

where h is the barrier to linearity for the Born-Oppenheimer component and f is the harmonic oscillator force constant for the bending near ρ_e (the equilibrium angle). The relationship between the sets of parameters have been derived in [14, 6]. In addition to the above bending potentials, it is necessary to include the corrections terms to quartic order [147]:

$$V^b_2(\bar{\rho}) = k_4 \frac{\bar{\rho}^2\left(\bar{\rho}^2 - \rho_e^2\right)^3}{\left(\bar{\rho}^2 + \rho_e^2\right)^2} \tag{3.70}$$

The terms from (3.70) has a cubic dependence near the minimum and become quartic for $\bar{\rho} \gg \rho_e$.

In order to obtain an expansion in terms of the reference bending coordinates, rather that the instantaneous one, we use the eq.(3.11), written to the first order.

The bending potential energy, in the reference frame is given by:

$$V^b(\bar{\rho}) = V^b_0(\rho) + \sum_{i=s,a}\left(\frac{\partial V^b(\rho)}{\partial \bar{\rho}}\right)_0 \left(\frac{\partial \bar{\rho}}{\partial S^i}\right)_0 S^i \tag{3.71}$$

The $\left(\frac{\partial \bar{\rho}}{\partial S^i}\right)_0$, $i = s, a$ are done in eq. (3.12).

The final bending potential become:

$$V^b(\bar{\rho}) = V_0^b(\rho) - \left(\frac{\partial V^b(\rho)}{\partial \rho}\right)_0 \frac{R_2(r^0,\rho)}{\sqrt{2}\,r^0(\rho)} S^s \tag{3.72}$$

Here the second term is a stretch bender interaction term and will be introduced to the stretching potential.

The Anharmonic Term of Potential

We must emphasis some aspects of anharmonic term arising from the eq.(3.64) and (3.71). The anharmonic term, linear in S^s (term which represents the cause of the Fermi effect) is:

$$-f_{22}\frac{R_2(\rho)}{\sqrt{2}r^0}(\rho-\rho_e) + \sqrt{2}\cdot f_{eff}^s(\rho)\,\frac{r'(\rho)}{R_1(\rho)}\,(\rho-\rho_e) \qquad [\,\mathrm{cm}^{-1}/\mathrm{\AA}] \tag{3.73}$$

where we suppose that, for $\rho_e \to 0$, $V_0^b(\rho) \approx \frac{1}{2} f_{22}\rho^2$ (from (3.68 and (3.69)). We discuss the term arising from the bending potential(3.71) :

1. If $V_0^b(\rho) = \frac{1}{2} f_{22}\rho^2$ (purely harmonic potential in the case of a linear molecule), we have for small ρ angles in the rigid - bender limit, $R_2(\rho) \approx -(p-1)\cdot\rho$, and then:

$$-\left(\frac{\partial\, V_0^b(\rho)}{\partial\rho}\right)_0 \frac{R_2(r^0,\rho)}{\sqrt{2}\,r_\rho} S^s \approx f_{22}\,\frac{p-1}{\sqrt{2}\,r_\rho}\,\rho^2 S^s \tag{3.74}$$

   This term is identical with $(K_{122}+K_{322})$ from [5, eq.(55)-(56)], where $\left[\frac{u_{13}(u_1+u_3)}{r(u_1u_3-u_{13}^2)}\right]|_{sym} = \frac{m_1}{r(\rho)\,m_2}$. The term arise during the transformation of the generalized coordinates to curvilinear ones. This term is similar with the A_1 term from [6, table 1], in the case of $\rho \to 0$.

2. In the case of the rigid-bender limit, apparently, only the term from the eq. (3.74) contributes to the anharmonic constant. But it is to remember the term $F_{122} = \frac{1}{2} f_{122}$, from eq. (3.55), which will not vanish, and therefore it will be added to the potential constant.

3. In the semirigid bender approach, the term has a component which depends on $r'(\rho)$ and to the square of the bending angle.

4. The term of eq.(3.73) is correct in the case of a linear molecule, when $\rho_e = 0$, but in the case of a bent molecule it is probably to be necessary other definition of eq.(3.14).

The term from the stretching potential (3.64) arises only in the semirigid bender approach (dependence on $r'(\rho)$ as it can be seen in eq. (3.73)). It should be noted that even if the anharmonic term vanishes in the semirigid approach, as expressed in the eq. (3.57) and [153], when we are changing the terms from the instantaneous frame to the reference frame, the terms of eq. (3.73) will appear.

For $\rho_e \to 0$, when we are using eq. (3.56), (3.25) for $R_1(r^0, \rho)$ and $\rho \to \rho_e$, the term of order of magnitude $(\rho^2 \cdot S^s)$ is

$$(p-1)\cdot\frac{f_{22}}{\sqrt{2}\,r^0} - 2\sqrt{2}\cdot F_{122} \qquad [\,\mathrm{cm}^{-1}/\mathrm{\AA}] \tag{3.75}$$

What it is interesting in eq.(3.73) is that we have a cubic Fermi interaction term which depends on the potential function as well as on the masses, bond lengths and their derivatives. This is obviously the consequence of:

- on adjusting the bond length on each angle ρ^0

- our definition for the stretching displacement S^s and S^a such that the stretch-bend kinetic energy operator (eq. (3.40), pag. 69) is separable.

Obs. *1* In the case of the "asymmetric" transformation

$$\begin{array}{l} S^s = S_1 + S_2 \\ S^a = S_1 - S_2 \end{array} \quad \left(\begin{array}{l} S_1 = \frac{1}{2}(S^s + S^a) \\ S_2 = \frac{1}{2}(S^s - S^a) \end{array} \right) \tag{3.76}$$

used in [186], the formula (3.73) for the interaction term will change,

$$f_{22}\frac{R_2(r^0,\rho)}{r^0}\ (\rho - \rho_e) + f^s_{eff}(\rho)\frac{r'(\rho)}{R_1(r^0,\rho)}\ (\rho - \rho_e) \tag{3.77}$$

where the constants f_{22} and f^s_{eff} are those from the "asymmetric" transformation.

Obs. *2* The formula (3.66) for the effective harmonic stretching constants will be, for the "asymmetric" transformation:

$$\begin{aligned} f^s_{eff} &= 2\left[f_{11}(\rho) + f_{13}(\rho)\right]\left(R_1(r^0,\rho)\right)^2 \\ f^a_{eff} &= 2\left[f_{11}(\rho) - f_{13}(\rho)\right]\left(R_5(r^0,\rho)\right)^2 \end{aligned} \tag{3.78}$$

Obs. *3* If we are comparing the eq.(3.66), (3.73) with the eq.(3.77), (3.78), we can define the "stretching" mass, as $m_{str} = 2 \cdot m_1$

3.3.4 The Relations between Literature and the Stretch-Bender Model Potential Constants

The conversion of the potential constants between different types of coordinates may be done only in the case of $\rho \to 0$. This is due to the fact that the Taylor expansion in power series of terms has an limited number of terms (usually up to fourth-order terms). In our case we are concerned only with the term $F_{s\rho\rho}$ (third order term) and $F_{\rho\rho\rho\rho}$ (fourth order term), because our potential type (§3.3.3) has a small number of parameters.

There are some points to be emphasized:

Obs. *1* The quadratic term in the bending potential [eq. (3.68) or (3.69)] take into account some terms of higher degree when expanded in Taylor series, near $\rho \simeq \rho_e$. For values $\rho \to \rho_e$ (with $\rho_e = 0$ in the case of the eq. (3.68)), both potentials have the known expression of the harmonic oscilator potential:

$$\frac{1}{2}k\rho^2$$

Obs. *2* The effective stretch potential coefficients in eq. (3.66) , include some higher order terms interactions between the stretching and bending coordinate if expanded in Taylor series (the $R_1(r^0,\rho)$ and $R_5(r^0,\rho)$ functions). Instead of this, we will use the eq. (3.67) which drops the series after the first terms.

Obs. *3* The quartic term correction in the bending potential (3.70), for values $\rho \to \rho_e$, has the approximate form:

$$V^b_2(\rho)|_{\rho\to\rho_e} \simeq k_4\,\rho^4 \tag{3.79}$$

The real $V^b_2(\rho)$ term from the eq.(3.70) take into account higher order terms because it can itself be expanded in Taylor series near $\rho \simeq \rho_e$.

Obs. *4* The only anharmonic term that mix bending and stretching vibrations is a cubic term, the cause for the Fermi interaction, eq.(3.73). We will neglect the upper terms because their weight seems to be small. Also, the cubic term from eq.(3.73) can be expanded in Taylor series, due to $R_1(r^0,\rho)$ and $R_5(r^0,\rho)$ functions, but we will drop the series after the first terms, and in consequence, the term will have the form from eq.(3.75).

Using the above observations, the potential from literature that we use is:

$$V = \frac{1}{2}f_{11}\left(x_1^2+x_3^2\right) + f_{13}x_1x_3 + \frac{1}{2}f_{22}x_2^2 + F_{122}(x_1+x_3)x_2^2 + F_{2222}x_2^4 \tag{3.80}$$

where,as in [46], the force constants are defined as:

$$\begin{aligned} f_{ij} &= \frac{\partial^2 V}{\partial x_i\,\partial x_j} \\ f_{122} &= \frac{\partial^3 V}{\partial x_2^2\,\partial x_1} = 2\,F_{122} \\ f_{2222} &= \frac{\partial^4 V}{\partial x_2^4} = 24\,F_{2222} \end{aligned} \tag{3.81}$$

(x_1, x_3) are the stretching coordinates and x_2 is the bending one.

We need these conversion relations in order to compare our constants with those from the literature, or to take the literature potential constants as initial values in our model.

We will consider geometrically defined coordinates:

- Cartesian coordinates, useful when the displacements are small [3, 4].
- generalized internal coordinates (valence coordinates), employed in variational and non-rigid bender calculations [6, 17].
- symmetric coordinates: S^s and S^a for the stretching displacement and ρ, for the bending displacement, used in the stretch-bending model [186]

Conversion to and from Internal Generalized Coordinates (Valence Force Displacement coordinates)

In the case of the internal generalized coordinates we will adopt for the bending coordinate the convention used by [5, 6, 17] and not the convention from [43].

Using the eq. (3.25), together with (3.11)-(3.15), we find from the eq. (3.19) the required relations between the generalized and curvilinear coordinates (§C.4):

$$\begin{aligned} \mathbf{R}^1 &\simeq \frac{1}{\sqrt{2}}\left[S^s\left(1+A_a\rho^2\right) + S^a\left(p - A_a\rho^2\right)\right] + d\rho^2 \\ \mathbf{R}^3 &\simeq \frac{1}{\sqrt{2}}\left[S^s\left(1+A_a\rho^2\right) - S^a\left(p - A_a\rho^2\right)\right] + d\rho^2 \\ \bar{\rho} &= \rho\left[1 + \frac{A_\rho}{\sqrt{2}r}S^s\right] \end{aligned} \tag{3.82}$$

where we use the following notations:

$$\begin{aligned} A_\rho &= R_2^\rho = (p-1) - 8p\frac{d}{r} \\ A_a &= \frac{1}{4}R_1^\rho = \frac{1}{4}(p-1)\left(1 - 8\frac{d}{r}\right) \\ A_s &= \frac{1}{4}R_1^\rho - 2\frac{d}{r}A_\rho \end{aligned} \tag{3.83}$$

S^s and S^a are the symmetric and antisymmetric stretching coordinates, while R_1^ρ and R_2^ρ are derived from the eq. (3.25) and are defined in (A-63) and in (A-67).

Here and in the following considerations we take for $r_i(\rho)$ the same dependence of ρ like in eq. (3.56):

$$\mathcal{R}(\rho) = d\rho^2 \tag{3.84}$$

If we use the method from [46], or the method from [3, 4], we find the general relations between the cubic and the quartic potential constants (§C.5):

$$\begin{aligned}
f_{ss} &= f_{11} + f_{13} \\
f_{aa} &= [f_{11} - f_{13}] \cdot p^2 \\
f_{\rho\rho} &= f_{22} \\
F_{s\rho\rho} &\simeq f_{22}\frac{A_\rho}{\sqrt{2}r} + \sqrt{2} \cdot d\,(f_{11} + f_{13}) \cdot \frac{(g_D - 1)}{g_D} \\
F_{\rho\rho\rho\rho} &= F_{2222} + 2dF_{122} + d^2\,(f_{11} + f_{13}) + \mathcal{O}(upper\ terms)
\end{aligned} \tag{3.85}$$

The equations from the harmonic constants in (3.85) are identical with those from (3.67), discussed previously. The g_D factor defined below in eq.(3.152), is used when d is not defined as in (3.56), otherwise it is equal to unit ($g_D = 1$).

If we consider the d expression from (3.84) and (3.56), the cubic potential constant from the eq.(3.85) is the same as in eq. (3.75). The relations between the curvilinear and generalized coordinates are, (§C.5):

$$\begin{aligned}
S^s &= \frac{1}{\sqrt{2}}\left(\mathbf{R}^1 + \mathbf{R}^3\right)\left(1 - A_s\bar{\rho}^2\right) - \sqrt{2}d\bar{\rho}^2 + \mathcal{O}(upper\ terms) \\
S^a &= \frac{1}{\sqrt{2}p}\left(\mathbf{R}^1 - \mathbf{R}^3\right)\left(1 + A_a\frac{1}{p}\bar{\rho}^2\right) \\
\rho &\simeq \bar{\rho}\left[1 - \frac{A_\rho}{2r}\left(\mathbf{R}^1 + \mathbf{R}^3\right)\right] + \frac{d}{r}A_\rho\bar{\rho}^3 + \mathcal{O}(upper\ terms)
\end{aligned} \tag{3.86}$$

The equations corresponding to the stretching coordinates (3.86) are identical, in the rigid-bender limit with the eq. (3.26). We compute the potential constants, from the eq. (3.86) as:

$$\begin{aligned}
f_{11} &= \frac{1}{2}\left(f_{ss} + \frac{1}{p^2}f_{aa}\right) \\
f_{13} &= \frac{1}{2}\left(f_{ss} - \frac{1}{p^2}f_{aa}\right) \\
f_{22} &= f_{\rho\rho} \\
F_{122} &= \frac{1}{\sqrt{2}}F_{s\rho\rho} - d\,f_{ss} - \frac{A_\rho}{2r}f_{\rho\rho} \\
F_{2222} &= F_{\rho\rho\rho\rho} - \sqrt{2}\,dF_{s\rho\rho} + d^2\,f_{ss} + \frac{A_\rho\,d}{r}f_{\rho\rho} + \mathcal{O}(upper\ terms)
\end{aligned} \tag{3.87}$$

For the harmonic stretching potential constants we see that the antisymmetric stretching potential terms is weighted with $\frac{1}{p^2}$, in connection with the corresponding term in (3.67).

Conversion to and from Linearized Generalized Internal Coordinates

The linearized coordinates are mainly used in the small amplitude treatment of all vibrational displacements. In order to do the calculus, we use the relations between the linearized and internal generalized coordinates previously obtained by [3] and [4]. Using the eq. (3.82) together

with the formulas from [3] and [4], we find the required relations between the linearized and curvilinear coordinates (§C.6):

$$\begin{aligned}
q_0^1 &\simeq \frac{1}{\sqrt{2}} S^s \left\{1+\left[A_a-\frac{1}{4}\left(A_\rho+1\right)\right]\rho^2\right\}+\frac{1}{\sqrt{2}} S^a\left(p-A_a\rho^2\right) \\
&- \frac{r}{8}\left(1-8\frac{d}{r}\right)\rho^2+\mathcal{O}(upper\ terms) \\
q_0^3 &\simeq \frac{1}{\sqrt{2}} S^s \left\{1+\left[A_a-\frac{1}{4}\left(A_\rho+1\right)\right]\rho^2\right\}-\frac{1}{\sqrt{2}} S^a\left(p-A_a\rho^2\right) \\
&- \frac{r}{8}\left(1-8\frac{d}{r}\right)\rho^2+\mathcal{O}(upper\ terms) \\
\gamma_0 &\simeq \rho\left[1+\frac{1}{\sqrt{2}r}\left(A_\rho+1\right)S^s\right]-\frac{1}{24}\left[1-24\frac{d}{r}\right]\rho^3+\mathcal{O}(upper\ terms)
\end{aligned} \tag{3.88}$$

The constants A_s,A_a and A_ρ are defined in (3.83) and the dependence of the bond length on the bending angle is the same as in (3.84). We find the general relations between quadratic, cubic and quartic potential constants, by using the method from [3], (§C.6):

$$\begin{aligned}
f_{ss} &= f_{11}^0+f_{13}^0 \\
f_{aa} &= p^2\cdot\left(f_{11}^0-f_{13}^0\right) \\
f_{\rho\rho} &= f_{\rho\rho}^0 \\
F_{s\rho\rho} &= \sqrt{2}F_{122}^0-\frac{r}{4\sqrt{2}}\left(1-8\frac{d}{r}\right)\left(f_{11}^0+f_{13}^0\right)+\frac{A_\rho+1}{\sqrt{2}r}f_{22}^0+2\sqrt{2}d\left(f_{11}^0+f_{13}^0\right) \\
F_{\rho\rho\rho\rho} &\simeq F_{2222}^0-\frac{r}{4}\left(1-8\frac{d}{r}\right)F_{122}^0+\frac{r^2}{64}\left(1-8\frac{d}{r}\right)^2\left(f_{11}^0+f_{13}^0\right) \\
&- \frac{1}{24}\left(1-24\frac{d}{r}\right)f_{22}^0+\mathcal{O}(upper\ terms)
\end{aligned} \tag{3.89}$$

The relations between the curvilinear and linearized coordinates are (§C.7):

$$\begin{aligned}
S^s &= \frac{1}{\sqrt{2}}\left(q_0^1+q_0^3\right)\left[1-\left(A_s-2\frac{d}{r}\right)\gamma_0^2\right]+\frac{r}{4\sqrt{2}}\left(1-8\frac{d}{r}\right)\gamma_0^2+\mathcal{O}(upper\ terms) \\
S^a &= \frac{1}{\sqrt{2}p}\left(q_0^1-q_0^3\right)\left(1+A_a\frac{1}{p}\gamma_0^2\right) \\
\rho &= \gamma_0\left[1-\frac{A_\rho+1}{2r}\left(q_0^1+q_0^3\right)\right]-\frac{A_\rho}{8}\left(1-8\frac{d}{r}\right)\gamma_0^3 \\
&- \frac{1}{12}\gamma_0^3+\mathcal{O}(upper\ terms)
\end{aligned} \tag{3.90}$$

The symmetric stretching coordinate has the same weight ($\frac{1}{p}$) as the corresponding equation from (3.86). The transformation (3.90) leads to the following relations between the quadratic, cubic and quartic constants of the potential energy expansion in terms of the linearized valence force coordinates and the curvilinear coordinates:

$$\begin{aligned}
f_{11}^0 &= \frac{1}{2}\left(f_{ss}+\frac{f_{aa}}{p^2}\right) \\
f_{13}^0 &= \frac{1}{2}\left(f_{ss}-\frac{f_{aa}}{p^2}\right) \\
f_{22}^0 &= f_{\rho\rho} \\
F_{122}^0 &= \frac{1}{\sqrt{2}}F_{s\rho\rho}+\frac{r}{8}\left(1-8\frac{d}{r}\right)f_{ss}-\frac{\left(A_\rho+1\right)}{2r}f_{\rho\rho}-2d\,f_{ss} \\
F_{2222}^0 &= F_{\rho\rho\rho\rho}+\frac{r}{4\sqrt{2}}\left(1-8\frac{d}{r}\right)F_{s\rho\rho}+\frac{r^2}{64}\left(1-8\frac{d}{r}\right)^2 f_{ss}
\end{aligned} \tag{3.91}$$

$$- \left[\frac{1}{12}+\frac{1}{8}A_\rho\left(1-8\frac{d}{r}\right)\right] f_{\rho\rho} + \mathcal{O}(upper\ terms)$$

In the case of the rigid bender limit ($d = 0$), the cubic and quartic terms from the eq. (3.91) are the well known formula from [4].

3.4 Solving the Eigenvalue Problem

In order to solve the Schrödinger equation we diagonalize the Hamiltonian matrix for each vibronic state. This matrix is set up using basis functions which are products of numerical bending functions and stretching functions that depend parametrically on ρ. These basis functions, $\Phi(\rho, \varphi, S^s, S^a)$ can be written as:

$$\Phi^i_{v_1,v_2,v_3,K}(\rho, \varphi, S^s, S^a) = \Phi^i_{v_2,K}(\rho)\frac{1}{\sqrt{2\pi}} e^{iK\varphi}\, \chi^{ss}_{v_1}(S^s;\rho)\, \chi^{aa}_{v_3}(S^a;\rho) \tag{3.92}$$

In (3.92) we introduce the signed quantum number K as the eigenvalue for the N_z operator [15]:

$$N_z = J_z - S_z = -i\hbar\frac{\partial}{\partial\varphi}$$

where as previously noted, φ describes the orientation of the molecular plane with respect to an arbitrary reference orientation. $\Phi^i_{v_2,K}(\rho)$ is the bending wavefunction and $\chi^{ss}_{v_1}(S^s;\rho), \chi^{aa}_{v_3}(S^a;\rho)$ are the symmetric and antisymmetric wavefunctions, respectively. The basis function (3.92) must be multiplied by an electronic factor, to give a Born-Oppenheimer basis function.

We may evaluate the vibronic coupling matrix elements involving the L_z operator by using approximate electronic factors which become exactly correct for $\rho \to 0$, only. These factors must transform accordingly to the representations of the C_2v point group and have to be [15]:

$$\psi^{\pm}_{el}(\nu-\varphi;\rho=0) = \frac{1}{\sqrt{4\pi}}\left[e^{i\Lambda(\nu-\varphi)} \pm e^{-i\Lambda(\nu-\varphi)}\right] \tag{3.93}$$

which transform as the C_{2v} point group A_1 and B_1 representations respectively.

In the above considerations, the variable ν is the azimuth angle describing respectively the averaged motion of the electrons with respect to an arbitrary reference configuration, and the operator L_z is: $L_z = -i\hbar\frac{\partial}{\partial(\nu-\varphi)}$ describing the averaged motion of the electrons with respect to the molecular plane. An alternative formulation [15] can be obtained by choosing basis functions which are symmetric and antisymmetric linear combinations of the Born-Oppenheimer functions (3.92)-(3.93). In the linear limit this amounts to taking electronic angular factors:

$$\psi^{\pm}_{el}(\nu-\varphi;\rho=0) = \frac{1}{\sqrt{2\pi}} e^{\pm i\Lambda(\nu-\varphi)} \tag{3.94}$$

These factors represent waves moving freely around the linear molecule axis in opposite directions, rather than standing waves as implied by (3.93).

With the electronic wavefunction (3.94), the vibrational wavefunction (3.92) is written as:

$$\Phi^i_{v_1,v_2,v_3,l}(\rho, \varphi, S^s, S^a) = \Phi^i_{v_2,l}(\rho)\frac{1}{\sqrt{2\pi}} e^{i(K-\Lambda)\varphi}\, \chi^{ss}_{v_1}(S^s;\rho)\, \chi^{aa}_{v_3}(S^a;\rho) \tag{3.95}$$

where Λ is a signed quantity- the eigenfunction of L_z operator when $\rho = 0$. The term in φ is just the angular factor for the two-dimensional oscillator with vibrational angular momentum quantum number l, $\frac{1}{\sqrt{2\pi}} e^{il\varphi}$, so that we obtain the well known relation:

$$l = K - \Lambda \quad \text{or} \quad K = l + \Lambda \tag{3.96}$$

The functions (3.95) will be called the l-basis, $|\Lambda\, v\, l\rangle$, instead of the K-basis functions from (3.92). It may appear that the l basis introduces l as a new quantum number, but in fact l merely replaces the parity quantum number implied by the form of (3.93) [15]. More arguments in using the l-basis instead of the K-basis are done in [15].

Obs. In the eq. (3.93) and (3.94) only the dependence $(\nu - \varphi)$ has been specifically indicated in the electronic factor and the radial part of the electronic wavefunction has been omitted since L_z (electronic operator) does not act on it.

3.4.1 The Stretching Equations

In our approach to solving the equations we assume that we may use the harmonic oscillator approximation to evaluate the necessary integrals, and hence the potential stretching energy may be written as:

$$V^{as}(S^s, S^a; \rho) = \frac{1}{2} f^s_{eff}(\rho)(S^s)^2 + \frac{1}{2} f^a_{eff}(\rho)(S^a)^2 \tag{3.97}$$

where the stretching part as well as f^s_{eff} and f^a_{eff} are taken from eq. (3.66).

The equations for the symmetric and antisymmetric motions are then solved separately for each value of ρ, i.e.:

$$\left[-\frac{\hbar^2}{2} g^{\varepsilon\varepsilon} \frac{\partial^2}{\partial (S^\varepsilon)^2} + \frac{1}{2} f^\varepsilon_{eff}(\rho)(S^\varepsilon)^2 \right] \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon; \rho) = E^\varepsilon_{v_i}(\rho) \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon; \rho) \tag{3.98}$$

with $\varepsilon = s, a$ and $i = 1, 3$ respectively, for eq. (3.98) and below. The solutions of these equations are:

$$E^\varepsilon_{v_i} = hc\omega_\varepsilon(\rho) \left[v_i + \frac{1}{2} \right] \tag{3.99}$$

The ρ-dependent stretching frequencies (cm^{-1}) are obtained by using the eq. (3.38) and (3.66) as:

$$\begin{aligned} hc\omega_1(\rho) &= \hbar \sqrt{g^{ss} f^s_{eff}} = \hbar \sqrt{\frac{R_1^2(r^0,\rho) f^s_{rr}(\rho)}{m_1 R_3(r^0,\rho)}} \\ &\text{and} \\ hc\omega_3(\rho) &= \hbar \sqrt{g^{aa} f^a_{eff}} = \hbar \sqrt{\frac{R_5^2(r^0,\rho) f^a_{rr}(\rho)}{m_1 R_4(r^0,\rho)}} \end{aligned} \tag{3.100}$$

The eigenfunctions of the eq.(3.98) are normalized harmonic oscillator functions which depend parametrically on ρ, e.g.:

$$\chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon; \rho) = N^\varepsilon_{v_i}(\rho)\, e^{-\frac{\xi_\varepsilon^2}{2}} H_{v_i}(\xi_\varepsilon) \tag{3.101}$$

where ξ_ε is related to the stretching coordinate by $\xi_\varepsilon = (\alpha_\varepsilon)\, S^\varepsilon$ and

$$N^\varepsilon_{v_i}(\rho) = \sqrt{\frac{\alpha_\varepsilon(\rho)}{\pi^{\frac{1}{2}} 2^{v_i} (v_i!)}} \tag{3.102}$$

The functions $\alpha(\rho)$ are related to the $\gamma(\rho)$ functions (used by [6]) by the relation: $g^{\varepsilon\varepsilon}\alpha^2(\rho) = \gamma(\rho)$, hence the α functions are connected to the harmonic stretching frequencies of eq.(3.100) by:

$$\alpha_\varepsilon(\rho) = \sqrt{\frac{2\pi c}{\hbar} \frac{\omega_\varepsilon(\rho)}{g^{\varepsilon\varepsilon}}} \tag{3.103}$$

3.4.2 Minimization of the Renner-Teller Coupling Terms

In the approach so far we have described a model for an isolated state of a molecule. From the infinite manifold of electronic states, we shall now pick a pair which becomes degenerate in the linear limit. The two potential functions are denoted as $V^+(\rho)$ (upper) and $V^-(\rho)$ (lower), respectively [15]. Following [15], we start with a completely general simplified equation which leaves out the spin-orbit effects and the x,y rotation:

$$\left[H_b(\rho) + H_{rot}^{(z)}(\nu\,,\varphi\,,\rho) + V^{(i)}(\rho) - E\right]\psi^{(i)}(\nu\,,\varphi\,,\rho) = 0 \tag{3.104}$$

In eq. (3.104) $H_b(\rho)$ is the bending Hamiltonian (first row of eq. (3.40) and $H_{rot}^{(z)}(\nu\,,\varphi\,,\rho)$ is the rotational Hamiltonian (second row in eq. (3.40)).

In the semirigid bender limit, Jungen and Merer [15], could reduced (3.104) to a pair of equations for each value of l, which involves only the bending angle ρ. The pair of differential equations is coupled through an electrostatic splitting. When we include the interaction between two states, which may become degenerate when linear, the resultant coupled equations may be written, in the original l basis adopted in [15], as:

$$\begin{bmatrix} H_b(\rho) + U_k^-(\rho) - E & H_K(\rho) \\ H_K(\rho) & H_b(\rho) + U_k^+(\rho) - E \end{bmatrix} \begin{bmatrix} \bar{\Phi}_{v_2,l}^-(\rho) \\ \bar{\Phi}_{v_2,l}^+(\rho) \end{bmatrix} = 0 \tag{3.105}$$

where we have essentially two effective potential functions $U_k^{\pm}(\rho)$ and a coupling function $H_K(\rho)$. The potential and the coupling functions are:

$$\begin{aligned} U_k^{\pm}(\rho) &= V^-(\rho) + \frac{1}{2}V_{2\Lambda}(\rho) + \left[\frac{1}{2}\hbar^2\, g_0^{\varphi\varphi}(\rho)\right](K \pm \Lambda)^2 \\ H_K(\rho) &= \frac{1}{2}V_{2\Lambda}(\rho) \end{aligned} \tag{3.106}$$

where

$$V_{2\Lambda}(\rho) = V^+(\rho) - V^-(\rho) \tag{3.107}$$

Obs. The sign $\pm$ refers to upper and lower state, and are different from the signs in eq. (3.93) or (3.94), where the signs are refering to the symmetry of the wavefunctions.

The term in $(K \pm \Lambda)$ in eq. (3.106) is recognized as the angular part of the Hamiltonian for the two dimensional oscillator, with l taking the values $(K \pm \Lambda)$, corresponding to the two values $\mp\Lambda$ for the orbital angular momentum.

In order to solve these equations Jungen and Merer [15] proposed and implemented the following strategy. First of all, energies and numerical bending wavefunctions are obtained in the l basis using one of the potential energy curves (3.106), usually the lower one. Using these basis functions, the matrix elements of the perturbation (3.107) are evaluated and used to construct a H matrix. This is then subject to an unitary transformation using a $\mathbf{S}$ matrix, which is a generalized form of Renner's original transformation. This preserves the identity of the unique level.

The matrix after the transformation is referred to as the $\mathbf{H}'$ matrix:

$$\mathbf{H}' = \hat{\mathbf{S}}^+\,\mathbf{H}\,\hat{\mathbf{S}} \tag{3.108}$$

Finally, the energies and the numerical bending wavefunctions are obtained by using one set of the l basis functions for the second state. These are used to construct the final matrix to be diagonalized, the $\mathbf{H}''$ matrix:

$$\mathbf{H}'' = \hat{\mathbf{T}}^+\,\mathbf{H}'\,\hat{\mathbf{T}} \tag{3.109}$$

where the off-diagonal Renner-Teller coupling is minimized.

In (3.109) $\hat{\mathbf{T}}$ is the overlap integral matrix, defined as:

$$T^{--}_{v,v'} = \delta_{v,v'} \qquad T^{+-}_{v,v'} = T^{-+}_{v,v'} = 0$$
$$T^{++}_{v,v'} = \langle \bar{\Phi}^{-}_{v,l=K+\Lambda}(\rho) | \bar{\Phi}^{+}_{v',l=K+\Lambda}(\rho) \rangle \tag{3.110}$$

In eq. (3.110) the sign $\mp$ refer to the wavefunctions computed using the $V^{\mp}(\rho)$ potentials in (3.104).

The final interaction matrix which is to be diagonalized, the $\mathbf{H}''$ matrix from (3.109), has the size of the Renner-Teller coupling elements minimized so that in general they are smaller than a typical vibrational interval. We will refer to the wavefunctions with which the final interaction matrix is constructed as the "primitive" wavefunctions, and the matrix of the numerical wavefunctions $\mathbf{U}$, as the "primitive" eigenvector matrix. There are these wavefunctions which are used to construct the off diagonal coupling elements of the final interaction matrix.

In the expression (3.105) and (3.106), in the place of $V^{\pm}(\rho)$ we use the zeroth order effective bending potential, $V^{\pm}_{eff}(\rho)$. By taking into account the eq. (3.68) - (3.70) for the bending potential and the eq. (3.100) for the stretching energies, we find:

$$V^{\pm}_{eff}(\rho\,, v_1\,, v_3) = hcV_0^{\mp b}(\rho\,, S^s\,, S^a) + hc\omega_1^{\pm}(\rho)\left[v_1 + \frac{1}{2}\right] + hc\omega_3^{\pm}(\rho)\left[v_3 + \frac{1}{2}\right] \tag{3.111}$$

Obs. *1* It can be also included in this potential the diagonal terms due to the stretch-bend interactions discussed below.

Obs. *2* The difference between the eq. (3.105), (3.106), (3.111) and the initial method of Jungen [15] is that in the present model we have included in the pseudo-potential term $f(\rho)$ (3.46) the elements arising from the tensor elements corresponding to the symmetric and antisymmetric stretching displacements (see (3.50).

Obs. *3* In our method, first of all we will solve the Renner-Teller coupling elements and find the bending eigenvalues and only after that we deal with explicit anharmonic stretch-bender coupling.

Obs. *4* One of the advantages of building the vibronic interaction in the present way using the Jungen and Merer [15] transformations is that at the intermediate stage of the calculation (the $\mathbf{H}''$ matrix), the Renner-Teller matrix elements are *off diagonal* between the coupled electronic states in the primitive basis functions used to construct the final interaction or $\mathbf{H}''$ matrix.

3.4.3 Introduction of Anharmonic Coupling

In the stretch-bender model the stretch-bend interactions are introduced in two ways:

- the effective bending potential $hcV_0^b(\bar{\rho}, S^s\,, S^a)$, given in eq. (3.71) contains the term $-hc\left(\frac{\partial V_0}{\partial \bar{\rho}}\right)\frac{R_2(r^0,\rho)}{\sqrt{2}\,r^0}S^s$, which causes a cubic stretch-bend interaction.
- the effective stretching potential $hcV^{as}(\bar{\rho}, \bar{S}^s\,, \bar{S}^a)$, given in eq.(3.64) contains the term $\left(\frac{\partial V^{as}}{\partial S^s}\right)\frac{\mathcal{R}'(\rho)}{R_1(r^0,\rho)}\,(\rho - \rho_e)$, which causes a cubic stretch-bend interaction.

These corrections involve at this point only the potential energy. It exist also a correction involving the kinetic energy operator, because the bending kinetic energy operator acts on the ρ dependent stretching functions (3.101) and (3.103). The last one represents the "fast" stretching motion. If we use in the l basis the wavefunction from (3.94) and (3.95), we have the total wavefunction (electronic and vibrational):

$$\psi^{\pm}_{v_1,v_2,v_3,l} = \frac{1}{2\pi}\,e^{\pm i\Lambda\nu}\,\Phi^{\pm}_{v_2,l,v_1,v_3,}(\rho)\,e^{i(K\mp\Lambda)\varphi}\,\chi^{ss,\pm}_{v_1}(S^s\,;\rho)\chi^{aa,\pm}_{v_3}(S^a\,;\rho) \tag{3.112}$$

If we introduce the wavefunction (3.112) in the eq. (3.104) and we are taking into account the potential energy (3.111) and the above observations, we obtain two equations, each of them involving the two vibrational factors $\Phi^{+}_{v_2,l,v_1,v_3}(\rho)$ and $\Phi^{-}_{v_2,l,v_1,v_3}(\rho)$. The equation are obtained by multiplying the eq.(3.104) on the left side by $\frac{1}{\sqrt{2\pi}} e^{\pm i\Lambda\nu} e^{i(K\mp\Lambda)\varphi}$ (electronic and rotational wavefunctions) and by integrating over ν and φ (§D.1). We have then the interaction matrix (for simplicity we neglect at the first step the $\chi^{aa\pm}_{v_3}(S^a;\rho)$ function):

$$(\mathbf{A} - E\,\mathbf{I})\,\mathbf{B} = 0 \tag{3.113}$$

where:

$\mathbf{I}$ – is the identity matrix

$$\mathbf{A} = \begin{bmatrix} \boxed{\begin{matrix} H^{l=K+\Lambda}_{v_1,v_2}(\rho) & \frac{1}{2}V_{2\Lambda}(\rho,v_1) \\ \frac{1}{2}V_{2\Lambda}(\rho,v_1) & H^{l=K-\Lambda}_{v_1,v_2}(\rho) \end{matrix}} & \cdots & \begin{matrix} H^{l=K+\Lambda}_{v_1,v_1',v_2}(\rho) & H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) \\ H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) & H^{l=K-\Lambda}_{v_1,v_1',v_2}(\rho) \end{matrix} & \cdots \\ \vdots & \ddots & \vdots & \vdots \\ \begin{matrix} H^{l=K+\Lambda}_{v_1,v_1',v_2}(\rho) & H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) \\ H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) & H^{l=K-\Lambda}_{v_1,v_1',v_2}(\rho) \end{matrix} & \cdots & \boxed{\begin{matrix} H^{l=K+\Lambda}_{v_1',v_2}(\rho) & \frac{1}{2}V_{2\Lambda}(\rho,v_1') \\ \frac{1}{2}V_{2\Lambda}(\rho,v_1') & H^{l=K-\Lambda}_{v_1',v_2}(\rho) \end{matrix}} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{3.114}$$

$$\mathbf{B} = \begin{bmatrix} \psi^{K+\Lambda,+}_{v_2,v_1,v_3}(\rho,s^s) \\ \psi^{K-\Lambda,-}_{v_2,v_1,v_3}(\rho,s^s) \\ \vdots \\ \psi^{K+\Lambda,+}_{v_2,v_1',v_3}(\rho,s^s) \\ \psi^{K-\Lambda,-}_{v_2,v_1',v_3}(\rho,s^s) \\ \vdots \end{bmatrix} \tag{3.115}$$

The matrix elements of the $\mathbf{A}$ matrix are the following:

$$\begin{aligned} H^{l=K\pm\Lambda}_{v_1,v_2}(\rho) &= H_b(\rho) + V^{-}_{eff}(\rho;v_1) + \frac{1}{2}V_{2\Lambda}(\rho;v_1) + \frac{\hbar^2}{2}g^{\varphi\varphi}l^2 \\ H^{l=K\pm\Lambda}_{v_1,v_1',v_2}(\rho) &= \frac{1}{2}\left\{ -\left[\left(\frac{\partial V^{+}_{eff}(\rho;v_1)}{\partial\rho}\right)_0 + \left(\frac{\partial V^{-}_{eff}(\rho;v_1)}{\partial\rho}\right)_0\right]\frac{R_2(r^0,\rho)}{\sqrt{2}\,r^0(\rho)}\,S^s \right. \\ &+ \left.\left[\left(\frac{\partial V^{as,+}(S^s,\rho)}{\partial S^s}\right)_0 + \left(\frac{\partial V^{as,-}(S^s,\rho)}{\partial S^s}\right)_0\right]\frac{\mathcal{R}'(\rho)}{R_1(r^0,\rho)}(\rho-\rho_e)\right\} F^{l,l}_{v_1,v_1'}(\rho) \end{aligned} \tag{3.116}$$

$$H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) = \frac{1}{2}\left\{ -\left[\left(\frac{\partial V^{+}_{eff}(\rho;v_1)}{\partial\rho}\right)_0 - \left(\frac{\partial V^{-}_{eff}(\rho;v_1)}{\partial\rho}\right)_0\right]\frac{R_2(r^0,\rho)}{\sqrt{2}\,r^0(\rho)}\,S^s \right.$$

$$+ \quad \left[\left(\frac{\partial V^{as,+}(S^s,\rho)}{\partial S^s}\right)_0 - \left(\frac{\partial V^{as,-}(S^s,\rho)}{\partial S^s}\right)_0\right] \frac{\mathcal{R}'(\rho)}{R_1(r^0,\rho)}(\rho-\rho_e)\Bigg\} F^{l,l'}_{v_1,v_1'}(\rho)$$

The wavefunctions from eq. (3.113) which enter as matrix elements in **B** vector are the following:

$$\begin{aligned}
\psi^{K+\Lambda,+}_{v_2,v_1,v_3}(\rho,s^s) &= \bar{\Phi}^{+}_{v_2,K+\Lambda,v_1,v_3}(\rho)\,\chi^{ss}_{v_1}(S^s;\rho) \\
\psi^{K-\Lambda,-}_{v_2,v_1,v_3}(\rho,s^s) &= \bar{\Phi}^{-}_{v_2,K-\Lambda,v_1,v_3}(\rho)\,\chi^{ss}_{v_1}(S^s;\rho)
\end{aligned} \tag{3.117}$$

In eq. (3.116), $F^{l,l'}_{v_1,v_1'}(\rho)$ is the Fermi resonance integral, issued when the stretching coordinate of the anharmonic term is integrated over the harmonic oscillator wavefunction:

$$F^{l,l'}_{v_i,v_i'}(\rho) = \int_{-\infty}^{\infty}\left(\chi^{\varepsilon\varepsilon}_{v_i}\right)^{*} S^i\,\chi^{\varepsilon\varepsilon}_{v_i'}\,dS^i = \delta_{v_i,v_i'+1}\frac{1}{\alpha_i^{l,l'}(\rho)}\sqrt{\frac{v_i'+1}{2}} + \delta_{v_i,v_i'-1}\frac{1}{\alpha_i^{l,l'}(\rho)}\sqrt{\frac{v_i'}{2}} \tag{3.118}$$

where $\alpha_i^{l,l'}(\rho)$ is function of $\omega_i^{l}(\rho)$ and $\omega_i^{l'}(\rho)$.

Obs. From the last two terms in eq. (3.116), we observe that, if the l basis of Jungen and Merer is used, the resultant anharmonic coupling terms are:

$$\left\{\left[\left(\frac{\partial V^{+}}{\partial \rho}\right)+\left(\frac{\partial V^{+}}{\partial S^s}\right)\right]+\left[\left(\frac{\partial V^{-}}{\partial \rho}\right)+\left(\frac{\partial V^{-}}{\partial S^s}\right)\right]\right\}$$

within each electronic state and

$$\left\{\left[\left(\frac{\partial V^{+}}{\partial \rho}\right)+\left(\frac{\partial V^{+}}{\partial S^s}\right)\right]-\left[\left(\frac{\partial V^{-}}{\partial \rho}\right)+\left(\frac{\partial V^{-}}{\partial S^s}\right)\right]\right\}$$

between the states.

This result is similar to the Fermi resonance parameters $W_1 \sim (f'+f'')$ and $W_2 \sim (f'-f'')$, introduced by Hougen [37],[153] in order to treat the Fermi resonance in linear teriatomic molecules.

3.4.4 Adiabatic and non-Adiabatic Terms

The adiabatic and non-adiabatic terms are connected with the correction involving the kinetic energy operator. This represent, as mention above, the "fast" stretching motion. The treatment involving the kinetic energy operator can be carried out at three levels:

1. Born-Oppenheimer approximation

   We suppose that:

$$\frac{\partial^2}{\partial\rho^2}\left[\Phi^{i}_{v_2,l,v_1,v_3}(\rho)\,\chi^{ss}_{v_1}(S^s;\rho)\right] \simeq \chi^{ss}_{v_1}(S^s;\rho)\,\frac{\partial^2}{\partial\rho^2}\,\Phi^{i}_{v_2,l,v_1,v_3}(\rho) \tag{3.119}$$

   and the Fermi interactions arise uniquely through the S^s-dependence of $V_0(\rho,S^s,S^a)$. This should correspond to the semirigid bender model of Bunker and Landsberg [14], but it does not exactly since the terms in $(r^0)' = \frac{\partial r^0}{\partial\rho}$ are missing in their expressions.

2. Adiabatic approximation

   In eq. (3.119) we add a second term and the equation become:

$$\begin{aligned}
\frac{\partial^2}{\partial\rho^2}\left[\Phi^{j}_{v_2,l,v_1,v_3}(\rho)\,\chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)\right] &\simeq \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)\,\frac{\partial^2}{\partial\rho^2}\,\Phi^{j}_{v_2,l,v_1,v_3}(\rho) \\
&+ \Phi^{j}_{v_2,l,v_1,v_3}(\rho)\,\frac{\partial^2}{\partial\rho^2}\,\chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)
\end{aligned} \tag{3.120}$$

In eq. (3.120) and below, $j = (+,-)$, $i = 1,3$ and $\varepsilon = s,a$ respectively. The second term generates the matrix element:

$$-\frac{\hbar^2}{2}\, g^{\rho\rho}\, I^{(2)}_{v_i',v_i}(\rho) = -\frac{\hbar^2}{2}\, g^{\rho\rho} \int_{-\infty}^{\infty} \left[\chi^{\varepsilon\varepsilon}_{v_i'}(S^\varepsilon;\rho)\right]^* \frac{\partial^2}{\partial\rho^2}\, \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)\, dS^\varepsilon \tag{3.121}$$

which is the adiabatic correction to the effective potential (eq. (3.59),(3.64) and (3.71)). The value of the correction term $I^{(l)}_{v_i',v_i}(\rho)$ is given by (§D.2):

$$\begin{aligned}
I^{(2)}_{v_i',v_i}(\rho) &= \int_{-\infty}^{\infty} \left[\chi^{\varepsilon\varepsilon}_{v_i'}(S^\varepsilon;\rho)\right]^* \frac{\partial^2}{\partial\rho^2}\, \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho) dS^\varepsilon \\
= \;& \delta_{v_i',v_i+4}\, \frac{1}{4}\left(\frac{1}{\alpha_i(\rho)}\frac{\partial\alpha_i(\rho)}{\partial\rho}\right)^2 \sqrt{(v_i+1)\,(v_i+2)\,(v_i+3)\,(v_i+4)} \\
& -\delta_{v_i',v_i+2}\, \frac{1}{2}\left[\frac{1}{\alpha_i(\rho)}\frac{\partial^2\alpha_i(\rho)}{\partial\rho^2} - \left(\frac{1}{\alpha_i(\rho)}\frac{\partial\alpha_i(\rho)}{\partial\rho}\right)^2\right] \sqrt{(v_i+1)\,(v_i+2)} \\
& +\delta_{v_i',v_i}\, \frac{1}{2}\left(\frac{1}{\alpha_i(\rho)}\frac{\partial\alpha_i(\rho)}{\partial\rho}\right)^2 \left(v_i^2+v_i+1\right) \\
& +\delta_{v_i',v_i-2}\, \frac{1}{2}\left[\frac{1}{\alpha_i(\rho)}\frac{\partial^2\alpha_i(\rho)}{\partial\rho^2} - \left(\frac{1}{\alpha_i(\rho)}\frac{\partial\alpha_i(\rho)}{\partial\rho}\right)^2\right] \sqrt{(v_i-1)v_i} \\
& +\delta_{v_i',v_i-4}\, \frac{1}{4}\left(\frac{1}{\alpha_i(\rho)}\frac{\partial\alpha_i(\rho)}{\partial\rho}\right)^2 \sqrt{(v_i-3)\,(v_i-2)\,(v_i-1)\,v_i}
\end{aligned} \tag{3.122}$$

3. Non adiabatic approximation

One now has bending momentum coupling terms:

$$-\hbar^2 g^{\rho\rho} I^{(1)}_{v_i',v_i}(\rho)\frac{\partial}{\partial\rho} = -\hbar^2 g^{\rho\rho} \int_{-\infty}^{\infty} \left[\chi^{\varepsilon\varepsilon}_{v_i'}(S^\varepsilon;\rho)\right]^* \frac{\partial}{\partial\rho}\, \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho) dS^\varepsilon \frac{\partial}{\partial\rho} \tag{3.123}$$

which couple different stretching states v_i and v_i'. The term from the eq. (3.123) arise from the eq. (3.120) when we are considering all the terms:

$$\begin{aligned}
\frac{\partial^2}{\partial\rho^2}\left[\Phi^j_{v_2,l,v_1,v_3}(\rho)\, \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)\right] &= \underbrace{\chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)\frac{\partial^2}{\partial\rho^2}\Phi^j_{v_2,l,v_1,v_3}(\rho)}_{B.O.approx.} \\
+ \;\underbrace{\Phi^j_{v_2,l,v_1,v_3}(\rho)\frac{\partial^2}{\partial\rho^2}\chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)}_{adiabatic\,approx.} &+ \underbrace{2\frac{\partial}{\partial\rho}\chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho)\frac{\partial}{\partial\rho}\Phi^j_{v_2,l,v_1,v_3}(\rho)}_{non-adiabatic\,approx}
\end{aligned} \tag{3.124}$$

The value of the integral $I^{(1)}_{v_i',v_i}(\rho)$ is (§D.2):

$$\begin{aligned}
I^{(1)}_{v_i',v_i}(\rho) &= \int_{-\infty}^{\infty} \left[\chi^{\varepsilon\varepsilon}_{v_i'}(S^\varepsilon;\rho)\right]^* \frac{\partial}{\partial\rho}\, \chi^{\varepsilon\varepsilon}_{v_i}(S^\varepsilon;\rho) dS^\varepsilon \\
&= \frac{1}{2}\left(\frac{1}{\alpha_i(\rho)}\frac{\partial\alpha_i(\rho)}{\partial\rho}\right)\left[-\delta_{v_i',v_i+2}\sqrt{(v_i+1)(v_i+2)} + \delta_{v_i',v_i-2}\sqrt{v_i(v_i-1)}\right]
\end{aligned} \tag{3.125}$$

The eq. (3.123) gives an additional contribution to stretch-bend interaction (3.64) and (3.71), which also produces off-diagonal elements in v_i.

3.4.5 Symmetry of Matrix Elements

We can see from the eq. (3.122) and (3.125) that these equations don't have an evident symmetry. For this reason we must evaluate the symmetry of the energy matrix. We are interested only in analyzing the eq. (3.122 and 3.125) , the other terms of the energy matrix are multiplicative and, for this reason, symmetric.

We must find the symmetry of the matrix element:

$$H_{ik\,,jl} = \int_0^{\pi} \int_{-\infty}^{\infty} \Phi_i \chi_k \left[2\Phi'_j \chi'_l + \Phi_j \chi''_l \right] d\rho \, dS^{\varepsilon} \tag{3.126}$$

in the base $\{\Phi_i(\rho)\,\chi_k(S^s;\rho)\}$. In this section the following shortcuts are used:

$$\begin{aligned} &\Phi_i \equiv \Phi^{\pm}_{\nu_2,l,\nu_1,\nu_3}(\rho) \quad \chi_k \equiv \chi^{\varepsilon\varepsilon}_{\nu_i}(S^{\varepsilon};\rho) \\ &' \equiv \tfrac{\partial}{\partial\rho} \qquad\qquad '' \equiv \tfrac{\partial^2}{\partial\rho^2} \end{aligned} \tag{3.127}$$

The eq.(3.126) can be written in an other form, as:

$$H_{ik\,,jl} = 2\int_0^{\pi} \Phi_i \, f_{kl}(\rho) \, \Phi'_j \, d\rho + \int_0^{\pi} \Phi_i \, g_{kl}(\rho) \, \Phi_j \, d\rho \tag{3.128}$$

where:

$$\begin{aligned} f_{kl}(\rho) &= \int_{-\infty}^{\infty} \chi_k \, \chi'_l \, dS^{\varepsilon} \\ g_{kl}(\rho) &= \int_{\infty}^{\infty} \chi_k \, \chi''_l \, dS^{\varepsilon} \end{aligned} \tag{3.129}$$

are the integrals corresponding to $I^{(1)}_{kl}$ and $I^{(2)}_{kl}$ respectively. The properties of the functions $f_{kl}(\rho)$ and $g_{kl}(\rho)$ are (§D.3):

$$f_{kl} = -f_{lk} \quad g_{kl} = g_{lk} + 2f'_{kl} \tag{3.130}$$

By taking into account the eq. (3.130) and by integrating by parts, we find that:

$$\begin{aligned} H_{ik\,,jl} &= \underbrace{2\,\Phi_i \, f_{kl} \, \Phi_j \,|_0^{\pi}}_{=0} - 2\int_0^{\pi} [\Phi_i f_{kl}]' \, \Phi_j \, d\rho + \int_0^{\pi} \Phi_i g_{kl} \, \Phi_j \, d\rho \\ &= -2\int_0^{\pi} \Phi'_i \, f_{kl} \, \Phi_j \, d\rho - 2\int_0^{\pi} \Phi_i f'_{kl} \, \Phi_j \, d\rho + \int_0^{\pi} \Phi_i \left[g_{lk} + 2f'_{kl} \right] \Phi_j \, d\rho \\ &= \int_0^{\pi} \Phi_j \, f_{lk} \, \Phi_i \, d\rho + \int_0^{\pi} \Phi_j \, g_{lk} \, \Phi_i \, d\rho \\ &= H_{jl\,,ik} \end{aligned} \tag{3.131}$$

As it can be seen from the eq. (3.131), the matrix element is symmetric.

Obs. *1* The formula (3.131) is valid only for the wavefunction with the volume element $dV = \frac{1}{g^{\rho\rho}} d\rho \, dS^s \, dS^a$, because in that case we have:

$$\begin{aligned} H_{ik\,,jl} &\sim \hbar^2 \int_0^{\pi} g^{\rho\rho} \Phi_i \int_{-\infty}^{\infty} \left[2f_{kl}\Phi'_j + g_{kl}\,\Phi_j \right] \frac{d\rho \, dS^s}{g^{\rho\rho}} \\ &= \hbar^2 \int_0^{\pi} \Phi_i \int_{\infty}^{\infty} \left[2f_{kl}\Phi'_j + g_{kl}\,\Phi_j \right] d\rho \, dS^s \end{aligned} \tag{3.132}$$

and in this case the eq. (3.132) is identical with (3.126).

Obs. *2* When the volume element is $dV = d\rho \, dS^s \, dS^a$, the matrix element of the kinetic energy is not symmetric (§D.3).

3.4.6 The Final Interaction Matrix Elements

The equations which therefore lead to the calculation of the bending and stretching energies, before integrating over $\Phi^{\pm}_{v_2,l,v_1,v_3}(\rho)$ bending functions are:

$$\Big[\langle\chi^{ss}_{v_1'}(S^s;\rho)\,\chi^{aa}_{v_3'}(S^a;\rho)|\mathbf{H}_b(\rho)+V_{eff}(\rho)|\chi^{ss}_{v_1}(S^s;\rho)\,\chi^{aa}_{v_3}(S^a;\rho)\rangle$$
$$-\ \delta_{v_1'\,v_1}\,\delta_{v_3'\,v_3}\,E_{v_1v_2v_3}\Big]\,\Phi^{\pm}_{v_2,l,v_1,v_3}(\rho)=0 \tag{3.133}$$

The equation (3.133) takes into account the effects previously analyzed:

1. the anharmonic coupling (3.116)
2. the stretching equations (by using for the $V_{eff}(\rho)$ the formula (3.111)
3. the adiabatic and non-adiabatic couplings (3.121) and (3.125), respectively.

In order to solve the eq.(3.133) we split the problem into two parts:

1. In the first part, the zeroth order Hamiltonian $\hat{H}^0$, contains the diagonal contributions of the stretching to the bending potential energy curves. This was discussed above in the section (§3.4.2), and it has the eigenvalues $E^{0,\pm}_{v_1,v_2,v_3}$.
2. In the second part, the perturbation Hamiltonian $\hat{H}'$, contains all the remaining perturbations terms due to the stretch-bend interactions. The perturbation Hamiltonian, $\hat{H}'$ results from the kinetic and potential energy operators, acting on the functions $\Phi^{\pm}_{v_2,lv_1,v_3}(\rho)$.

After integration over the stretching functions, the resultant off-diagonal stretch-bend interaction terms in the final interaction matrix, may be written in the l-basis as:

$$\hat{\mathbf{H}}'\quad\Phi^{-}_{v_2,K\pm\Lambda,v_1,v_3}(\rho) \tag{3.134}$$
$$=\ \Bigg\{\underbrace{-\frac{\hbar^2}{2}\,g^{\rho\rho}\left[I^{(2)}_{v_1'v_1}+I^{(2)}_{v_3'v_3}\right]}_{adiab.\ approx.}\underbrace{-\hbar^2\,g^{\rho\rho}\left[I^{(1)}_{v_1'v_1}+I^{(1)}_{v_3'v_3}\right]}_{non-adiab.\ approx.}\frac{\partial}{\partial\rho}\underbrace{-\hbar^2\,g^{\rho\rho}\,I^{(1)}_{v_1'v_1}\,I^{(1)}_{v_3'v_3}}_{D-D\ resonances}$$
$$\underbrace{-\frac{1}{2}\left[\left(\frac{\partial V_0^+}{\partial\rho}\right)_0+\left(\frac{\partial V_0^-}{\partial\rho}\right)_0\right]\frac{R_2(r^0,\rho)}{\sqrt{2}r^0(\rho)}F_{v_1'v_1}+\frac{1}{2}\left[\left(\frac{\partial V^+}{\partial S^s}\right)_0+\left(\frac{\partial V^-}{\partial S^s}\right)_0\right]\frac{\mathcal{R}'(\rho)}{R_1(r^0,\rho)}(\rho-\rho_e)\,F_{v_1'v_1}}_{anharmonic\ potential\ terms}\Bigg\}$$
$$\times\quad\Phi^{-}_{v_2,K\pm\Lambda,v_1,v_3}(\rho)$$
$$+\frac{1}{2}\left\{-\left[\left(\frac{\partial V_0^+}{\partial\rho}\right)_0-\left(\frac{\partial V_0^-}{\partial\rho}\right)_0\right]\frac{R_2(r^0,\rho)}{\sqrt{2}\,r^0(\rho)}+\left[\left(\frac{\partial V^+}{\partial S^s}\right)_0-\left(\frac{\partial V^-}{\partial S^s}\right)_0\right]\frac{\mathcal{R}'(\rho)}{R_1(r^0,\rho)}(\rho-\rho_e)\right\}F_{v_1'v_1}$$
$$\times\quad\Phi^{-}_{v_2,K\mp\Lambda,v_1,v_3}(\rho)$$

In the case when $\Lambda=0$ ($V^+(\rho,S^s,S^a)=V^-(\rho,S^s,S^a)$ and do not exist the Renner-Teller effect), the last term from the eq.(3.134) vanish. In the evaluation of the matrix elements, the "primitive" wavefunctions discussed in (§3.4.2), $\Phi^{\pm}_{v_2,l,v_1,v_3}$ depend upon v_1 and v_3, since the effective bending potential (3.111) is a function both of v_1 and v_3. The treatment of the coupling in the stretching-bender model can be carried out at four levels:

1. Neglect all perturbation terms, this is the semirigid bender limit, as derived by Jungen and Merer [15].
2. Include the potential coupling only and then evaluate:

$$\langle\Phi^{-}_{v_2',K\pm\Lambda,v_1',v_3'}|f_{Fermi}(\rho)|\Phi^{-}_{v_2,K\pm\Lambda,v_1,v_3}(\rho)\rangle \tag{3.135}$$

where we have the coupling function

$$f_{Fermi}(\rho) = \frac{1}{2}\left\{-\left[\left(\frac{\partial V_0^+}{\partial \rho}\right)_0 \pm \left(\frac{\partial V_0^-}{\partial \rho}\right)_0\right]\frac{R_2(r^0,\rho)}{\sqrt{2}r^0(\rho)} + \left[\left(\frac{\partial V^+}{\partial S^s}\right)_0 \pm \left(\frac{\partial V^-}{\partial S^s}\right)_0\right]\frac{\mathcal{R}'(\rho)}{R_1(r^0,\rho)}(\rho-\rho_e)\right\} F_{v_1' v_1}(\rho) \tag{3.136}$$

3. Add the adiabatic correction to the effective potential, by evaluating:

$$\langle \Phi^-_{v_2',l,v_1',v_3'}(\rho)| - \frac{\hbar^2}{2} g^{\rho\rho} I^{(2)}_{v_i v_i'} |\Phi^-_{v_2,l,v_1,v_3}(\rho)\rangle \tag{3.137}$$

4. Include the off-diagonal coupling terms arising from the non-adiabatic approximation, the main terms of this type are the following:

$$\langle \Phi^-_{v_2',l,v_1',v_3'}(\rho)| - \hbar^2 g^{\rho\rho} I^{(1)}_{v_i v_i'} \frac{\partial}{\partial \rho} |\Phi^-_{v_2,l,v_1,v_3}(\rho)\rangle \tag{3.138}$$

where v_i is either v_1 or v_3.

The other significant terms arising from the non-adiabatic coupling is the resonance between stretching states with two quanta of excitation, the Darling- Denison resonances. These are calculated using the product of the integrals:$I^{(1)}_{v_1 v_1'} \times I^{(1)}_{v_3 v_3'}$, and writing $\alpha_i'(\rho) = \frac{\partial \alpha_i(\rho)}{\partial \rho}$, giving rise to (together with the formula (3.125):

$$\begin{aligned} -I^{(1)}_{v_1' v_1}(\rho) \times I^{(1)}_{v_3' v_3}(\rho) &= -\frac{1}{4}\left[\frac{\alpha_1'(\rho)}{\alpha_1(\rho)} \cdot \frac{\alpha_3'(\rho)}{\alpha_3(\rho)}\right] \\ &\times \left[-\delta_{v_1',v_1+2}\sqrt{(v_1+1)(v_1+2)} + \delta_{v_1',v_1-2}\sqrt{v_1(v_1-1)}\right] \\ &\times \left[-\delta_{v_3',v_3+2}\sqrt{(v_3+1)(v_3+2)} + \delta_{v_3',v_3-2}\sqrt{v_3(v_3-1)}\right] \end{aligned} \tag{3.139}$$

We must add in the eq. (3.135) the term arising from the kinetic energy, term which is linear in S^s symmetric stretching coordinate (the fourth row of the eq. (3.50)). This will give the next term:

$$\langle \Phi^-_{v_2',K\pm\Lambda,v_1',v_3'}(\rho)|\frac{1}{2} f^{\pm}_{lin}(\rho) F_{v_1' v_1}(\rho)|\Phi^-_{v_2,K\pm\Lambda,v_1,v_3}(\rho)\rangle \tag{3.140}$$

where:

$$f^i_{lin} = -a_s^{\rho\rho,i}\left(g_0^i\right)^{-\frac{1}{4}}\left[P_\rho, \left(g_0^i\right)^{\frac{1}{2}}\left[P_\rho, \left(g_0^i\right)^{-\frac{1}{4}}\right]\right]\left(g_0^{\rho\rho,i}\right)^2 \tag{3.141}$$

and $i = (+,-)$ for the upper or lower potential state, respectively. From the kinetic energy, the third row of the eq. (3.50) add a value function depending only of ρ to the bending potential energy:

$$f^i_\rho(\rho) = -\frac{1}{2}\left(g_0^{\rho\rho,i}\right)\left(g_0^i\right)^{\frac{1}{4}}\left[P_\rho, \left(g_0^i\right)^{-\frac{1}{4}}\right]\left\{g_0^{ss,i}\left[P_s, g^i_{s\rho}\right]_0 + g_0^{aa,i}\left[P_a, g^i_{a\rho}\right]_0\right\} \tag{3.142}$$

and $i = (+,-)$ as above.

Obs. We can introduce in our calculus the last two lines from the eq. (3.50), and in this case, we will have terms arising from:

$$\int_{-\infty}^{\infty} \chi^{\varepsilon\varepsilon}_{v_i'}(S^i)^2 \chi^{\varepsilon\varepsilon}_{v_i} dS^i \sim \delta_{v_i',v_i+2} + \delta_{v_i',v_i} + \delta_{v_i',v_i-2}$$

but these terms have a lower weight (an order of $\frac{1}{\alpha_i}$).

If we introduce all the previous terms together, we get the interaction matrix (for simplicity we neglect at the first step the $\chi^{aa}_{v_3}(S^a;\rho)$ function):

$$(\mathbf{A} - E\,\mathbf{I})\,\mathbf{B} = 0 \tag{3.143}$$

where:

$\mathbf{I}$ – is the identity matrix

$$\mathbf{A} = \begin{bmatrix} \boxed{\begin{matrix} H^{l=K+\Lambda}_{v_1,v_2}(\rho) & 0 \\ 0 & H^{l=K-\Lambda}_{v_1,v_2}(\rho) \end{matrix}} & \cdots & H^{l=K+\Lambda}_{v_1,v_1',v_2}(\rho) \quad H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) & \cdots \\ \vdots & \ddots & \vdots & \vdots \\ H^{l=K+\Lambda}_{v_1,v_1',v_2}(\rho) \quad H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) & \cdots & \boxed{\begin{matrix} H^{l=K+\Lambda}_{v_1',v_2}(\rho) & 0 \\ 0 & H^{l=K-\Lambda}_{v_1',v_2}(\rho) \end{matrix}} & \cdots \\ H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) \quad H^{l=K-\Lambda}_{v_1,v_1',v_2}(\rho) & & & \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{3.144}$$

$$\mathbf{B} = \begin{bmatrix} \Phi^{-}_{v_2,K+\Lambda,v_1,v_3}(\rho) \\ \Phi^{-}_{v_2,K-\Lambda,v_1,v_3}(\rho) \\ \vdots \\ \Phi^{-}_{v_2,K+\Lambda,v_1',v_3}(\rho) \\ \Phi^{-}_{v_2,K-\Lambda,v_1',v_3}(\rho) \\ \vdots \end{bmatrix} \tag{3.145}$$

The matrix elements of the final interaction matrix, before integrating over the bending functions are the following:

$$\begin{aligned} H^{l=K\pm\Lambda}_{v_1,v_2}(\rho) &= E^{0,\pm}_{v_1,v_2,v_3} - \frac{\hbar^2}{2} g^{\rho\rho,\pm}\, I^{(2)}_{v_1,v_1} + f^{\pm}_{\rho}(\rho) \\ H^{l=K\pm\Lambda}_{v_1,v_1',v_2}(\rho) &= -\frac{\hbar^2}{2} g^{\rho\rho,\pm}\, I^{(2)}_{v_1,v_1'} - \hbar^2\, g^{\rho\rho,\pm}\, I^{(1)}_{v_1,v_1'}\, \frac{\partial}{\partial\rho} + \frac{1}{2} F^{ll}_{v_1v_1'}(\rho)\, \Big\{ f^{\pm}_{lin}(\rho) \\ &\quad - \left[\left(\frac{\partial V_0^{+}}{\partial\rho} \right)_0 + \left(\frac{\partial V_0^{-}}{\partial\rho} \right)_0 \right] \frac{R_2(r^0,\rho)}{\sqrt{2}\, r^0(\rho)} + \left[\left(\frac{\partial V^{+}}{\partial S^s} \right)_0 + \left(\frac{\partial V^{-}}{\partial S^s} \right)_0 \right] \frac{\mathcal{R}'(\rho)(\rho-\rho_e)}{R_1(r^0,\rho)} \Big\} \\ H^{l=K+\Lambda}_{l'=K-\Lambda\,v_1,v_1',v_2}(\rho) &= \frac{1}{2} \left\{ - \left[\left(\frac{\partial V_0^{+}}{\partial\rho} \right)_0 - \left(\frac{\partial V_0^{-}}{\partial\rho} \right)_0 \right] \frac{R_2(r^0,\rho)}{\sqrt{2}\, r^0(\rho)} \right. \\ &\quad \left. + \left[\left(\frac{\partial V^{+}}{\partial S^s} \right)_0 - \left(\frac{\partial V^{-}}{\partial S^s} \right)_0 \right] \frac{\mathcal{R}'(\rho)(\rho-\rho_e)}{R_1(r^0,\rho)} \right\} F^{ll'}_{v_1v_1'}(\rho) \end{aligned} \tag{3.146}$$

Obs. We can introduce from formula (3.146) the terms:

$$f_{\rho}^{\pm}(\rho) - \frac{\hbar^2}{2} g^{\rho\rho,\pm} I^{(2)}_{v_1,v_1} \tag{3.147}$$

in $V_{eff}^{\pm}(\rho)$ from (3.111) and in that case the "primitive " bending wavefunctions will be better adapted to the stretching perturbations.

3.5 Numerical Calculus Considerations

3.5.1 Bond Length Parameters and Connection with Rotational Constants

The bond lengths of the component electronic states are treated as independent quantities which are permitted to be different except at $\rho = 0$, where they must be equal. In order to find the linear bond length and the ρ dependence of the bond length, we follow the algorithm described in [147] (§E.1):

1. We consider the formula for the mean rotational constant:

   - for the linear molecules

   $$B_{v_2}^{lin} \sim B_e - \alpha_e(v_2 + 1) + \mathcal{O}(v_1, v_3) \tag{3.148}$$

   - for the bent molecules [5, 190]

   $$B_{v_2}^{bent} = B_e - \alpha_e(v_2 + \frac{1}{2}) + \mathcal{O}(v_1, v_3) \tag{3.149}$$

   In the previous equations $B_e \sim \frac{1}{I_e^0}$, is the equilibrium rotational constant and α_e is the vibration-rotation coupling term. The bond length is that which reproduce in the best way $\bar{B}_v = \frac{1}{2}(B + C)$ rotational constant, for $v_2^{(bent)} = -\frac{1}{2}$ or $v_2^{lin} = -1$. In the same time it must reproduce the unperturbed levels corresponding to the specific electronic state.

2. After finding the r^0 value it is necessary to fit the positions of the unperturbed bending levels which correspond to an electronic state by taking into account a bending potential function as discussed in (§3.3.3) simultaneously with the rotational constants B_{v_2}, corresponding to those levels. In this iterative approach, we find the dependence of the bond length with the angle. This dependence is taken as in [147, eq.(15)], near the linear configuration(as in eq. (3.56)):

   $$r^i(\rho) = r^0 + d_1^i \tan^2\left(\frac{\rho}{2}\right) + d_2^i \rho^2 \tag{3.150}$$

   where $i = (+, -)$, corresponding to upper or lower state, respectively. If we consider the previous algorithm and the $r = f(\rho)$ dependence from (3.150), we find the analytical expression for the bond length and the d factor (§E.1):

   $$\begin{aligned} r_0 &= \sqrt{\frac{C_{g^{\rho\rho}}}{2\, m_1\, B_e}} \\ d &= \sqrt{\frac{C_{g^{\rho\rho}}}{2\, m_1\, B_e}} \cdot \frac{1}{4}\left(\frac{2p-1}{4p} + \frac{\alpha_e \tilde{\omega}_2}{4pB_e^2}\right) \end{aligned} \tag{3.151}$$

Obs. The iterative approach discussed above work well for linear molecules. For the bent molecule, we must consider these two steps:

- find the bond length ($r_{ech} = f(\rho_{min})$) and the ρ_{min} value.
- determine the variation of the bond length with ρ, preserving $r_{ech} = f(\rho_{min})$ value (it means that r^0 value change, when d_1^i and d_2^i values change in (3.150)).

Now we must emphasizes some important aspects:

1. The eq. (3.150) , for $\rho \to 0$ can be expanded in power series and has more terms that the eq.(3.56), taking into account upper term influence of the potential constants.

2. The eq. (3.56) which describes the dependence of the length with the angle, was obtained in the approximation $\rho \to 0$, from the potential constants in the generalized internal coordinates. The $\left(\frac{\partial V}{\partial r_i}\right)_0 = 0$ condition simplify the stretching potential in the reference frame as shown above, in (§3.3.1).

3. The dependence of the bond length with ρ angle from the eq.(3.150) is obtained after a fit of rotational levels, but it is not obtained from a minimum condition of the potential constants.

4. From the previous two items, and after some easy transformations in (§E.2), it seems that the two approaches are not identical. Indeed, $\mathcal{R}^{(rot.const)}(\rho) \sim \mathcal{R}^{(theor)}(\rho)$, because the functions have the same dependence type in ρ^2 for small angles, but the multiplication coefficients are quite different.

   For this reason we introduce a new parameter which describe the matching of the two approaches as:

$$g_D = \frac{\mathcal{R}^{(rot.const.)}(\rho)}{\mathcal{R}^{(theor.)}(\rho)} \tag{3.152}$$

   The g_D parameter needs some additional comments:

   - In the generalized internal coordinates, the bending potential must go to *infinity* for $\rho = \pi$, as have been considered by Pliva *et al.* [191], and emphasized in [5]. But in the same time, Hougen, Bunker and Johns [5] and Jungen, Hallin and Merer [147] find that such a potential give no practical advantages and the bending potential (3.68)-(3.70) does serve to reproduce the experimental data much better. The semi-rigid bender model proposed by Bunker and Landsberg [14] is described without any reference to the bending potential shape.
   - Obviously something has to go to infinity at $\rho = \pi$, either the potential energy or the bond length. Jungen *et al.* [147] have chosen the bond length, because from physical point of view the two outer atoms of the molecule must interact when the vibration bring them together, and a more realistic picture of the molecule would then be a diatomic molecule (consisting of the two outer atoms) loosely bonded to the central atom which is already on the way to dissociation according to

$$B - A - B \to A + B_2$$

     In this method, when the stretch - bend interactions were introduced (coupling between the normal coordinates Q_1 and Q_2), the possibility of dissociation along the pathway previously mentioned was allowed. This dissociation pathway is just as important as the more familiar one

$$B - A - B \to B + A - B$$

     which correspond to a superposition of Q_1 and the antisymmetric coordinate Q_3, as mentioned in [147].

Let analyses in detail the algorithms to obtain the bond length dependences of the bending angle. The algorithm of Bunker *et al.* [14] was analyzed in detail in (§3.3.1). In order to establish the formula for the approach of Jungen *et al.* [147, 150], we start from [150, eq.(8)]. After some calculus, we find that α_e, the dependence of the rotational constant over the bending angle is (§E.1):

$$-\alpha_e = 4p\frac{B_e^2}{\tilde{\omega}_2}\left(\frac{m+2m_1}{4m} - \frac{4\,d^{ChJ}}{r_0}\right) = B_e p\left(\frac{B_e}{\tilde{\omega}_2}\right)\left(\frac{2p-1}{p} - \frac{4\,d_1^{ChJ}}{r_0}\right) \tag{3.153}$$

In order to find the same constant in the generalized internal coordinates, we start from [5, eq.(64)-(67)]. These equations have been obtained from the Hamiltonian [5, eq.(62)], using the contact transformation [45], and is done in (§E.3), in the case of the semirigid bender model. In the calculus we have considered only the leading terms in (v_2+1) from [5, eq.(64)-(67)], because the other terms are multiplied by

$$\frac{\hbar^2}{a^2} = 64\,p^2\left(\frac{B_e}{\tilde{\omega}_2}\right)^2 \leq 10^{-3}$$

and can be neglected in the first approach.

With these observations, we find from (§E.3) the values for the α_i terms (notations from [5]), in the case of a symmetrical molecule:

$$\begin{aligned}
-\alpha^{harm} &= B_e p\left(\frac{B_e}{\tilde{\omega}_2}\right)\cdot\left(\frac{2p-1}{p} - \frac{4\,d_1^{th}}{r_0}\right)\\
-\alpha^{Cor} &= B_e p\left(\frac{B_e}{\tilde{\omega}_2}\right)\cdot\frac{2\tilde{\omega}_2^2}{p^2}\left[\frac{1}{(\tilde{\omega}_2^2-\tilde{\omega}_1^2)} + \frac{p}{(\tilde{\omega}_2^2-\tilde{\omega}_3^2)}\right]\\
-\alpha^{Anh} &= -B_e p\left(\frac{B_e}{\tilde{\omega}_2}\right)\cdot\frac{2\tilde{\omega}_2^2}{p}\left[\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2}\right]
\end{aligned} \tag{3.154}$$

Because the rotational constants in the two approaches must be equal, and with (3.153) - (3.154), we have (§E.3):

$$\begin{aligned}
g_D &= 1 + \frac{1}{B_e p}\left(\frac{\tilde{\omega}_2}{B_e}\right)\frac{1}{32B_e(-r_0\tilde{K}_{122})\left(\frac{1}{\tilde{\omega}_1^2}+\frac{p}{\tilde{\omega}_3^2}\right)}\cdot\left(\alpha^{Cor}+\alpha^{Anh}\right)\\
&= 1 + \frac{\tilde{\omega}_2^2}{16pB_e(-r_0\tilde{K}_{122})}\left[1 + \frac{1}{p\left(\frac{1}{\tilde{\omega}_1^2}+\frac{p}{\tilde{\omega}_3^2}\right)}\left(\frac{1}{\tilde{\omega}_1^2-\tilde{\omega}_2^2}+\frac{p}{\tilde{\omega}_3^2-\tilde{\omega}_2^2}\right)\right]\\
&= 1 + \frac{r_0}{2d_1^{BL}}\frac{\tilde{\omega}_2^2}{p}\left[\frac{1}{\tilde{\omega}_1^2}+\frac{p}{\tilde{\omega}_3^2}\right]\left[1 + \frac{1}{p\left(\frac{1}{\tilde{\omega}_1^2}+\frac{p}{\tilde{\omega}_3^2}\right)}\left(\frac{1}{\tilde{\omega}_1^2-\tilde{\omega}_2^2}+\frac{p}{\tilde{\omega}_3^2-\tilde{\omega}_2^2}\right)\right]
\end{aligned} \tag{3.155}$$

where d_1^{BL} is defined in [14, eq.(21)] and in (E-147). In (§E.3) there are also underlined some important considerations concerning the calculus of the g_D factor in the rigid bender or in the semirigid bender approach.

The formula (3.155) needs some special considerations:

- The deviation of the g_D factor from unity is done because the Coriolis and the anharmonic perturbation is considered. The anharmonic term arise when passing from generalized internal coordinated to the curvilinear ones, as in [5, eq.(56)] and eq. (3.64), (3.71). This means that the g_D factor is in some extent an indirect measurement of the anharmonic and Coriolis perturbations.

- Even in the absence of the Coriolis coupling, the g_D factor is greater than unity, due to the last term in the parenthesis of eq. (3.155), and which arise from the change of coordinate (3.11) and (3.14), from generalized to curvilinear frame.
- From the previous considerations result that formula (3.150), used in Jungen approach for the unidimensional bending motion take into account in an indirect way the anharmonic coupling which imply Fermi interactions, as pointed out in [153], as well as Coriolis coupling. This can explain why the model, with a small number of parameters, can reproduce the experimental data much better than other formalisms.
- The value for the g_D factor must be considered when comparing the results issued from this model, with variational techniques potential surface results, as well as results from linearized coordinates formalism in the case of small amplitude bending motions.
- If we consider a quadratic dependence of the bond length with the angle, as in the eq.(3.150), the relation between d_1^{ChJ} and d_1^{BL} constants may be rewritten with formula (3.155), in a more visible form. Putting (3.152) into another form

$$d_1^{ChJ} = g_D \, d_1^{BL} \tag{3.156}$$

and because $g_D = 1 + \frac{\bar{g}_D}{d_1^{BL}}$, we have

$$d_1^{ChJ} = d_1^{BL} + \bar{g}_D \tag{3.157}$$

The previous formula has the main advantage that the $\bar{g}_D$ term depend only on the bond length and the vibrational frequency for the stretching and bending motions,

$$\bar{g}_D = \frac{r_0}{2}\frac{\tilde{\omega}_2^2}{p}\left[\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2}\right]\left[1 + \frac{1}{p\left(\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2}\right)}\left(\frac{1}{\tilde{\omega}_1^2 - \tilde{\omega}_2^2} + \frac{p}{\tilde{\omega}_3^2 - \tilde{\omega}_2^2}\right)\right] \tag{3.158}$$

and then it is easier to be computed and used in the calculus.

5. Because in the stretch-bender formalism that describes the Fermi interaction, we have $\mathcal{R}^{(theor)}(\rho)$, and the bond length dependence with the ρ angle done by $\mathcal{R}^{(rot.const.)}(\rho)$, we must substitute the former by the last, using the formula (3.152). Then the eq.(3.73) become:

$$\left[-f_{\rho\rho}\frac{R_2(r^0,\rho)}{\sqrt{2}\,r(\rho)}(\rho - \rho_e) + \sqrt{2}\frac{f_{eff}^s(\rho)}{R_1(r^0,\rho)} \cdot \frac{r'(\rho)}{g_D} \cdot (\rho - \rho_e)\right] S^s \tag{3.159}$$

The eq.(3.159) ensure a correct use of the $\left(\frac{\partial V}{\partial r_i}\right)_0 = 0$ condition and in the same time allow the use of the Renner-Teller formalism for the bending displacement, as it was developed by Jungen and Merer [15, 147].

3.5.2 Connection between Renner-Teller Formalism and the Total Interaction Matrix of Stretch-Bender Model

As it was pointed out in the section (§3.5.1), for the bending coordinate we use the formalism developed by Jungen [15]. With the potential parameters for the bending potential (eq. (3.68)-(3.70)) and the bond length dependence with the angle (eq. (3.150)), the bending energies, the bending eigenfunctions and $(\hat{\mathbf{S}}\,\hat{\mathbf{T}}\,\hat{\mathbf{U}})$ matrix of [15, eq.(38) and (42)] are computed.

We see that the $(\hat{\mathbf{S}}\,\hat{\mathbf{T}}\,\hat{\mathbf{U}})$ matrix is computed for each value of the stretching quantum number and the total $(\hat{\mathbf{S}}\,\hat{\mathbf{T}}\,\hat{\mathbf{U}})$ matrix has a block structure. The matrix is:

$$(\mathbf{STU})^{(total)} = \begin{pmatrix} \boxed{(\mathbf{STU})^{(v_1)}} & 0 & 0 & \dots \\ 0 & \boxed{(\mathbf{STU})^{(v_1+1)}} & 0 & \dots \\ \vdots & \vdots & \ddots & \dots \\ 0 & \dots & 0 & \boxed{(\mathbf{STU})^{(v_1')}} \end{pmatrix} \tag{3.160}$$

where each $(\mathbf{STU})^{(v_1')}$ matrix is orthonormalized.

Also, the initial total interaction matrix, $\mathbf{H}^{(total)}$, has a block structure, where the terms are:

- $E_i^{0(v_1)}$= initial bending and stretching energies
- W_1 = Matrix for the anharmonic coupling Fermi resonances of type:

$$\sum_{\alpha}\left[\left(\frac{\partial V^{+}}{\partial \alpha}\right)_0+\left(\frac{\partial V^{-}}{\partial \alpha}\right)_0\right]$$

  with $\alpha = \rho\,, S^s$, (the same as the term $H^{l=K\pm\Lambda}_{v_1,v_1\pm1,v_2}$ from the eq. (3.146)).
- W_2 = Matrix for the anharmonic coupling Fermi resonances of type:

$$\sum_{\alpha}\left[\left(\frac{\partial V^{+}}{\partial \alpha}\right)_0-\left(\frac{\partial V^{-}}{\partial \alpha}\right)_0\right]$$

  with $\alpha = \rho\,, S^s$ (it is the term $H^{l=K+\Lambda}_{v_1,v_1\pm1,v_2}{}^{l'=K-\Lambda}(\rho)$ from the eq. (3.146))
- $N^{(2)}_{a+n}$ = Matrix for the adiabatic and non-adiabatic couplings, proportional with $\left[I^{(1)}_{v_1,v_1'}+I^{(2)}_{v_1,v_1'}\right]$ (the same with $H^{l=K\pm\Lambda}_{v_1,v_1\pm2,v_2}$ from the eq. (3.146)).

$$\mathbf{H}^{(total)} = \begin{pmatrix} \overbrace{\boxed{\begin{matrix} E_1^{0(v_1)} & & 0 \\ & \ddots & \\ 0 & & E_n^{0(v_1)} \end{matrix}}}^{\text{Bend Block}} & \overbrace{\begin{matrix} W_1 & W_2 \\ W_2 & W_1 \end{matrix}}^{\text{Fermi Block}} & \overbrace{\begin{matrix} N_{a+n}^{(2)} & 0 \\ 0 & N_{a+n}^{(2)} \end{matrix}}^{\text{Adiab. and non-Adiab Block}} & 0 & \cdots \\ \begin{matrix} W_1 & W_2 \\ W_2 & W_1 \end{matrix} & \boxed{\begin{matrix} E_1^{0(v_1+1)} & & 0 \\ & \ddots & \\ 0 & & E_n^{0(v_1+1)} \end{matrix}} & \begin{matrix} W_1 & W_2 \\ W_2 & W_1 \end{matrix} & \begin{matrix} N_{a+n}^{(2)} & 0 \\ 0 & N_{a+n}^{(2)} \end{matrix} & \cdots \\ \begin{matrix} N_{a+n}^{(2)} & 0 \\ 0 & N_{a+n}^{(2)} \end{matrix} & \begin{matrix} W_1 & W_2 \\ W_2 & W_1 \end{matrix} & \boxed{\begin{matrix} E_1^{0(v_1+2)} & & 0 \\ & \ddots & \\ 0 & & E_n^{0(v_1+2)} \end{matrix}} & \begin{matrix} W_1 & W_2 \\ W_2 & W_1 \end{matrix} & \cdots \\ 0 & \begin{matrix} N_{a+n}^{(2)} & 0 \\ 0 & N_{a+n}^{(2)} \end{matrix} & \begin{matrix} W_1 & W_2 \\ W_2 & W_1 \end{matrix} & \boxed{\begin{matrix} E_1^{0(v_1+3)} & & 0 \\ & \ddots & \\ 0 & & E_n^{0(v_1+3)} \end{matrix}} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{3.161}$$

The matrix blocks situated on the diagonal position, are already diagonal, due to the multiplication with:

$$\mathbf{H}_{diag}^{(v_i)} = (\mathbf{STU})^{+}\ \mathbf{H}^{(v_i)}\ (\mathbf{STU}) \tag{3.162}$$

This situation determines a pre-diagonalization of the initial interaction matrix (3.161), by multiplying with $(\mathbf{STU})^{(total)}$ from (3.160). We can write the $\mathbf{H}^{(total)}$ in a block structure as:

$$\mathbf{H}^{(total)} = \begin{pmatrix} \mathbf{H}_{diag}^{(v_1)} & \mathbf{H}_{v_1,v_1+1} & \cdots \\ \mathbf{H}_{v_1,v_1+1} & \mathbf{H}_{diag}^{(v_1+1)} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \tag{3.163}$$

where each $\mathbf{H}_{diag}^{(v_1)}, \mathbf{H}_{v_1,v_1+1}$ is a matrix of dimension twice the bending base (in the case of Renner-Teller coupling) or of the bending base. We will have:

$$\left[(\mathbf{STU})^{(total)}\right]^{+}\ \mathbf{H}^{(total)}\ (\mathbf{STU})^{(total)} \tag{3.164}$$

The pre-diagonalization is easy to do, because in the $H^{(total)}$ matrix, each non-diagonal block from the row v_1 and the column v_1' will be multiplied by:

$$\left[(\mathbf{STU})^{(v_1)}\right]^{+}\ \mathbf{H}_{v_1,v_1'}\ (\mathbf{STU})^{v_1'} \tag{3.165}$$

This means that is not need to do a full matrix multiplication.

After the multiplication (3.165), each non-diagonal block will have the terms like:

$$\boxed{\begin{matrix} g & & S \\ & g & \\ & & g \\ S & & g \end{matrix}} \quad \begin{cases} g - \text{large elements} \\ S - \text{small elements} \end{cases}$$

As it can be seen in the above block, the large elements are on the diagonal of the matrix.

Another problem to be taken into account is the phase of the bending wavefunctions computed above. As a limit case for the bending functions, in the rigid bender limit, for linear molecules, we consider as wavefunctions, those of a bidimensional oscillator. In the literature, there are three phase conventions:

1. The convention used by Shaffer [44], [11], where the wavefunction is:

$$\psi^{sh}_{v,l}(x,\varphi) \sim x^{\frac{l}{2}}\, e^{-\frac{x}{2}}\, L^{l}_{\frac{v+l}{2}}(x)\, e^{il\varphi} \tag{3.166}$$

where $x \sim \rho^2$ and $L^l_s(x)$ is the associated Laguerre polynomials. If we consider the above functions, we have the matrix elements for

$$q_{\pm} \;=\; q_x \pm i q_y \;=\; q e^{\pm i\varphi} \tag{3.167}$$

as:

$$\begin{aligned}
\langle v+1, l+1|q_+|v,l\rangle &= -\frac{1}{\sqrt{2}}\,(v+l+2)^{\frac{1}{2}} \\
\langle v-1, l+1|q_+|v,l\rangle &= \frac{1}{\sqrt{2}}\,(v-l)^{\frac{1}{2}} \\
\langle v-1, l-1|q_-|v,l\rangle &= -\frac{1}{\sqrt{2}}\,(v+l)^{\frac{1}{2}} \\
\langle v+1, l-1|q_-|v,l\rangle &= \frac{1}{\sqrt{2}}\,(v-l+2)^{\frac{1}{2}}
\end{aligned} \tag{3.168}$$

2. The convention used by [47], [49] and others, where the wavefunction is defined as:

$$\psi^{Msh}_{v,l}(x,\varphi) \sim x^{\frac{l}{2}}\, e^{-\frac{x}{2}}\, L^{l}_{\frac{v-l}{2}}(x)\, e^{il\varphi} \tag{3.169}$$

and $x \sim \rho^2$, $L^l_{\frac{v-l}{2}}(x)$ is the associated Laguerre polynomials with other definition and slightly different behavior.

The connection between the definition (3.166) and (3.169) is:

$$\psi^{Msh}_{v,l}(x,\varphi) = (-1)^l\, \psi^{sh}_{v,l}(x,\varphi) \tag{3.170}$$

This means that near $x \to 0$, the new wavefunction will be always positive:

$$\psi^{Msh}_{v,l}(x,\varphi)|_0 \sim \rho^{l+\frac{1}{2}} \tag{3.171}$$

If we consider the eq. (3.170), the matrix elements (3.168), will change the sign.

3. A convention used by Hougen [37], Jungen and Merer [33], where the matrix elements have the formula:

$$\begin{aligned}
\langle v\pm 1, l+1|q_+|v,l\rangle &\sim [(v+1)\pm(l+1)]^{\frac{1}{2}} \\
\langle v\pm 1, l-1|q_-|v,l\rangle &\sim [(v+1)\mp(l-1)]^{\frac{1}{2}}
\end{aligned} \tag{3.172}$$

The relation between the Shaffer phase convention and Jungen phase convention is:

$$\psi^{ChJ}_{v,l}(x) = (-1)^{v_b+l}\, \psi^{sh}_{v,l}(x) \tag{3.173}$$

The relation between the Messiah phase convention and Jungen phase convention is:

$$\psi_{v,l}^{ChJ}(x) = (-1)^{v_b}\,\psi_{v,l}^{Msh}(x) \tag{3.174}$$

The relation between the linear and bent molecule bending quantum numbers is $v = 2v_b + |l|$ and we introduced in (3.173) and (3.174) the quantum number v_b.

Obs. *1* In [33, eq.(11), eq.(14)] it is a mismatch between the definition of the wavefunction and the matrix elements.

Obs. *2* Moffitt [52] use another phase convention for this wavefunctions which can be related to those of Shaffer's function by:

$$\psi_{v,l}^{M}(x) = e^{i\frac{\pi}{2}l}\psi_{v,l}^{sh}(x) \tag{3.175}$$

Obs. *3* It is important to know the matrix elements for q_+, q_-, because we can find the matrix elements for q^2, as:

$$q^2 = \frac{1}{2}(q_+q_- + q_-q_+) \tag{3.176}$$

All of the wavefunctions used in the bending computation have, near $\rho \to 0$, the behavior [15]:

$$\bar{\Phi}^{i}_{v_2,l,v_1,v_3}(\rho) \sim \rho^{l+\frac{1}{2}}$$

and are computed with the phase convention used by Messiah [47].

Because in the stretch-bender model we use the Hougen [37] convention for the anharmonic coupling matrix elements, the phase of the wavefunctions must be changed, as in eq. (3.174). We must change also the rotation matrix $(\mathbf{STU})^{(v_i)}$, after the formula (§E.4):

$$(\mathbf{STU})_{v_i}^{Stretch-Bender} = (\mathbf{S}^l)^+\,(\mathbf{STU})^{(v_i)} \tag{3.177}$$

where $(\mathbf{S}^l)$ is a diagonal matrix:

$$(\mathbf{S}^l)_{n,m} = (-1)^{n-1}\,\delta_{n,m} \tag{3.178}$$

The "primitive" wavefunctions are computed with a volume element of $dV = d\rho$, instead of $dV = \frac{d\rho}{g^{\rho\rho}}$, as was pointed out in the section (§3.2.4) and in the eq.(3.132). For this reason, we must scale the bending wavefunctions with $\sqrt{g^{\rho\rho}}$:

$$\Phi^{i}_{v_2,l,v_1,v_3}(\rho) = \sqrt{g^{\rho\rho}}\bar{\Phi}^{i}_{v_2,l,v_1,v_3}(\rho) \tag{3.179}$$

The last problem to be pointed out in this section, is the bending potential constant, used to compute the initial bending energies and the "primitive" wavefunctions (3.179). The effective potential to be used is (3.111), but the algorithm for the bending displacement take into account the $V_0^{\mp b}(\rho)$ potential from (3.111), instead of $V_{eff}(\rho)$. For this reason we must adapt the potential constant in $V_0^{\mp b}(\rho)$ (the eq. (3.68) - (3.70)) to take into account the stretching component to the bending potential (last two terms in (3.111)).

We have two cases:

1. Bent molecules (eq. (3.69) and (3.70)).

   The minimum angle value ρ_{min} and the barrier to linearity (h) can be computed directly from the shape of $V_0^{\mp b}(\rho)$ function. The harmonic force constant (f) and the anharmonic parameter (k_4), are found by using an iterative least-square fit, to match better the $V_0^{\mp b}(\rho)$ function.

2. Linear molecules (eq. (3.68) and (3.70)).

   The harmonic force constant (K) and the anharmonic parameter (k_4) are computed directly from the shape of the $V_0^{\mp b}(\rho)$ function. The parameters for the Lorentz perturbation are found using a least-square fit of the function:

$$\frac{1}{y_i} = \frac{1}{a'} + \frac{\rho_i^2 b'}{a'} \quad \text{where} \quad \begin{cases} b' = \frac{1}{b}\ ,\ a' = \frac{a}{b} \\ y_i = V_0^{\mp b}(\rho_i) - \frac{1}{2}k\rho_i^2 - V_2^b(\rho_i) \end{cases} \tag{3.180}$$

   y_i is the difference between the "correct" potential $V_0^{\mp b}(\rho)$ and the "approximate" one $\frac{1}{2}k\rho^2 + V_2^b(\rho)$.

In the above procedure the terms from (3.147) are supposed to be enough small.

3.5.3 Computational Details

In the previous section (§3.4.6) we have not take into account that the dependence of the bond length with the ρ angle is function of the upper and/or lower state, too. If we consider this dependence, the auxiliary functions $R_i(r^{0\pm}, \rho)$, $i = \overline{1,5}$, defined in (3.16) are different for the two states and therefore they must be written as $R_i^{\pm}(r^0, \rho)$. We have to make the same consideration for $\mathcal{R}(\rho)$, defined in (3.1), which, in connection with (3.150), gives:

$$\mathcal{R}^{\pm}(\rho) = d_1^{\pm} \tan^2\left(\frac{\rho}{2}\right) + d_2^{\pm}\,\rho^2 \tag{3.181}$$

We must write the expressions involving $R_i^{\pm}(r^0, \rho)$ and $\mathcal{R}^{\pm}(\rho)$ from the eq. (3.134) and (3.146) by taking into account the previous observations:

$$\begin{aligned} &-\left[\left(\frac{\partial V_0^+}{\partial \rho}\right)_0 \frac{R_2^+(r^{0,+},\rho)}{\sqrt{2}r^{0,+}(\rho)} \pm \left(\frac{\partial V_0^-}{\partial \rho}\right)_0 \frac{R_2^-(r^{0,-},\rho)}{\sqrt{2}r^{0,-}(\rho)}\right] \\ &+\left[\frac{1}{g_D^+}\left(\frac{\partial V^+}{\partial S^s}\right)_0 \frac{(\mathcal{R}^+(\rho))'}{R_1^+(r^{0,+},\rho)}(\rho - \rho_e^+) \pm \frac{1}{g_D^-}\left(\frac{\partial V^-}{\partial S^s}\right)_0 \frac{(\mathcal{R}^-(\rho))'}{R_1^-(r^{0,-},\rho)}(\rho - \rho_e^-)\right] \end{aligned} \tag{3.182}$$

In the same time, the stretching energy, (3.100) is a function of the upper and lower state. In the W_2 integrals from the eq. (3.161), there are involved harmonic oscillator functions between upper and lower bending states (bias the bond length dependence with the ρ angle). We have the integrals of type:

$$\int_{-\infty}^{\infty} \chi_{ss}^+(S^s;\rho)(S^s)^n\ \chi_{ss}^-(S^s;\rho)\,dS^s \sim \frac{1}{\alpha^n} \tag{3.183}$$

where α is a constant to obtain the dimensionless constant $\xi = \alpha S^s$ for the Hermite polynomials. In the case of the integrals (3.183), we have made the crude approximation:

$$\alpha(\rho) = \frac{1}{2}\left[\alpha^+(\rho) + \alpha^-(\rho)\right] \tag{3.184}$$

In the same time, the dependence of the stretching energy with the bending angle, involved in (3.100) was approximated with:

$$\omega_i^{\pm}(\rho) = \omega_i^0 + (\omega_i^{(2)})^{\pm}\rho^2 + (\omega_i^{(4)})^{\pm}\rho^4 \tag{3.185}$$

where $i = 1, 3$ for the symmetric and antisymmetric stretching respectively. The formula (3.185) is obtained by expanding in Taylor series as function of the ρ angle, the expressions in (3.100) and by canceling the series after the quartic term.

In the stretching potential we must include the contribution of an anharmonic term in the usual way by using the parameters x_i:

$$\sum_{i=1,3} \omega_i(\rho) \left(v_i + \frac{1}{2}\right) \left[1 + x_i \left(v_i + \frac{1}{2}\right)\right] \tag{3.186}$$

This contribution includes the potential terms proportional with S_i^3 in the second order approximation and S_i^4 in the first order approximation.

When computing the integrals from (3.161), we have various types of terms (we use the CGS system and the spectroscopic units, instead of the MKS system):

1. The Fermi integrals, of type:

$$\int_o^\pi \underbrace{\left[\int_{-\infty}^{\infty} \left(\chi_{v_1}^{ss,i}(S^s;\rho)\right)^* S^s \chi_{v_1'}^{ss,i'}(S^s;\rho) dS^s\right]}_{(B)} \times \underbrace{\left(\Phi_{v_2,l,v_1,v_3}^{i}(\rho)\right)^* \Phi_{v_2',l',v_1',v_3'}^{i'}(\rho)\, f_{Fermi}^{ii'}(\rho) \times \frac{d\rho}{g^{\rho\rho}}}_{(A)} \tag{3.187}$$

where $i, i' = (+,-)$ for the upper and/or lower state respectively and:

$$\begin{aligned} f_{Fermi}^{ii'}(\rho) &= (\delta_{i,+}\delta_{i',+} + \delta_{i,-}\delta_{i',-}) \left\{ -\left[\left(\frac{\partial V_0^+}{\partial \rho}\right)_0 \frac{R_2^+(r^{0,+},\rho)}{\sqrt{2} r^{0,+}(\rho)} + \left(\frac{\partial V_0^-}{\partial \rho}\right)_0 \frac{R_2^-(r^{0,-},\rho)}{\sqrt{2} r^{0,-}(\rho)}\right] \right. \\ &+ \left. \left[\left(\frac{\partial V^+}{\partial S^s}\right)_0 \frac{(\mathcal{R}^+(\rho))'(\rho - \rho_e^+)}{R_1^+(r^{0,+},\rho)} + \left(\frac{\partial V^-}{\partial S^s}\right)_0 \frac{(\mathcal{R}^-(\rho))'(\rho - \rho_e^-)}{R_1^-(r^{0,-},\rho)}\right] \right\} \\ &+ (\delta_{i,+}\delta_{i',-} + \delta_{i,-}\delta_{i',+}) \left\{ -\left[\left(\frac{\partial V_0^+}{\partial \rho}\right)_0 \frac{R_2^+(r^{0,+},\rho)}{\sqrt{2} r^{0,+}(\rho)} - \left(\frac{\partial V_0^-}{\partial \rho}\right)_0 \frac{R_2^-(r^{0,-},\rho)}{\sqrt{2} r^{0,-}(\rho)}\right] \right. \\ &+ \left. \left[\left(\frac{\partial V^+}{\partial S^s}\right)_0 \frac{(\mathcal{R}^+(\rho))'(\rho - \rho_e^+)}{R_1^+(r^{0,+},\rho)} - \left(\frac{\partial V^-}{\partial S^s}\right)_0 \frac{(\mathcal{R}^-(\rho))'(\rho - \rho_e^-)}{R_1^-(r^{0,-},\rho)}\right] \right\} \end{aligned} \tag{3.188}$$

The bending wavefunctions were multiplied with $\sqrt{g^{\rho\rho}}$ (eq. (3.179)) and then the part (A) from eq.(3.187) has a dimension of $\left[\frac{cm^{-1}}{cm}\right]$. The matrix element has the dimension $[cm^{-1}]$, dimension of energy, as it must be, due to the fact that the part (B) from eq.(3.187) has a dimension $[cm]$.

The constants which enter into the metric tensor element $g^{\rho\rho}$ from eq. (3.187) vanish because we have:$\sqrt{g^{\rho\rho}}\sqrt{g^{\rho\rho}} \cdot \frac{1}{g^{\rho\rho}} = 1$ and the others are in $[cm^{-1}]$. The integral (B) is proportional with $\frac{1}{\alpha(\rho)}$, where $\alpha(\rho)$ is the known constant from the adiabatic harmonic oscillator,

$$\alpha_i(\rho) = \sqrt{\frac{\omega_i(\rho)\mu}{\hbar}} \tag{3.189}$$

In the previous formula we have $\omega_i(\rho)$ in (s^{-1}) and μ is the reduced mass of the stretching atoms. The value of $\alpha(\rho)$ is (§E.5):

$$\alpha_i(\rho) = 17.222085 \cdot 10^6 \sqrt{\mu\,[amu]\ \omega_i\,[cm^{-1}]} \tag{3.190}$$

The value used effectively during the computation is not that from (3.190), the value is

$$\underbrace{0.17222085}_{C_\alpha} \sqrt{\mu\,[amu]\ \omega_i\,[cm^{-1}]} \tag{3.191}$$

because we multiply $\alpha_i(\rho)\cdot 10^{-8}$, where 10^{-8} is the conversion factor between

$$\frac{1}{r^0\,[\mathring{\mathrm{A}}]} \rightarrow \frac{1}{r^0\,[cm]}$$

2. The adiabatic and non-adiabatic integrals , of type:

$$-\frac{\hbar^2}{2}\int_0^{\pi}\underbrace{\left[\int_{-\infty}^{\infty}\left[\chi^{ss,\pm}_{v_1}(S^s,\rho)\right]^*\frac{\partial^2}{\partial\rho^2}\chi^{ss,\pm}_{v_1'}(S^s,\rho)dS^s\right]}_{(B)}\times$$
$$\underbrace{g^{\rho\rho,\pm}(\rho)\left[\Phi^{\pm}_{v_2,l,v_1,v_3}(\rho)\right]^*\Phi^{\pm}_{v_2',l,v_1',v_3'}(\rho)\frac{d\rho}{g^{\rho\rho}}}_{(A)} \qquad (3.192)$$
$$-\hbar^2\int_0^{\pi}\underbrace{\left[\int_{-\infty}^{\infty}\left[\chi^{ss,\pm}_{v_1}(S^s,\rho)\right]^*\frac{\partial}{\partial\rho}\chi^{ss,\pm}_{v_1'}(S^s,\rho)dS^s\right]}_{(B)}\times$$
$$\underbrace{g^{\rho\rho,\pm}(\rho)\left[\Phi^{\pm}_{v_2,l,v_1,v_3}(\rho)\right]^*\frac{\partial}{\partial\rho}\Phi^{\pm}_{v_2',l,v_1',v_3'}(\rho)\frac{d\rho}{g^{\rho\rho}}}_{(A)}$$

The bending wavefunctions are multiplied with $\sqrt{g^{\rho\rho}}$ eq. (3.179) and therefore have the dimension of $\sqrt{g^{\rho\rho}}$. The (B) integrals are function of $\frac{\alpha'(\rho)}{\alpha(\rho)}$ and $\frac{\alpha''(\rho)}{\alpha(\rho)}$, eq. (3.122) and (3.125) and therefore are dimensionless. The dimension of (A) integrals is that of $(\hbar^2\,g^{\rho\rho})$, because, as above, we have $\sqrt{g^{\rho\rho}}\cdot\sqrt{g^{\rho\rho}}\cdot\frac{1}{g^{\rho\rho}}=1$ The integrals (3.192) must have the dimension of $[cm^{-1}]$ and for this reason are divided by (hc).

After some calculus, we replace (§E.5)the factor $(\hbar^2 g^{\rho\rho})$ in (3.192) with:

$$\underbrace{16.85771}_{\mathbf{C}_{g^{\rho\rho}}}\,g^{\rho\rho}\,\left[amu^{-1}\cdot\mathring{\mathrm{A}}\right] \qquad (3.193)$$

3. The integrals from the kinetic energy terms $f(\rho)^{\pm}$ and $f(\rho)^{\pm}_{lin}$ defined in eq. (3.141), (3.142).

   After some calculus we find that the numerical constant is equal with

$$\mathbf{C}_{g^{\rho\rho}} = 16.85771$$

   and in the metric tensor elements all masses are expressed in [amu] and the lengths in [Å].

Obs. The connection between the numerical constant in $\alpha(\rho)$ factor and that from adiabatic and non-adiabatic factor is: $\mathbf{C}_{g^{\rho\rho}}=\frac{1}{\sqrt{2}\mathbf{C}_{\alpha}}$

3.6 Extension of the Formalism for non-Symmetric Molecules

3.6.1 Reference Configuration, Displacements and Instantaneous Configuration

Following the approach originated by HBJ [5], we consider the reference configuration of a molecule which lies in the plane making the angle φ with the xz plane. This means that we must multiply all a_{ix} , a_{iy} $i=\overline{1,3}$ from [5, eq.(2)] with $\cos\varphi$ and $\sin\varphi$ respectively. The values of $\vec{a}_i(\rho)$ are chosen so that satisfy the eq. (3.5) which will fix the angle ε between the local Oz axis

and the bond length r_{23} (Fig.2.1 and Fig.F.1). The displacements are subject to the constraints (3.6)-(3.7), discussed previously. We compute the relations between the displacements and the stretching coordinates in a similar manner as in (§3.1.2). We get the instantaneous coordinates (§F.1):

$$
\begin{aligned}
x_1 &= \left[-\frac{m_2+m_3}{m}r_{12} - S_1\right]\sin(\rho-\varepsilon)\cos\varphi + \frac{m_3}{m}r_{23}\sin\varepsilon\cos\varphi \\
&+ S_1\frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\cos\varphi \\
y_1 &= \left[\frac{m_2+m_3}{m}r_{12} + S_1\right]\sin(\rho-\varepsilon)\sin\varphi - \frac{m_3}{m}r_{23}\sin\varepsilon\sin\varphi \\
&- S_1\frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\sin\varphi \\
z_1 &= -\left[\frac{m_2+m_3}{m}r_{12} + S_1\right]\cos(\rho-\varepsilon) - \frac{m_3}{m}r_{23}\cos\varepsilon - S_1\frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon) \\
x_2 &= \left[\frac{m_1}{m}r_{12} + \frac{m_1}{m_2}S_1\right]\sin(\rho-\varepsilon)\cos\varphi + \left[\frac{m_3}{m}r_{23} + \frac{m_3}{m_2}S_3\right]\sin\varepsilon\cos\varphi \\
&- S_1\frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\frac{m_1}{m_2}\cos(\rho-\varepsilon)\cos\varphi - S_3\frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\frac{m_3}{m_2}\cos\varepsilon\cos\varphi \\
y_2 &= -\left[\frac{m_1}{m}r_{12} + \frac{m_1}{m_2}S_1\right]\sin(\rho-\varepsilon)\sin\varphi - \left[\frac{m_3}{m}r_{23} + \frac{m_3}{m_2}S_3\right]\sin\varepsilon\sin\varphi \\
&+ S_1\frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\frac{m_1}{m_2}\cos(\rho-\varepsilon)\sin\varphi + S_3\frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\frac{m_3}{m_2}\cos\varepsilon\sin\varphi \\
z_2 &= \left[\frac{m_1}{m}r_{12} + \frac{m_1}{m_2}S_1\right]\cos(\rho-\varepsilon) - \left[\frac{m_3}{m}r_{23} + \frac{m_3}{m_2}S_3\right]\cos\varepsilon \\
&+ S_1\frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\frac{m_1}{m_2}\sin(\rho-\varepsilon) - S_3\frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\frac{m_3}{m_2}\sin\varepsilon \\
x_3 &= \frac{m_1}{m}r_{12}\sin(\rho-\varepsilon)\cos\varphi - \left[\frac{m_1+m_2}{m}r_{23} + S_3\right]\sin\varepsilon\cos\varphi + S_3\frac{1}{\varepsilon'}\frac{r'_{23}}{r_23}\cos\varepsilon\cos\varphi \\
y_3 &= -\frac{m_1}{m}r_{12}\sin(\rho-\varepsilon)\sin\varphi + \left[\frac{m_1+m_2}{m}r_{23} + S_3\right]\sin\varepsilon\sin\varphi - S_3\frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\varepsilon\sin\varphi \\
z_3 &= \frac{m_1}{m}r_{12}\cos(\rho-\varepsilon) + \left[\frac{m_1+m_2}{m}r_{23} + S_3\right]\cos\varepsilon + S_3\frac{1}{\varepsilon'}\frac{r'_{23}}{r_23}\sin\varepsilon
\end{aligned}
\tag{3.194}
$$

In the following equations we will use the quantities[5, 14, 6]:

$$
\begin{aligned}
u_1 &= m_1\,(m_2+m_3)\,(r^0_{12})^2 \\
u_3 &= m_3\,(m_2+m_3)\,(r^0_{32})^2 \\
u_{13} &= m_1 m_3 r^0_{12} r^0_{32} \\
m &= m_1+m_2+m_3
\end{aligned}
\tag{3.195}
$$

As in (§3.1.2), in the case of the potential energy, we need to obtain an expression in terms of the reference angle ρ, rather than the instantaneous angle, $\bar{\rho}$. We find, similarly with (3.11) that:

$$
\bar{\rho}(\rho, S_1, S_3) \simeq \rho + \left(\frac{\partial\rho}{\partial S_1}\right)_{S_1=0} S_1 + \left(\frac{\partial\rho}{\partial S_3}\right)_{S_3=0} S_3 \tag{3.196}
$$

With the same assumptions as for the eq. (3.12), we obtain the derivatives of ρ (§F.2) relative to the stretching coordinate, as:

$$
\left(\frac{\partial\rho}{\partial S_1}\right)_{S_1=0} = -\left[\left(\frac{m_1+m_2}{m_2}\right)\cdot\frac{(r^0_{12})'}{r^0_{12}}\left(\frac{1}{1-\varepsilon'}\right)\frac{1}{r^0_{12}} - \left(\frac{m_1}{m_2}\right)\frac{1}{r^0_{23}}\sin\rho\right.
$$

$$
\begin{aligned}
&+ \left(\frac{m_1}{m_2}\right)\left(\frac{1}{1-\varepsilon'}\right)\frac{(r_{12}^0)'}{r_{12}^0}\frac{\cos\rho}{r_{23}^0}\Bigg] \\
\left(\frac{\partial\rho}{\partial S_3}\right)_{S_3=0} &= -\Bigg[\left(\frac{m_3+m_2}{m_2}\right)\cdot\frac{(r_{23}^0)'}{r_{23}^0}\left(\frac{1}{\varepsilon'}\right)\frac{1}{r_{23}^0} - \left(\frac{m_3}{m_2}\right)\frac{1}{r_{12}^0}\sin\rho \\
&+ \left(\frac{m_3}{m_2}\right)\left(\frac{1}{\varepsilon'}\right)\frac{(r_{23}^0)'}{r_{23}^0}\frac{\cos\rho}{r_{12}^0}\Bigg]
\end{aligned}
\tag{3.197}
$$

The relations between the stretching coordinate of Jensen [6, eq.(31),(33)] and the stretching coordinates in our model, S_1 and S_3, are (§F.3):

$$
\begin{aligned}
\Delta r_1 &= r_{12} - r_{12}^0(\rho) = \frac{m_1+m_2}{m_2}S_1 - \frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\sin\rho\right]S_3 \\
\Delta r_3 &= r_{23} - r_{23}^0(\rho) = -\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin\rho\right]S_1 + \frac{m_3+m_2}{m_2}S_3
\end{aligned}
\tag{3.198}
$$

Δr_1 and Δr_3 are the displacements from the equilibrium position in the "potential valley", as in the relations (3.13). We consider also the relation in terms of the reference stretching coordinates (§F.4):

$$
\begin{aligned}
\left(\frac{\partial S_1}{\partial\rho}\right)_0 &= \frac{1}{D}\Bigg\{[\mathcal{R}'_{12}(\rho)+\mathcal{R}'_{23}(\rho)]\left[\left(1+\frac{m_3}{m_2}\right)+\frac{m_3}{m_2}\left(\cos\rho+\frac{1}{\varepsilon'}\cdot\frac{(r_{23}^0)'}{r_{23}^0}\sin\rho\right)\right] \\
&+ [\mathcal{R}'_{12}(\rho)-\mathcal{R}'_{23}(\rho)]\left[\left(1+\frac{m_3}{m_2}\right)-\frac{m_3}{m_2}\left(\cos\rho+\frac{1}{\varepsilon'}\cdot\frac{(r_{23}^0)'}{r_{23}^0}\sin\rho\right)\right]\Bigg\} \qquad (3.199) \\
\left(\frac{\partial S_3}{\partial\rho}\right)_0 &= \frac{1}{D}\Bigg\{[\mathcal{R}'_{12}(\rho)+\mathcal{R}'_{23}(\rho)]\left[\left(1+\frac{m_1}{m_2}\right)+\frac{m_1}{m_2}\left(\cos\rho+\frac{1}{1-\varepsilon'}\cdot\frac{(r_{12}^0)'}{r_{12}^0}\sin\rho\right)\right] \\
&- [\mathcal{R}'_{12}(\rho)-\mathcal{R}'_{23}(\rho)]\left[\left(1+\frac{m_1}{m_2}\right)-\frac{m_1}{m_2}\left(\cos\rho+\frac{1}{1-\varepsilon'}\cdot\frac{(r_{12}^0)'}{r_{12}^0}\sin\rho\right)\right]\Bigg\}
\end{aligned}
$$

where the denominator D is:

$$
\begin{aligned}
D &= 2\Bigg\{\left(1+\frac{m_1}{m_2}\right)\left(1+\frac{m_3}{m_2}\right) - \frac{m_1m_3}{m_2^2}\left[\cos\rho+\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin\rho\right]\times \\
&\left[\cos\rho+\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\sin\rho\right]\Bigg\}
\end{aligned}
\tag{3.200}
$$

In the rigid-bender limit, the eq. (3.197)-(3.199) become:

$$
\begin{aligned}
&\left(\tfrac{\partial\rho}{\partial S_1}\right)_{r'=0} = \tfrac{m_1}{m_2}\cdot\tfrac{1}{r_{23}^0}\sin\rho \qquad \left(\tfrac{\partial\rho}{\partial S_3}\right)_{r'=0} = \tfrac{m_3}{m_2}\cdot\tfrac{1}{r_{12}^0}\sin\rho \\
&\Delta r_1|_{r'=0} = \left(1+\tfrac{m_1}{m_2}\right)S_1 - \tfrac{m_3}{m_2}\cos\rho\, S_3 \quad \Delta r_3|_{r'=0} = \left(1+\tfrac{m_3}{m_2}\right)S_3 - \tfrac{m_1}{m_2}\cos\rho\, S_1 \qquad (3.201) \\
&\left(\tfrac{\partial S_1}{\partial\rho}\right)_{r'=0} = 0 \qquad \left(\tfrac{\partial S_3}{\partial\rho}\right)_{r'=0} = 0
\end{aligned}
$$

We see that again, the derivatives of the stretching coordinates to the bending angle vanish in the rigid bender limit, as it must be.

3.6.2 Kinetic Energy

In order to obtain the kinetic energy in curvilinear coordinates, we assume that, if the reference configuration is close to that of the instantaneous configuration, the derivatives of the displacements may be evaluated **after** setting $S_1 = 0$ and $S_3 = 0$ [186], i.e.:

$$
\left(\frac{\partial f}{\partial\alpha}\right)_0 = \frac{\partial\left(f|_{S_1=S_3=0}\right)}{\partial\alpha} \tag{3.202}
$$

The quantum kinetic energy operator is given by (3.36), where the quantum operators are:

$$\begin{aligned} P_\rho &= -i\hbar\frac{\partial}{\partial\rho} \quad P_1 = -i\hbar\frac{\partial}{\partial S_1} \\ P_\varphi &= -i\hbar\frac{\partial}{\partial\varphi} \quad P_3 = -i\hbar\frac{\partial}{\partial S_3} \end{aligned} \tag{3.203}$$

Elements of the metric tensor

We must consider (3.202) in order to evaluate the metric tensor elements, in the "0" point only and in this situation we will not have a stretching coordinate dependence, $g^0_{ij} = f(\rho)$. The metric tensor elements are diagonal for the ρ and φ coordinates and will be (§F.5):

$$\begin{aligned} g^0_{\rho\rho} &= \frac{1}{m}\left\{(1-\varepsilon')^2\left[1+\frac{1}{(1-\varepsilon')^2}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)^2\right]u_1 + (\varepsilon')^2\left[1+\frac{1}{(\varepsilon')^2}\left(\frac{(r^0_{23})'}{r^0_{23}}\right)^2\right]u_3\right. \\ &- 2u_{13}(1-\varepsilon')\,\varepsilon'\left[\left[1-\frac{1}{(1-\varepsilon')}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)\frac{1}{\varepsilon'}\left(\frac{(r^0_{23})'}{r^0_{23}}\right)\right]\cos\rho\right. \\ &+ \left.\left.\left[\frac{1}{\varepsilon'}\left(\frac{(r^0_{23})'}{r^0_{23}}\right)+\frac{1}{(1-\varepsilon')}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)\right]\sin\rho\right]\right\} \\ g^0_{\varphi\varphi} &= \frac{1}{m}\left[u_1\sin^2(\rho-\varepsilon)+u_3\sin^2\varepsilon-2u_{13}\sin(\rho-\varepsilon)\sin\varepsilon\right] \\ g^0_{11} &= \frac{m_1(m_1+m_2)}{m_2}\left[1+\frac{1}{(1-\varepsilon')^2}\cdot\left(\frac{(r^0_{12})'}{r^0_{12}}\right)^2\right] \\ g^0_{33} &= \frac{m_3(m_3+m_2)}{m_2}\left[1+\frac{1}{(\varepsilon')^2}\cdot\left(\frac{(r^0_{23})'}{r^0_{23}}\right)^2\right] \\ g^0_{13} &= -\frac{m_1m_3}{m_2}\left\{\left[1-\frac{1}{(1-\varepsilon')\,\varepsilon'}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)\left(\frac{(r^0_{23})'}{r^0_{23}}\right)\right]\cos\rho\right. \\ &+ \left.\left[\frac{1}{\varepsilon'}\left(\frac{(r^0_{23})'}{r^0_{23}}\right)+\frac{1}{(1-\varepsilon')}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)\right]\sin\rho\right\} \\ g^0_{\rho\alpha} &= g^0_{\varphi\beta} = 0 \\ &\text{where } \alpha = \varphi\,,1\,,3 \text{ and } \beta = \rho\,,1\,,3 \end{aligned} \tag{3.204}$$

The Jacobian of the metric tensor is function of ρ only:

$$g_0 = g^0_{\rho\rho}\,g^0_{\varphi\varphi}\left[g^0_{11}\,g^0_{33}-(g^0_{13})^2\right] \tag{3.205}$$

Obs.*1* In the case of the rigid bender approach, $g^0_{\varphi\varphi}$ and $g^0_{\rho\rho}$ have the same values as in [5, eq.(37)].

Obs.*2* The $g^0_{\rho\rho}$ from the eq. (3.204) is different from the value of [14], in the semirigid bender limit, with:

$$\begin{aligned} g^0_{\rho\rho} &= g^{BL}_{\rho\rho}+\frac{1}{m}\left\{u_1\left(\frac{(r^0_{12})'}{r^0_{12}}\right)^2+u_3\left(\frac{(r^0_{23})'}{r^0_{23}}\right)^2+2u_{13}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)\left(\frac{(r^0_{23})'}{r^0_{23}}\right)\cos\rho\right. \\ &- \left.2u_{13}\left[\varepsilon'\left(\frac{(r^0_{12})'}{r^0_{12}}\right)+(1-\varepsilon')\left(\frac{(r^0_{23})'}{r^0_{23}}\right)\right]\sin\rho\right\} \end{aligned} \tag{3.206}$$

Obs.*3* The contravariant metric tensor elements are the following:

$$\begin{aligned} g_0^{\rho\rho} &= \left(g^0_{\rho\rho}\right)^{-1} \qquad g_0^{11} = \frac{g^0_{33}}{g^0_{11}\, g^0_{33} - \left(g^0_{13}\right)^2} \\ g_0^{\varphi\varphi} &= \left(g^0_{\varphi\varphi}\right)^{-1} \qquad g_0^{33} = \frac{g^0_{11}}{g^0_{11}\, g^0_{33} - \left(g^0_{13}\right)^2} \\ g_0^{\rho\alpha} &= g_0^{\varphi\beta} = 0 \qquad g_0^{13} = -\frac{g^0_{13}}{g^0_{11}\, g^0_{33} - \left(g^0_{13}\right)^2} \\ &\text{with } \alpha = \varphi\,, 1\,, 3 \qquad \text{and } \beta = \rho\,, 1\,, 3 \end{aligned} \tag{3.207}$$

The Kinetic Hamiltonian

We consider the kinetic energy operator by taking into account the eq. (3.36) and (3.203), and Appendix (§F.6):

$$\begin{aligned} T &= \frac{1}{2} g_0^{\rho\rho}\, P_\rho^2 + \frac{1}{2}\left[P_\rho, g_0^{\rho\rho}\right] P_\rho + \frac{1}{2} g_0^{-\frac{1}{4}} \left[P_\rho\,, g_0^{\rho\rho}\, g_0^{\frac{1}{2}} \left[P_\rho\,, g_0^{-\frac{1}{4}}\right]\right] \\ &+ \frac{1}{2} g_0^{\varphi\varphi}\, P_\varphi^2 \\ &+ \frac{1}{2} g_0^{11}\, P_1^2 + \frac{1}{2} g_0^{33}\, P_3^2 + g_0^{13}\, P_1 P_3 \end{aligned} \tag{3.208}$$

In the formula (3.208):

- the first row is the BL semirigid bender Hamiltonian [14]
- the second row is the rotational Hamiltonian around Oz axis
- the third row is the stretching kinetic Hamiltonian

The stretching part of the kinetic Hamiltonian is not diagonal. We must change the coordinates in order to make it diagonal:

$$\begin{aligned} \tilde{S}_1 &= \sin\zeta\, S_1 + \cos\zeta\, S_3 \\ \tilde{S}_3 &= \cos\zeta\, S_1 - \sin\zeta\, S_3 \end{aligned} \tag{3.209}$$

We get the condition for g^{13} to vanish by using (3.209) in the stretching kinetic Hamiltonian (§F.6):

$$\tan 2\zeta = \frac{2 g_0^{13}}{g_0^{33} - g_0^{11}} = \frac{2 g^0_{13}}{g^0_{33} - g^0_{11}} \tag{3.210}$$

We make the changes in the previous section by taking into account the new coordinates defined in (3.209):

1. The ρ derivatives to the new stretching coordinates, from (3.197) and (3.209) can be computed as:

$$\begin{aligned} \left(\frac{\partial\rho}{\partial\tilde{S}_1}\right)_0 &= \left(\frac{\partial\rho}{\partial S_1}\right)_0 \sin\zeta + \left(\frac{\partial\rho}{\partial S_3}\right)_0 \cos\zeta \\ \left(\frac{\partial\rho}{\partial\tilde{S}_3}\right)_0 &= \left(\frac{\partial\rho}{\partial S_1}\right)_0 \cos\zeta - \left(\frac{\partial\rho}{\partial S_3}\right)_0 \sin\zeta \end{aligned} \tag{3.211}$$

2. The derivatives of the new stretching coordinates to ρ become (with the eq. (3.199) and (3.209)):

$$\left(\frac{\partial \tilde{S}_1}{\partial \rho}\right)_0 = \left(\frac{\partial S_1}{\partial \rho}\right)_0 \sin\zeta + \left(\frac{\partial S_3}{\partial \rho}\right)_0 \cos\zeta$$
$$\left(\frac{\partial \tilde{S}_3}{\partial \rho}\right)_0 = \left(\frac{\partial S_1}{\partial \rho}\right)_0 \cos\zeta - \left(\frac{\partial S_3}{\partial \rho}\right)_0 \sin\zeta \qquad (3.212)$$

3. The relations between the stretching coordinates of Jensen [6] and the new stretching coordinates of our model, are found to be (from the eq. (3.209) and (3.198)):

$$\begin{aligned}
\Delta r_1 &= \left\{\frac{m_1+m_2}{m_2}\sin\zeta - \cos\zeta\frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\left(\frac{(r^0_{23})'}{r^0_{23}}\right)\sin\rho\right]\right\}\tilde{S}_1 \\
&+ \left\{\frac{m_1+m_2}{m_2}\cos\zeta + \sin\zeta\frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\left(\frac{(r^0_{23})'}{r^0_{23}}\right)\sin\rho\right]\right\}\tilde{S}_3 \\
\Delta r_3 &= \left\{\frac{m_3+m_2}{m_2}\cos\zeta - \sin\zeta\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{1-\varepsilon'}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)\sin\rho\right]\right\}\tilde{S}_1 \\
&- \left\{\frac{m_3+m_2}{m_2}\sin\zeta + \cos\zeta\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{1-\varepsilon'}\left(\frac{(r^0_{12})'}{r^0_{12}}\right)\cos\rho\right]\right\}\tilde{S}_3
\end{aligned} \qquad (3.213)$$

We make the substitution (3.44) for the bending wavefunction and the kinetic energy will be [192]:

$$T = T^0_{rb} + T^0_{str} \qquad (3.214)$$

with

- T^0_{rb} the same as in eq. (3.45)
- $$T^0_{str} = \frac{1}{2}g_0^{\tilde{1}\tilde{1}}P^2_{\tilde{1}} + \frac{1}{2}g_0^{\tilde{3}\tilde{3}}P^2_{\tilde{3}} \qquad (3.215)$$

where the new contravariant tensor elements are the following:

$$\begin{aligned}
g_0^{\tilde{1}\tilde{1}} &= g_0^{11}\sin^2\zeta + g_0^{33}\cos^2\zeta + g_0^{13}\sin 2\zeta \\
g_0^{\tilde{3}\tilde{3}} &= g_0^{11}\cos^2\zeta + g_0^{33}\sin^2\zeta - g_0^{13}\sin 2\zeta
\end{aligned} \qquad (3.216)$$

3.6.3 Potential Energy

We introduce the auxiliary functions $R^{(1)}_{\tilde{1}}(\rho)$, $R^{(3)}_{\tilde{1}}(\rho)$, $R^{(1)}_{\tilde{5}}(\rho)$, $R^{(3)}_{\tilde{5}}(\rho)$ in a similar manner with previously defined $R_1(r,\rho)$ $R_5(r,\rho)$ functions, in order to simplify the expressions. With these new functions, the eq. (3.213) can be written as:

$$\begin{aligned}
\Delta r_1 &= R^{(1)}_{\tilde{1}}(\rho)\,\tilde{S}_1 + R^{(1)}_{\tilde{5}}(\rho)\,\tilde{S}_3 \\
\Delta r_3 &= R^{(3)}_{\tilde{1}}(\rho)\,\tilde{S}_1 - R^{(3)}_{\tilde{5}}(\rho)\,\tilde{S}_3
\end{aligned} \qquad (3.217)$$

If we consider [6, eq.(3.1) (3.3)], the relation between our stretching coordinates and the generalized stretching internal coordinates is similar with(3.18):

$$\begin{aligned}
\Delta r_{12} &= R^{(1)}_{\tilde{1}}(\rho)\,\tilde{S}_1 + R^{(1)}_{\tilde{5}}(\rho)\,\tilde{S}_3 + \mathcal{R}_1(\rho) \\
\Delta r_{23} &= R^{(3)}_{\tilde{1}}(\rho)\,\tilde{S}_1 - R^{(3)}_{\tilde{5}}(\rho)\,\tilde{S}_3 + \mathcal{R}_3(\rho)
\end{aligned} \qquad (3.218)$$

The Semirigid Bender Approach

To find the dependence of the bond length with the ρ coordinate, we use the potential expanded in Taylor series up to the Fermi cubic term in the instantaneous coordinates:

$$\begin{aligned} V^{str}(\Delta r_{12}\,,\Delta r_{23}\,,\bar{\rho}) &= \frac{1}{2}f_{11}\Delta r_{12}^2+\frac{1}{2}f_{33}\Delta r_{23}^2+f_{13}\Delta r_{12}\Delta r_{23} \\ &+ F_{122}\Delta r_{12}\rho^2+F_{322}\Delta r_{23}\rho^2 \end{aligned} \tag{3.219}$$

With the minimum conditions $\left(\frac{\partial V^{str}}{\partial \Delta r_{12}}\right)_{\tilde{S}_1=\tilde{S}_3=0}=0$ and $\left(\frac{\partial V^{str}}{\partial \Delta r_{23}}\right)_{\tilde{S}_1=\tilde{S}_3=0}=0$ we find the angle variation for the bond lengths as (§F.7):

$$\begin{aligned} \mathcal{R}_1 &= -\frac{(f_{33}F_{122}-f_{13}F_{322})}{f_{11}f_{33}-f_{13}^2}(\rho-\rho_e)^2 \\ \mathcal{R}_3 &= -\frac{(f_{11}F_{322}-f_{13}F_{122})}{f_{11}f_{33}-f_{13}^2}(\rho-\rho_e)^2 \end{aligned} \tag{3.220}$$

If we introduce the equations (3.218) in the potential function (3.219), by taking into account the condition (3.220), we find the potential energy in the instantaneous configuration (§F.7), as:

$$V^{as}(\tilde{S}_1\,,\tilde{S}_3\,,\rho)=\frac{1}{2}f_{\tilde{1}\tilde{1}}(\rho)\,\tilde{S}_1^2+\frac{1}{2}f_{\tilde{3}\tilde{3}}(\rho)\,\tilde{S}_3^2+f_{\tilde{1}\tilde{3}}(\rho)\,\tilde{S}_1\,\tilde{S}_3 \tag{3.221}$$

where the effective potential constants are the following:

$$\begin{aligned} f_{\tilde{1}\tilde{1}}(\rho) &= f_{11}\left[R_{\tilde{1}}^{(1)}(\rho)\right]^2+f_{33}\left[R_{\tilde{1}}^{(3)}(\rho)\right]^2+2f_{13}R_{\tilde{1}}^{(1)}(\rho)R_{\tilde{1}}^{(3)}(\rho) \\ f_{\tilde{3}\tilde{3}}(\rho) &= f_{11}\left[R_{\tilde{5}}^{(1)}(\rho)\right]^2+f_{33}\left[R_{\tilde{5}}^{(3)}(\rho)\right]^2-2f_{13}R_{\tilde{5}}^{(1)}(\rho)R_{\tilde{5}}^{(3)}(\rho) \\ f_{\tilde{1}\tilde{3}}(\rho) &= f_{11}R_{\tilde{1}}^{(1)}(\rho)R_{\tilde{5}}^{(1)}(\rho)-f_{33}R_{\tilde{1}}^{(3)}(\rho)R_{\tilde{5}}^{(3)}(\rho)+f_{13}\left[R_{\tilde{1}}^{(3)}(\rho)R_{\tilde{5}}^{(1)}(\rho)-R_{\tilde{1}}^{(1)}(\rho)R_{\tilde{5}}^{(3)}(\rho)\right] \end{aligned} \tag{3.222}$$

The comments made for the eq.(3.57) are valid for the previous equations too.

The Potential Hamiltonian

If we change from the instantaneous configuration to the reference configuration, we must use the formulas (3.11) and (3.14). The derivatives are those from the eq. (3.211) and (3.212). If we make the same changes as for the symmetric molecule, the final potential energy , in the reference frame, is:

$$\begin{aligned} V^{ref}(\tilde{S}_1\,,\tilde{S}_3\,;\rho) &= V_0^b(\rho)+V_0^{as}(\tilde{S}_1\,,\tilde{S}_3\,;\rho) \\ &+ \left[\left(\frac{\partial V_0^b}{\partial\rho}\right)_0\left(\frac{\partial\rho}{\partial\tilde{S}_1}\right)+f_{\tilde{1}\tilde{1}}(\rho)\left(\frac{\partial\tilde{S}_1}{\partial\rho}\right)(\bar{\rho}-\rho_e)\right]\tilde{S}_1 \\ &+ \left[\left(\frac{\partial V_0^b}{\partial\rho}\right)_0\left(\frac{\partial\rho}{\partial\tilde{S}_3}\right)+f_{\tilde{3}\tilde{3}}(\rho)\left(\frac{\partial\tilde{S}_3}{\partial\rho}\right)(\bar{\rho}-\rho_e)\right]\tilde{S}_3 \end{aligned} \tag{3.223}$$

and $V_0^b(\rho)$ is the bending potential defined in eq.(3.68)-(3.70).

3.6.4 Comparison with Symmetric Molecule Model

In the case of the symmetric molecules, we have the relations:

$$\begin{array}{ll} \varepsilon'=\frac{1}{2} & \varepsilon=\frac{\rho}{2} \\ m_1=m_3 & r_{12}^0=r_{23}^0 \end{array} \tag{3.224}$$

If we use the relation (3.224) we find that $g_{11}^0=g_{33}^0$, from the eq. (3.204), and then from (3.210), the rotation angle is $\zeta=\frac{\pi}{4}$. In that case the eq.(3.209) is similar with (3.22) and $\tilde{S}_1\equiv S^s$ and $\tilde{S}_3\equiv S^a$ coordinates.

The Jacobian of the pseudo-metric tensor is unchanged , as it must be (§F.7):

$$g^0_{11}\, g^0_{33} - (g^0_{13})^2 = g^{ss}_0\, g^{aa}_0 \tag{3.225}$$

The new functions are the following (§F.8):

$$\begin{aligned} R^{(1)}_{\tilde{1}}(\rho) &= R^{(3)}_{\tilde{1}}(\rho) = \frac{1}{\sqrt{2}} R_1(r,\rho) \\ R^{(1)}_{\tilde{5}}(\rho) &= R^{(3)}_{\tilde{5}}(\rho) = \frac{1}{\sqrt{2}} R_5(r,\rho) \end{aligned} \tag{3.226}$$

If we consider the eq. (3.226), the equation (3.218)become identical with (3.19).The bond length variation with the angle is equal and

$$\mathcal{R}_1(\rho) = \mathcal{R}_3(\rho) = -\frac{F_{122}}{f_{11} + f_{13}} (\rho - \rho_e)^2 \tag{3.227}$$

The potential constants, defined in (3.222) become (§F.8):

$$\begin{aligned} f_{\tilde{1}\tilde{1}}(\rho) &= f^s_{eff}(\rho) \\ f_{\tilde{3}\tilde{3}}(\rho) &= f^a_{eff}(\rho) \\ f_{\tilde{1}\tilde{3}}(\rho) &= 0 \end{aligned} \tag{3.228}$$

If we consider the formula (3.227), the derivatives (3.199) will be:

$$\left(\frac{\partial S_1}{\partial \rho}\right)_0 = \left(\frac{\partial S_3}{\partial \rho}\right)_0 = \frac{\mathcal{R}'(\rho)}{R_1(r,\rho)} \tag{3.229}$$

and from (3.212), the derivatives are:

$$\begin{aligned} \left(\frac{\partial \tilde{S}_1}{\partial \rho}\right)_0 &= \sqrt{2}\frac{\mathcal{R}'}{R_1(r,\rho)} = \left(\frac{\partial S^s}{\partial \rho}\right) \\ \left(\frac{\partial \tilde{S}_3}{\partial \rho}\right)_0 &= \left(\frac{\partial S^a}{\partial \rho}\right)_0 = 0 \end{aligned} \tag{3.230}$$

The formula (3.211), become for the symmetric molecules (§F.8):

$$\begin{aligned} \left(\frac{\partial \rho}{\partial \tilde{S}_1}\right)_0 &= \left(\frac{\partial \rho}{\partial S_s}\right)_0 = -\frac{R_2(r,\rho)}{\sqrt{2} r^0(\rho)} \\ \left(\frac{\partial \rho}{\partial \tilde{S}_3}\right)_0 &= \left(\frac{\partial \rho}{\partial S_a}\right)_0 = 0 \end{aligned} \tag{3.231}$$

From the equations (3.225) - (3.231), we found the formulas for the symmetric molecules with the assumption that the derivatives of the functions are *evaluated* after setting the stretching coordinates to 0 ($\tilde{S}_1 = \tilde{S}_3 = 0$) [186].

3.7 Conclusions

In this thesis we have derived a vibration-rotation Hamiltonian for a symmetric molecule, the Stretch-Bender model, which is based on the use of a stretch-bender frame, chosen so that as the molecule bends the reference geometry follows the minimum in the potential energy surface. This therefore minimizes the size of the displacements required to reach the instantaneous axis geometry. This new Stretch-Bender Hamiltonian has been combined with the Jungen and Merer [15] method of solving the Renner-Teller coupling problem to produce a compact method for the variational calculation of the energies for a symmetrical molecule possessing a degenerate electronic state when linear. A key role in the understanding of the combined stretching - bending motions is played by the g_D term, introduced here for the first time, which relates the end-over-end rotational motion to the angle-dependent reference geometry. The Fermi coupling arises naturally from the change of the configuration during vibrational motion. The extension to asymmetric molecules is outlined.

Chapter 4

Linear Triatomic Molecules Treated with the Stretch-Bender Model: CO_2 and CO_2^+ Molecules

In order to test the Stretch-Bender model described in the previous chapter, a series of linear molecules was considered. The CO_2 molecule is a perfect example for testing only the Fermi interaction, because the great majority of its levels are modified by this effect.

For testing the coupling of electronic, electron spin and ro-vibrational angular momenta, in order to explain the pattern of the ro-vibronic state, the CO_2^+ ion of the former molecule was considered. The Fermi interaction shift a limited number of energy levels, hence the influence of the ro-vibronic coupling can be taken into account with the Fermi coupling.

4.1 Linear Molecules without Renner-Teller Effect: CO_2

4.1.1 Introduction

The carbon dioxide is one of the most important components of the environment. Although it is considered a trace gas in the terrestrial atmosphere, its strong opacity in the IR domain has a major impact on the environment. Accurate knowledge of the spectroscopic properties of the carbon dioxide molecule is necessary for understanding the greenhouse effect and planetary atmosphere. It is a prime factor in atmospheric remote sensing of temperature and constituent profiles. CO_2 is often a contaminant in spectra.

From the spectroscopist point of view CO_2 is a case particularly simple, with $\Lambda = 0$ and a linear geometrical configuration. Then no couple occur between the orbital angular momentum, electronic spin and bending vibrational motion and which is commonly referred to as the Renner-Teller effect.

In exchange the vibronic energy levels exhibit a pure and large Fermi interaction and it is why the Fermi resonance has been discovered by analysing the Raman spectra of CO_2 molecule. Then CO_2 is an ideal molecule to test the new Stretch-Bender model. Due to its great interest and the simple behaviour, a large number of vibronic levels have been identified, which make the fit procedure to be more reliable [155, 193, 194, 195, 196]. The analysis some of phenomena that contribute to absorption is done in [197, 198].

4.1.2 Results and Discussion

Bond length parameters

The first step is to determine the ground state geometric structure of the molecule. The algorithm to find the bond length parameters was explained in (§3.5.1), and follows [147]. The most

practical quantity to work with, is the structure for $v_2^{linear} = -1$, $v_1 = v_3 = 0$, because good rotational constants are available for $0\,,\, l^l\,,\, 0$ levels, which are not subject to interactions. The mean value $\frac{1}{2}(B+C)$ was considered. The C constant is subject to vibrational Coriolis effects [150], and then the C constant has to be corrected for this.

For the ground state of CO_2 the accurate rotational constants of Rothman *et all* [194], when treated iteratively as in (§3.5.1), give the $v_2^{(linear)} = -1$ structure as in Figure 4.1

$$r(C-O) = 1.1631\,\text{Å} \tag{4.1}$$

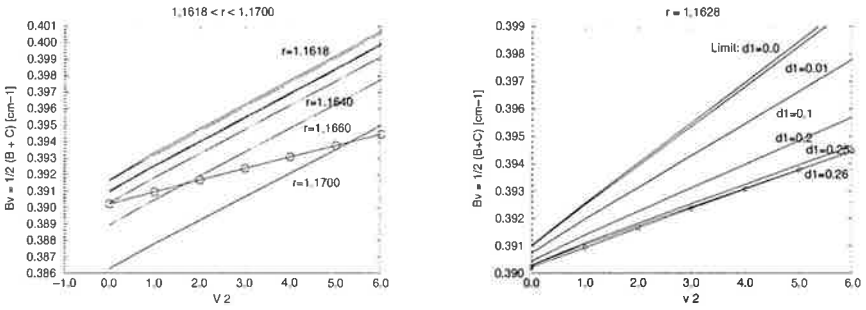

Figure 4.1: Changements in the rotational constants due to various settings for the bond length and the dependence of the bond length with the ρ angle. It is an iterative process to find the best parameters for the bond length. The maximum slope of the rotational constants is for $d_1^{(ChJ)} = 0$. The experimental points are represented with circles.

The value was then kept fixed for the rest of the calculation. After fixing $v_2^{(linear)} = -1$ bond lenghts, we determined the variation of the bond length with ρ, using the observed variation of $\bar{B} = \frac{1}{2}(B+C)$ with v_2. For the ground state we set $d_2 = 0$ in (3.150) and we found, with (4.1), (see Figure 4.1):

$$r(\rho) = \left(1.1631 + 0.2449\tan^2\left(\frac{\rho}{2}\right)\right)\,\text{Å} \tag{4.2}$$

The vibrational Coriolis effects have been included. More considerations about the form of the eq.(4.2) is done in (§3.5.1).

The accuracy of the small bending amplitude (harmonic oscillator) for the CO_2 molecule can be verified if the values from eq.(4.1) and eq.(4.2) are compared with the values computed with (3.151).

A comparison between the values found using the two ways is given in Table 4.1. The small error in the bond length (1.05 %) and the dependence of the bond length with the angle (3.69 %) indicate that the harmonic oscillator approach can be used successfully for the CO_2 molecule. This also explain the good results previously obtained with this approach [155].

Also, in the case of the small amplitude approach it is no difference between d_1 and d_2 parameters in (3.150), because the higher order terms in the power series expansion of the $\tan^2\left(\frac{\rho}{2}\right)$ have a limited influence.

If we use the definition of the bond length variation with ρ from [14] and the potential force constants from [39, 46] we have $d_1^{(th)} = 0.1429$ from Pliva and $d_1^{(th)} \in [0.1218 - 0.1539]$ from Pariseau, depending on the data sets. If we use the contour map of the potential energy from [46, Fig.2], we have $d_1^{(th)} = 0.1917$. With these values, the g_D parameter defined in (3.152) takes a value of:

$$g_D = 1.722 \pm 0.103 \tag{4.3}$$

Table 4.1: Comparison between the values obtained with the Stretch- Bender formalism and the values obtained from the harmonic oscillator approach, or from the literature.

$r(\rho=0)$	1.16188^a	1.1631^b
		1.1618^j
d_1	0.26134^a	0.2449^b
g_D	1.8067^e	1.8730^b
W	32.19^h	22.99^g
x_1	-0.00247^b	-0.00276^i
		-0.00262^f
B_e	0.3894^c	0.3902406^d
		0.39025^j
$-\alpha_e \cdot 10^4$	7.5804^c	7.076429^d

^{a} Equation (3.151)
^{b} Data from Table.4.2
^{c} Computed with r_0 from [155]
^{d} From unperturbated rotational constant fit
^{e} Equation (3.155)
^{g} Computed from the Fermi matrix element fit in Fig.(4.7)
^{h} Computed from [37]
^{i} Computed from [39]
^{f} Computed from [46]
^{j} Computed from [155]

Potential parameters

By now it will be appreciated that it is necessary to go through the calculations twice, the first time to get certain expectation values based on the potential parameters, which are then used to optimize the input parameters for the second attempt. Seven potential parameters were found to be necessary to describe the shapes of the Born-Oppenheimer curve for the bending potential, as well as the stretching potential behaviour. These are k_1 , k_4 for the bending potential (described in §3.3.3)) and ω_1 , $\omega_1^{(2)}$, $\omega_1^{(4)}$ (defined in (3.185)) for the stretching potential.

An anharmonic term x_1 for the stretching potential is found enough important to be included between the fitting parameters. The g_D factor, describing the influence of the Coriolis coupling and anharmonic perturbation is taken into account as a variable parameter. The dependence of the stretching energy with the bending angle, described in (3.185), allows for the stretch-bend interaction and is similar with the f bending parameter dependence on the degree of excitation of the stretching states, as defined in [186].

The full list of molecular parameters for the CO_2 molecule are given in Table 4.2. The results

Table 4.2: Parameters used to model the Fermi resonance structure of the ground state $\tilde{X}^1\Sigma_g^+$ of CO_2. The zero point energy corrections for the stretching vibrations are included in the effective potential energy functions for the bending

Bond length variation		
$r(\rho=0)$	1.1631	Å
d_1 , coefficient of $\tan^2\frac{\rho}{2}$	0.2449	Å
k	38833.67 ± 29.91	$cm^{-1}rad^{-2}$
k_4	8145.35 ± 121.79	$cm^{-1}rad^{-4}$
ω_1^0	1345.25 ± 1.15	cm^{-1}
$\omega_1^{(2)}$	81.94 ± 10.45	$cm^{-1}rad^{-2}$
x_1	-0.00248 ± 0.00021	
g_D	1.8730 ± 0.0029	

of the calculation using the parameters from the Table 4.2 are given in the Table 4.3 together with the effective rotational constants. The standard deviation in the least square treatment normalized to the unit weight was 0.625. In order to see the influence of the different parameters to the energy levels, each parameter was initialized with zero value and the differences to the initial computed levels are given in Table 4.4. In the case of the k_4 parameter, the behaviour is normal, because if the anharmonic bending term vanish, the levels will be lower than the initial values. The levels which change sign are supposed to be subject of a strong Fermi interaction, which change the order of levels. The behaviour for $\omega_1^{(2)}$ and $\omega_1^{(4)}$ parameters suggest that they

Table 4.3: Observed and calculated band origins and rotational constants for $\tilde{X}^1\Sigma_g^+$ ground state of CO_2. All parameters are given in cm^{-1}

v_1	v_2^l	v_3	Band origin	Diff. o-c	Rotational constants B	C	$\frac{1}{2}(B+C)$	$\frac{1}{2}(B+C)^r$	Ref.
0	0^0	0	0		0.3905	0.3896	0.3901	0.3901	h
			0				0.3902	0.3902	c
			0					0.3902	d
			0					0.3902	exp
0	1^1	0	667.18	-0.20	0.3914	0.3904	0.3909	0.3909	h
			667.400	-0.02			0.3909	0.3909	c
			667.381	-0.001				0.3906	d
			667.38					0.3912	exp
0	2^0	0	1286.39	-0.982	0.3923	0.3903	0.3913	0.3907	h
			1285.39	0.018			0.3916	0.3904	c
			1285.414	-0.006				0.3905	d
			1285.408					0.3905	exp
0	2^2	0	1334.89	0.242	0.3924	0.3909	0.3916	0.3916	h
			1335.14	-0.008			0.3916	0.3916	c
			1335.123	0.009				0.3917	d
			1335.132					0.3917	exp
1	0^0	0	1387.43	0.754	0.3905	0.3896	0.3901	0.3901	h
			1388.19	-0.006			0.3890	0.3902	c
			1388.188	-0.004				0.3902	d
			1388.184					0.3900	exp
0	3^1	0	1933.44	-0.970	0.3933	0.3910	0.3921	0.3915	h
			1932.46	0.01			0.3924	0.3912	c
			1932.482	-0.012				0.3907	d
			1932.470					0.3917	exp
0	3^3	0	2003.06	0.186	0.3933	0.3913	0.3923	0.3923	h
			2003.28	-0.034			0.3924	0.3924	c
			2003.234	0.012				0.3924	d
			2003.246					0.3924	exp
1	1^1	0	2075.96	0.896	0.3914	0.3903	0.3909	0.3915	h
			2076.85	0.006			0.3897	0.3909	c
			2076.875	-0.019				0.3904	d
			2076.856					0.3913	exp
0	4^0	0	2549.61	-1.243	0.3942	0.3910	0.3926	0.3915	h
			2548.24^x	0.127			0.3931	0.3910	c
			2548.380	-0.013				0.3911	d
			2548.367					0.3911	exp
0	4^2	0	2585.83	-0.808	0.3942	0.3915	0.3928	0.3919	h
			2585.01	0.012			0.3931	0.3920	c
			2585.049	-0.027				0.3920	d
			2585.022					0.3919	exp
1	2^0	0	2671.29	-0.147	0.3923	0.3903	0.3913	0.3915	h
			2670.83^x	0.313			0.3903	0.3885	c
			2671.122	0.021				0.3895	d
			2671.143					0.3896	exp

^{r} Perturbed rotational constants [155, eq.(25)]
^{h} This work
^{c} Reference [155]
^{d} Reference [195]
^{exp} Reference [194]
^{x} Levels not considered in the fit in [155]

Table 4.3: *(continued)*

v_1	v_2^l	v_3	Band origin	Diff. o-c	Rotational constants B	C	$\frac{1}{2}(B+C)$	$\frac{1}{2}(B+C)^r$	Ref.
0	4^4	0	2671.65	0.065	0.3942	0.3918	0.3930	0.3930	h
			2671.88	-0.165					c
			2671.725	-0.010				0.3931	d
			2671.715					0.3931	exp
1	2^2	0	2759.98	0.745	0.3924	0.3908	0.3911	0.3919	h
			2760.69	0.035			0.3903	0.3915	c
			2760.778	-0.053				0.3915	d
			2760.725					0.3915	exp
2	0^0	0	2796.06	1.076	0.3905	0.3896	0.3901	0.3909	h
			2797.03	0.106			0.3877	0.3906	c
			2797.135	0.001				0.3906	d
			2797.136					0.3906	exp
0	5^1	0	3182.29	-0.826	0.3951	0.3916	0.3933	0.3922	h
			3181.35[x]	0.114					c
			3181.472	-0.008				0.3910	d
			3181.464					0.3923	exp
0	5^3	0	3241.13	-0.507	0.3951	0.3919	0.3935	0.3929	h
			3241.48	-0.857					c
			3240.688	-0.065				0.3927	d
			3240.623					0.3927	exp
1	3^1	0	3339.41	-0.054	0.3933	0.3910	0.3921	0.3922	h
			3339.10	0.256					c
			3339.306	0.050				0.3900	d
			3339.356					0.3912	exp
0	5^5	0	3340.59	-0.062	0.3951	0.3923	0.3937	0.3937	h
			3341.00	-0.472					c
			3340.605	-0.077				0.3938	d
			3340.528					0.3938	exp
1	3^3	0	3441.82	0.395	0.3933	0.3913	0.3923	0.3929	h
			3442.93	-0.715					c
			3342.342	-0.127				0.3922	d
			3442.215					0.3922	exp
2	1^1	0	3499.90	0.772	0.3914	0.3903	0.3909	0.3919	h
			3500.46	0.112					c
			3500.677	-0.005				0.3904	d
			3500.672					0.3917	exp
0	6^0	0	3793.04	-0.356	0.3959	0.3916	0.3937	0.3914	h
			3792.45[x]	0.234					c
			3792.673	0.011				0.3918	d
			3792.684					0.3918	exp
0	6^2	0	3822.09	-0.078	0.3959	0.3921	0.3940	0.3929	h
			3822.038	-0.026				0.3924	d
			3822.012					0.3923	exp
0	6^4	0	3898.34	-0.026	0.3960	0.3924	0.3942	0.3930	h
			3898.05[x]	0.264					c
			3898.460	-0.146				0.3934	d
			3898.314					0.3937	exp

[r] Perturbed rotational constants [155, eq.(25)]
[h] This work
[c] Reference [155]
[d] Reference [195]
[exp] Reference [194]
[x] Levels not considered in the fit in [155]

Table 4.3: *(continued)*

			Band	Diff.	Rotational constants				
v_1	v_2^l	v_3	origin	o-c	B	C	$\frac{1}{2}(B+C)$	$\frac{1}{2}(B+C)^r$	Ref.
1	4^0	0	3942.55	-0.007	0.3941	0.3910	0.3926	0.3923	h
			3942.15[x]	0.393					c
			3942.561	-0.018				0.3896	d
			3942.543					0.3896	exp
1	4^2	0	4007.92	-0.006	0.3942	0.3915	0.3928	0.3929	h
			4007.873	0.041				0.3914	d
			4007.914					0.3914	exp
0	6^6	0	4009.83	-0.154	0.3960	0.3927	0.3943	0.3944	h
			4009.884	0.208				0.3945	d
			4009.676					0.3945	exp
2	2^0	0	4064.11	0.165	0.3923	0.3903	0.3913	0.3924	h
			4063.97[x]	0.305					c
			4064.197	0.078				0.3896	d
			4064.275					0.3896	exp
1	4^4	0	4122.33	-0.061	0.3942	0.3918	0.3930	0.3936	h
			4122.29	-0.021					c
			4122.527	-0.258				0.3929	d
			4122.269					0.3929	exp
2	2^2	0	4197.20	0.161	0.3924	0.3908	0.3916	0.3926	h
			4197.426	-0.065				0.3916	d
			4197.361					0.3916	exp
3	0^0	0	4224.92	0.177	0.3905	0.3896	0.3901	0.3915	h
			4224.71	0.387					c
			4225.043	0.054				0.3910	d
			4225.097					0.3910	exp
0	7^1	0	4415.31	0.839	0.3968	0.3922	0.3945	0.3922	h
			4416.121	0.028				0.3926	d
			4416.149					0.3931	exp
0	7^3	0	4466.13	0.986	0.3968	0.3925	0.3947	0.3936	h
			4467.223	-0.107				0.3931	d
			4467.116					0.3930	exp
0	7^5	0	4556.97	0.625	0.3969	0.3928	0.3948	0.3943	h
			4557.883	-0.288				0.3941	d
			4557.595					0.3941	exp
1	5^1	0	4590.95	0.166	0.3950	0.3916	0.3933	0.3930	h
			4591.027	0.089				0.3907	d
			4591.116					0.3912	exp
1	5^3	0	4676.70	0.09	0.3951	0.3919	0.3935	0.3935	h
			4676.812	-0.022				0.3922	d
			4676.790					0.3922	exp
2	3^1	0	4753.71	-0.257	0.3933	0.3910	0.3921	0.3930	h
			4753.270	0.183				0.3903	d
			4753.453					0.3912	exp
1	5^5	0	4801.94	-0.575	0.3951	0.3923	0.3937	0.3942	h
			4801.836	-0.471				0.3935	d
			4801.365					0.3935	exp

[r] Perturbed rotational constants [155, eq.(25)]
[h] This work
[c] Reference [155]
[d] Reference [195]
[exp] Reference [194]
[x] Levels not considered in the fit in [155]

Table 4.3: *(continued)*

			Band	Diff.	Rotational constants				
v_1	v_2^l	v_3	origin	o-c	B	C	$\frac{1}{2}(B+C)$	$\frac{1}{2}(B+C)^r$	Ref.
2	3^3	0	4890.74	-0.644	0.3933	0.3913	0.3923	0.3934	h
			4890.277	-0.181				0.3922	d
			4890.096					0.3922	exp
3	1^1	0	4939.18	-0.827	0.3914	0.3903	0.3909	0.3924	h
			4938.324	0.031				0.3912	d
			4938.353					0.3911	exp

^{r} Perturbed rotational constants [155, eq.(25)]
^{h} This work
^{d} Reference [195]
^{exp} Reference [194]

are not so important for the fit, which we can also see from the great relative errors in Table 4.2. The parameters act through the bending parameters, but also in the interaction matrix, because the behaviour is not the same as for the k_4 parameter. $\omega_1^{(4)}$ parameter is less important than $\omega_1^{(2)}$ one. The major influence of these parameters seems to be mainly bias the interaction matrix due to the $\alpha(\rho)$ functions and not bias the bending potential.

The anharmonic stretching parameter x_1 act in the same way, bias the bending potential shape, because it is linked to $\omega_1(\rho)$ stretching frequency, and due to the minus sign, the main influence is opposite to the k_4 parameter.

The stretching part in the transformation Jacobian (as was discussed in the theoretical chapter, which is contained in $f_1(\rho)$ pseudo-potential term), have only a minor influence on the fit of the levels. This could explain the success of the Jungen and Merer formalism, even if they do not consider the whole transformation. Because the shitf trend is uniform, it can easily be compensated by another parameter variation.

The g_D parameter act only bias the Fermi interaction, which explain the apparent chaotic spread of plus or minus signs in the terms. Because k_4 column has the same behaviour, this suggest that the main influence is from the derivative of the bending potential to the bending coordinate, in the Fermi interaction.

The Lorentz potential parameters a and b (3.68), seems not to have any influence in the improvement of the actual fit of the experimental data.

Using the conversion formulas for the potential force constants (3.87) from the curvilinear to the generalized coordinates system, the force constants from Table 4.5 are obtained. It must be emphasized that in the formulas (3.86) the *theoretical* $d_1^{(th)}$ *are used* and not our value $d_1^{(ChJ)}$, because the formulas for the convertion were obtained in the Bunker and Landsberg approach [14]. The change between the two values is done with (3.152), as:

$$d_1^{(th)} = \frac{d^{(ChJ)}}{g_D} \tag{4.4}$$

If we compute the value of g_D parameter theoretically, with the (3.155) formula, we obtain the value from the Table 4.1. The difference between theoretical and fitted value is about 4.7 %, which confirm the valability of the formula (3.155) obtained in the frame of the harmonic oscillator approach. The theoretical value from Table 4.1 is in the error range of (4.3) value and all the g_D values are correlated each other, which is quite normal due to the conversion relations between the formalisms. The influence of the stretching vibrations on the bending potential is shown in Figure (4.2), where the potential contour map is drawn in a (ρ, v_1) coordinate system. It is important to mention that in the curvilinear coordinates, the potential valley is a "straight" ascend line, compared with [46, Fig.2], where it is a bend line, with a minimum point.

Table 4.4: The influence of the various parameters used in computation of the vibronic energy levels. The relative influence is obtained by considering each parameter equal to 0 (excepting from $\omega_1^{(4)}$ which initially was zero), in Table.4.2 and is measured by using the shift of the computed energy levels ($\Delta E = E_{real} - E_{p_i=0}$). The band origins are the calculated values with the parameters from Table.4.2

v_1	v_2^l	v_3	Band origin	Par. $k_4 = 0$	Par. $\omega_1^{(2)} = 0$	Par. $\omega_1^{(4)} = 45.39$	Par. $x_1 = 0$	Par. $g_D = 1$	$f_1(\rho)^\dagger$
0	0^0	0	0	0	0	0	0	0	0
0	1^1	0	667.18	9.29	0.55	-0.05	-0.11	12.16	-0.12
0	2^0	0	1286.34	16.55	1.19	-0.04	-3.21	54.34	-0.13
0	2^2	0	1334.90	23.30	1.13	-0.05	-0.18	31.78	-0.19
1	0^0	0	1387.41	11.25	1.13	-0.07	-3.70	-18.74	-0.15
0	3^1	0	1933.37	34.14	2.34	0.00	-3.41	92.99	-0.20
0	3^3	0	2003.09	42.04	1.69	-0.01	-0.25	59.25	-0.22
1	1^1	0	2075.92	26.19	2.35	-0.05	-3.75	-13.38	-0.24
0	4^0	0	2549.52	49.87	3.95	-0.11	-6.63	85.43	-0.19
0	4^2	0	2585.75	56.77	3.47	-0.10	-3.56	137.57	-0.22
1	2^0	0	2671.27	27.54	2.39	0.02	-13.55	36.32	-0.11
0	4^4	0	2671.69	65.51	2.30	0.12	-0.28	95.03	-0.19
1	2^2	0	2759.95	45.51	3.57	0.03	-3.84	2.37	-0.27
2	0^0	0	2796.01	33.91	3.51	0.03	-7.37	161.11	-0.25
0	5^1	0	3182.21	75.05	5.21	0.27	-7.53	-84.88	-0.20
0	5^3	0	3241.06	84.38	4.55	0.26	-3.69	-173.22	-0.19
1	3^1	0	3339.33	53.18	4.39	0.10	-12.23	72.25	-0.17
0	5^5	0	3340.65	93.74	2.76	0.28	-0.29	139.64	-0.12
1	3^3	0	3441.80	69.27	4.76	0.17	-3.94	27.52	-0.26
2	1^1	0	3499.91	52.76	5.20	0.15	-8.11	232.82	-0.28
0	6^0	0	3793.00	-88.14	7.08	0.51	-10.79	-29.51	-0.15
0	6^2	0	3822.02	-103.75	6.81	0.50	-8.05	-70.82	-0.16
0	6^4	0	3898.30	116.99	5.57	0.48	-3.81	-162.04	-0.11
1	4^0	0	3942.60	61.46	4.93	0.26	-22.79	-96.37	-0.02
1	4^2	0	4007.80	82.03	6.22	0.25	-11.86	114.96	-0.16
0	6^6	0	4009.91	126.76	3.24	0.48	-0.28	193.72	-0.01
2	2^0	0	4064.20	50.29	4.88	0.24	-23.12	25.22	-0.05
1	4^4	0	4122.33	97.54	5.94	0.37	-4.05	62.00	-0.20
2	2^2	0	4197.23	271.46	6.96	0.35	-8.53	304.39	-0.28
3	0^0	0	4225.02	66.69	7.01	0.36	-11.40	186.04	-0.27
0	7^1	0	4415.34	-80.46	9.13	0.82	-12.49	3.34	-0.10
0	7^3	0	4466.11	-95.37	8.34	0.79	-8.45	-44.54	-0.07
0	7^5	0	4556.95	-114.68	6.53	0.74	-3.93	-138.92	0.02
1	5^1	0	4590.92	-81.00	7.53	0.44	-21.78	-110.22	-0.03
1	5^3	0	4676.57	-109.54	7.95	0.47	-11.74	-165.92	-0.11
2	3^1	0	4753.73	-96.72	7.41	0.41	-21.90	52.59	-0.07
1	5^5	0	4801.96	130.33	7.08	0.62	-4.14	106.09	-0.01
2	3^3	0	4890.82	329.35	8.71	0.60	-8.87	-262.74	-0.23
3	1^1	0	4939.35	443.55	9.12	0.62	-12.97	238.22	-0.25

† The pseudo-potential function $f_1(\rho)$ in the bending hamiltonian is computed without the stretching contribution

Table 4.5: Force constants in the generalised coordinate system, computed with the stretch - bender force constants from the Table.4.2

Force constants	*Ref.*[h]	*Ref.*[a]	*Ref.*[b]
$K_{122}(F_{122})$ $[\frac{\mathring{A}\cdot aJ}{rad^2}]$	-0.647	-0.618	-0.570 ; -0.588
$F_{2222}(K_{2222})$ $[\frac{aJ}{rad^4}]$	0.171	-0.041	-0.065 ; -0.010 ; 0.002
$F_{11}(K_{11})$ $[\frac{aJ}{\mathring{A}^2}]$	8.530	8.014	8.095
$F_{22}(K_{22})$ $[\frac{aJ}{rad^2}]$	0.386	0.393	0.393

[h] This work
[a] Reference [39]
[b] Reference [46]

Rotational constants B and C for the CO_2 molecule

The bond lengths given previously refer to the $v_2^{(linear)} = -1$ structure (corresponding to the equilibrum with respect to the bending vibration) and were obtained using the values of $\bar{B} = \frac{1}{2}(B + C)$ for the $0\,,\, l^l\,,\, 0$ levels ($v_2 = l$ levels), which are unperturbed. In fact the constants B and C vary with the vibrational quantum number in a fairly complicated way because of the large amplitude and the vibrational Coriolis effects [150].

The levels are not affected by the rotational-electronic Coriolis perturbation, so that in order to reproduce their $\bar{B}$ values, we calculate both B and C constants as expectation values over the vibrational basis functions. The inertial contributions are done in [150] and in (§E.1).

The observed C constant includes also the effects of the vibrational Coriolis interaction between the antisymmetric stretching vibration v_3 and the two vibrations v_1 and v_2. The procedure to evaluate them it is explained in [150]. A comparison of the observed and the calculated rotational constants for the levels of the ground state in CO_2 molecule is given in Table 4.3. The calculated values are based on the potential parameters and the geometrical structure from Table 4.2. The importance of the vibrational Coriolis effects is very clearly seen from Figure (4.3). As we can observe, if the Coriolis correction is neglected, $\bar{B}$ increases too rapidly with v_2^{linear}. The Coriolis contribution to the C constant has been evaluated using the value $\omega_3 = 2349.49\, cm^{-1}$ of the antisymmetric stretching frequences from [155]. In the general case, the fit of the levels is not so good, due to the perturbations which arise (see Figure 4.4). In order to have a quite similar behaviour with the experimental values, we must use the relations between the perturbed B_i^0 and the unperturbed B_i rotational constants [155, eq.(25)]. In this case the general behaviour of the $B = f(v_2)$ dependence is the same for the levels with $v_1 = 0$ (no stretching levels), but it is not so good for the levels with $v_1 = 1$. These results can be due to the method of rotational constants computation: the expectation values are computed using only the bending wavefunctions. The stretching contribution is included indirectly, in the harmonic and the anharmonic bending potential constants. It seems that this approach is good only for the bending wavefunctions with $v_1 = v_3 = 0$, but for the stretching wavefunctions a more direct influence in the stretching wavefunctions must be used. From the Table 4.3 it can be seen that the error in the rotational constant is nearby of the same order of magnitude as in the case of Courtoy study [155] and the rotational structure is resonably well described by the effective asymmetric top hamiltonian for a semi-rigid molecule.

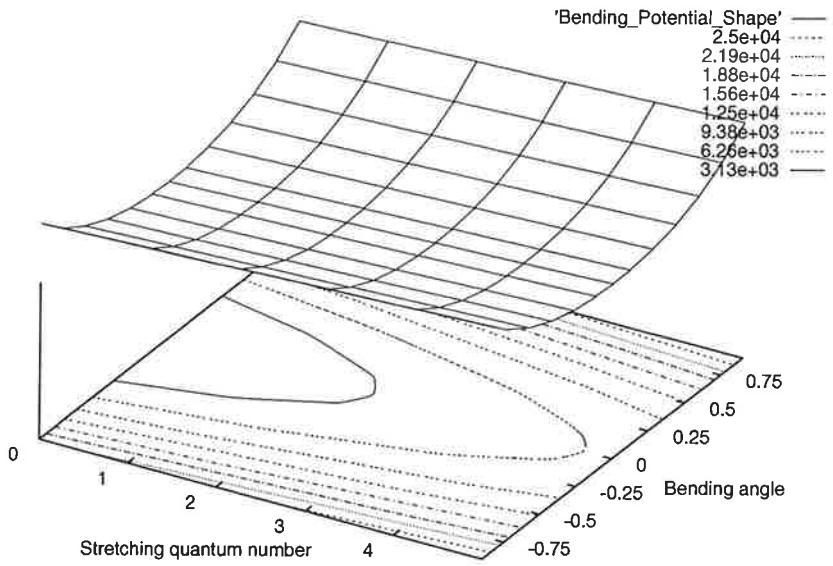

Figure 4.2: Potential energy of CO_2 valley and contour map as a function of the stretching quantum number (stretching displacement of one oxigen atom) and the bending angle. Contours are drawn at intervals of $3.13\,10^3\ cm^{-1}$, which correspond to approximatively 5 quanta of bending mode.

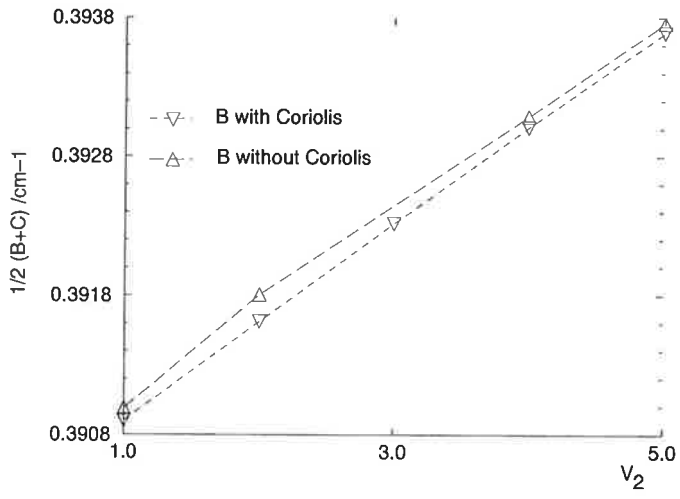

Figure 4.3: Values of $\bar{B} = \frac{1}{2}(B + C)$ for the levels of $0, l^l, 0$ type, as a function of $v_2^{(linear)}$, calculated with and without Coriolis correction to C.

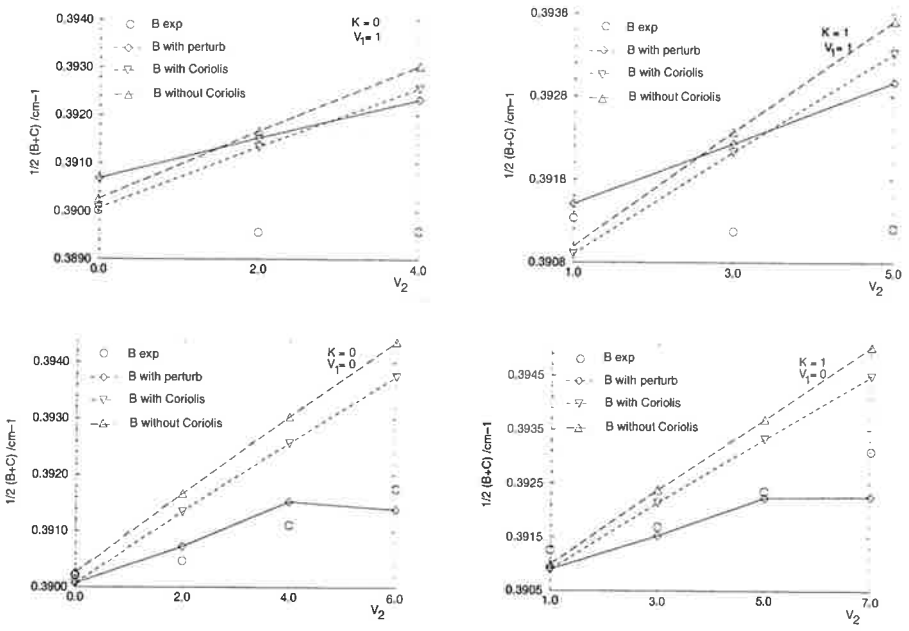

Figure 4.4: Vibrational variation of the $\bar{B} = \frac{1}{2}(B + C)$ rotational constants, with $v_2^{(linear)}$. The experimental values are taken from [194].

Fermi Interaction in the CO_2 Molecule

From the 74 vibrational levels of the $^{12}C^{16}O$ molecule reported by Courtoy [155], only 12 are not in resonance; they are of the type $0\,,\, l^l\,,\, v_3$, with l=0,1,... The most important resonances in CO_2 are determined by the cubic force constant f_{122}, which has been discussed in (§3.3.3), and for CO_2 this is found to have slightly different values in the various calculations [39, 46, 155].

In the Table 4.3 and Table 4.4 it was used the traditional labeling of CO_2 levels involved in the Fermi resonance from [155]. The real labels for the energy levels have to be interchanged [190, 199] in the case of the CO_2 molecule. The Table 4.3 needs some special comments concerning the algorithm used to fit the levels. In the fit done by Courtoy [155], 20 parameters were used, without the Fermi interaction analysis. The Fermi interaction analysis was done by groups of interacting levels, solving matrices of dimension 2x2, 3x3 and so on, for two sets of interacting levels, respective three sets, or more. After this, all the effective Fermi interaction parameters are fitted with a general formula allowing for the dependence of the Fermi interaction constant with a linear function like $f(v_1, v_2, v_3, l)$.

In our approach the Fermi interaction is introduced in a more natural way and do not need special parameters. Then, the interaction arises in the moment of construction of the interaction matrix with the general bending and stretching potential constants, but without a special term f_{122} in the curvilinear coordinate system. In the Fermi interaction analysis we have some distinct groups of levels (see Figure 4.5). For $K = 0$ and $K = 1$ levels, the Fermi interaction analysis can be done up to four sets of interacting levels, for $K = 2$ and $K = 3$, up to three sets of interacting levels and for $K = 4$ and $K = 5$ only for two sets of interacting levels. In the figure it can be observed the reverse order of the unperturbed levels. 02^00 has a greater energy than 10^00 level, for example. This is due to the initial unperturbed levels, and to the magnitude of the $\langle v_1, v_2^l, v_3|H^1|v_1 + 1, v_2^l, v_3\rangle$ term, which is not enough great to change the initial order. As an example, $\langle 0, 0^0, 0|H^1|1, 0^0, 0\rangle \simeq 51$ cm^{-1}, $E^0_{0,0^0,0} \simeq 674$ cm^{-1}, $E^0_{1,0^0,0} \simeq 2013$ cm^{-1} and the perturbation $\Delta V \simeq \frac{(H_{12})^2}{E^0_{0,0^0,0} - E^0_{0,0^0,0}} \simeq 1.9\,\text{cm}^{-1}$ can not change the order. In fact $E_{0,0^0,0} \simeq E^0_{1,0^0,0} - \Delta V \simeq 672.1\text{cm}^{-1}$, $E_{1,0^0,0} \simeq E^0_{1,0^0,0} + \Delta V \simeq 2015\,\text{cm}^{-1}$ and the

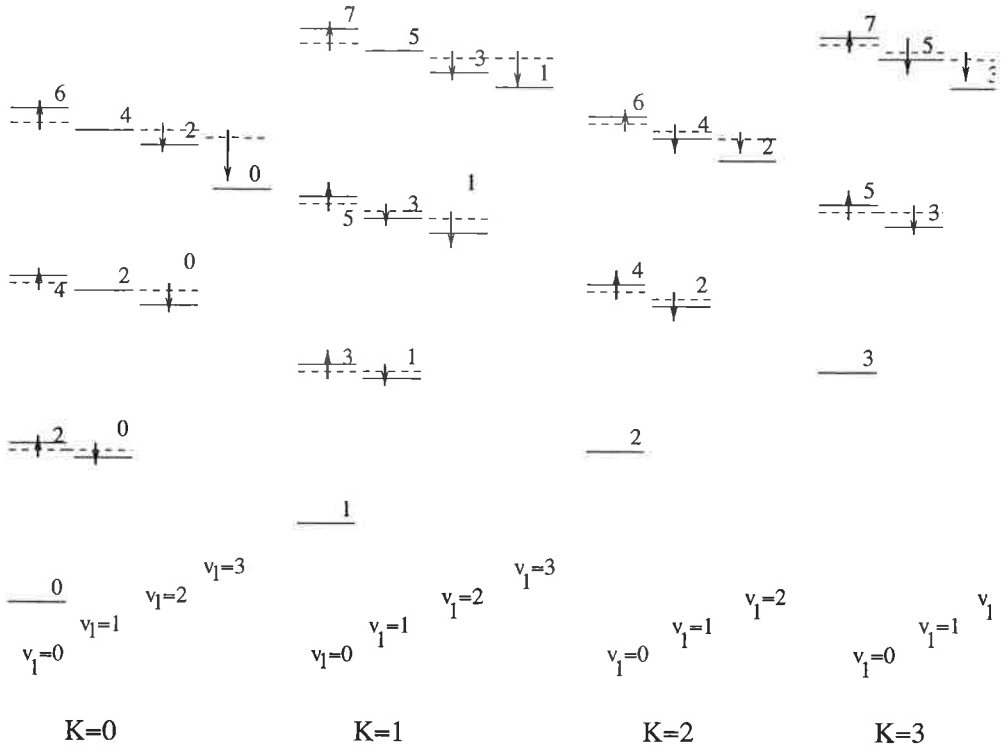

Figure 4.5: Patterns of the bending vibronic and stretching vibrational levels for the ground state $\tilde{X}^1\Sigma_g^+$ of CO_2. Arrows indicate the shifts of the levels due to the Fermi interaction.

$1, 0^0, 0$ level was shifted only with $\simeq 1.9\,\mathrm{cm}^{-1}$.

In order to show that the assumptions about the angular dependence of the force constant (from $\omega_1(\rho)$) and the bond length are resonable, the calculated matrix elements of the Fermi resonance coupling $0, v_2^l, 0$ and $1, (v_2 - 2)^l, 0$ states of the CO_2 molecule are plotted in Figure 4.6. It can be seen that, as in [186, Fig.3], the slope is almost linear when plotted against $[(v_2 + 1)(v_2 + 2)]^{\frac{1}{2}}$, as one would expect in the harmonic oscillator limit. But, contrarily to [186], the behaviour of the matrix elements is almos linear up to great v_2 numbers, even if the individual terms from the matrix elements (3.159) are not linear for large v_2 values.

The purely vibrational coupling is exemplified by the resultant energy pattern shown in Figure 4.7. The comparison with the [186, Fig.4], let us to observe that in our case there is not curves crosing, and always the levels with smaller v_1 stretching numbers belong to a higher energy (as was shown in Figure 4.5). More than this, the Fermi resonance occur for all sets of levels, contrarily to the case of CH_2 molecule, discussed in [186]. The two dimensional wavefunctions used to demonstrate the Fermi interaction mixing in the case of CO_2 molecule were carried out using the parameter set from Table 4.2. The effects of strong vibrational mixing in this case is evident from the asymmetric pattern of the final wavefunction in Figure 4.8. This asymmetry suggest the strong coupling between the stretching and the bending motion, in a similar fashion as was described in [186]. From the figure we see that the small oscillation approximation works for the CO_2 molecule, because the bending wavefunction domain do not exceed 0.4 rad ($\simeq 23°$), and the stretching oscillation is about 0.12 Å.

The Hougen interaction parameter for the Fermi resonance can be computed using the equations from [37, 153]:

$$W = f_{122}^0 \left(\frac{\tilde{\omega}_1}{2\tilde{f}_{11}}\right)^{\frac{1}{2}} \left(\frac{\tilde{\omega}_2}{2\tilde{f}_{22}}\right) \tag{4.5}$$

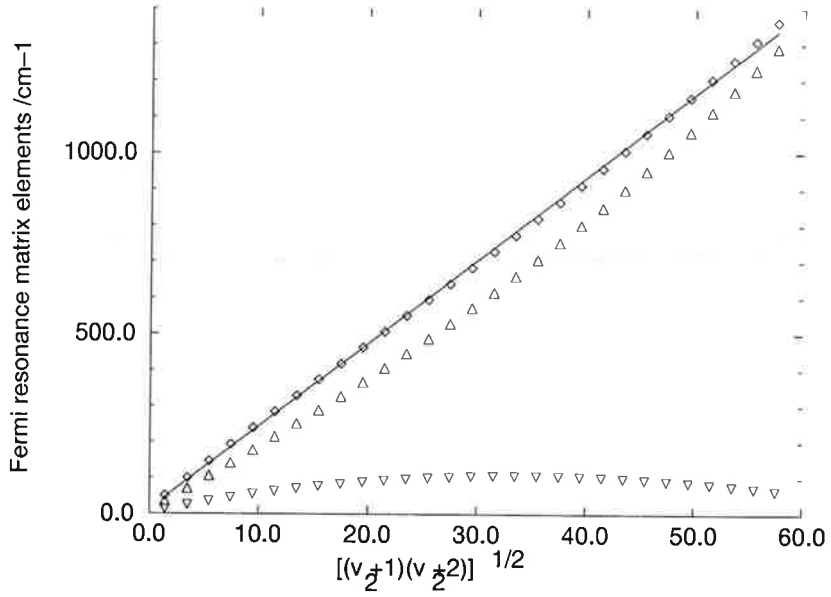

Figure 4.6: The calculated Fermi resonance matrix elements between the levels $0, v_2^0, 0$ and $1, (v_2-2)^0, 0$ of the ground state $\tilde{X}^1\Sigma_g^+$ of CO_2 plotted against the expected function for a harmonic oscillator basis. The total element matrix shows the almost harmonic oscillator relationship, while the individual components from (3.159) deviate from linearity ($\triangledown$ - component issued from the bending potential derivative; $\triangle$ - component issued from stretching potential derivative).

where all the values are in cm^{-1} and the equation is valid in the linearized generalized internal coordinates. If we use the equation (3.91) for the conversion of the coordinates, with *theoretical* $d_1^{(th)}$ *for the d variable*, we find $W = 38.56\text{cm}^{-1}$.

From the Table 4.1 we see that the value computed using the slope from the Figure 4.7 is about 22.9 cm^{-1}. The value computed from the W^0 parameter of Courtoy is approximately 32.89 cm^{-1} (we use the formula $W = \frac{W^0}{\sqrt{2}}$ because W^0 has another definition).

The anharmonic stretching parameter from Table 4.1 has both the same sign and order of magnitude as the values from [39, 46], if we put $x_1 = \frac{x_{11}}{\omega_1}$ (which represent the definition of x_1 from (3.186)).

From the previous discussion we can see that the parameters found in Table 4.1 are consistent with the literature data, but our approach has the major advantage of using a much smaller number of parameters in order to fit the experimental levels.

4.2 Linear Molecules with Renner-Teller Effect: CO_2^+

4.2.1 Introduction

The CO_2^+ ion belongs to the familly of triatomic molecules possessing fifteen valence electrons, including radicals and ions such as NCO, BO_2, N_2O^+ and CS_2^+. All these molecules have $^2\Pi$ ground states exhibiting an orbital as well as a spin degeneracy, and they are characterized by a strong $^2\Sigma^+ - ^2\Pi$ electronic transition, situated in the near UV domain.

Several ro-vibronic states of the electronic ground state have been detected in the electronic spectra of CO_2^+ [110, 180, 200, 201, 202, 203, 204, 205, 206, 207, 208]. In addition, vibronic components of the bending mode have been measured by infrared diode laser absorbtion spectroscopy [209]. Recently Frye and Sears [112] have applied the diode laser spectroscopy to the

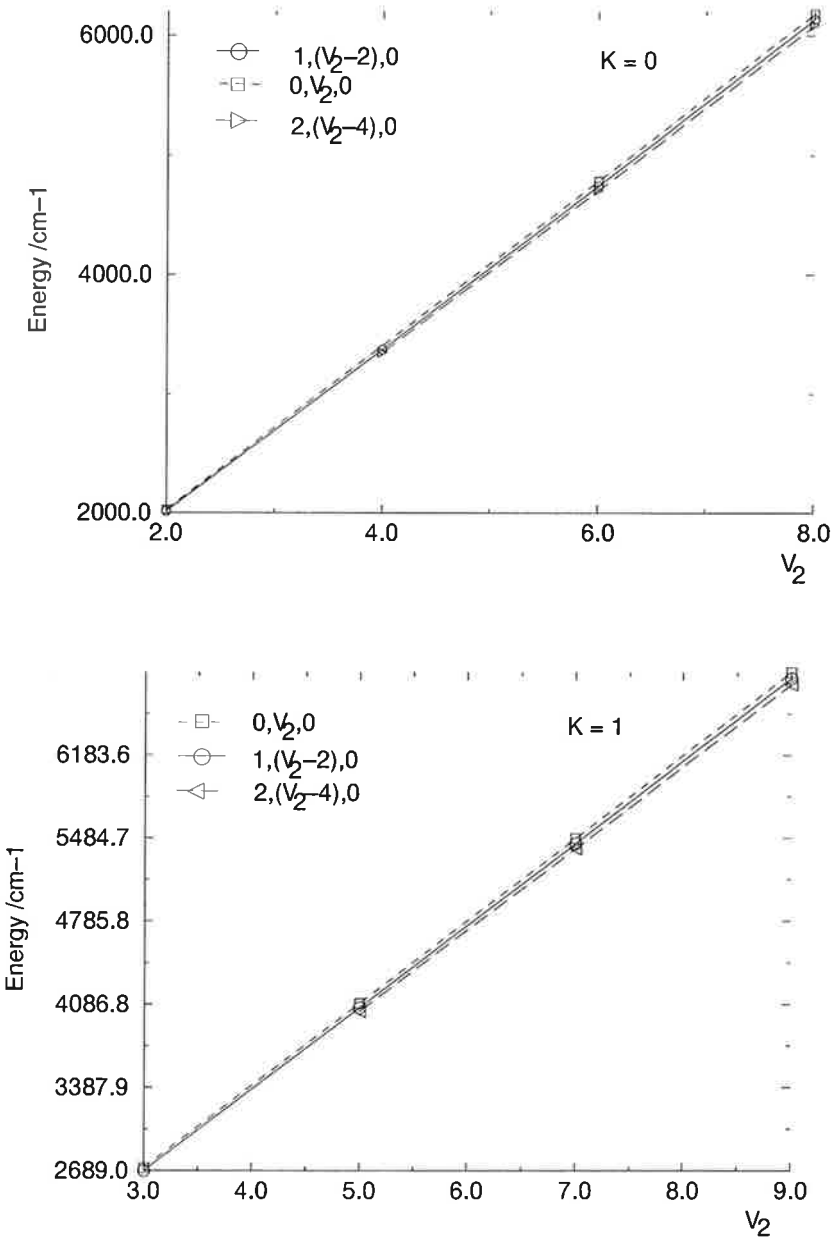

Figure 4.7: The calculated vibronic energy levels with $K = 0$ and $K = 1$ of the ground state $\tilde{X}^1\Sigma_g^+$ of CO_2. Always the levels with smaller v_1 stretching number belongs to a higher energy.

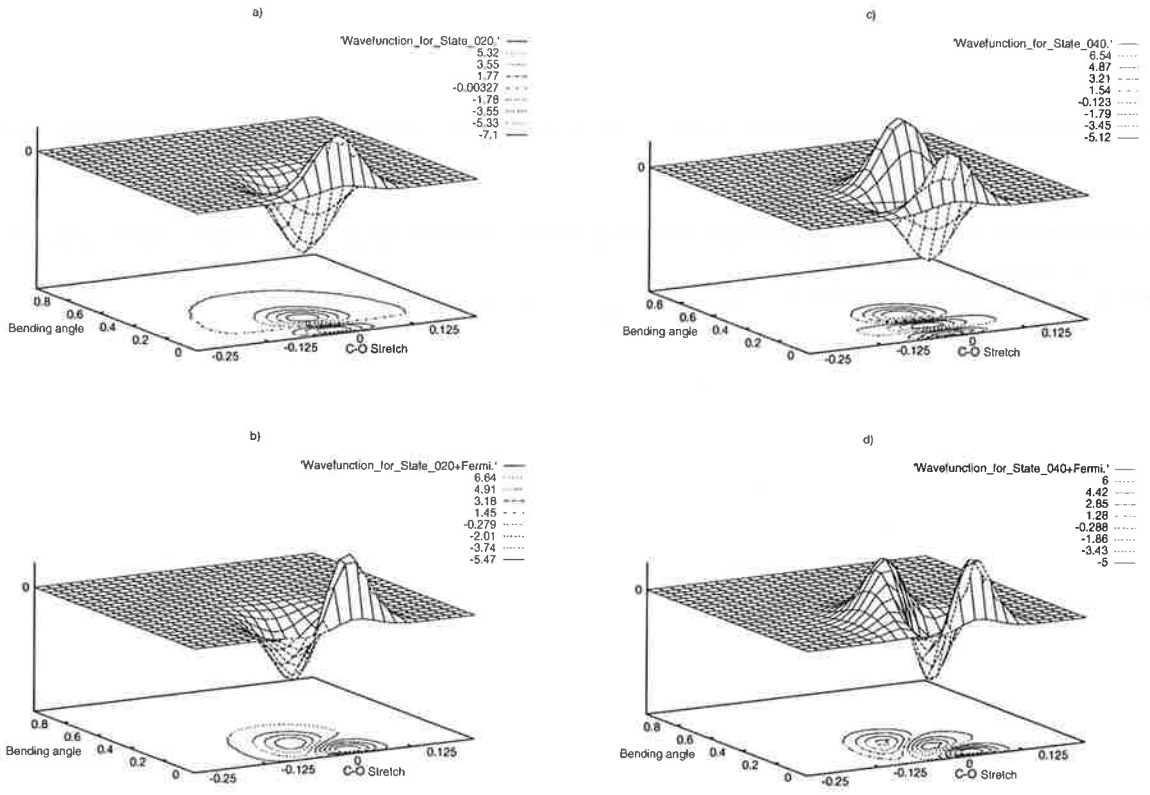

Figure 4.8: Three-dimensional wavefunctions for $K = 0$, (a) (020) and (c) (040) vibronic levels of the ground state $\tilde{X}^1\Sigma_g^+$ of CO_2. For each state the primitive wavefunctions , as well as the final wavefunctions are represented. For the (020) state, the final parentage is (b): 49.8 % (020) and 47.6 % (100). For the (040) state, the final parentage is (d): 28.1 % (040) and 45.2 % (120) and 19.5 % (200).

CO_2 ion and determined the lower spin-vibronic states associated with the $v = 0, 1$ and 2 bending levels, with very high precision. They used a hamiltonian operator for a linear triatomic molecule in a $^2\Pi$ electronic state, derived by Brown and Jorgensen [111] to fit the observed data, together with the previously reported infrared measurements.The A-X system vibrational analysis was further revised and extended [180] by unambiguous identification of bands involving several members of the "Fermi polyades".

The bending anharmonicity in the $^2\Pi_g$ state of CO_2^+ and the geometry variation of the $\langle L_z \rangle$ electronic angular momentul expectation value have been interpreted by Gauyacq and Jungen [113, 210], and Larzilliere and Jungen [153]. According to this model, vibronic coupling and bending anharmonicity in the $\tilde{X}^2\Pi_g$ state have a common physical origin, namely the Hertzberg-Teller interaction between the $\tilde{X}^2\Pi$ and $\tilde{A}^2\Sigma_u^+$ states.

Brommer *et all* [179], followed by Chambaud *et all* [180] which used the last available data, have obtained the three-dimensional APEF's for the electronic ground state of CO_2^+ from the highly correlated electronic wavefunctions and calculated the ro-vibronic energy levels of this species by considering full dimensionality, anharmonicity, rotation-vibration, electronic angular momenta and electron spin coupling effects. The electron correlation effects have been analysed in terms of anharmonic force fields. As was seen, one of the best experimentally investigated examples of the $^2\Pi_g$ states in linear molecule is the CO_2^+ ion, which provides a very good basis for testing the coupling effects, especially in connection with the CO_2 case, analysed in the previously section.

4.2.2 Results and discussion

Potential parameters

The determination of the bond lengths and potential energy curves is based on the knowledge of the rotational constants and the vibronic energy levels deduced from the band origin. Initially we used the bond lengths given by Larzilliere and Jungen [153, Table A1], and these ones have been adjusted to take into account the coupling terms derived from eq.(3.185), which allow for the stretch-bend excitation [186].

We have assumed the bond lengths and their variation with the bending angle to have the form from eq.(3.150), as in [153, 186], where the bond length parameters $r_{CO}(\rho = 0)$ and d_{CO} are to be determinate from the rotational structure. We must remember that eq.(3.150) makes r vary as ρ^2 near $\rho = 0$, which is equivalent to the semi-rigid bender model of [14]. For a given bending potential of type (3.68) or (3.69) the bending levels are calculated numerically, as mentioned in (§3.5.2) and in (§3.5.3).

Using this form of the bending potential we have calculated the rotational constants by using the method from [147], used previously for CO_2 molecule. We have found that in order to reproduce the observed B_0 and α_B value, as well as the observed energy levels, the bond lengths and the d_1 parameter must be the same as in [153]. In the first moment this may seems unusual because our formalism is more general than the formalism of Jungen and Merer [15], but, as was pointed out in the study of CO_2 molecule, the rotational constants have been computed using the bending wavefunctions and the stretching part seems not play an important role in the rotational analysis.

We are choosing to use only the d_1 parameter, but we have found that d_1 and d_2 parameters are nearby equivalents (it means, a variation of the parameter $d_2 \simeq \frac{d_1}{4}$ will produces the same influence on the rotational constants, which suggest that CO_2^+ exist mainly in the region of the small amplitude bending vibration).

The algorithm to find the bond lengths parameters was explained for the CO_2 molecule. For the ground state, we found the bond length equation:

$$r(\rho) = (1.178 + 0.22 \tan^2 \frac{\rho}{2}) \text{ Å} \tag{4.6}$$

The contribution of the vibrational Coriolis interaction to the rotational constant has been included in the calculations following [150]. The value $\omega_3 = 1435.4\ cm^{-1}$ of the antisymmetric stretching frequency from [179] has been used.

Having established the bond lengths parameters from the rotationl constants, we can evaluate the levels positions for the $\tilde{X}^2\Pi$ state of CO_2^+. For the bending analyse we have used the numerical treatment introduced by Jungen and Merer [15], as explained in (§3.4). The treatments accounts for the combined effects of the large amplitude bending motion in each orbital component of the Π electronic state, the a -axis Coriolis coupling between the components (the Renner-Teller effect), as well as the spin-orbit coupling.

The Fermi interaction treatment was explained in the theoretical chapter. The results are given in Table 4.6.

The spin-orbit constant was assumed to vary with the bending angle according to [153, 112]:

$$A^{so}(\rho) = A^{so}(\rho = 0) + d^{so}\rho^2 \tag{4.7}$$

The ρ dependent electronic Coriolis coupling matrix element between the Born-Oppemheimer component states has the form [15, 153]:

$$h^{-1}\langle {}^2\Pi^+|L_z|{}^2\Pi^-\rangle = \Lambda - \frac{g_K}{2A(\rho)} \tag{4.8}$$

where $\Lambda = 1$ for a Π electronic state. $A(\rho)$ is the a - axis rotational constant which tends toward infinity proportional to $\frac{1}{\rho^2}$ when ρ approaches to zero. The eq.(4.8) therefore makes $\langle L_z \rangle$ vary

Table 4.6: Parameters used to fit the bending levels of the $\tilde{X}^2\Pi$ state of the CO_2^+ molecule. Error limits are one standard deviation (standard deviation: 0.351^a,0.230^b,1.87^c)

Bond length variation				
$r(\rho=0)$	1.178			Å
d_1 , coeff. of $\tan^2\frac{\rho}{2}$	0.22			Å
$A^{so}(\rho=0)$	$-160.66^a \pm 0.051$	$-161.57^b \pm 0.151$	$-161.23^c \pm 2.32$	cm^{-1}
d^{so}, var. of A^{so} with ρ^2	$-48.89^a \pm 1.25$	$-10.91^b \pm 3.63$	$-45.51^c \pm 6.11$	$cm^{-1}rad^{-2}$
g_K, var. of $\langle L_z\rangle$ with ρ	3.11 (fixed)	$3.45^b \pm 0.06$	3.11 (fixed)	cm^{-1}
k^+	$18979.5^a \pm 55.0$	$18952.1^b \pm 190.7$	$18618.5^c \pm 19.2$	$cm^{-1}rad^{-2}$
k_4^+	$8785.2^a \pm 143.1$	$8574.3^b \pm 298.9$	$10891.6^c \pm 111.3$	$cm^{-1}rad^{-4}$
k^-	$28037.0^a \pm 51.1$	$28075.2^b \pm 181.9$	$27609.8^c \pm 24.5$	$cm^{-1}rad^{-2}$
k_4^-	$8036.2^a \pm 101.2$	$7825.9^b \pm 253.4$	$11880.7^c \pm 138.9$	$cm^{-1}rad^{-4}$
ω_1^0	$1244.6^a \pm 0.91$	$1244.1^b \pm 3.57$	$1267.1^c \pm 4.0$	cm^{-1}
$\omega_1^{(2)+}$	$212.6^a \pm 45.2$	$245.6^b \pm 156.7$	$-33.0^c \pm 14.1$	$cm^{-1}rad^{-2}$
$\omega_1^{(2)-}$	$269.7^a \pm 46.4$	$287.4^b \pm 161.2$	$-108.8^c \pm 62.3$	$cm^{-1}rad^{-2}$
g_D^+	$1.3735^a \pm 0.0077$	$1.3944^b \pm 0.0738$	$1.441^c \pm 0.093$	
g_D^-	$1.5931^a \pm 0.0065$	$1.6108^b \pm 0.1031$	$1.652^c \pm 0.087$	
x_1^+			$0.4926^c \pm 0.183$	
x_1^-			$-0.0057^c \pm 0.0011$	

[a] Experimental data from [112]

[b] Experimental data from [180], only the levels assigned in [112]
Obs: The differences are due to a different treatment for finding the vibrational band origin.

[c] Experimental data from [180]

as ρ^2 near $\rho = 0$. g_K is a small constant which measures the departure of the Coriolis coupling from the pure precession value Λ as the molecule bends [34, 15].

The g_D factor which describes the influence of the anharmonic perturbation and Coriolis coupling in the rotational constants is taken into account as a variable parameter.

In the Table 4.6 three sets of data have been computed. The first is the data set related to the experimental values given by [112]. These data are important because all the literature analysis are based on them. The second set of data consider the new experimental values from [180], but take into account only the levels previously assigned. We consider this step, because we want to observe the change of the parameters when the full available data are taken into account. The last parameter set are obtained when all new levels are considered. It is easy to see that the first two sets of parameter are quite equivalent, as it must be, because the new refined data are not significant different from the old ones. In the second minimization, even if the match of data is better, the errors assigned are greater, due to numerical procedures. When all data are taken into account, some new parameters must be introduced, as in the case of the CO_2 molecule. The new parameters are the anharmonicity of the stretching potential (the x_1 parameter) and the dependence of the stretching frequency with the quartic term of the bending angle. We see that in fact all the potential parameters are nearly the same (in the range of errors), except the dependence of the stretching frequency with the bending angle. But we must remember that the behaviour of the ω_1 parameter, described in eq.(3.100), is only approximatively described by equation (3.185). The last equation is used for numerical reasons, as discussed in (§3.5.3), and allow the bending potential parameters to depend on the degree of excitation of the stretching states, as was pointed out in [186].

With the parameters used to describe the levels of the $\tilde{X}^2\Pi$ state for CO_2^+ from the Table 4.6, the results from the Table 4.7 are found, together with the effective rotational constants.

The data in Table 4.7 needs some comments. The energy levels obtained by Frye and Sears [112] are based on a harmonic oscillator basis, with matrix elements and wavefunctions which are orthonormalized. This fact ensures that in the interaction matrix there are only a few non -

Table 4.7: Vibronic energy levels and rotational constants in the $\tilde{X}^2\Pi$ state of CO_2^+ (cm^{-1})

v_1	v_2^l	K	Σ	State	Band origin	Diff o-c^B	$B_{v,K}$	Ref.
0	0^0	1	$\frac{1}{2}$	$^2\Pi_{\frac{3}{2}}$	0.0		0.380506	e1
					-0.011		0.38052	j
					0.0		0.380548	h1
					0.0		0.380548	h2
					0.0		0.380546	h3
0	0^0	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	159.598		0.380506	e1
					159.33			e2
					159.608	-0.01	0.38052	j
					159.502	0.096		f
					158.6	0.958		c
					158.3	1.298		a
					159.33	0.0		r
					159.239	0.359	0.380548	h1
					159.21	0.12	0.380550	h2
					159.70	-0.37	0.380546	h3
0	1^1	0	$\frac{1}{2}$	$^2\Sigma^+$	467.259		0.381672	e1
					467.18			e2
					467.259	0.0	0.381750	j
					467.244	0.015		f
					473.6	-6.341		c
					472.4	-5.141		a
					468.36	-1.18		r
					467.371*	-0.112	0.381709*	h1
					467.12*	0.06	0.381714*	h2
					466.04*	1.14	0.381695*	h3
0	1^1	2	$\frac{1}{2}$	$^2\Delta_{\frac{1}{2}}$	511.599		0.381682	e1
					512.36			e2
					511.622	-0.023	0.38167	j
					511.588	0.011		f
					511.2	0.399		c
					512.9	-1.301		a
					508.98	3.38		r
					511.748	-0.149	0.381710	h1
					512.61	-0.25	0.381710	h2
					510.13	2.23	0.381696	h3
0	1^1	2	$-\frac{1}{2}$	$^2\Delta_{\frac{3}{2}}$	668.040		0.381682	e1
					667.78			e2
					668.020	0.02	0.38167	j
					668.091	-0.051		f
					667.9	0.14		c
					668.0	0.04		a
					665.28	2.76		r
					668.077	-0.037	0.381709	h1
					667.99	-0.21	0.381714	h2
					666.88	0.90	0.381696	h3

^{e1} Experimental values from [112]

^{e2} Experimental values from [180]

^{j} Reference [153]

^{f} Reference [112]

^{a} Reference [179]

^{r} Reference [180]

^{h1} This work, using experimental values from [112]

^{h2} This work, using experimental values from [180], but only the previous found in [112]

^{h3} This work, using experimental values from [180]

* Mean values from the spin projection levels (differences due to numerical errors).

^{B} The values from the sets ^{j}, ^{f}, ^{a}, ^{h1}, are compared with ^{e1}; the sets ^{r}, ^{h2} and ^{h3} are compared with ^{e2}.

Table 4.7: (continued)

v_1	v_2^l	K	Σ	State	Band origin	Diff o-c^B	$B_{v,K}$	Ref.
0	1^1	0	$\frac{1}{2}$	$^2\Sigma^-$	719.174		0.381443	e1
					719.22			e2
					719.174	0.0	0.381450	j
					719.154	0.02		f
					727.6	-8.426		c
					726.4	-7.226		a
					723.64	-4.42		r
					719.308*	-0.134	0.381383*	h1
					719.18*	0.04	0.381381*	h2
					717.51*	1.71	0.381373*	h3
0	2^0	1	$\frac{1}{2}$	$^2\Pi_{\frac{3}{2}}$	939.684		0.383273	e1
					939.8			e2
					945.915	-6.231	0.38264	j
					939.667	0.017		f
					942.2	-2.516		c
					942.2	-2.516		a
					939.65	0.15		r
					939.773	-0.089	0.382327	h1
					939.85	-0.05	0.382320	h2
					942.08	-2.28	0.382274	h3
0	2^0	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	949.995		0.383273	e1
					949.7			e2
					952.792	-2.797	0.38264	j
					950.014	-0.019		f
					957.6	-7.605		c
					956.9	-6.905		a
					952.80	-3.1		r
					950.063	-0.068	0.382317	h1
					949.76	-0.06	0.382326	h2
					950.68	-0.98	0.382274	h3
0	2^2	3	$\frac{1}{2}$	$^2\Phi_{\frac{7}{2}}$	1021.000		0.382916	e1
					1022.5			e2
					1020.988	0.012	0.38274	j
					1021.079	-0.079		f
					1016.9	4.1		c
					1022.2	-1.2		a
					1016.65	5.85		r
					1020.742	0.258	0.382728	h1
					1022.33	0.17	0.382731	h2
					1020.56	1.94	0.382698	h3
0	2^2	3	$-\frac{1}{2}$	$^2\Phi_{\frac{5}{2}}$	1173.052		0.382916	e1
					1172.7			e2
					1173.060	-0.01	0.38274	j
					1173.112	-0.06		f
					1171.3	1.752		c
					1172.9	0.152		a
					1168.69	3.91		r
					1172.831	0.221	0.382728	h1
					1172.56	0.14	0.382736	h2
					1173.07	-0.37	0.382697	h3

^{e1} Experimental values from [112]

^{e2} Experimental values from [180]

^{j} Reference [153]

^{f} Reference [112]

^{c} Reference [129]

^{a} Reference [179]

^{r} Reference [180]

^{h1} This work, using experimental values from [112]

^{h2} This work, using experimental values from [180], but only the previous found in [112]

^{h3} This work, using experimental values from [180]

* Mean values from the spin projection levels (differences due to numerical errors).

^{B} The values from the sets ^{j}, ^{f}, ^{a}, ^{h1}, are compared with ^{e1}; the sets ^{r}, ^{h2} and ^{h3} are compared with ^{e2}.

Table 4.7: (continued)

v_1	v_2^l	K	Σ	State	Band origin	Diff o-c^B	$B_{v,K}$	Ref.
1	0^0	1	$\frac{1}{2}$	$^2\Pi_{\frac{3}{2}}$	1242.023		0.383273	e1
					1241.6			e2
					1242.025	-0.002		f
					1242.5	-0.477		c
					1242.5	-0.477		a
					1243.39	-1.79		r
					1241.763	0.260	0.380535	h1
					1241.51	0.09	0.380533	h2
					1241.44	0.16	0.380559	h3
0	2^2	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	1250.606		0.383273	e1
					1251.0			e2
					1257.162	-6.556	0.382740	j
					1250.616	-0.01		f
					1258.7	-8.094		c
					1258.1	-7.494		a
					1255.96	-4.96		r
					1250.879	-0.273	0.382266	h1
					1251.13	-0.13	0.382264	h2
					1252.56	-1.56	0.382238	h3
0	2^2	1	$\frac{1}{2}$	$^2\Pi_{\frac{3}{2}}$	1287.489		0.383273	e1
					1287.2			e2
					1265.535	21.954	0.382240	j
					1287.495	-0.006		f
					1297.1	-9.611		c
					1297.1	-9.611		a
					1293.74	-6.54		r
					1287.226	0.263	0.382265	h1
					1287.14	0.06	0.382267	h2
					1287.74	-0.54	0.382237	h3
0	3^1	0	$\frac{1}{2}$	$^2\Sigma^+$	1405.3			e2
					1398.40	6.9		r
					1402.39*	2.91		h3
1	0^0	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	1425.153		0.383273	e1
					1425.1			e2
					1425.149	0.004		f
					1423.6	1.553		c
					1422.9	2.253		a
					1424.95	0.15		r
					1425.402	-0.250	0.380534	h1
					1425.17	-0.07	0.380535	h2
					1426.14	-1.04	0.380559	h3
0	3^1	2	$\frac{1}{2}$	$^2\Delta_{\frac{5}{2}}$	1426.6			e2
					1422.20	4.4		r
					1427.43	-0.83		h3

^{e1} Experimental values from [112]

^{e2} Experimental values from [180]

^{j} Reference [153]

^{f} Reference [112]

^{c} Reference [129]

^{a} Reference [179]

^{r} Reference [180]

^{h1} This work, using experimental values from [112]

^{h2} This work, using experimental values from [180], but only the previous found in [112]

^{h3} This work, using experimental values from [180]

* Mean values from the spin projection levels (differences due to numerical errors).

^{B} The values from the sets ^{j}, ^{f}, ^{a}, ^{h1}, are compared with ^{e1}; the sets ^{r}, ^{h2} and ^{h3} are compared with ^{e2}.

Table 4.7: (continued)

v_1	v_2^l	K	Σ	State	Band origin	Diff o-c	$B_{v,K}$	Ref.
0	3^1	2	$-\frac{1}{2}$	$^2\Delta_{\frac{3}{2}}$	1440.4			e2
					1447.63	-7.23		r
					1446.14	-5.74		h3
1	1^1	0	$\frac{1}{2}$	$^2\Sigma^+$	1738.7			e2
					1739.66	-0.96		r
					1738.06*	0.63		h3
1	1^1	2	$\frac{1}{2}$	$^2\Delta_{\frac{5}{2}}$	1757.0			e2
					1761.29	-4.29		r
					1758.63	-1.63		h3
0	3^1	0	$\frac{1}{2}$	$^2\Sigma^-$	1808.4			e2
					1813.45	-5.05		r
					1808.96*	-1.96		h3
1	1^1	2	$-\frac{1}{2}$	$^2\Delta_{\frac{3}{2}}$	1948.9			e2
					1948.21	0.69		r
					1948.72	0.18		h3
1	1^1	0	$\frac{1}{2}$	$^2\Sigma^-$	1998.4			e2
					2006.56	-8.16		r
					1998.15*	0.25		h3
2	0^0	1	$\frac{1}{2}$	$^2\Pi_{\frac{3}{2}}$	2496.9			e2
					2491.32	5.58		r
					2495.82	1.08		h3
1	2^2	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	2542.44			e2
					2546.44	-4.0		r
					2542.09	0.35		h3
1	2^2	1	$\frac{1}{2}$	$^2\Pi_{\frac{3}{2}}$	2578.7			e2
					2588.40	-9.7		r
					2578.86	-0.16		h3
2	0^0	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	2682.4			e2
					2677.65	4.75		r
					2682.63	-0.23		h3
2	1^1	0	$\frac{1}{2}$	$^2\Sigma^+$	3000.5			e2
					2995.76	4.74		r
					3000.75*	-0.25		h3
3	0^0	1	$\frac{1}{2}$	$^2\Pi_{\frac{3}{2}}$	3738.4			e2
					3724.36	14.04		r
					3737.71	0.69		h3
2	2^2	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	3820.5			e2
					3819.39	1.11		r
					3819.75	0.75		h3
3	0^0	1	$-\frac{1}{2}$	$^2\Pi_{\frac{1}{2}}$	3932.2			e2
					3923.28	8.92		r
					3933.18	-0.98		h3

e2 Experimental values from [180]

r Reference [180]

h3 This work, using experimental values from [180]

* Mean values from the spin projection levels (differences due to numerical errors).

zero elements. In our treatment, the bending wavefunctions are computed numerically, and even if they must be orthonormalized, in practice it is a factor of $f \in [0.01 - 0.3]$ of non-normalized interaction, which perturb our calculus, especially for the terms which belong to different Renner components (see Table 4.8). This may be the cause which determine that variational calculus

Table 4.8: Overlap integrals between wavefunctions corresponding to a bidimensional oscillator for the state $(00^00)^2\Pi_{\frac{3}{2}}$ and $(0v_2^00)^2\Pi_{\frac{3}{2}}$ and $(0v_2^20)^2\Pi_{\frac{3}{2}}$ states. The bending paramaters are: $r_0 = 1.178, d_1 = d_2 = 0, k^- = 28794\ cm^{-1}rad^{-2}, k^+ = 19372\ cm^{-1}rad^{-2}$

Π state							
	$(10^00)^2\Pi_{\frac{3}{2}}$	$(12^00)^2\Pi_{\frac{3}{2}}$	$(14^00)^2\Pi_{\frac{3}{2}}$	$\cdots$	$(12^20)^2\Pi_{\frac{3}{2}}$	$(14^20)^2\Pi_{\frac{3}{2}}$	$(16^20)^2\Pi_{\frac{3}{2}}$
$(00^00)^2\Pi_{\frac{3}{2}}$	0.99214	-0.00765	-0.00019	$\cdots$	0.69622	-0.40798	0.28865 $\cdots$
Σ state							
	$(11^10)^2\Sigma^+$	$(13^10)^2\Sigma^+$	$(15^10)^2\Sigma^+$	$\cdots$	$(11^10)^2\Sigma^+$	$(13^10)^2\Sigma^+$	$(15^10)^2\Sigma^+$
$(01^10)^2\Sigma^+$	0.98465	-0.01042	0.00032	$\cdots$	0.98465	-0.01042	0.00032 $\cdots$
Δ state							
	$(11^10)^2\Delta_{\frac{5}{2}}$	$(13^10)^2\Delta_{\frac{5}{2}}$	$(15^10)^2\Delta_{\frac{5}{2}}$	$\cdots$	$(13^30)^2\Delta_{\frac{5}{2}}$	$(15^30)^2\Delta_{\frac{5}{2}}$	$(17^30)^2\Delta_{\frac{5}{2}}$
$(01^10)^2\Delta_{\frac{5}{2}}$	0.98465	-0.01042	0.00032	$\cdots$	0.79794	-0.40777	0.25817 $\cdots$

could not obtain better results. We see from Table 4.7 that the APEF analysis, could not fit better the available data, in the two cases taken into account. Our model fit remarcably well the experimental data, with a smaller number of parameters than in the variational techniques. Another observation is that with the 14 initialy levels available, the match is much better, probably due to the fact that only two Fermi levels were involved, and the algorithm of Jungen and Merer [15] which we use, was designed to handle very well the bending levels.

Numerical Tests

In order to verify the symmetry of the adiabatic and non-adiabatic terms from (§3.4.4) and (§3.4.5), a special numerical calculus was done. The test was used to verify the formula (D-36), and bias this formula the volum element for the bending wave function. The results are done in Table 4.9. As we can see from this table, the volume element of the wavefunctions must be

$$\frac{1}{g^{\rho\rho}(\rho)} d\rho\, dS_1\, dS_2$$

in order to obtain in our formalism a symmetric energy matrix, as was pointed out in (§3.4.5).

As in the case of the CO_2 molecule, in order to verify the importance of different parameters, each parameter was initialised with zero and the differences to the initial computed levels are given in Table 4.10. It must be emphasized the influence of the k_4^+ , k_4^- parameters, especially for the k_4^- parameter which is not zero, as in the case of [153]. These results concerning the anharmonic parameters are discussed below, with another anharmonic terms. From the non uniform behaviour of the anharmonic parameters, we presume that the main influence is in the matrix interaction parameters, as in the case of the CO_2 molecule.

The behaviour of the $g_D^{\pm}$ parameters are quite uniform, in contrast with the case in CO_2 molecule. We know that the g_D parameter acts only in the interaction matrix, and we suppose that the apparent uniformity arrises only due to small number of levels taken into account. As in the case of CO_2, the stretching part from the pseudo-potential function has a minimum influence, and the same comments are valid.

In contrast with the anharmonic parameters, the behaviour of $\omega_1^{(2)\pm}$ is quite uniform and indicate that the main effect is done bias the quadratic bending potential constant, in contrast with the case of the CO_2 molecule. If we use the formula (3.100) for the ρ-dependent stretching

Table 4.9: Integrals from adiabatic and non-adiabatic approximation, computed with wavefunctions defined for a volume element $dV = d\rho dS_1 dS_3$. The integrals are computed over 2000 points with the Simpson method.

$H_{vv'} - H_{v'v}$							
	1	2	3	...	21	22	23
1					-0.277258	0.263225	0.01236
2					0.2461143	-0.742649	0.461691
3					0.027229	0.400883	-1.101677
...							
21	0.277258	-0.246143	-0.027229				
22	-0.263225	0.742649	-0.400883				
23	-0.012360	-0.461691	1.101677				
Formula (D-36)							
	1	2	3	...	21	22	23
1					-0.277245	0.263239	0.012375
2					0.246157	-0.742634	0.461706
3					0.027243	0.400897	-1.101663
...							
21	0.277245	-0.246157	-0.027243				
22	-0.263239	0.742634	-0.400897				
23	-0.012375	-0.461706	1.101663				

Table 4.10: The influence of the various parameters used in computation of the vibronic energy levels. The relative influence is obtained by considering each parameter equal to 0, in Table 4.6 and is measured by using the shift of the computed energy levels ($\Delta E = E_{real} - E_{p_i} = 0$). The band origins are the calculated values with the parameters from Table.4.6

Band origin	Par. k_4^+	Par. k_4^-	Par. $\omega_1^{(2)+}$	Par. $\omega_1^{(2)-}$	Par. g_D^+	Par. g_D^-	Par. f_1
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
159.614	0.581	-0.24	0.09	-0.06	0.30	-0.16	0.0
467.488	21.08	-0.55	3.05	-0.51	11.42	-0.19	-0.06
511.871	12.05	5.21	1.59	0.89	6.38	4.07	-0.06
668.138	14.51	4.27	1.81	0.71	7.71	3.39	-0.06
719.345	-1.67	13.31	-0.81	3.22	-0.36	10.32	-0.05
939.842	55.45	1.15	4.65	-0.24	36.02	1.89	-0.08
950.009	53.10	0.25	4.25	0.27	32.50	-0.34	-0.09
1020.923	32.83	12.03	3.15	1.49	17.89	9.75	-0.10
1172.512	39.10	9.79	3.50	1.21	21.32	8.03	-0.10
1241.721	1.75	17.35	2.24	3.15	-9.69	33.14	0.06
1251.062	2.82	31.73	0.07	4.46	2.74	34.51	-0.05
1287.169	-2.84	16.20	0.18	4.61	3.83	-7.39	-0.02
1425.616	1.84	1.64	3.07	2.54	-3.43	-7.29	0.11

† The pseudo-potential function $f_1(\rho)$ in the bending hamiltonian is computed without the stretching contribution

frequencies, together with (3.25), we find for small ρ values, after expanding in power series:

$$\begin{aligned}\omega_1(\rho) &\simeq \omega_1^0 + \omega_1^{(2)Th}\rho^2 + O(\rho^4) \\ &\simeq \omega_1^0 + \frac{1}{8}(p-1)\omega_1^0\rho^2 + O(\rho^4) \simeq \omega_1^0\left[1 + \frac{1}{8}(p-1)\rho^2\right] + O(\rho^4)\end{aligned} \tag{4.9}$$

The previous formulas need some special comments. It is very important to note that the $\omega_1 = f(\rho)$ dependence exist even in the case of the *rigid-bender* approach (case with $d_1 = 0$), as well as in the case of our formalism, as was explained in the theoretical chapter. This fact is due to the very existence of our functions $R_i(\rho, r_0)$, defined in (3.16). If we take for the quadratic stretching force constant a formula similar with [186, Eq.(47)], we will have for (4.9):

$$\omega_1(\rho) = \omega_1^0\left\{1 + \frac{1}{8}\left[(p-1) - 3\,d_1\right]\rho^2\right\} \tag{4.10}$$

Here we used the approximation for the small ρ angles:

$$\frac{1}{\left[1 + \frac{d_1}{4}\rho^2\right]^{\frac{3}{2}}} \simeq \frac{1}{\left[1 + \frac{3}{2}\frac{d_1}{4}\rho^2\right]} \simeq 1 - \frac{3d_1}{8}\rho^2 \tag{4.11}$$

When comparing the results obtained with (4.10) and (4.9) with the values from Table 4.6, we find find the results listed in Table 4.11. As we can see, the values from Table 4.11 indicate that

Table 4.11: Comparison of the molecular parameters for $X^2\Pi_g$ state of CO_2^+

	This work	Other sources	Units
r_0	1.178	1.1785^b ; 1.11769^i	Å
d	0.22	0.1642^b	Å
g_D^+	1.3735	1.651^{c1} ; 1.518^{c2} ; 1.98^d	
g_D^-	1.5931	1.371^{c1} ; 1.448^{c2} ; 1.139^d	
g_D^{mean}	1.4833	1.45^d ; 1.57^e	
ω_1	1244.6	1244.4^g ; 1244.0^f ; 1278.0^h	cm^{-1}
$\omega_1^{(2)+}$	212.6	341.1^j ; 414.76^k	cm^{-1}
$\omega_1^{(2)-}$	269.7	351.0^j ; 414.76^k	cm^{-1}
A^{so}	-160.66	-161.022^g ; $-161.48.0^f$; -160.0^h	cm^{-1}
ε	-0.193	-0.193^g ; -0.196^f ; -0.198^h	
ε_1	-0.451	-0.451^f	
ε_2	0.345	0.343^f	
g_4	3.99	4.91^g ; 5.35^h	cm^{-1}
$\tilde{g}_4$	0.18	0.556^g ; 1.48^h	cm^{-1}
W_1	47.54	35.47^g ; 30.63^f ; 39.74^h	cm^{-1}
W_2	-0.077	2.65^g ; 0.87^f ; 6.62^h	cm^{-1}

[b] Equation (3.152)
[c1] Equation (3.155) with ω_2^{mean}, [c2] equation (3.155) with $\omega_2^{\pm}$
[d] Values computed from [179] with BL formula [14] and definition of g_D
[e] From contour map of the potential from [179]
[f] Reference [153]
[g] Reference [112]
[h] Reference [179]
[i] Reference [204]
[j] Equation (4.10)
[k] Equation (4.9)

the formula used in [186] seems real, because otherwise the $\omega_i^{(2)}$ parameters will be too high. This is a difference from the CO_2 case, where the computed value is too high, compared with the fitted value. More than this, it suggest that these parameters must be positive, at least for $d_1 \leq \frac{p-1}{6}$. Because in the case of the CH_2 molecule, analysed in [186], the p value is near unity

($p \simeq 1.1666$), it explains the δf_1 negative value obtained. When we analyze the data set for all the experimental levels, we see that this parameter is negative. This suggest that when higher excited stretching states are involved, we could not expand in power series, as in the case of the equation (4.10).

It is interesting to note, that in the case of all levels fit, the value of the stretching frequency is closer to the value obtained by the variational techniques (a value of 1268.0), rather that with the value obtained with the harmonic oscillator (a value close to 1244.0).

The anaharmonic stretching parameter x_1 act in the same way as $\omega_1^{(2)Th}$, bias the bending potential shape, because it is linked to $\omega_1(\rho)$ stretching frequency. The introduction of this parameter is suggested by the existence of the f_{1111} potential constant [179, Table XII], [180, Table II] in a similar way with the parameter introduced for the CO_2 molecule.

Using the conversion formulas for the potential force constants (3.87) from the curvilinear to the generalized system, as well as to the linearized coordinates (3.91), the force constants from the Table 4.12 are obtained.

Table 4.12: Force constants in the generalised coordinate system, computed with the stretch - bender force constants from Table.4.6

Force constants	This work	Ref. [179, 180]
$K_{122}(F_{122})$ $[\frac{aJ}{\mathring{A}\cdot rad^2}]$ upper state	-0.563	-0.371, -0.359
lower state	-0.586	-0.213, -0.203
$F_{2222}(K_{2222})$ $[\frac{aJ}{rad^4}]$ upper state	0.251	0.119, 0.131
lower state	0.240	0.061, 0.068
$f_{11}(2\,K_{11})$ $[\frac{aJ}{\mathring{A}^2}]$	15.16	15.395, 15.550
$f_{22}(2\,K_{22})$ $[\frac{aJ}{rad^2}]$ upper state	0.546	0.573, 0.566
lower state	0.370	0.383, 0.378

Again, as for the CO_2 molecule, it must be emphasized that in the formula (3.91) *the theoretical* $d_1^{(th)}$ *are used* and not $d_1^{(ChJ)}$, because the equations are obtained in the frame of the semi-rigid approach. The change is done with the formula (4.4). The theoretical value for the g_D parameter computed with (3.155) formula, and the values from the force constant field (with $d_1^{(th)}$) are listed in Table 4.11, with our parameters. It can be seen that the agreement between the values is enough good, the only mismatch are the constants for anharmonic interaction. But this fact may be linked to the g_D parameter used in the fit. The g_D factor in the Table 4.11 needs some comments. First of all, the mean value is nearly the same for the theoretical value and for the fitted value. Meanwhile, the two components are not so close as we would, and it seems that the values obtained in the fiting procedure are reversed. The difference is about 15 %. We believe that in the fitting procedure, these parameters substitute themself to other anharmonic parameters, which could explain the mismatch observed in Table 4.12. Another explanation could be the algorithm for computing the theoretical value. From [§E.3], we see that g_D is find as a mean value (see eq.(E-156)), and we are not taken into account any perturbation like the Renner-Teller effect on the rotational constants. This could explain the better match for CO_2, and in the same time for the mean value of CO_2^+.

Rotational Constants and Spin-Orbit Effects $B_{v,k}$ for the CO_2^+ molecule

The bond lengths given previously refer to the $v_1^{(linear)} = -1$ structure and was obtained using the values of $\bar{B} = \frac{1}{2}(B + C)$ for the unique $v_2 = K + 1$ levels, which exhibit a nearby $B \simeq$

$B_0 - \alpha_e(v_2 + 1)$ behaviour, as in Figure 4.9. For the rest of the levels, as pointed out by Frye and Sears [112], the increase is not linear in the bending quantum number. This may be due to the anharmonic bending potential constants, which are enough high, as it was find in the [112] study. In our curvilinear coordinates one obtain the simplest and more realistic expresion for the force field, as was pointed out in [154]. As an example, in this system the behaviour of the rotational constant B (larger in the (010) Σ^+ level than in the (010) Σ^- level) arises naturally, without upper term constants [153].

The observed and calculated rotational constants $B_{v,K}$ are done in Table 4.7. Figure 4.9 showes the agreement between the observed and the calculated rotational constants graphically. It can be seen a slight improvement of the constants, but this is not sure to be linked to the introduced stretching displacement, because the rotational constants for the states $(100)^2\Pi$ are not enough accurate computed.

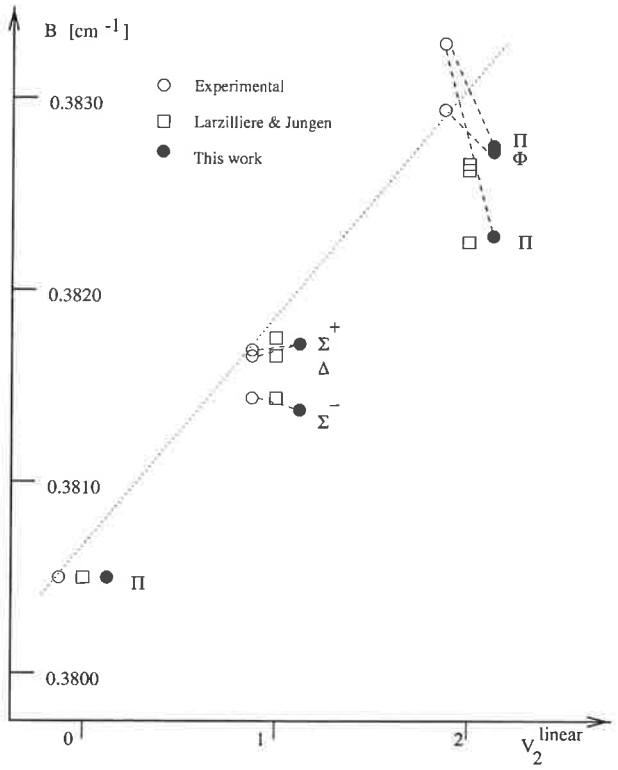

Figure 4.9: Observed and calculated rotational constants of the $\tilde{X}^2\Pi$ electronic state in CO_2^+, versus v_2^{linear}.

In a multiplet electronic state the presence of the spin-orbit coupling represented by the operator $A^{so}L_zS_z$, leads to shifts and splittings to vibronic levels with $K > 0$. As a first approximation one may consider the spin-orbit operator as contributing an amount $A^{so}\langle L_z\rangle\Sigma$ to the vibronic energy, where the erratic behaviour of $\langle L_z\rangle$ is responsible for the strong variation from level to level. The discrepancies between the observed and the computed levels could be mostly removed by the introduction of the parameter $g_K = 3.19\,\mathrm{cm}^{-1}$, to account for the variation of the electronic orbital angular momentum quantum number Λ with the bond angle, as in (4.8).

The spin-orbit coupling constant can be determined by comparing the observed splitting to the expectation values $\langle L_z\rangle$. Given the molecular constants listed in Table 4.6, it is possible, using the method described in [15], to calculate the complete pattern of the spin-orbit splittings for all the levels, as is shown in the Table 4.13, for the $K = 1$ levels. The table shows a good agreement between $\langle L_z\rangle$ behaviour and the $\left(A_{eff}^{so}\right)$ values computed with Jungen and Merer

Table 4.13: Effective spin-orbit splittings computed with the Stretch-Bender and Jungen and Merer method respectively, compared with $\langle L_z \rangle$ values, for $K = 1$ vibronic levels of the $^1\Pi_g$ state of CO_2^+

$K = 1$	$\|000;10\rangle$	$\|020;10\rangle$	$\|040;10\rangle$	$\|060;10\rangle$	$\|020;-12\rangle$
$\langle \bar{L}_z \rangle^a$	0.9912	0.0073	0.0228	0.0323	-0.0164
$\left(A_{eff}^{so}\right)^a$	159.77	1.46	3.90	5.24	-2.64
$\left(A_{eff}^{so}\right)^b$	159.61	10.18	9.47	11.48	-36.11

[a] Reference [15]
[b] This work

method. In our method, the Fermi interaction as well the adiabatic and non-adiabatic effects into the interaction matrix perturb the non-unique levels. Unfortunately, there are no experimental data for comparing other levels that the unique ones and for this reason an improvement of the spin-orbit constant could not be done.

In order to compare our method with the three states model from [113] some properties of the unique levels are listed in Table 4.14 and in Figure 4.10.

Table 4.14: Bending energies (cm^{-1})and the effective spin-orbit constants of the lowest unique levels in the $^2\Pi_g$ state of CO_2^+, compared with different hamiltonians for the three-state model of [113]

Vibronic level	Energy levels			Spin-orbit constants		
K	[a]	[b]	[c]	[a]	[b]	[c]
1	515.363	515.52	515.70	-159.61	-157.92	-157.88
2	1025.547	1030.97	1031.47	-156.27	-155.03	-154.96
3	1532.238	1546.91	1547.83	-151.59	-151.63	-151.55

[a] This work
[b] Reference [113, Table 4(a)]
[c] Reference [113, Table 4(b)]

The slope of the unique levels line, as seen in Figure 4.10, is lower than that one computed in [113]. This follows the trend observed in [113] and this means that the levels computed with the approximate formula [113, eq.(23)] are greater than those computed with the vibronic matrix from [113]. We suppose that if the interaction matrix will be more complete, the energy levels will have a lower energy, but this difference might arise simply due to a different choice of parameters.

The spin-orbit constants are different from those of [113], but it seems that the difference is due uniquelly from a different choice of A^{so}, g_K parameters. The Table 4.14 shows a good agreement between our data and those obtained with the three states modes from [113], which can be explained in the framework of the small oscillations approximation.

The formula (4.7) used, allowed the effective spin-orbit parameters to vary with the vibrational states, as it was shown in the previous section. As previously discussed in [112], the spin-rotation interaction has been neglected in the $(000)^2\Pi$, $(010)^2\Delta$, $(020)^2\Phi$ states (see Table 4.7) since its contributions to the energy are not distinguished, and the model do not permit explicitely this type of computation in this stage of the development. For the same reason, the rotational dependence of the spin-orbit coupling was ignored in the (020) or $(100)\Pi$ state. From the Table 4.7 it can be seen that the error in the rotational constant are nearby of the same order of magnitude as in the case of [153], which is normal because the same formalism

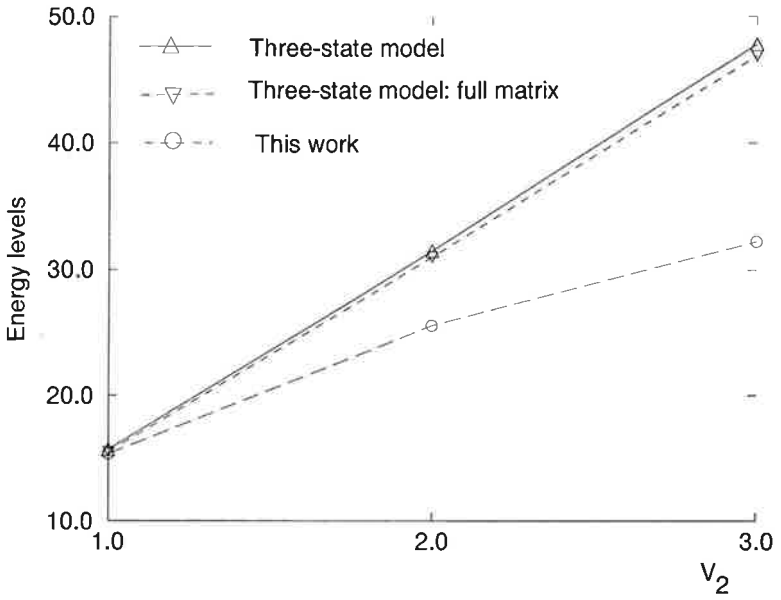

Figure 4.10: Energy of the unique levels ($K = 1$ to 3). The values used for the three states model are $\varepsilon = -0.188$, $\omega_m = 513\ cm^{-1}$ and $g_K = 3.22\ cm^{-1}$. (◯) this work; (▽) numerical diagonalization of the matrix in the three states model; (△) Ref.[113, eq.(23)].

was used, and taking into account of the stretching vibrations do not improve the match of the levels.

Vibronic and Anharmonic Effects

The splittings upon slight bending of the Π^- and Π^+ Born-Oppemheimer potential energy curves of a linear triatomic molecule has two distinct origin. The electrostatic dipole field created by the displaced nuclei mixes the Π electronic state with the Σ states. The mixing leads to a splitting of the initially degenerate Π^+ and Π^- components; it also causes the Coriolis coupling matrix element $\langle L_z \rangle$, discussed previously, to vary with ρ because the Π wavefunction acquire non Σ character.

The displacement of the nuclei create a quadrupole electrostatic field which also contribute to the splitting of the Π^+ and Π^- component states, in the first order, without changing the orbital character of the electronic wavefunction. If we consider the Π electronic ground state together with the first excitated Σ^+ state we have a three model state, where the potential $V^-(\rho)$ is affected by the quadrupolar interaction only, $V^+(\rho)$ is determined by the combined effects of the quadrupolar and dipolar terms, and g_K depends primarly on the magnitude of the dipolar interaction [31, 96, 34, 108]. Gauyacq and Jungen [113] showed that the dipolar interaction introduce an anharmonicity in the potantial $V^+(\rho)$, too. The resulting anharmonic level shifts are expected to be comparable in size to those arising from the vibronic parameter g_K. The quantities involved are related to the potential curve parameters given in Table 4.6,

$$\begin{aligned} k_m &= \frac{k^+ + k^-}{2} \\ \varepsilon &= \frac{(k^+ - k^-)}{(k^+ + k^-)} = \frac{\varepsilon_1 + \varepsilon_2}{(1 + \varepsilon_1)} \\ \Delta E &= T_0\left(\tilde{B}^2\Sigma_u^+\right) - T_0\left(\tilde{X}^2\Pi_g\right) \end{aligned}$$

$$g_{22} = \frac{1}{2}k_4^+\left(\frac{\omega_m}{k_m}\right)^2 \tag{4.12}$$

In the previous formulas, ε_1 is the dipole contribution and the ε_2 is the quadrupole contribution in the Renner parameter ε.

Within the three state model, g_{22} and g_K can be expressed in terms of ω_m , ΔE , ε_1 , ε_2 as in [113, 153]:

$$\begin{aligned} g_{22} &= \frac{\omega_m^2\varepsilon_1\left(2\varepsilon_1+\varepsilon_2\right)}{4\Delta E\left(1+\varepsilon_1\right)^2}\left(1-\alpha\right) \\ g_K &= -\frac{\omega_m^2\varepsilon_1}{2\Delta E\left(1+\varepsilon_1\right)} \end{aligned} \tag{4.13}$$

where $\alpha = \frac{k'-k}{k}\cdot\frac{1}{(2\varepsilon_1+\varepsilon_2)}$, and k and k' represent the unperturbed quadratic force constants in the Π and Σ states, respectively. The parameters corresponding to the ground state $\tilde{X}^2\Pi_g$ of CO_2^+ are: $\omega_m = 513\,cm^{-1}$, $\varepsilon = -0.188$, $\Delta E = 34600\,cm^{-1}$ [113] and these parameters are reprezentative for most of the 15-valence electron molecules. More precise paramaters are given in [153]: $\omega_m = 512\,cm^{-1}$, $\varepsilon = -0.196$, $\Delta E = 34598\,cm^{-1}$.

With the data from Table 4.6 we find the parameters given in Table 4.11. By analysing this table we see that the strong dipolar interaction ε_1 which pushes the Π^+ potential energy curve below the Π^- curve for $\rho \neq 0$, is partly balanced by the quadrupolar interaction ε_2 which acts in the opposite sense.

The Renner-Teller parameter ε and the harmonic vibrational interval ω_2, are determined from our parameters to be -0.193 and 511.76 cm^{-1} respectively, in good agreement with the literature.

Some comments are necessarily for the anharmonic terms $k_4^{\pm}$. In the analysis of the data some different algorithms are used. The generalized force field constants, obtained from conversion formulas are done in Table 4.12. The constants from [112, 179, 180] and those of the present work are easily to be converted. In the same time, the data from [153] are difficult to be compared, because the stretching coordinates are not uniquelly defined. This work, which use symmetrized stretching coordinates is a possibility, the choice of the nonsymmetrized stretching coordinates from Duxbury *et all* [186] is another one, and the "standard" one was used by Jensen [6, 7]. Thus each set of parameters can be valid in its framework, but not always the direct comparison is possible. In the Larzilliere and Jungen [153] analysis with the three state model [113], the parameter k_4^- equal zero. But in the case of the wider model based on rectilinear coordinates from Frye and Sears [112] as well as in the variational calculus from [179, 180], the parameter k_4^- do not vanish. We tried to fit the data with $k_4^- = 0$, but we not succed to do this in a reasonable measure. It means that the anharmonic parameters need to exist because they must adjust the shape of the potential curves to the new interactions which arise when solving the interaction matrix. Meanwhile, it is not an unique conclusion about this, due to the mathematical and numerical algorithms, and this parameter simply can arise due to computational algorithms, or can manifest itself as a cumulative processus, in place of other "invisible" parameters. This aspect was well underlined in the paper of Frye and Sears [112], when results from different methods using various degree of approximation are done. The same type of analysis was done in [113]. Further analysis maybe can succed in finding the right value.

Fermi Interactions

As it was underlined in the case of the CO_2 molecule, the Fermi interaction is introduced due to our choice of instantaneous configuration and reference frame. Then we do not need explicitely a f_{122} quadratic interaction term.

In the same time, CO_2^+ is now one of the best characterized examples of the complicated coupling situation which occur in a linear triatomic molecule in an orbitally degenerate electronic state, and provides a benchmark to assess the best models of vibronic interactions.

Even if in this moment multiple groups of Fermi levels are available, we illustrate our interaction analysis on only two groups of two interacting sets of levels. This is seen in Figure 4.11, where the two-dimensional wavefunctions are done for the interacting levels in the case of the $\Sigma = -\frac{1}{2}$ spin. The same behaviour as in the CO_2 as well as in [186] is observed. Also, the Renner-Teller coupling is very clear observed in this plot. The plot show the same behaviour as the ones displayed in [180, fig. 4] As in the case of the neutral molecule, we see that the wavefunction domain is in the limit of the small oscillation approximation, which of course will not be the case when higher stretching modes are involved (as can be seen in [180, fig. 5]).

In order to see the degree of consistence of the harmonic oscillator framework for small amplitude oscillations, the matrix elements of Fermi interaction between $0v_2^l0$ and $1(v_2-2)^l0$ for the CO_2^+ molecule are plotted in Figure 4.12. It can be seen from the plot that the linearity against the function for a harmonic oscillator basis is preserved, as in the case of the CO_2 molecule. Also, as in the case of CO_2, the linearity is preserved for large v_2 even if each component of the matrix element is not linear. If compared with the CH_2 molecule [186], it seems that this can be a feature of a linear molecule, though this aspect must be investigated further.

The vibronic energy levels for the interacting sets are represented in Figure 4.13, and we can see that it has the same characteristics as in the case of the CO_2 molecule: the levels from the stretching states do not cross each other, contrarily to the CH_2 molecule. The same comments as for the previous figure are valid. The Fermi interactions are smaller in CO_2^+, because the distance between levels are greater than in the neutral molecule. Also, in the ion, the levels with a smaller stretching quantum number lie lower than the coupled levels, contrarily as in CO_2.

Finally, in order to compare the results from various parameters, the Hougen parameters W_1 and W_2 must be computed, using equations similar with (4.5), from [37, 153, 154] in linearized generalized internal coordinates. The values computed from our data are listed in Table 4.11, together with the values previously obtained from [112, 153, 179]. Our values were computed using the conversion formulas (3.91) with theoretical $d_1^{(th)}$ parameter. The parameter obtained from the slope of Figure 4.12 is about 28.93. It is seen that the element obtained from the graph has the same feature as the element find in the case of the CO_2 molecule.

In Table 4.15 the interaction matrix for the Fermi interacting levels is done. We see that the magnitude of the Fermi matrix element is the same as those derived with the Hougen W_1 and W_2 parameters. After the multiplication with STU matrix (from Table 4.16), we see that the behaviour of the matrices for the two spin projection is changed. For the $\Sigma = -\frac{1}{2}$, the element between $|100;10\rangle$ and $|020;-12\rangle$ is greater than those for $|100;10\rangle$ and $|020;10\rangle$. But in the same time, the eigenvector matrix show the same behaviour for the two spin projection (see Table 4.16). The composition of the complete ro-vibronic wavefunction for the analysed Fermi polyades is the same (in the limit of numerical errors), as in the [180, Table VI], which prove that our approach is consistent with the more elaborate variational techniques.

Some important remarks concerning the parameters from the Table 4.11 must be done. As was pointed out in [179] in the framework of the same approach we can obtain multiple sets of parameters which fit well the same experimental data. The choice between the different sets is a difficult task, because the literature data are not consistent, as it can be seen in Table 4.11.

The inclusion of the g_D parameter, which is characterized by the anharmonic constant f_{122}, in the bond length description, confirm the assertion from [153] that the semi-rigid bender model used by Jungen and Merer [15] implies Fermi interaction constants of the correct order of magnitude despite the fact that it does not explicitely allow for the stretching motion.

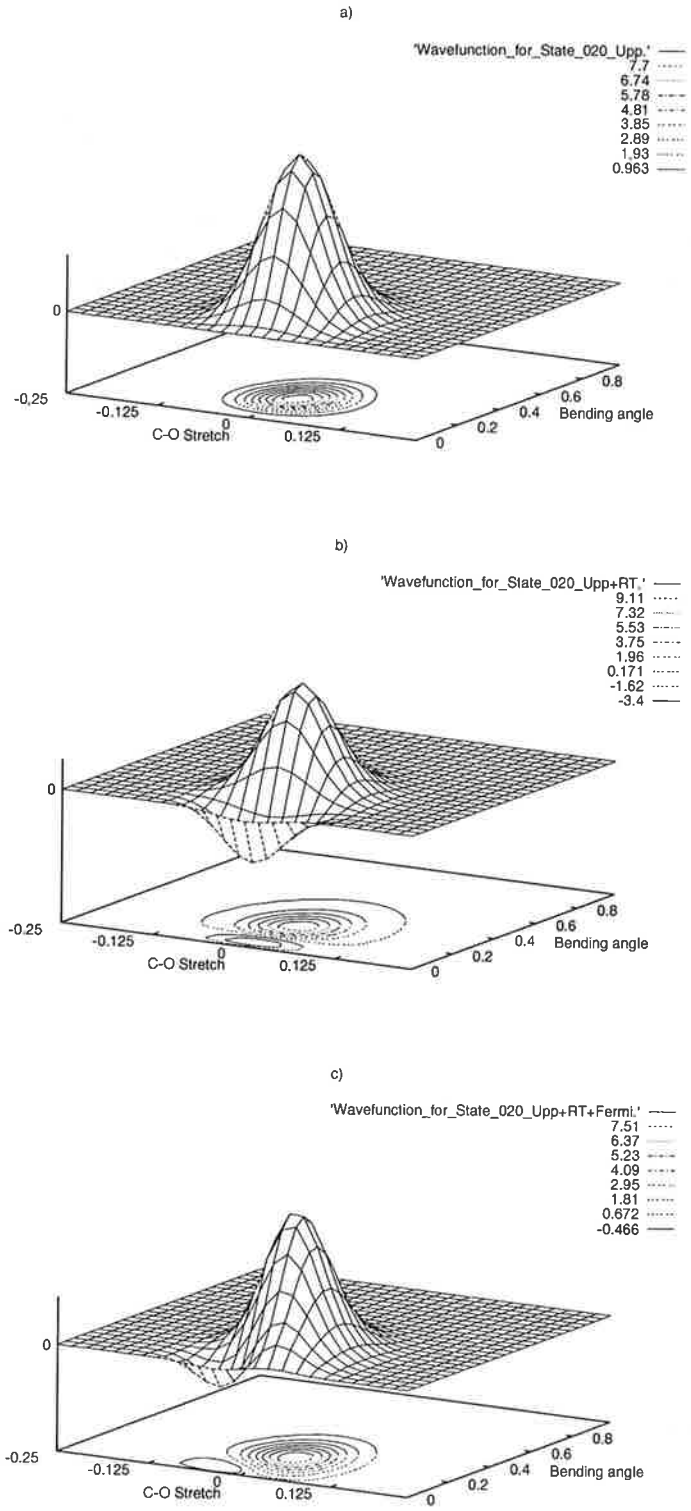

Figure 4.11: Three-dimensional wavefunctions for the $K = 1$, $\Sigma = -\frac{1}{2}$, $|020;-12\rangle$ $\kappa^2\Pi_{g1/2}$ vibronic level of the ground state $\tilde{X}^2\Pi$ of CO_2^+. There are represented: (a) the primitive wavefunction; (b) the Renner-Teller coupling and (c) the Fermi resonance. For the Renner-Teller coupling, the parentage is: 73.2 % $|020;10\rangle$ $\mu^2\Pi_{g1/2}$ and 23.4 % $|020;-12\rangle$ $\kappa^2\Pi_{g1/2}$. For the Fermi resonance, the parentage is: 0.4 % $|020;10\rangle$ $\mu^2\Pi_{g1/2}$, 89.9 % $|020;-12\rangle$ $\kappa^2\Pi_{g1/2}$ and 7.7 % $|100;10\rangle$ $^2\Pi_{g1/2}$. In figure (c), it is a phase shift of 180°, compared with Table 4.16.

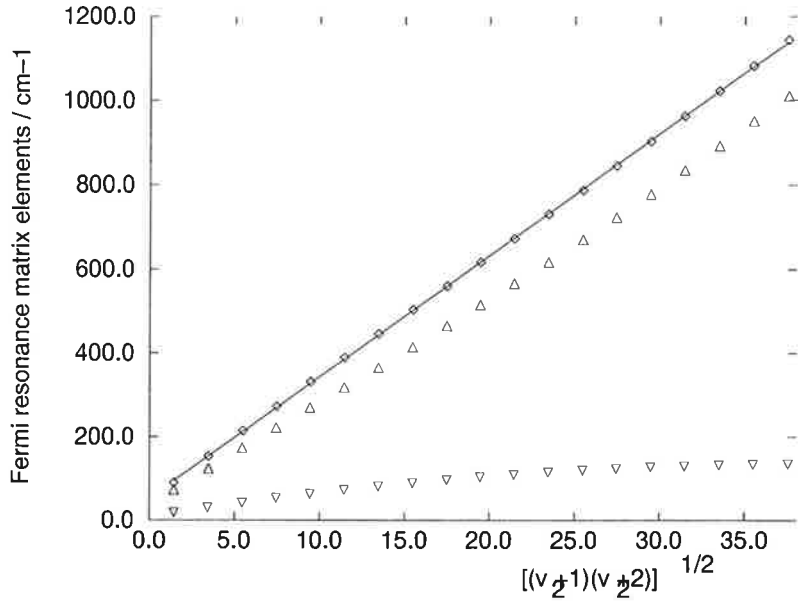

Figure 4.12: The calculated Fermi resonance matrix elements between the levels $(0, v_2^0, 0)^2\Pi_{3/2}$ and $(1, (v_2 - 2)^0, 0)^2\Pi_{3/2}$ of the $\tilde{X}^2\Pi$ electronic state in CO_2^+, plotted against the expected function for a harmonic oscillator basis. The total element matrix shows the almost harmonic oscillator relationship, while the individual components from (3.159) deviate from linearity (∇ - term issued from the bending potential derivative; $\triangle$ - term from the stretching potential derivative).

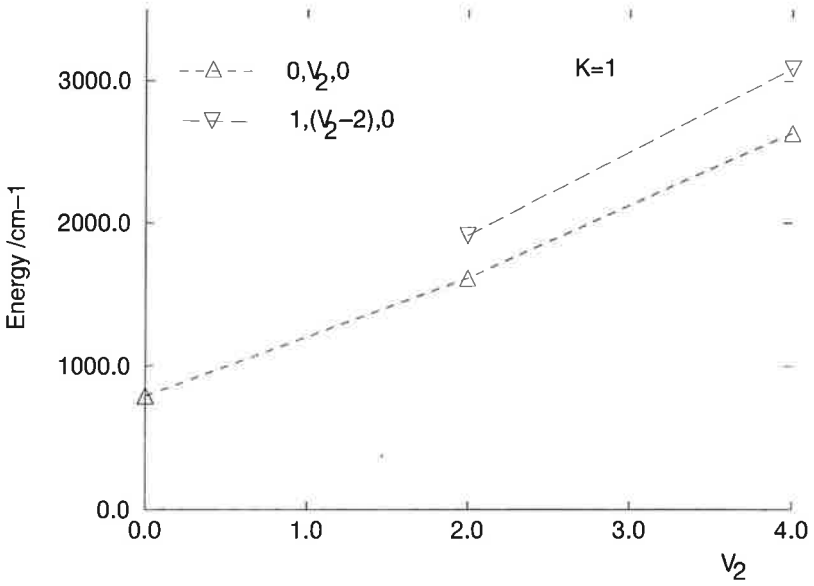

Figure 4.13: The calculated vibronic energy levels with $K = 1$ of the $\tilde{X}^2\Pi$ electronic state, $2\Pi_{3/2}$ vibrational state of CO_2^+. The levels with smaller v_1 stretching number belongs to a smaller energy.

Table 4.15: The Fermi interaction matrix for the interacting levels in the state $\tilde{X}^2\Pi$ of CO_2^+ molecule. The initial Fermi interaction matrix, and the one obtained by multiplication with the STU matrix [37] is given.

$\Sigma = -\frac{1}{2}$						
	H^{Fermi}			$(STU)^+ H^{Fermi} (STU)$		
$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$		$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$
1414.2	-65.5	-2.0	$\|100;10\rangle$	1414.2	-39.1	-47.5
-64.5	990.5	0.0	$\|020;10\rangle$	-39.1	990.5	0.0
-2.0	0.0	1297.7	$\|020;-12\rangle$	-47.5	0.0	1297.7
$\Sigma = \frac{1}{2}$						
	H^{Fermi}			$(STU)^+ H^{Fermi} (STU)$		
$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$		$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$
1253.5	-64.4	-2.0	$\|100;10\rangle$	1253.5	56.4	22.0
-64.4	989.7	0.0	$\|020;10\rangle$	56.4	989.7	0.0
-2.0	0.0	1295.3	$\|020;-12\rangle$	22.0	0.0	1295.3

Table 4.16: The Renner-Teller and the final eigenvectors for the interacting levels in the state $\tilde{X}^2\Pi$ of CO_2^+ molecule.

$\Sigma = -\frac{1}{2}$						
	STU eigenvectors			Fermi eigenvectors		
$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$		$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$
-0.9964	-0.0465	0.0709	$\|100;10\rangle$	-0.9523	0.0887	-0.2769
-0.0387	-0.4964	-0.8157	$\|020;10\rangle$	0.0758	0.9804	0.0596
0.0755	-0.8667	0.4839	$\|020;-12\rangle$	0.2799	0.0301	-0.9481
$\Sigma = \frac{1}{2}$						
	STU eigenvectors			Fermi eigenvectors		
$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$		$\|100;10\rangle$	$\|020;10\rangle$	$\|020;-12\rangle$
-0.9976	-0.009	-0.0684	$\|100;10\rangle$	-0.7677	-0.1810	-0.6079
-0.0142	0.8702	0.4763	$\|020;10\rangle$	-0.1436	0.9675	-0.1100
0.0554	0.4895	-0.8645	$\|020;-12\rangle$	0.6136	0.0054	-0.7771

4.3 Conclusion

As an example of the application of the Stretch-Bender model we have choosen to use test calculations of the vibronic energies inside a series of linear molecule which exhibit Fermi interaction, as well as Renner-Teller effect.

The CO_2 molecule was choosen because has a pure Fermi interaction and it is an ideal benchmark for a model, like the hydrogen atom in the case of the atomic physics. More than this, carbon dioxide play an important role in the Earth atmosphere and in the laser physics. Our results are in good agreement with the previous results and define very sharp the applicability limits in the case of the literature models. The energy levels and the behaviour of the molecule are very well described with a small number of parameters.

The ion of the CO_2 molecule belongs to the familly of the triatomic molecules possessing 15 valence electrons, including radicals and ions such as NCO, BO_2, CO_2 and CS_2. All these molecules have $^2\Pi$ ground states exhibiting an orbital as well as a spin degeneracy, and they are characterized by a strong $^2\Sigma^+ - ^2\Pi$ electron transition situated in the near UV domain. CO_2^+ is an important component in the astrophysics and ionosphere. It provides a benchmark to test models of vibronic interactions in these cases. The $^2\Pi$ states of the CO_2^+ ion have been used to demonstate the application of the Stretch-Bender method for the analysis of the behaviour of strong coupled electronic and vibrational states. The model could explain some

surprisingly features to fit energy levels of some methods [15], as well as to validate the use of some "semi-empirical" formulas [186], in the framework of a specific approach.

It defines the limits for the small amplitude approaches used by [112]. The g_D factor, introduced here for the first time, plays a key role in order to understand the indirect action of some couplings as in the case of the Coriolis coupling, and elucidate the problem of conversion the bond length parameters in [179].

The test calculations presented here were made using the Jungen and Merer [15] l-basis, which is adapted for all the molecules, especially for those with a linear equilibrium geometry in both states.

In this work we have given a more satisfactory account of the vibrational effects combined with the Fermi interaction, in an enough simple and in the same time more general model, where the Fermi coupling arises naturally from the change of the molecule frame in a reference configuration which follows the minimum in the potential energy surfaces.

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Part III

Appendix

Appendix A

Coordinates

A.1 The Cartesian Coordinates of the Reference Configuration in the Molecule Fixed Axis System

From Fig.3.1 we define the relations for the φ angle as:

$$\begin{aligned}
\cos\varphi &= -\frac{a_{1x}-a_{2x}}{\sqrt{(a_{1x}-a_{2x})^2+(a_{1y}-a_{2y})^2}} = -\frac{a_{3x}-a_{2x}}{\sqrt{(a_{3x}-a_{2x})^2+(a_{3y}-a_{2y})^2}} \\
\sin\varphi &= \frac{a_{1y}-a_{2y}}{\sqrt{(a_{1x}-a_{2x})^2+(a_{1y}-a_{2y})^2}} = \frac{a_{3y}-a_{2y}}{\sqrt{(a_{3x}-a_{2x})^2+(a_{3y}-a_{2y})^2}}
\end{aligned} \tag{A-1}$$

The angle θ is $\frac{\rho}{2}$ and $p = 1 + \frac{2m_1}{m_2}$, like in eq.(3.4), for a symmetric molecule (which have $m_1 = m_3$).

We define the relation for the angle θ as:

$$\cos\theta = -\frac{a_{1z}-a_{2z}}{r^0} = \frac{a_{3z}-a_{2z}}{r^0} \tag{A-2}$$

With the equations (A-1) and (A-2) we find:

$$\left\{\begin{array}{l} a_{1x} = a_{2x} - r^0\sin\theta\cos\varphi \\ a_{1y} = a_{2y} + r^0\sin\theta\sin\varphi \\ a_{1z} = a_{2z} - r^0\cos\theta \end{array}\right. \quad \left\{\begin{array}{l} a_{3x} = a_{2x} - r^0\sin\theta\cos\varphi \\ a_{3y} = a_{2y} + r^0\sin\theta\sin\varphi \\ a_{3z} = a_{2z} + r^0\cos\theta \end{array}\right. \tag{A-3}$$

The relation for the center of the mass are:

$$\begin{aligned}
m_1a_{1x} + m_2a_{2x} + m_3a_{3x} &= 0 \\
m_1a_{1y} + m_2a_{2y} + m_3a_{3y} &= 0 \\
m_1a_{1z} + m_2a_{2z} + m_3a_{3z} &= 0
\end{aligned} \tag{A-4}$$

If we introduce the relations (A-3) into the equation for the center of mass, we obtain the following expressions:

$$\begin{aligned}
a_{1x} &= -\frac{r^0}{p}\sin\theta\cos\varphi \\
a_{2x} &= \frac{2m_1}{m_2}\cdot\frac{1}{p}r^0\sin\theta\cos\varphi \\
a_{3x} &= -\frac{r^0}{p}\sin\theta\cos\varphi
\end{aligned} \tag{A-5}$$

For the second axis the coordinates are,

$$\begin{aligned}
a_{1y} &= \frac{r^0}{p}\sin\theta\sin\varphi \\
a_{2y} &= -\frac{2m_1}{m_2}\cdot\frac{1}{p}r^0\sin\theta\sin\varphi \\
a_{3y} &= \frac{r^0}{p}\sin\theta\sin\varphi
\end{aligned} \tag{A-6}$$

and for the third axis:

$$\begin{aligned} a_{1z} &= -r^0 \cos\theta \\ a_{2z} &= 0 \\ a_{3z} &= r^0 \cos\theta \end{aligned} \tag{A-7}$$

A.2 The Angular Momentum in the Reference Configuration

We consider that the angular momentum of the reference configuration vanish in the molecule-fixed system:

$$\sum_i \vec{a}(\rho) \times \left(m_i \frac{d\vec{a}}{dt} \right) = 0 \tag{A-8}$$

We introduce the ρ coordinate in the above relation and the angular momentum expression become:

$$\sum_i \vec{a}(\rho) \times \left(m_i \frac{d\vec{a}}{dt} \right) = \sum_i \vec{a}(\rho) \times m_i \left(\frac{d\vec{a}}{d\rho} \right) \cdot \dot{\rho} \tag{A-9}$$

The derivative of ρ to time is simplified and for this reason, the relation for the angular momentum of the reference configuration become:

$$\sum_i m_i \vec{a}(\rho) \times \left(\frac{d\vec{a}}{d\rho} \right) = 0 \tag{A-10}$$

A.3 Displacements for Symmetric and Antisymmetric Stretching

The conditions for the symmetric molecule, when the ν_3 is not excited (Fig.3.1, (a)):

$$\begin{aligned} d^s_{3z} &= -d^s_{1z} \\ d^s_{2z} &= 0 \\ d^s_{3x} &= d^s_{1x} \\ d^s_{3y} &= d^s_{1y} \end{aligned} \tag{A-11}$$

The conditions for the center of mass are:

$$\begin{aligned} m_2 d^s_{2x} + 2m_1 d^s_{1x} = 0 \qquad & d^s_{2x} = -2\frac{m_1}{m_2} \cdot d^s_{1x} \\ m_2 d^s_{2y} + 2m_1 d^s_{1y} = 0 \qquad & d^s_{2y} = -2\frac{m_1}{m_2} \cdot d^s_{1y} \end{aligned} \tag{A-12}$$

The displacement S^s must lie in the molecule plane, due to the Eckart conditions [40]:

$$\frac{d^s_{1y}}{d^s_{1x}} = \frac{a_{1y}}{a_{1x}} \quad \rightarrow \quad \tan\varphi = \frac{d^s_{1y}}{d^s_{1x}} = \frac{a_{1y}}{a_{1x}} \tag{A-13}$$

The other Eckart conditions are already fulfilled through symmetry. The Sayvetz condition of [5, eq.(7c)] become:

$$\begin{aligned} m_1 \left(\frac{\partial a_{1x}}{\partial \rho} d^s_{1x} + \frac{\partial a_{1y}}{\partial \rho} d^s_{1y} + \frac{\partial a_{1z}}{\partial \rho} d^s_{1z} \right) + m_3 \left(\frac{\partial a_{3x}}{\partial \rho} d^s_{3x} + \frac{\partial a_{3y}}{\partial \rho} d^s_{3y} + \frac{\partial a_{3z}}{\partial \rho} d^s_{3z} \right) & \\ + m_2 \left(\frac{\partial a_{2x}}{\partial \rho} d^s_{2x} + \frac{\partial a_{2y}}{\partial \rho} d^s_{2y} + \frac{\partial a_{2z}}{\partial \rho} d^s_{2z} \right) &= 0 \end{aligned} \tag{A-14}$$

The previous condition means in essence that $\vec{S}^s$ and $\frac{\partial \vec{r}_\rho}{\partial \rho}$ are "at right angles" which ensures the separations of bending and stretching. If we use the equations (3.3) and (A-11)-(A-12), we find the relation:

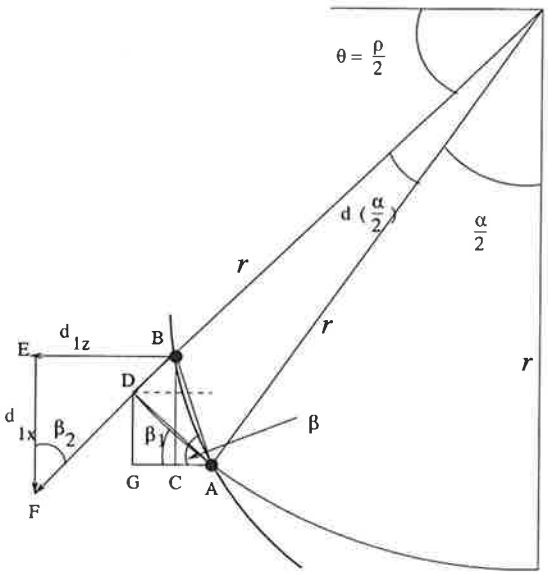
$$\left.\begin{aligned} &\left(\tfrac{r_\rho}{2}\cos\theta + r'_\rho \sin\theta\right) d^s_{1x} \cos\varphi + \left(\tfrac{r_\rho}{2}\cos\theta + r'_\rho \sin\theta\right) d^s_{1y} \sin\varphi \\ &- \left(\tfrac{r_\rho}{2}\cos\theta + r'_\rho \sin\theta\right) d^s_{1z} \cos\varphi = 0 \end{aligned}\right\} \Rightarrow \tag{A-15}$$

$$\left(\frac{r_\rho}{2}\cos\theta + r'_\rho \sin\theta\right)\left(d^s_{1x}\cos\varphi + d^s_{1z}\sin\varphi\right) = \left(\frac{r_\rho}{2}\sin\theta - r'_\rho\cos\theta\right) d^s_{1z} \tag{A-16}$$

and then the final displacement as function of the stretching coordinate are:

$$\begin{aligned} d^s_{1x} &= -\left(\sin\theta - 2\frac{r'_\rho}{r_\rho}\cos\theta\right)\frac{S^s}{\sqrt{2}}\cdot\cos\varphi \\ d^s_{1y} &= \left(\sin\theta - 2\frac{r'_\rho}{r_\rho}\cos\theta\right)\frac{S^s}{\sqrt{2}}\cdot\sin\varphi \\ d^s_{1z} &= -\left(\cos\theta + 2\frac{r'_\rho}{r_\rho}\sin\theta\right)\frac{S^s}{\sqrt{2}} \end{aligned} \tag{A-17}$$

The factor $\frac{1}{\sqrt{2}}$ is for normalization. From the previous equation and equations (A-11), we find the expressions for all the displacements due to the symmetric stretching coordinate. A geometrical approach for the displacement coordinates is in Fig.A.1.



The relations between displacement coordinates is:

$$\frac{d_{1z}}{d_{1x}} = \frac{\cos\theta + \frac{2r'}{r}\sin\theta}{\sin\theta - \frac{2r'}{r}\cos\theta}$$

Proof: for infinitesimal variations, $d\left(\frac{\alpha}{2}\right) \to 0$,
$\beta_1 = \beta_2$ ($FD \perp AD$ and $EB \perp DG$)
$\beta_1 \simeq \beta$ (infinitesimal variations)
$AD = \frac{r}{2}d\rho$ (length of arc)
$BD = r'd\rho$ (semirigid bender approx.)
$AG = AD\cos\beta_1 \quad DG = AD\sin\beta_1$
$BC = BD\cos\beta_2 + DG$
$AC = AG - BD\sin\beta_1$
$\Delta ABC \sim \Delta BEF$ ($FB \perp AB$ and $EB \perp BC$)
$\to \frac{d_{1z}}{d_{1x}} = \frac{BC}{AC}$
q.e.d.

Figure A.1: Geometrical representation of the displacement coordinates in the approximation of the semirigid bender approach (see eq.(A-17)).

The conditions for the symmetric molecule, when the ν_1 is not excited (Fig.3.1, (b)):

$$\begin{aligned} d^a_{3z} &= d^a_{1z} \\ d^a_{2x} &= 0 \\ d^a_{2y} &= 0 \\ d^a_{3x} &= -d^a_{1x} \\ d^a_{3y} &= -d^a_{1y} \end{aligned} \tag{A-18}$$

The conditions for the center of mass are:

$$m_2\, d^a_{2z} + 2m_1\, d^s_{1z} = 0 \quad \to \quad d^a_{2z} = -2\frac{m_1}{m_2} d^a_{1z} \tag{A-19}$$

The displacement in the molecular plane S^a is obtained by taking into account the condition:

$$\frac{d^a_{1y}}{d^a_{1x}} = -\frac{a_{1y}}{a_{1x}} \tag{A-20}$$

The Sayvetz condition from [5, eq.(7c)] become:

$$\begin{aligned} m_1\left(\frac{\partial a_{1x}}{\partial\rho}d^a_{1x} + \frac{\partial a_{1y}}{\partial\rho}d^a_{1y} + \frac{\partial a_{1z}}{\partial\rho}d^a_{1z}\right) + m_3\left(\frac{\partial a_{3x}}{\partial\rho}d^a_{3x} + \frac{\partial a_{3y}}{\partial\rho}d^a_{3y} + \frac{\partial a_{3z}}{\partial\rho}d^a_{3z}\right) \\ + m_2\left(\frac{\partial a_{2x}}{\partial\rho}d^a_{2x} + \frac{\partial a_{2y}}{\partial\rho}d^a_{2y} + \frac{\partial a_{2z}}{\partial\rho}d^a_{2z}\right) = 0 \end{aligned} \tag{A-21}$$

The previous equation vanishes identically. Taking into account (A-18), and similar with eq.(A-17) we assume that:

$$\begin{aligned} d^a_{1x} &= -\left(\sin\theta - 2\frac{r'_\rho}{r_\rho}\cos\theta\right)\frac{S^a}{\sqrt{2}}\cdot\cos\varphi \\ d^a_{1y} &= \left(\sin\theta - 2\frac{r'_\rho}{r_\rho}\cos\theta\right)\frac{S^a}{\sqrt{2}}\cdot\sin\varphi \\ d^a_{1z} &= -\left(\cos\theta + 2\frac{r'_\rho}{r_\rho}\sin\theta\right)\frac{S^a}{\sqrt{2}} \end{aligned} \tag{A-22}$$

The factor $\frac{1}{\sqrt{2}}$ is for normalization. From the previous equation and equations (A-18), we find the expressions for all the displacements due to the antisymmetric stretching coordinate. The relation between symmetric and antisymmetric displacements, $\vec{d}^s$, and $\vec{d}^a$ and the total displacements $\vec{d}$ is:

$$\vec{d}_i = \vec{d}^s_i + \vec{d}^a_i$$

A.4 The Derivative of the Bending Angle to the Stretching Coordinates

First we will analyze the derivative to the antisymmetric stretching coordinate. From Fig.A.2, we obtain the relation (here we will use ρ instead of $\bar{\rho}$ for the instantaneous bending angle),

$$\rho = -\arctan\frac{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2}}{z_1-z_2} + \arctan\frac{\sqrt{(x_3-x_2)^2+(y_3-y_2)^2}}{z_3-z_2} \tag{A-23}$$

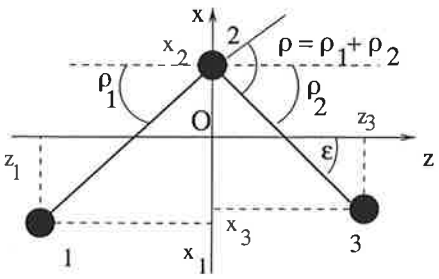


Figure A.2: Geometrical configuration need to obtain the relations between the ρ coordinate and the cartesian ones.

From the previous equation and equations (3.10) we have:

$$\begin{aligned} &\left(\tfrac{\partial\rho}{\partial x_1}\right)_0 = \left(\tfrac{\partial\rho}{\partial x_3}\right)_0 \\ &\left(\tfrac{\partial\rho}{\partial y_1}\right)_0 = \left(\tfrac{\partial\rho}{\partial y_3}\right)_0 \qquad \tfrac{\partial x_1}{\partial S^a} = -\tfrac{\partial x_3}{\partial S^a} \qquad \tfrac{\partial x_2}{\partial S^a} = 0 \\ &\left(\tfrac{\partial\rho}{\partial z_1}\right)_0 = -\left(\tfrac{\partial\rho}{\partial z_3}\right)_0 \qquad \tfrac{\partial y_1}{\partial S^a} = -\tfrac{\partial y_3}{\partial S^a} \qquad \tfrac{\partial y_2}{\partial S^a} = 0 \\ &\left(\tfrac{\partial\rho}{\partial z_2}\right)_0 = 0 \qquad \tfrac{\partial z_1}{\partial S^a} = \tfrac{\partial z_3}{\partial S^a} \qquad \tfrac{\partial z_2}{\partial S^a} = -\tfrac{2m_1}{m_2}\left(\tfrac{\partial z_1}{\partial S^a}\right) \end{aligned} \tag{A-24}$$

Now we can compute the derivative:

$$\begin{aligned} \left(\frac{\partial\rho}{\partial S^a}\right) &= \frac{\partial\rho}{\partial x_1}\cdot\frac{\partial x_1}{\partial S^a} + \frac{\partial\rho}{\partial x_3}\cdot\frac{\partial x_3}{\partial S^a} + \frac{\partial\rho}{\partial y_1}\cdot\frac{\partial y_1}{\partial S^a} + \frac{\partial\rho}{\partial y_3}\cdot\frac{\partial y_3}{\partial S^a} \\ &+ \frac{\partial\rho}{\partial z_1}\cdot\frac{\partial z_1}{\partial S^a} + \frac{\partial\rho}{\partial z_3}\cdot\frac{\partial z_3}{\partial S^a} \\ &= \left(\frac{\partial\rho}{\partial x_1} - \frac{\partial\rho}{\partial x_3}\right)\frac{\partial x_1}{\partial S^a} + \left(\frac{\partial\rho}{\partial y_1} - \frac{\partial\rho}{\partial y_3}\right)\frac{\partial y_1}{\partial S^a} + \left(\frac{\partial\rho}{\partial z_1} + \frac{\partial\rho}{\partial z_3}\right)\frac{\partial z_1}{\partial S^a} \\ &= 0 \end{aligned} \tag{A-25}$$

For the symmetric stretching coordinate, eq.(A-23) may be written as:

$$\left.\begin{array}{l}\rho^0 = 2\arctan p\frac{\sqrt{(x_1^0)^2+(y_1^0)^2}}{z_1^0} \\ \rho = 2\arctan p\frac{\sqrt{(x_1)^2+(y_1)^2}}{z_1}\end{array}\right\} \quad \rho = \rho^0 + \left(\frac{\partial\rho}{\partial S^s}\right)_0 \cdot S^s \tag{A-26}$$

We express the derivative of ρ as function of the symmetric coordinate:

$$\begin{aligned}\frac{\partial\rho}{\partial S^s} &= \frac{\partial\rho}{\partial x_1}\frac{\partial x_1}{\partial S^s} + \frac{\partial\rho}{\partial y_1}\frac{\partial y_1}{\partial S^s} + \frac{\partial\rho}{\partial z_1}\frac{\partial z_1}{\partial S^s} \\ &= \frac{2pz_1^2}{z_1^2 + p^2\left(x_1^2+y_1^2\right)} \cdot \left[\frac{x_1}{z_1}\frac{1}{\sqrt{x_1^2+y_1^2}}\frac{\partial x_1}{\partial S^s} + \frac{y_1}{z_1}\frac{1}{\sqrt{x_1^2+y_1^2}}\frac{\partial y_1}{\partial S^s}\right. \\ &- \left.\frac{\sqrt{x_1^2+y_1^2}}{z_1^2}\frac{\partial z_1}{\partial S^s}\right]\end{aligned} \tag{A-27}$$

If we introduce the ρ coordinate, the above derivative become:

$$\frac{\partial\rho}{\partial S^s} = \frac{2p}{\sqrt{2}\,r^0}\cos\theta\left(\sin\theta - \frac{2r'_\rho}{r_\rho}\cos\theta\right) - \frac{2}{\sqrt{2}\,r_\rho}\sin\theta\left(\cos\theta + \frac{2r'_\rho}{r_\rho}\sin\theta\right) \tag{A-28}$$

The derivative of ρ as function of S^s, near 0 is:

$$\begin{aligned}\frac{\partial\rho}{\partial S^s}|_0 &= \frac{2}{\sqrt{2}\,r_\rho}(p-1)\sin\theta\cos\theta - \frac{4r'_\rho}{\sqrt{2}\,r_\rho^2}\left(p\cos^2\theta + \sin^2\theta\right) \\ &= -\frac{1}{\sqrt{2}\,r_\rho}R_2(r_\rho\,,\rho)\end{aligned} \tag{A-29}$$

For small values of ρ, $R_2(r_\rho\,,\rho) < 0$, which means that the derivative is positive.

A.5 The Change of the Bond Length from the Reference Configuration as Function of the Stretching Coordinates in the Stretch-Bender Model

The bond length for the atoms 1 and 2, expressed in Cartesian coordinates is:

$$r_{12} = \sqrt{(x_1 - x_2) + (y_1 - y_2) + (z_1 - z_2)} \tag{A-30}$$

By taking into account the equations (3.10), we are obtaining from the bond length the formula:

$$r_{12} = r_{12}^0(\rho)\sqrt{1 + 2\left(\frac{S^s}{\sqrt{2}\,r_{12}^0}R_1\left(r^0,\rho\right) + \frac{S^a}{\sqrt{2}\,r_{12}^0}R_5\left(r^0,\rho\right)\right) + \mathcal{O}\left((S^s)^2\,,(S^a)^2\right)} \tag{A-31}$$

with $R_1\left(r^0,\rho\right)$, $R_5\left(r^0,\rho\right)$ from (3.16).

Similar with above, the bond length between the atoms 2 and 3 is given, in Cartesian coordinates, by:

$$r_{23} = \sqrt{(x_2 - x_3) + (y_2 - y_3) + (z_2 - z_3)} \tag{A-32}$$

By taking into account the equations (3.10), we are obtaining from the bond length the formula:

$$r_{23} = r_{23}^0(\rho)\sqrt{1 + 2\left(\frac{S^s}{\sqrt{2}\,r_{23}^0}R_1\left(r^0,\rho\right) - \frac{S^a}{\sqrt{2}\,r_{23}^0}R_5\left(r^0,\rho\right)\right) + \mathcal{O}\left((S^s)^2\,,(S^a)^2\right)} \tag{A-33}$$

If we are expanding in power series the square root, we are obtaining, by taking into account only the terms of the first order:

$$\begin{array}{l}\sqrt{1 + 2\left(\frac{S^s}{\sqrt{2}\,r_{12}^0}R_1\left(r^0,\rho\right) + \frac{S^a}{\sqrt{2}\,r_{12}^0}R_5\left(r^0,\rho\right)\right) + \mathcal{O}\left((S^s)^2\,,(S^a)^2\right)} \approx \\ 1 + \left(\frac{S^s}{\sqrt{2}\,r_{12}^0}R_1\left(r^0,\rho\right) + \frac{S^a}{\sqrt{2}\,r_{12}^0}R_5\left(r^0,\rho\right)\right) + \mathcal{O}\left((S^s)^2\,,(S^a)^2\right) + \ldots\end{array} \tag{A-34}$$

The change of the bond length corresponding the atoms 1 and 2 is, in this approximation:

$$\Delta r_1 = r_{12} - r_{12}^0(\rho) \approx \frac{1}{\sqrt{2}} R_1\left(r^0, \rho\right) S^s + \frac{1}{\sqrt{2}} R_5\left(r^0, \rho\right) S^a \tag{A-35}$$

In a similar manner we are obtaining the formula for the change of the bond length corresponding to the atoms 2 and 3 and we will obtain the second equation of (3.13):

$$\Delta r_3 = r_{23} - r_{23}^0(\rho) \approx \frac{1}{\sqrt{2}} R_1\left(r^0, \rho\right) S^s - \frac{1}{\sqrt{2}} R_5\left(r^0, \rho\right) S^a \tag{A-36}$$

A.6 The Derivative of the Stretching Coordinates in the Reference Frame

In order to evaluate the derivatives of the stretching coordinates in the reference frame: $\frac{\partial \bar{S}^s}{\partial \rho}$ and $\frac{\partial \bar{S}^a}{\partial \rho}$ we will consider the change of the bond length and its derivative, as function of the bending coordinate from (3.1):

$$r(\rho) = r^e + \mathcal{R}(\rho) \quad \text{and} \quad r'(\rho) = \mathcal{R}'(\rho)$$

We will consider the change of the bond length for the atoms (1,2) or (2,3), by using the formula (A-35) and (A-36) from the appendix (§A.5).

In the case of the infinitesimal displacements we have, for the bending angle: $\rho = \rho_0 + d\rho$ where ρ_0 is the bending angle for a reference configuration and $d\rho$ is the infinitesimal displacement.

For the reference bond length (from §A.5) we have: $r_{i2}^0 = r(\rho_0)$ and $r_{i2} = r(\rho)$ with i =1,3.

If we are introducing the formula (3.1) into the relations (A-35 and A-36) we will obtain the relations which characterize the changing of the bond length with the angle:

$$\begin{aligned} \mathcal{R}\left(\rho_0 + d\rho\right) - \mathcal{R}\left(\rho_0\right) &\approx \frac{1}{\sqrt{2}} \left[R_1(\rho_0) d\bar{S}^s + R_5(\rho) d\bar{S}^a\right] \\ \mathcal{R}\left(\rho_0 + d\rho\right) - \mathcal{R}\left(\rho_0\right) &\approx \frac{1}{\sqrt{2}} \left[R_1(\rho_0) d\bar{S}^s - R_5(\rho) d\bar{S}^a\right] \end{aligned} \tag{A-37}$$

Because we have: $\mathcal{R}\left(\rho + d\rho\right) - \mathcal{R}\left(\rho\right) = \mathcal{R}'\left(\rho\right) d\rho$, we can use this relation in (A-37) and we will obtain:

$$\begin{aligned} \mathcal{R}'\left(\rho\right) d\rho &= \frac{1}{\sqrt{2}} \left[R_1(\rho_0)\, d\bar{S}^s + R_5(\rho)\, d\bar{S}^a\right] \\ \mathcal{R}'\left(\rho\right) d\rho &= \frac{1}{\sqrt{2}} \left[R_1(\rho_0)\, d\bar{S}^s - R_5(\rho)\, d\bar{S}^a\right] \end{aligned} \tag{A-38}$$

By analyzing the relations (A-38) we can obtain the derivatives of the stretching coordinates (3.15):

$$\left(\frac{\partial \bar{S}^s}{\partial \rho}\right)_0 = \sqrt{2}\, \frac{\mathcal{R}'(\rho_0)}{R_1(\rho_0)} \quad \text{and} \quad \left(\frac{\partial \bar{S}^a}{\partial \rho}\right)_0 = 0 \tag{A-39}$$

A.7 The Conversion from the Displacements in the Reference Frame to the Stretching Generalized Coordinates

The stretching generalized coordinates are defined in [6, page 7] as:

$$\begin{aligned} \mathbf{R}^1 &= r_{12} - r_{12}^e \\ \mathbf{R}^3 &= r_{23} - r_{23}^e \end{aligned} \tag{A-40}$$

If we will introduce in eq. (3.13) the value of the bond length for the reference point in the semirigid bender approach (3.1), we will obtain:

$$\begin{aligned} \Delta r_1 &= r_{12} - [r_{12}^e + \mathcal{R}_{12}(\rho)] \\ \Delta r_3 &= r_{23} - [r_{23}^e + \mathcal{R}_{23}(\rho)] \end{aligned} \tag{A-41}$$

We will introduce in the previous relations, the formula for $\mathbf{R}^i$ as in (A-40) and we will get the relations (3.19):

$$\Delta r_{i2} = \Delta r_i + \mathcal{R}_{i2}(\rho)$$

with $i = 1, 3$ and $\Delta r_{i2} = \mathbf{R}^i$.

Let take a closer look on the previous formula. In fact, we will consider the generalized displacements in two different formulas and we prove that they are equivalent in our approximation.

Using eq. (3.13), (3.14), (A-39) and (A-37) - (A-38), we have:

$$\begin{aligned}
\Delta r_{12} &= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s + R_5\left(r^0,\rho\right)S^a\right] + \mathcal{R}_{12}\left(\rho\right) \\
&\approx \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s + R_5\left(r^0,\rho\right)S^a\right] + \mathcal{R}_{12}\left(\rho_e\right) + \mathcal{R}'_{12}\left(\rho\right)\ \left(\rho-\rho_e\right) \\
&= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s + R_5\left(r^0,\rho\right)S^a\right] + \frac{R_1(\rho)}{\sqrt{2}}\sqrt{2}\frac{\mathcal{R}'_{12}\left(\rho\right)}{\sqrt{2}R_1}\left(\rho-\rho_e\right) + \mathcal{R}_{12}\left(\rho_e\right) \\
&= \frac{1}{\sqrt{2}}\left\{R_1\left[S^s + \sqrt{2}\frac{\mathcal{R}'_{12}\left(\rho\right)}{R_1}\left(\rho-\rho_e\right)\right] + R_5\left(r^0,\rho\right)S^a\right\} + \mathcal{R}_{12}\left(\rho_e\right) \qquad \text{(A-42)} \\
&= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)\bar{S}^s + R_5\left(r^0,\rho\right)\bar{S}^a\right] + \mathcal{R}_{12}\left(\rho_e\right)
\end{aligned}$$

In a similar way we found that

$$\begin{aligned}
\Delta r_{32} &= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)S^s - R_5\left(r^0,\rho\right)S^a\right] + \mathcal{R}_{32}\left(\rho\right) \\
&= \frac{1}{\sqrt{2}}\left[R_1\left(r^0,\rho\right)\bar{S}^s - R_5\left(r^0,\rho\right)\bar{S}^a\right] + \mathcal{R}_{32}\left(\rho_e\right) \qquad \text{(A-43)}
\end{aligned}$$

In the previous formulas, we can see the way the instantaneous and the reference coordinates are considered together. We have to verify the limits of this approach, using eq. (3.11) and (3.12), in the formula

$$\mathcal{R}_{i2}\left(\rho\right) = \mathcal{R}_{i2}\left(\rho_e\right) + \mathcal{R}'_{i2}\left(\rho\right)\ \left(\rho-\rho_e\right)$$

We shall consider for the $\mathcal{R}\left(\rho\right)$ a quadratic dependence with ρ,

$$\mathcal{R}_{i2}\left(\rho\right) = d_i\,\rho^2$$

Then, we have (with eq.(3.25)):

$$\begin{aligned}
\mathcal{R}_{i2}\left(\rho\right) &= d_i\left(\rho - \frac{R_2|_{\rho_e\to 0}\,\rho}{\sqrt{2}r}S^s\right)^2 \qquad \text{(A-44)} \\
&= d_i\rho^2\left[1 - \sqrt{2}\frac{R_2|_{\rho_e\to 0}}{r}S^s + \frac{\left(R_2|_{\rho_e\to 0}\right)^2}{2r^2}\left(S^s\right)^2\right] \qquad \text{(A-45)}
\end{aligned}$$

and

$$\mathcal{R}_{i2}\left(\rho\right) + \mathcal{R}'_{i2}\left(\rho\right)\ \left(\rho-\rho_e\right) = d_i\rho^2\left(1 - \sqrt{2}\frac{R_2|_{\rho_e\to 0}}{r}S^s\right) \qquad \text{(A-46)}$$

We have from the previous two equations,

$$\mathcal{R}_{i2}\left(\rho\right)|_{\rho_e\to 0} - \left[\mathcal{R}_{i2}\left(\rho\right) + \mathcal{R}'_{i2}\left(\rho\right)\ \left(\rho-\rho_e\right)\right]|_{\rho_e\to 0} \approx \mathcal{O}\left(\left(S^s\right)^2\right) \qquad \text{(A-47)}$$

We see that in our degree of approximation, these equations are equivalents.

A.8 Conversion Relations between the Stretching Coordinates of the Semi-Rigid Bender Model and Generalized Valence Stretching Coordinates

In order to get the conversion relations between the stretching coordinates of the semirigid bender model and generalized valence stretching coordinates we will take into account the atom 2 , because it's both of stretching coordinates are orthogonal. We can consider for this calculus neither the atom 1, because for it, both vibrations are added, nor the atom 3 because for it, the S^s is added and the S^a is subtracted. We will consider the A matrix from [6] which is defined is such a way that there are negative values for the displacement d_{2y} (connected with positive values for the y coordinates of the atoms 1 and 3). In our

reference system, the y values for the atoms 1 and 3 are negatives and the d_{2y} displacement is positive. The displacements of the atom 2 corresponding to the symmetric stretching coordinate, with A matrix and in our formalism are:

$$\begin{aligned} d_{2y} &= -\left\{ -\frac{\left[m_1\left(m_2+m_3\right)\sin\frac{\rho}{2}+m_1 m_3\cos\rho\sin\frac{\rho}{2}\right]}{D} S_1^{Jen} \right. \\ &- \left. \frac{\left[m_1 m_3\cos\rho\sin\frac{\rho}{2}+m_3\left(m_1+m_2\right)\sin\frac{\rho}{2}\right]}{D} S_3^{Jen} \right\} \\ &= \frac{2m_1}{m_2}\left(\sin\frac{\rho}{2}+\frac{2r'}{r}\cos\frac{\rho}{2}\right)\frac{S^s}{\sqrt{2}} \end{aligned} \tag{A-48}$$

The matrix A is calculated for $r \not= f(\rho)$ and for this reason the second term in the parenthesis, from the right side of the equation (A-48) will vanish.

If we are considering $m_1 = m_3$ we can obtain the formula for S^s from the eq. (A-48):

$$S^s = \frac{1}{\sqrt{2}}\frac{m_2\left[m_2+m_1\left(1+\cos\rho\right)\right]}{D}\cdot\left(S_1^{Jen}+S_3^{Jen}\right) \tag{A-49}$$

We will do a similar calculus in order to obtain the relation for the antisymmetric coordinate S^a. The symmetric displacement d_{2z} vanishes and this imply $S_1^{Jen} = S_3^{Jen}$. The same relation is obtained by using the antisymmetric displacement d_{2y} which vanishes too.

The displacements of the atom 2 corresponding to the anti-symmetric stretching coordinate are:

$$\begin{aligned} d_{2z} &= \frac{1}{D}\left\{\left[m_1\left(m_2+m_3\right)\cos\frac{\rho}{2}-m_1 m_3\cos\rho\cos\frac{\rho}{2}\right]S_1^{Jen} \right. \\ &- \left. \left[m_1 m_3\cos\rho\cos\frac{\rho}{2}-m_3\left(m_1 m_2\right)\cos\frac{\rho}{2}\right]S_3^{Jen}\right\} \\ &= +\frac{2m_1}{m_2}\left(\cos\frac{\rho}{2}+\frac{2r'}{r}\sin\frac{\rho}{2}\right)\cdot\frac{S^a}{\sqrt{2}} \end{aligned} \tag{A-50}$$

The same consideration for the matrix A, as above, will determine the second term in the parenthesis, from the right side of the equation (A-48) will vanish.

If we are considering that $m_1 = m_3$ we can obtain the formula for S^a from the eq. (A-50):

$$S^a = \frac{1}{\sqrt{2}}\frac{m_2\left[m_2+m_1\left(1-\cos\rho\right)\right]}{D}\cdot\left(S_1^{Jen}-S_3^{Jen}\right) \tag{A-51}$$

In both formula (A-49), (A-51) the definition for D is the same as in [7, 186]:

$$D = m_2\left(2m_1+m_2\right)+m_1^2\sin^2\rho = m_2^2 p + m_1^2\sin^2\rho$$

We can obtain the formula for S_1^{Jen} and S_3^{Jen} by using the eq.(A-49,A-51):

$$\begin{aligned} S_1^{Jen} &= \frac{1}{\sqrt{2}}\left[\frac{D}{m_2\left[m_2+m_1\left(1+\cos\rho\right)\right]}\cdot S^s+\frac{D}{m_2\left[m_2+m_1\left(1-\cos\rho\right)\right]}\cdot S^a\right] \\ S_3^{Jen} &= \frac{1}{\sqrt{2}}\left[\frac{D}{m_2\left[m_2+m_1\left(1+\cos\rho\right)\right]}\cdot S^s-\frac{D}{m_2\left[m_2+m_1\left(1-\cos\rho\right)\right]}\cdot S^a\right] \end{aligned} \tag{A-52}$$

We will introduce the definition of D in the relations (A-51) and we will get the conversion relations between the Cartesian vibrational coordinates S^s and S^a and the coordinates S_1^{Jen} and S_3^{Jen}, used by [6, 7] to define the A matrix for a general triatomic molecule:

$$\begin{aligned} S_1^{Jen} &= \frac{1}{\sqrt{2}}\frac{1}{m_2^2}\left\{m_2\left[m_2+m_1\left(1-\cos\rho\right)\right]\cdot S^s+m_2\left[m_2+m_1\left(1+\cos\rho\right)\right]\cdot S^a\right\} \\ S_3^{Jen} &= \frac{1}{\sqrt{2}}\frac{1}{m_2^2}\left\{m_2\left[m_2+m_1\left(1-\cos\rho\right)\right]\cdot S^s-m_2\left[m_2+m_1\left(1+\cos\rho\right)\right]\cdot S^a\right\} \end{aligned} \tag{A-53}$$

If we introduce the relation for the coefficient p, we have:

$$\frac{m_1}{m_2} = \frac{(p-1)}{2} \tag{A-54}$$

the above transformations relations (A-53) will be:

$$\begin{aligned} S_1^{Jen} &= \frac{1}{\sqrt{2}}\left\{\left[\frac{p+1}{2}-\frac{p-1}{2}\cos\rho\right]\cdot S^s+\left[\frac{p+1}{2}+\frac{p-1}{2}\cos\rho\right]\cdot S^a\right\} \\ S_3^{Jen} &= \frac{1}{\sqrt{2}}\left\{\left[\frac{p+1}{2}-\frac{p-1}{2}\cos\rho\right]\cdot S^s-\left[\frac{p+1}{2}+\frac{p-1}{2}\cos\rho\right]\cdot S^a\right\} \end{aligned} \tag{A-55}$$

In the case of the symmetric transformation and $r'=0$, from eq.(3.16), R_3 and R_4 functions have the formula:

$$\begin{aligned} R_3|_{r'=0} &= \frac{1}{2}\left[(p+1)-(p-1)\cos\rho\right] \\ R_4|_{r'=0} &= \frac{1}{2}\left[(p+1)+(p-1)\cos\rho\right] \end{aligned} \tag{A-56}$$

We will introduce the above relations into the transformation equations (A-55) and we will get the final relations for the Jensen's coordinates:

$$\begin{aligned} S_1^{Jen} &= \frac{1}{\sqrt{2}}\left[R_3\cdot S^s+R_4\cdot S^a\right] \\ S_3^{Jen} &= \frac{1}{\sqrt{2}}\left[R_3\cdot S^s-R_4\cdot S^a\right] \end{aligned} \tag{A-57}$$

A.9 Relations between the Stretching Coordinates and S_1 , S_3 from [6]

We will obtain the dependence of S_1 and S_3 coordinates in our formalism as function of the coordinates S_1^{Jen} and S_3^{Jen} from [6] by using the relations (A-49) and (A-51)

$$\begin{aligned} S_1 &= \frac{1}{\sqrt{2}}\left(S^s+S^a\right)=\frac{1}{2D}\left[\left(2m_2^2+2m_1m_2\right)S_1^{Jen}+2m_1m_2\cos\rho S_3^{Jen}\right] \\ &= \frac{m_2}{D}\left[\left(m_1+m_2\right)S_1^{Jen}+\left(m_1\cos\rho\right)S_3^{Jen}\right] \end{aligned} \tag{A-58}$$

$$S_3=\frac{1}{\sqrt{2}}\left(S^s-S^a\right)=\frac{m_2}{D}\left[\left(m_1\cos\rho\right)\ S_1^{Jen}+\left(m_1+m_2\right)S_3^{Jen}\right] \tag{A-59}$$

If we are considering the above relations in a matrix form we will have: $S=\hat{C}S^{Jen}$ where

$$\hat{C}=\begin{pmatrix} \frac{m_2}{D}\left(m_1+m_2\right) & \frac{m_1m_2}{D}\cos\rho \\ \frac{m_1m_2}{D}\cos\rho & \frac{m_2}{D}\left(m_1+m_2\right) \end{pmatrix} \tag{A-60}$$

The $\tilde{A}$ matrix, obtained from (3.8) and defined in a similar manner with the $\hat{A}$ matrix from [7] is (in the rigid-bender limit):

$$\tilde{A}|_{\substack{r'=0\\ \varphi=0}}=\begin{pmatrix} -\sin\theta & 0 \\ \sin\theta & 0 \\ -\cos\theta & 0 \\ \frac{m_1}{m_2}\sin\theta & \frac{m_1}{m_2}\sin\theta \\ -\frac{m_1}{m_2}\sin\theta & -\frac{m_1}{m_2}\sin\theta \\ \frac{m_1}{m_2}\cos\theta & -\frac{m_1}{m_2}\cos\theta \\ 0 & -\sin\theta \\ 0 & \sin\theta \\ 0 & \cos\theta \end{pmatrix} \tag{A-61}$$

As we know, from [5, 6], the relation between the displacements d_i and the coordinates S^{Jen} is: $d=\hat{A}\,S^{Jen}$. We has a similar relation $d=\tilde{A}\,S$.

The relations above together with the (A-60) let us to obtain the connection between the two matrix:$\hat{A}$ and $\tilde{A}$:

$$\hat{A}=\tilde{A}\cdot\hat{C} \tag{A-62}$$

A.10 Behavior of the $R_1(r^0,\rho)\ -\ R_5(r^0,\rho)$ near $\rho \to 0$

If we are considering the definitions of the functions from (3.16) and $r(\rho) = r_0 + d_r\rho^2$, we will have in the second order expansions in ρ ($\cos x \approx 1 - \frac{x^2}{2}$ and $\sin x \approx x$):

$$R_1|_{\rho\to 0} \simeq 1 + \rho^2\left[-\frac{1}{4} + \frac{p}{4} - \frac{2d_r(p-1)}{r_0}\right] = 1 + R_1^\rho\frac{\rho^2}{4} \tag{A-63}$$

where $R_1^\rho = \left[p - 1 - 2(p-1)\frac{4d_r}{r_0}\right]$

$$R_5|_{\rho\to 0} \simeq p + \rho^2\left[\frac{1}{4} - \frac{p}{4} + \frac{2d_r(p-1)}{r_0}\right] = p + R_5^\rho\frac{\rho^2}{4} \tag{A-64}$$

where $R_5^\rho = \left[1 - p + 2(p-1)\frac{4d_r}{r_0}\right]$

It can be seen that $R_1^\rho = -R_5^\rho$, from the above relations.

$$R_3|_{\rho\to 0} \simeq 1 + \rho^2\left[-\frac{1}{4} + \frac{p}{4} - 4(p-1)\frac{d_r}{r_0} + 16p\left(\frac{d_r}{r_0}\right)^2\right] = 1 + R_3^\rho\frac{\rho^2}{4} \tag{A-65}$$

where $R_3^\rho = \left[p - 1 - 4(p-1)\frac{4d_r}{r_0} + 4p\left(\frac{4d_r}{r_0}\right)^2\right]$

$$R_4|_{\rho\to 0} \simeq p + \rho^2\left[\frac{1}{4} - \frac{p}{4} + 4(p-1)\frac{d_r}{r_0} + 16\left(\frac{d_r}{r_0}\right)^2\right] = p + R_4^\rho\frac{\rho^2}{4} \tag{A-66}$$

where $R_4^\rho = \left[1 - p + 4(p-1)\frac{4d_r}{r_0} + 4\left(\frac{4d_r}{r_0}\right)^2\right]$

$$R_2|_{\rho\to 0} \simeq \rho\left[-(p-1) + 2p\frac{4d_r}{r_0}\right] = -R_2^\rho\rho \tag{A-67}$$

where $R_2^\rho = \left[(p-1) - 2p\frac{4d_r}{r_0}\right]$

A.11 Transformation from Curvilinear to Generalized Stretching Coordinates for $\rho \to 0$

In order to obtain the inverse transformation, from the Jensen's coordinates to the vibrational coordinates, we will begin with the relations (A-49) and will consider the relation (A-54).The inverse transformation relations will be:

$$S^s = \left[\frac{1 + \frac{p-1}{2}(1+\cos\rho)}{p + \left(\frac{p-1}{2}\right)^2\sin^2\rho}\right]\cdot(S^s)^{Jen} \tag{A-68}$$

where $(S^s)^{Jen} = \frac{1}{\sqrt{2}}\left(S_1^{Jen} + S_3^{Jen}\right)$ and $(S^a)^{Jen} = \frac{1}{\sqrt{2}}\left(S_1^{Jen} - S_3^{Jen}\right)$.

In the case then $\rho \to 0$ it is possible to approximate $\sin\rho \approx \rho$ and the relation (A-68) will be:

$$S^s \approx \left[\frac{\frac{p+1}{2} + \frac{p-1}{2}\left(1 - \frac{\rho^2}{2}\right)}{p + \left(\frac{p-1}{2}\right)\rho^2}\right]\cdot(S^s)^{Jen} = \left[\frac{1 + \left(\frac{p-1}{4p}\right)\rho^2}{1 + \frac{1}{p}\left(\frac{p-1}{2}\right)^2\rho^2}\right]\cdot(S^s)^{Jen} \tag{A-69}$$

If we are expanding in power series up to the first order the denominator of the expression below, S^s will be approximated as:

$$S^s \approx \left[1 - \left(\frac{p-1}{4}\right)\rho^2\right]\cdot(S^s)^{Jen} \tag{A-70}$$

Similarly, from (A-51) we can deduce the transformation relation for the antisymmetric coordinate.

$$S^a = \frac{\left[\frac{p+1}{2} - \frac{p-1}{2}\cos\rho\right]}{\left[p + \left(\frac{p-1}{2}\right)^2\sin^2\rho\right]}\cdot(S^a)^{Jen} \tag{A-71}$$

In the case then $\rho \to 0$ and by expanding in power series the denominator until the first order, the relation of the transformation become:

$$S^a \approx \frac{1}{p}\left[1+\left(\frac{p-1}{4p}\right)\rho^2\right]\cdot(S^a)^{Jen} \tag{A-72}$$

If we consider the relations for R_1 and R_5 from (§A.10), and the formulas (3.13), (3.21) in the rigid bender limit, the inverse conversion transformation become:

$$\begin{aligned} S^s &= \frac{1}{R_1}(S^s)^{Jen} \\ S^a &= \frac{1}{R_5}(S^a)^{Jen} \end{aligned} \tag{A-73}$$

There relations are similar with the relations (3.30) and with (A-70), (A-72).

Appendix B

Kinetic Energy

B.1 Classical Change of Coordinates in the Kinetic Energy

The kinetic energy for a particle is in Cartesian coordinates:

$$T = \frac{1}{2} m_1 \left(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2 \right) \tag{B-1}$$

We are doing a change of coordinates: x , y , $z \rightarrow \rho$, θ , r

The kinetic energy in these coordinates is:

$$T = \frac{1}{2} m_1 \cdot \left[\left(\frac{\partial x_1}{\partial \rho}\dot{\rho} + \frac{\partial x_1}{\partial \varphi}\dot{\varphi} + \frac{\partial x_1}{\partial r}\dot{r} \right)^2 + \left(\frac{\partial y_1}{\partial \rho}\dot{\rho} + \frac{\partial y_1}{\partial \varphi}\dot{\varphi} + \frac{\partial y_1}{\partial r}\dot{r} \right)^2 + \left(\frac{\partial z_1}{\partial \rho}\dot{\rho} + \frac{\partial z_1}{\partial \varphi}\dot{\varphi} + \frac{\partial z_1}{\partial r}\dot{r} \right)^2 \right] \tag{B-2}$$

If we arrange the terms in function of the new coordinates derivatives, we get:

$$T = \frac{1}{2} m_1 \sum_{\alpha,\beta} g_{\alpha\beta}^{[1]} \dot{u}_\alpha \dot{u}_\beta \tag{B-3}$$

where $u_1 = \rho$, $u_2 = \varphi$, $u_3 = r$ and $g_{\alpha\beta}^{[i]}$ are the metric tensor elements due to the coordinate change [187, 211].

$$g_{\alpha\beta}^{[k]} = \left[\left(\frac{\partial x_k}{\partial u_\alpha} \right) \left(\frac{\partial x_k}{\partial u_\beta} \right) + \left(\frac{\partial y_k}{\partial u_\alpha} \right) \left(\frac{\partial y_k}{\partial u_\beta} \right) + \left(\frac{\partial z_k}{\partial u_\alpha} \right) \left(\frac{\partial z_k}{\partial u_\beta} \right) \right] \tag{B-4}$$

For a number n of particles, the kinetic energy is:

$$T = \frac{1}{2} \sum_{i=1}^{n} m_i \cdot v_i^2 = \frac{1}{2} \sum_{i=1}^{n} m_i \cdot \left(\dot{x}_1^2 + \dot{y}_1^2 + \dot{z}_1^2 \right) \tag{B-5}$$

The kinetic energy become when we are doing the same change of coordinates:

$$T = \frac{1}{2} \sum_{i=1}^{n} m_i \cdot \sum_{\alpha\beta} g_{\alpha\beta}^{[i]} \dot{u}_\alpha \dot{u}_\beta = \frac{1}{2} \sum_{\alpha\beta} g_{\alpha\beta} \dot{u}_\alpha \dot{u}_\beta \tag{B-6}$$

where

$$g_{\alpha\beta} = \sum_{k=1}^{n} m_k g_{\alpha\beta}^{[k]} \tag{B-7}$$

B.2 Change of the Classical Kinetic Energy from Coordinates to Conjugate Momenta

If we consider the metric tensor $g_{\alpha\beta}$, the contravariant metric tensor elements are the following [211]:

$$g^{\alpha\beta} = (g_{\alpha\beta})^{-1}$$

The metric tensor elements are orthogonal with the contravariant elements [211]:

$$\sum_{\gamma} g^{\alpha\gamma}\, g_{\gamma\beta} = \delta_{\alpha\beta} \tag{B-8}$$

We define the momenta as function of the coordinates as [187]:

$$p_\alpha = \frac{\partial T}{\partial u_\alpha} = \sum_{\beta} g_{\alpha\beta}\, \dot{u}_\beta \tag{B-9}$$

The inverse relation, which defines the coordinate as function of the momenta is:

$$\sum_{\gamma} g^{\gamma\alpha} \cdot p_\alpha = \sum_{beta} \delta_{\gamma\beta}\, \dot{u}_\beta = \dot{u}_\gamma \tag{B-10}$$

The kinetic energy (see B-6) as function of the momenta has the formula:

$$2T = \sum_{\alpha\beta} g_{\alpha\beta} \left(\sum_{\gamma} g^{\alpha\gamma}\, p_\gamma\right)\left(\sum_{\delta} g^{\beta\delta}\, p_\delta\right) = \sum_{\gamma\delta} g^{\gamma\delta}\, p_\gamma\, p_\delta \tag{B-11}$$

B.3 Metric Tensor Elements in the Stretch-Bender Model

The calculus of the metric tensor elements needs the eq. (3.10) which represent the connection of the Cartesian coordinates and the stretch-bender coordinates. Below we will use the shortcuts from eq. (3.4), eq. (3.9), and the following relations:

$$' = \tfrac{\partial}{\partial\rho} = \tfrac{1}{2}\tfrac{\partial}{\partial\theta} \qquad \tfrac{\partial r_\rho}{\partial\theta} = 2\tfrac{\partial r_\rho}{\partial\rho} = 2r' \qquad \tfrac{\partial b}{\partial\theta} = 2\tfrac{\partial b}{\partial\rho} = 2b' \tag{B-12}$$

The molecule is AB_2 and for this reason, $m_1 = m_3$.

We use the definition of metric tensor element given in (B-7) and (B-4), and the coordinates: $u_1 = \rho$, $u_2 = \varphi$, $u_3 = S^s$, $u_4 = S^a$

Obs. In all below calculus, the φ coordinate does not exist because $\cos^2\varphi + \sin^2\varphi = 1$.

The metric tensor elements are the following:

♣ The metric tensor element for the bending coordinate is, from the previous observations,

$$\begin{aligned} g_{\rho\rho} \;=\; & \left(\frac{\partial\theta}{\partial\rho}\right)^2 \left\{ m_1 \left[\left(\frac{\partial x_1}{\partial\theta}\right)^2 + \left(\frac{\partial y_1}{\partial\theta}\right)^2 + \left(\frac{\partial z_1}{\partial\theta}\right)^2\right] + \right. \\ & \left. m_2 \left[\left(\frac{\partial x_2}{\partial\theta}\right)^2 + \left(\frac{\partial y_2}{\partial\theta}\right)^2 + \left(\frac{\partial z_2}{\partial\theta}\right)^2\right] + m_1 \left[\left(\frac{\partial x_3}{\partial\theta}\right)^2 + \left(\frac{\partial y_3}{\partial\theta}\right)^2 + \left(\frac{\partial z_3}{\partial\theta}\right)^2\right] \right\} \end{aligned} \tag{B-13}$$

With equation (3.10), the previous formula become,

$$\begin{aligned} g_{\rho\rho} \;=\; & \frac{1}{4}\left\{ m_1 \left[-\frac{br}{p}\sin\theta - \frac{r}{p}\cos\theta - \frac{S^s + S^a}{\sqrt{2}}\cos\theta + \frac{2b'}{\sqrt{2}}(S^s + S^a)\cos\theta - \frac{b}{\sqrt{2}}(S^s + S^a)\sin\theta\right]^2 \right. \\ & + \; m_1 \left[-br\cos\theta + r\sin\theta + \frac{1}{\sqrt{2}}(S^s + S^a)\sin\theta - \frac{2b'}{\sqrt{2}}(S^s + S^a)\sin\theta - \frac{b}{\sqrt{2}}(S^s + S^a)\cos\theta\right]^2 \\ & \left. + \; \left(\frac{2m_1}{m_2}\right)^2 m_2 \left[\frac{br}{p}\sin\theta + \frac{r}{p}\cos\theta + \frac{1}{\sqrt{2}}S^s\cos\theta - \frac{2b'}{\sqrt{2}}S^s\cos\theta + \frac{b}{\sqrt{2}}\sin\theta\right]^2 \right. \end{aligned}$$

$$
\begin{aligned}
&- m_1\left[-\frac{br}{p}\sin\theta-\frac{r}{p}\cos\theta-\frac{1}{\sqrt{2}}(S^s-S^a)\cos\theta+\frac{2b'}{\sqrt{2}}(S^s-S^a)\cos\theta-\frac{b}{\sqrt{2}}(S^s-S^a)\sin\theta\right]^2\\
&+ 2(S^a)^2\left(\frac{m_1}{m_2}\right)^2 m_2\left[-\sin\theta+2b'\sin\theta+b\cos\theta\right]^2 \qquad \text{(B-14)}\\
&+ m_1\left[br\cos\theta-r\sin\theta-\frac{1}{\sqrt{2}}(S^s-S^a)\sin\theta+\frac{2b'}{\sqrt{2}}(S^s-S^a)\sin\theta+\frac{b}{\sqrt{2}}(S^s-S^a)\cos\theta\right]^2\Bigg\}
\end{aligned}
$$

After algebraic calculus, the final form of $g_{\rho\rho}$ is:

$$
\begin{aligned}
g_{\rho\rho} &= \frac{m_1 r^2}{2p}\left[(\cos\theta+b\sin\theta)^2+p\,(\sin\theta-b\cos\theta)^2\right]+\frac{m_1 r}{\sqrt{2}}S^s\left[1+b^2-2b'\right]\\
&+\frac{m_1}{4}(S^s)^2\left\{p\left[(1-2b')\cos\theta+b\sin\theta\right]^2+\left[(1-2b')\sin\theta-b\cos\theta\right]^2\right\}\\
&+\frac{m_1}{4}(S^a)^2\left\{p\left[(1-2b')\sin\theta-b\cos\theta\right]^2+\left[(1-2b')\cos\theta+b\sin\theta\right]^2\right\} \qquad \text{(B-15)}
\end{aligned}
$$

♣ The metric tensor element for the azimuthal angle coordinate,

$$
\begin{aligned}
g_{\varphi\varphi} &= m_1\left[-\frac{r}{p}\sin\theta-\frac{1}{\sqrt{2}}(S^s+S^a)\,(\sin\theta-b\cos\theta)\right]^2\\
&+ 4\frac{m_1^2}{m_2}\left[\frac{r}{p}\sin\theta+\frac{1}{\sqrt{2}}S^s\,(\sin\theta-b\cos\theta)\right]^2\\
&+ m_1\left[-\frac{r}{p}\sin\theta-\frac{1}{\sqrt{2}}(S^s-S^a)\,(\sin\theta-b\cos\theta)\right]^2 \qquad \text{(B-16)}
\end{aligned}
$$

The final form of $g_{\varphi\varphi}$ is:

$$
g_{\varphi\varphi}=\frac{2m_1}{p}\left[r\sin\theta+\frac{pS^s}{\sqrt{2}}\,(\sin\theta-b\cos\theta)\right]^2+m_1(S^a)^2(\sin\theta-b\cos\theta)^2 \qquad \text{(B-17)}
$$

♣ The metric tensor element for the symmetric stretching coordinate has the formula

$$
\begin{aligned}
g_{ss} &= m_1\left[\frac{1}{2}(\sin\theta-b\cos\theta)^2+\frac{1}{2}(\cos\theta+b\sin\theta)^2\right]+2\frac{m_1^2}{m_2}(\sin\theta-b\cos\theta)^2\\
&+ m_1\left[\frac{1}{2}(\sin\theta-b\cos\theta)^2+\frac{1}{2}(\cos\theta+b\sin\theta)^2\right] \qquad \text{(B-18)}
\end{aligned}
$$

The final form of g_{ss} is:

$$
g_{ss}=m_1\left[p\,(\sin\theta-b\cos\theta)^2+(\cos\theta+b\sin\theta)^2\right] \qquad \text{(B-19)}
$$

♣ The metric tensor element for the antisymmetric coordinate is

$$
\begin{aligned}
g_{aa} &= m_1\left[\frac{1}{2}(\sin\theta-b\cos\theta)^2+\frac{1}{2}(\cos\theta+b\sin\theta)^2\right]+2\frac{m_1^2}{m_2}(\cos\theta+b\sin\theta)^2\\
&= m_1\left[\frac{1}{2}(\sin\theta-b\cos\theta)^2+\frac{1}{2}(\cos\theta+b\sin\theta)^2\right] \qquad \text{(B-20)}
\end{aligned}
$$

The final form of g_{aa} become:

$$
g_{aa}=m_1\left[(\sin\theta-b\cos\theta)^2+p\,(\cos\theta+b\sin\theta)^2\right] \qquad \text{(B-21)}
$$

♣ The metric tensor element for the bending and azimuthal coordinate, from eq.(3.10) and (B-7) is

$$
\begin{aligned}
g_{\rho\varphi} &= \left(\frac{\partial\theta}{\partial\rho}\right)\Bigg\{m_1\left[\left(\frac{\partial x_1}{\partial\theta}\right)\left(\frac{\partial x_1}{\partial\varphi}\right)+\left(\frac{\partial y_1}{\partial\theta}\right)\left(\frac{\partial y_1}{\partial\varphi}\right)\right]+\\
&m_2\left[\left(\frac{\partial x_2}{\partial\theta}\right)\left(\frac{\partial x_2}{\partial\varphi}\right)+\left(\frac{\partial y_2}{\partial\theta}\right)\left(\frac{\partial y_2}{\partial\varphi}\right)\right]+\\
&m_1\left[\left(\frac{\partial x_3}{\partial\theta}\right)\left(\frac{\partial x_3}{\partial\varphi}\right)+\left(\frac{\partial y_3}{\partial\theta}\right)\left(\frac{\partial y_3}{\partial\varphi}\right)\right]\Bigg\}=0 \qquad \text{(B-22)}
\end{aligned}
$$

♣ The metric tensor element for the azimuthal angle and symmetric stretching coordinate vanishes,

$$g_{\varphi s} = 0 \tag{B-23}$$

♣ In a similar manner, the metric tensor element for the azimuthal angle and antisymmetric stretching coordinate vanish also,

$$g_{\varphi a} = 0 \tag{B-24}$$

♣ The metric tensor element for the bending and symmetric stretching coordinate is

$$\begin{aligned}
g_{\rho s} &= \left(\frac{\partial\theta}{\partial\rho}\right)\left\{m_1\left[\left(\frac{\partial x_1}{\partial\theta}\right)\left(\frac{\partial x_1}{\partial S^s}\right)+\left(\frac{\partial y_1}{\partial\theta}\right)\left(\frac{\partial y_1}{\partial S^s}\right)+\left(\frac{\partial z_1}{\partial\theta}\right)\left(\frac{\partial z_1}{\partial S^s}\right)\right]+\right.\\
&\quad m_2\left[\left(\frac{\partial x_2}{\partial\theta}\right)\left(\frac{\partial x_2}{\partial S^s}\right)+\left(\frac{\partial y_2}{\partial\theta}\right)\left(\frac{\partial y_2}{\partial S^s}\right)+\left(\frac{\partial z_2}{\partial\theta}\right)\left(\frac{\partial z_2}{\partial S^s}\right)\right]+\\
&\quad \left.m_1\left[\left(\frac{\partial x_3}{\partial\theta}\right)\left(\frac{\partial x_3}{\partial S^s}\right)+\left(\frac{\partial y_3}{\partial\theta}\right)\left(\frac{\partial y_3}{\partial S^s}\right)+\left(\frac{\partial z_3}{\partial\theta}\right)\left(\frac{\partial z_3}{\partial S^s}\right)\right]\right\}\\
&= \frac{1}{2}\left\{-\frac{1}{\sqrt{2}}m_1\cdot\right.\\
&\quad \left[\left(-\frac{br}{p}\sin\theta-\frac{r}{p}\cos\theta+\frac{(S^s+S^a)}{\sqrt{2}}\left(-\cos\theta+2b'\cos\theta-b\sin\theta\right)\right)\left(\sin\theta-b\cos\theta\right)\right.\\
&+ \left.\left(-br\cos\theta+r\sin\theta+\frac{(S^s+S^a)}{\sqrt{2}}\left(\sin\theta-2b'\sin\theta-b\cos\theta\right)\right)\left(\cos\theta+b\sin\theta\right)\right]\\
&+ \frac{2\sqrt{2}m_1^2}{m_2}\left[\frac{br}{p}\sin\theta+\frac{r}{p}\cos\theta+\frac{S^s}{\sqrt{2}}\left(\cos\theta-2b'\cos\theta+b\sin\theta\right)\right]\left(\sin\theta-b\cos\theta\right)\\
&+ \frac{1}{\sqrt{2}}m_1\left[\left(\frac{br}{p}\sin\theta+\frac{r}{p}\cos\theta+\frac{(S^s-S^a)}{\sqrt{2}}\left(\cos\theta-2b'\cos\theta+b\sin\theta\right)\right)\left(\sin\theta-b\cos\theta\right)\right.\\
&+ \left.\left.\left(br\cos\theta-r\sin\theta+\frac{(S^s-S^a)}{\sqrt{2}}\left(-\sin\theta+2b'\sin\theta+b\cos\theta\right)\right)\left(\cos\theta+b\sin\theta\right)\right]\right\}
\end{aligned} \tag{B-25}$$

The final form of $g_{\rho s}$ is:

$$\begin{aligned}
g_{\rho s} &= \frac{m_1}{2}S^s\left\{p\left[(1-2b')\cos\theta+b\sin\theta\right]\left(\sin\theta-b\cos\theta\right)\right.\\
&\quad \left.-\left[(1-2b')\sin\theta-b\cos\theta\right]\left(\cos\theta+b\sin\theta\right)\right\}
\end{aligned} \tag{B-26}$$

♣ The metric tensor element for the bending and antisymmetric stretching coordinate is similarly,

$$\begin{aligned}
g_{\rho a} &= \left(\frac{\partial\theta}{\partial\rho}\right)\left\{m_1\left[\left(\frac{\partial x_1}{\partial\theta}\right)\left(\frac{\partial x_1}{\partial S^a}\right)+\left(\frac{\partial y_1}{\partial\theta}\right)\left(\frac{\partial y_1}{\partial S^a}\right)+\left(\frac{\partial z_1}{\partial\theta}\right)\left(\frac{\partial z_1}{\partial S^a}\right)\right]+\right.\\
&\quad m_2\left[\left(\frac{\partial x_2}{\partial\theta}\right)\left(\frac{\partial x_2}{\partial S^a}\right)+\left(\frac{\partial y_2}{\partial\theta}\right)\left(\frac{\partial y_2}{\partial S^a}\right)+\left(\frac{\partial z_2}{\partial\theta}\right)\left(\frac{\partial z_2}{\partial S^a}\right)\right]+\\
&\quad \left.m_1\left[\left(\frac{\partial x_3}{\partial\theta}\right)\left(\frac{\partial x_3}{\partial S^a}\right)+\left(\frac{\partial y_3}{\partial\theta}\right)\left(\frac{\partial y_3}{\partial S^a}\right)+\left(\frac{\partial z_3}{\partial\theta}\right)\left(\frac{\partial z_3}{\partial S^a}\right)\right]\right\}\\
&= \frac{1}{2}\left\{\frac{m_1}{\sqrt{2}}\left[\left(\frac{br}{p}\sin\theta+\frac{r}{p}\cos\theta+\frac{(S^s+S^a)}{\sqrt{2}}\left(\cos\theta-2b'\cos\theta+b\sin\theta\right)\right)\left(\sin\theta-b\cos\theta\right)\right.\right.\\
&- \left.\left(-br\cos\theta+r\sin\theta+\frac{(S^s+S^a)}{\sqrt{2}}\left(\sin\theta-2b'\sin\theta-b\cos\theta\right)\right)\left(\cos\theta+b\sin\theta\right)\right]\\
&+ \frac{2m_1^2}{m_2}S^a\left[-\sin\theta+2b'\sin\theta+b\cos\theta\right]\left(\cos\theta+b\sin\theta\right)\\
&+ \frac{m_1}{\sqrt{2}}\left[\left(-\frac{br}{p}\sin\theta-\frac{r}{p}\cos\theta+\frac{(S^s-S^a)}{\sqrt{2}}\left(-\cos\theta+2b'\cos\theta-b\sin\theta\right)\right)\left(\sin\theta-b\cos\theta\right)\right.\\
&- \left.\left.\left(br\cos\theta-r\sin\theta+\frac{(S^s-S^a)}{\sqrt{2}}\left(-\sin\theta+2b'\sin\theta+b\cos\theta\right)\right)\left(\cos\theta+b\sin\theta\right)\right]\right\}
\end{aligned} \tag{B-27}$$

The final form of $g_{\rho a}$ is:

$$\begin{aligned} g_{\rho a} &= \frac{m_1}{2} S^a \left\{ \left[(1-2b') \cos\theta + b \sin\theta \right] (\sin\theta - b\cos\theta) \right. \\ &\quad \left. - p \left[(1-2b') \sin\theta - b\cos\theta \right] (\cos\theta + b\sin\theta) \right\} \end{aligned} \tag{B-28}$$

♣ The metric tensor element for antisymmetric stretching and symmetric stretching coordinate is

$$\begin{aligned} g_{as} &= \frac{m_1}{2} m_1 \left[(\sin\theta - b\cos\theta)^2 + (\cos\theta + b\sin\theta)^2 \right] \\ &+ \frac{m_1}{2} \left[-(\sin\theta - b\cos\theta)^2 - (\cos\theta + b\sin\theta) \right] = 0 \end{aligned} \tag{B-29}$$

The Jacobian of the transformation is:

$$g = g_{\varphi\varphi} \left[g_{aa} \left(g_{\rho\rho}\, g_{ss} - g_{\rho s}^2 \right) - g_{ss} g_{\rho a}^2 \right] \tag{B-30}$$

We have to introduce the above formula for the metric tensor elements and after algebraic treatment we will obtain the Jacobian as:

$$\begin{aligned} g &= \frac{m_1^4 \cdot r^4}{p^2} \left\{ \left[\sin\theta + \frac{pS^s}{\sqrt{2}r} (\sin\theta - b\cos\theta) \right]^2 + \frac{p}{2} \left(\frac{S^a}{r} \right)^2 (\sin\theta - b\cos\theta)^2 \right\} \\ &\quad \left\{ \left[(\sin\theta - b\cos\theta)^2 + p\,(\cos\theta + b\sin\theta)^2 \right] \right. \\ &\quad \left[(\cos\theta + b\sin\theta)^2 + p\,(\sin\theta - b\cos\theta)^2 + \frac{p}{\sqrt{2}} \frac{S^s}{r} \left(1 + b^2 - 2b'\right) \right]^2 \\ &\quad \left. + \frac{p^2}{2} \left(\frac{S^a}{r} \right)^2 \left(1 + b^2 - 2b'\right)^2 \left[p\,(\sin\theta - b\cos\theta)^2 + (\cos\theta + b\sin\theta)^2 \right] \right\} \end{aligned} \tag{B-31}$$

B.4 The Calculus of the Contravariant Metric Tensor Elements in the Reference Frame

We are mainly interested in metric tensor elements values for the reference configuration ($S^s = S^a = 0$), because we use them in the expansion of the kinetic energy.

Obs. In all below calculus, we use the shortcut: $g_0^{\alpha\beta} = g^{\alpha\beta}|_{S^s = S^a = 0}$.

Using the results of the (§B.2), the contravariant metric tensor elements are the following:

♢ The contravariant metric tensor element for the bending coordinate:

$$g^{\rho\rho} = \frac{g_{ss} g_{aa}}{g_{aa} \left(g_{\rho\rho} g_{ss} - g_{\rho s}^2 \right) - g_{ss} g_{\rho a}^2} \tag{B-32}$$

$$g_0^{\rho\rho} = \frac{2p}{m_1 r^2 \left[(\cos\theta + b\sin\theta)^2 + p\,(\sin\theta - b\cos\theta)^2 \right]} \tag{B-33}$$

Equation (B-33) is identical with $g^{\rho\rho}$ from [186, Table III] and in the rigid bender limit with $\frac{1}{I_{\rho\rho}}$ from [5, eq.(37)].

♢ The contravariant metric tensor element for azimuthal angle and the bending coordinate:

$$g^{\rho\varphi} = 0 \tag{B-34}$$

♢ The contravariant metric tensor element for the bending and symmetric stretching coordinate:

$$g^{\rho s} = -\frac{g_{\rho s} g_{aa}}{g_{aa} \left(g_{\rho s} g_{ss} - g_{\rho s}^2 \right) - g_{ss} g_{\rho a}^2} = S^s \cdot f(S^s, S^a, \rho) \tag{B-35}$$

$$g_0^{\rho s} = 0 \tag{B-36}$$

◇ The contravariant metric tensor element for the bending and antisymmetric stretching coordinate:

$$g^{\rho a} = -\frac{g_{\rho a} g_{ss}}{g_{aa}\left(g_{\rho s} g_{ss} - g_{\rho s}^2\right) - g_{ss} g_{\rho a}^2} = S^a \cdot f(S^s, S^a, \rho) \tag{B-37}$$

$$g_0^{\rho a} = 0 \tag{B-38}$$

◇ The contravariant metric tensor element for the azimuthal angle coordinate:

$$g^{\varphi\varphi} = \frac{1}{g_{\varphi\varphi}} \tag{B-39}$$

$$g_0^{\varphi\varphi} = \frac{p}{2 m_1 r^2 \sin^2\theta} \tag{B-40}$$

Equation (B-40) is identical with $\frac{1}{I_{\varphi\varphi}}$ from [5, eq.(37)] and with $A(\rho)$ from [186, Table III].

◇ The contravariant metric tensor element for the azimuthal angle and the symmetric stretching coordinate:

$$g^{\varphi s} = 0 \tag{B-41}$$

◇ The contravariant metric tensor element for the azimuthal angle and the antisymmetric stretching coordinate:

$$g^{\varphi a} = 0 \tag{B-42}$$

◇ The contravariant metric tensor element for the symmetric stretching coordinate:

$$g^{ss} = \frac{g_{\rho\rho} g_{aa} - g_{\rho a}^2}{g_{aa}\left(g_{\rho\rho} g_{ss} - g_{\rho s}^2\right) - g_{ss} g_{\rho a}^2} \tag{B-43}$$

$$g_0^{ss} = \frac{1}{m_1} \frac{1}{\left[(\cos\theta + b\sin\theta)^2 + p\,(\sin\theta - b\cos\theta)^2\right]} \tag{B-44}$$

Equation (B-44) is identical with g^{ss} from [186, Table III], without a $\frac{1}{2}$ factor due to a different choice of S^s coordinate.

◇ The contravariant metric tensor element for the symmetric stretching and antisymmetric stretching coordinate:

$$g^{sa} = \frac{g_{\rho s} g_{\rho a}}{g_{aa}\left(g_{\rho\rho} g_{ss} - g_{\rho s}^2\right) - g_{ss} g_{\rho a}^2} = S^s \cdot S^a \cdot f(S^s, S^a, \rho) \tag{B-45}$$

$$g_0^{sa} = 0 \tag{B-46}$$

◇ The contravariant metric tensor element for the antisymmetric stretching coordinate:

$$g^{aa} = \frac{g_{\rho\rho} g_{ss} - g_{\rho s}^2}{g_{aa}\left(g_{\rho\rho} g_{ss} - g_{\rho s}^2\right) - g_{ss} g_{\rho a}^2} \tag{B-47}$$

$$g_0^{aa} = \frac{1}{m_1} \frac{1}{\left[(\sin\theta - b\cos\theta)^2 + p\,(\cos\theta + b\sin\theta)^2\right]} \tag{B-48}$$

Equation (B-48) is identical with g^{aa} from [186, Table III], without a $\frac{1}{2}$ factor due to a different choice of S^a coordinate.

$\diamond$ The jacobian in the reference frame can be obtained directly from (B-31),

$$g_0 = \frac{m_1^4 r^4}{p^2}\sin^2\theta\left[(\cos\theta+b\sin\theta)^2+p\,(\sin\theta-b\cos\theta)^2\right]^2\cdot \left[(\sin\theta-b\cos\theta)^2+p\,(\cos\theta+b\sin\theta)^2\right] \tag{B-49}$$

Equation (B-49) is identical with $\frac{1}{g}$ from [186], without a $\frac{1}{4}$ factor due to a different choice of S^s and S^a coordinate.

In the case of small angles ($\rho \to 0$), the trigonometric functions can be expanded in power series up to the second order and we will have from (B-31):

$$\begin{aligned} g(\rho,r) &= \frac{m_1^4 r^4}{p}\left(\frac{\rho}{2}\right)^2\left\{\left[1+\frac{p}{\sqrt{2}}\left(\frac{S^s}{r}\right)\left(1-\frac{4d}{r^0}\right)\right]^2+\frac{p}{2}\left(\frac{S^a}{r}\right)^2\left(1-\frac{4d}{r^0}\right)^2\right\}\times \\ &\quad \left\{\left[1+\frac{p}{\sqrt{2}}\left(\frac{S^s}{r}\right)\right]^2+\frac{p}{2}\left(\frac{S^a}{r}\right)^2\right\} \\ &\simeq \frac{m_1^4 r^4}{p}\left(\frac{\rho}{2}\right)^2\left\{1+2\sqrt{2}p\left(\frac{S^s}{r}\right)\left(1-\frac{2d}{r^0}\right)+\left(\frac{p}{\sqrt{2}}\frac{S^s}{r}\right)^2\left[\left(1-\frac{4d}{r^0}\right)^2+1\right]\right. \\ &\quad \left.+\frac{p}{2}\left(\frac{S^a}{r}\right)^2\left[\left(1-\frac{4d}{r^0}\right)^2+1\right]+\mathcal{O}\left((S^s)^3,S^s(S^a)^2\right)\right\} \end{aligned} \tag{B-50}$$

In the above formula we made the assumption that the bond length dependence with the angle is:

$$r(\rho) = r^0+\frac{d}{2}\rho^2$$

and in the first order power series

$$\lim_{\rho\to 0}\left[\sin\left(\frac{\rho}{2}\right)-\left(\frac{2r'}{r}\right)\cos\left(\frac{\rho}{2}\right)\right] \simeq \left(1-\frac{4d}{r}\right)\frac{\rho}{2}$$

$$\lim_{\rho\to 0}\left[\cos\left(\frac{\rho}{2}\right)+\left(\frac{2r'}{r}\right)\sin\left(\frac{\rho}{2}\right)\right] \simeq 1$$

B.5 The non Vanishing Terms of the Kinetic Hamiltonian in the Stretch-Bender Model

The quantum kinetic energy, from [187] is, in the reference frame:

$$\begin{aligned} &\frac{1}{2}\left[g^{-\frac{1}{4}}\sum_{\alpha\beta}P_\alpha\,g^{\alpha\beta}\,g^{\frac{1}{2}}\,P_\beta\,g^{-\frac{1}{4}}\right]_0 \\ =\ &\left\{\frac{1}{2}g^{\frac{1}{4}}\sum_{\alpha\beta}\left[P_\alpha,g^{\alpha\beta}\right]\left[P_\beta,g^{-\frac{1}{4}}\right]+\frac{1}{2}g^{-\frac{1}{4}}\sum_{\alpha\beta}g^{\alpha\beta}\left[P_\alpha,g^{\frac{1}{2}}\right]\left[P_\beta,g^{-\frac{1}{4}}\right]\right. \\ +\ &\left.\frac{1}{2}g^{\frac{1}{4}}\sum_{\alpha\beta}g^{\alpha\beta}\left[P_\alpha,\left[P_\beta,g^{-\frac{1}{4}}\right]\right]+\frac{1}{2}\sum_{\alpha\beta}\left[P_\alpha,g^{\alpha\beta}\right]P_\beta+\frac{1}{2}\sum_{\alpha\beta}g^{\alpha\beta}P_\alpha P_\beta\right\}_{S^s=S^a=0} \\ =\ &\frac{1}{2}g^{\frac{1}{4}}\left\{\left[P_\rho,g^{\rho\rho}\right]\left[P_\rho,g^{-\frac{1}{4}}\right]+\left[P_s,g^{s\rho}\right]\left[P_\rho,g^{-\frac{1}{4}}\right]+\left[P_s,g^{ss}\right]\left[P_s,g^{-\frac{1}{4}}\right]+\left[P_a,g^{a\rho}\right]\left[P_\rho,g^{-\frac{1}{4}}\right]\right\} \\ +\ &\frac{1}{2}g^{-\frac{1}{4}}\left\{g^{\rho\rho}\left[P_\rho,g^{\frac{1}{2}}\right]\left[P_\rho,g^{-\frac{1}{4}}\right]+g^{ss}\left[P_s,g^{\frac{1}{2}}\right]\left[P_s,g^{-\frac{1}{4}}\right]\right\} \\ +\ &\frac{1}{2}g^{\frac{1}{4}}\left\{g^{\rho\rho}\left[P_\rho,\left[P_\rho,g^{-\frac{1}{4}}\right]\right]+g^{ss}\left[P_s,\left[P_s,g^{-\frac{1}{4}}\right]\right]+g^{aa}\left[P_a,\left[P_a,g^{-\frac{1}{4}}\right]\right]\right\} \\ +\ &\frac{1}{2}\left\{\left[P_\rho,g^{\rho\rho}\right]P_\rho+\left[P_s,g^{ss}\right]P_s\right\}+\frac{1}{2}\left\{g^{\rho\rho}P_\rho^2+g^{ss}P_s^2+g^{aa}P_a^2+g_0^{\varphi\varphi}P_\varphi^2\right\} \end{aligned} \tag{B-51}$$

It is easily to see from (§B.4) that the derivative of the contravariant metric tensor elements in the reference frame vanish:

$$
\begin{array}{lll}
[P_\alpha\,,g^{as}]_{S^s=S^a=0}=0 & \left[P_\rho\,,g^{\beta\rho}\right]_{S^s=S^a=0}=0 & \text{from eq.(B-35), (B-37), (B-45)} \\
(g^{as})_{S^s=S^a=0}=0 & \left(g^{\rho\beta}\right)_{S^s=S^a=0}=0 & \text{from eq.(B-36), (B-38), (B-46)} \\
[P_a\,,g^{\alpha\alpha}]_{S^s=S^a=0}=0 & [P_a\,,g]_{S^s=S^a=0}=0 & \text{because the } S^a \text{ is as a square} \\
[P_a\,,g^{\rho s}]_{S^s=S^a=0}=0 & [P_s\,,g^{\rho a}]_{S^s=S^a=0}=0 & \text{from eq.(B-35), (B-37)} \\
[P_s\,,g^{ss}]_{S^s=S^a=0}=0 & & \text{from eq.(B-86)} \\
\left[P_\varphi\,,g^{\alpha\beta}\right]_{S^s=S^a=0}=0 & \left(g^{\alpha\varphi}\right)_{S^s=S^a=0}=0 & \text{from eq.(B-32) - (B-48)} \\
\text{where:} & \alpha=\rho\,,S^s\,,S^a & \\
 & \beta=S^a\,,S^s &
\end{array}
\tag{B-52}
$$

With the formulas from (B-52), the kinetic energy (B-51) become:

$$
\begin{aligned}
& \frac{1}{2}\left[g^{-\frac{1}{4}}\sum_{\alpha\beta}P_\alpha\,g^{\alpha\beta}\,g^{\frac{1}{2}}\,P_\beta\,g^{-\frac{1}{4}}\right]_0 \\
= \;& \frac{1}{2}g^{\rho\rho}P_\rho^2+\frac{1}{2}\left[P_\rho\,,g^{\rho\rho}\right]P_\rho+\frac{1}{2}g^{-\frac{1}{4}}\left[P_\rho\,,g^{\frac{1}{2}}\,g^{\rho\rho}\left[P_\rho\,,g^{-\frac{1}{4}}\right]\right]+\frac{1}{2}g_0^{\varphi\varphi}\,P_\varphi^2 \\
+ \;& \frac{1}{2}g^{ss}P_s^2+\frac{1}{2}g^{aa}P_a^2 \\
+ \;& \frac{1}{2}g^{-\frac{1}{4}}\,g^{ss}\left[P_s\,,g^{\frac{1}{2}}\right]\left[P_s\,,g^{-\frac{1}{4}}\right]+\frac{1}{2}g^{\frac{1}{4}}\,g^{ss}\left[P_s\,,\left[P_s\,,g^{-\frac{1}{4}}\right]\right]+\frac{1}{2}g^{\frac{1}{4}}\,g^{aa}\left[P_a\,,\left[P_a\,,g^{-\frac{1}{4}}\right]\right] \\
+ \;& \frac{1}{2}g^{\frac{1}{4}}\left[P_s\,,g^{s\rho}\right]\left[P_\rho\,,g^{-\frac{1}{4}}\right]+\frac{1}{2}g^{\frac{1}{4}}\left[P_a\,,g^{a\rho}\right]\left[P_\rho\,,g^{-\frac{1}{4}}\right]
\end{aligned}
\tag{B-53}
$$

B.6 The Order of Magnitude for Terms in the Kinetic Hamiltonian

- We consider [1] the incertitude relations, applied to the atomic scale:

$$
\Delta P_e\,R_0\sim\hbar \;\Rightarrow\; \left\{\begin{array}{l} P_e\sim\Delta P_e\sim\frac{\hbar}{R_0}\sim\hbar \\ E_{el}\sim\frac{P_e^2}{m_e}\sim\frac{\hbar^2}{m_e R_0^2}\end{array}\right. \tag{B-54}
$$

$$
E_{rot}\simeq E_{el}\frac{m_e}{M}\simeq E_v\sqrt{\frac{m_e}{M}}=E_v k^2
$$

- The vibrational constant is :

$$
f^{vib}\sim\frac{\partial^2}{\partial R_0^2}\left(\frac{\hbar^2}{m_e R_0^2}\right)\sim\frac{\hbar^2}{m_e R_0^4} \qquad \left[\frac{J}{m^2}\right] \;\Rightarrow\; E_v\sim E_{el}\sqrt{\frac{m_e}{M}}=E_{el}\,k^2 \tag{B-55}
$$

Proof:

$$
\begin{array}{lll}
E_v\sim\hbar\omega\sim\hbar\sqrt{\frac{\hbar^2}{m_e R_0^4 M}} & \Rightarrow & E_{el}\sqrt{\frac{m_e}{M}} \\
f_r\,S_r^2\sim E_v & \Rightarrow & S_r\sim R_0\sqrt[4]{\frac{m_e}{M}} \\
k=\sqrt[4]{\frac{m_e}{M}} & \Rightarrow & S\sim R_0 k
\end{array}
\tag{B-56}
$$

- The potential terms can be obtained as following:

$$
f^{vib}S_r^2\sim E_v \;\Rightarrow\; f_{S_r^{n_1}\ldots S_r^{n_n}}\cdot S_r^{n_1}\ldots S_r^{n_n}|_{n_1+\ldots n_n=n}\sim k^{n-2}\,E_v \tag{B-57}
$$

- $$
\left.\begin{array}{l}\Delta P_r\,S^s\sim\hbar \\ S^s\sim S_r\sim R_o\sqrt[4]{\frac{m_E}{m}}=R_0\,k\end{array}\right\}\quad P_r\sim\Delta P_r\sim\frac{\hbar}{S_r}\sim\frac{\hbar}{k} \tag{B-58}
$$

- $$
\mu^0_{\alpha\beta}\sim\frac{k^2\,E_v}{\hbar^2} \tag{B-59}
$$

Proof:
$$\left.\begin{array}{l}\mu^0_{\alpha\beta} \sim \frac{1}{I^0_{\alpha\beta}} \\ E_{rot} \sim \frac{\hbar^2}{I_{\alpha\alpha}} \sim \hbar^2 \mu^0_{\alpha\beta}\end{array}\right\} \quad \mu^0_{\alpha\beta} \sim \frac{E_{rot}}{\hbar^2} \sim \frac{E_{el}\cdot\frac{m_e}{M}}{\hbar^2} \sim k^2\,\frac{E_v}{\hbar^2} \tag{B-60}$$

- $$I^0_{\alpha\beta} \sim \frac{\hbar^2}{k^2\,E_v} \tag{B-61}$$

Proof:
$$\frac{\hbar^2}{I^0_{\alpha\beta}} \sim E_{rot} \Rightarrow \quad I^0_{\alpha\beta} \sim \frac{\hbar^2}{k^2\,E_v} \tag{B-62}$$

- $$\mu^0_{\alpha\beta}\, a_r^{\beta\gamma} \mu^0_{\gamma\delta}\, S_r \sim \frac{k^2\,E_v}{\hbar^2} \tag{B-63}$$

Proof:
$$\left.\begin{array}{l}P_r \sim \frac{\hbar}{k} \rightarrow \frac{\partial}{\partial S_r} \sim k^{-1} \\ a_r^{\alpha\beta} = \left(\frac{\partial I^0_{\alpha\beta}}{\partial S_r}\right)_0\end{array}\right\} \quad \mu^0_{\alpha\beta}\left(\frac{\partial I^0_{\alpha\beta}}{\partial S_r}\right)_0 \mu^0_{\gamma\delta}\, S_r \sim \frac{k^2\,E_v}{\hbar^2} > k\mu^0_{\alpha\beta} \sim \frac{k^3\,E_v}{\hbar^2} \tag{B-64}$$

- $$\mu^0_{rs} \sim \frac{k^2\,E_v}{\hbar^2} \tag{B-65}$$

Proof: μ^0_{rs} can not be computed with an algorithm similar with (B-59), because $\mu^0_{rs} \sim frac1M$.
$$\mu^0_{rs}\, P_r^2 \sim E_v \quad \rightarrow \quad \mu^0_{rs} \sim \frac{E_v}{P_r^2} \sim \frac{k^2 E_v}{\hbar^2} \tag{B-66}$$

- The kinetic momentum for the Coriolis coupling:

$$p_i \sim P_r S_r \sim \frac{\hbar}{k}\cdot k = \hbar \tag{B-67}$$

- $$\langle J_\alpha \rangle = \hbar \quad \text{where:} \quad \alpha = x, y, z \tag{B-68}$$

Proof:
$$\left.\begin{array}{l}\langle J_\alpha \rangle = \left[\langle v|P_\alpha^2|v\rangle\right]^{\frac{1}{2}} \sim \hbar \\ \mu^0_{\alpha\beta} J_x^2 \sim E_{rot} \sim E_v\, k^2\end{array}\right\} \quad J_\alpha^2 \sim \hbar^2 \Rightarrow \langle J_\alpha \rangle \sim \hbar \tag{B-69}$$

- $$\langle J_\rho \rangle \sim \frac{k}{\hbar} \tag{B-70}$$

Proof:
$$\left.\begin{array}{l}P_2 \sim \hbar\frac{\partial}{\partial Q_2} \sim \hbar \\ \\ \mu^0_{\rho\rho}\, J_\rho^2 \sim E_v\end{array}\right\} \quad J_\rho^2 \sim \frac{E_v}{\mu^0_{\rho\rho}} = \frac{\hbar^2}{k^2} \tag{B-71}$$

B.7 The Pseudo-Potential in the Bending Kinetic Hamiltonian and its Behavior for $\rho \rightarrow 0$

We will consider the following expression, similar to the bending kinetic Hamiltonian, where the functions have the meanings:

$f(x)$	–	contravariant metric tensor element g^{xx}
$g(x)$	–	the jacobian of the metric tensor
$\varphi(x)$	–	the wavefunction for the coordinate x

$$\begin{aligned} & f^{\frac{1}{2}}\, g^{-\frac{1}{4}}\, \frac{\partial}{\partial x}\, g^{\frac{1}{2}}\, f \frac{\partial}{\partial x}\, g^{-\frac{1}{4}}\, f^{-\frac{1}{2}}\varphi \\ = \; & f^{\frac{1}{2}}\, g^{-\frac{1}{4}}\, \frac{\partial}{\partial x}\, g^{\frac{1}{2}}\, f \left[-\frac{1}{4}\, g^{-\frac{5}{4}}\, g'\, f^{-\frac{1}{2}}\varphi + g^{-\frac{1}{4}}\,(-\frac{1}{2})\, f^{-\frac{3}{2}}\, f'\varphi + g^{-\frac{1}{4}}\, f^{-\frac{1}{2}}\varphi'\right] \\ = \; & f^{\frac{1}{2}}\, g^{-\frac{1}{4}}\, \frac{\partial}{\partial x} \left[-\frac{1}{4}\, g^{-\frac{3}{4}}\, g'\, f^{\frac{1}{2}}\,\varphi - \frac{1}{2} g^{\frac{1}{4}}\, f^{-\frac{1}{2}}\, f'\varphi + g^{-\frac{1}{4}}\, f^{\frac{1}{2}}\varphi'\right] \end{aligned} \tag{B-72}$$

After doing all the terms reduction the relation become:

$$\begin{aligned} & f^{\frac{1}{2}} g^{-\frac{1}{4}} \frac{\partial}{\partial x} g^{\frac{1}{2}} f \frac{\partial}{\partial x} g^{-\frac{1}{4}} f^{-\frac{1}{2}} \varphi \\ = & \left[\frac{3}{16} \frac{(g')^2}{g^2} f - \frac{1}{4} \frac{g''}{g} f - \frac{1}{4} \frac{g'}{g} f' + \frac{1}{4} \frac{(f')^2}{f} - \frac{1}{2} f'' \right] \varphi + f \varphi'' \end{aligned} \tag{B-73}$$

We are considering now:

$$\begin{aligned} & -g^{-\frac{1}{4}} f^{\frac{1}{2}} \frac{\partial^2}{\partial x^2} \left(g^{\frac{1}{4}} f^{\frac{1}{2}} \right) = -g^{-\frac{1}{4}} f^{\frac{1}{2}} \frac{\partial}{\partial x} \left(\frac{1}{4} g^{-\frac{3}{4}} g' f^{\frac{1}{2}} + \frac{1}{2} g^{\frac{1}{4}} f^{-\frac{1}{2}} f' \right) \\ = & \frac{3}{16} \frac{(g')^2}{g^2} - \frac{1}{4} \frac{g''}{g} f - \frac{1}{4} \frac{g'}{g} f' + \frac{1}{4} \frac{(f')^2}{f} - \frac{1}{2} f'' \end{aligned} \tag{B-74}$$

And therefore:

$$\begin{aligned} & f^{\frac{1}{2}} g^{-\frac{1}{4}} \frac{\partial}{\partial x} g^{\frac{1}{2}} f \frac{\partial}{\partial x} g^{-\frac{1}{4}} f^{-\frac{1}{2}} \varphi \\ = & - \left[g^{-\frac{1}{4}} f^{\frac{1}{2}} \frac{\partial^2}{\partial x^2} \left(g^{\frac{1}{4}} f^{\frac{1}{2}} \right) \right] \varphi + f \frac{\partial^2}{\partial x^2} \end{aligned} \tag{B-75}$$

We use this relation below, in the equations (B-33), (B-49) for the reference configuration, and with the functions R_i, defined in (3.16).

$$\left. \begin{array}{l} g^{\frac{1}{4}} = \frac{\sqrt{2}m}{\sqrt{p}} \cdot r R_3^{\frac{1}{2}} \left(r^0, \rho \right) \sin^{\frac{1}{2}} \theta R_4^{\frac{1}{4}} \left(r^0, \rho \right) \\ \left(g^{\rho\rho} \right)^{\frac{1}{2}} = \frac{\sqrt{2p}}{\sqrt{m}} \frac{1}{r R_3^{\frac{1}{2}} (r^0, \rho)} \end{array} \right\} \longrightarrow \quad g^{\frac{1}{4}} \left(g^{\rho\rho} \right)^{\frac{1}{2}} = 2m^{\frac{1}{2}} \sin^{\frac{1}{2}} \theta R_4^{\frac{1}{4}} \left(r^0, \rho \right) \tag{B-76}$$

We consider the derivatives of $g^{\frac{1}{4}} \left(g^{\rho\rho} \right)^{\frac{1}{2}}$ on ρ:

$$\begin{aligned} \frac{\partial}{\partial \rho} \left(g^{\frac{1}{4}} \left(g^{\rho\rho} \right)^{\frac{1}{2}} \right) &= 2m^{\frac{1}{2}} \left[\frac{1}{4} \frac{\cos\theta}{\sin^{\frac{1}{2}} \theta} R_4^{\frac{1}{4}} + \frac{1}{4} \sin^{\frac{1}{2}} \theta \frac{R_4'}{R_4^{\frac{3}{4}}} \right] \\ \frac{\partial^2}{\partial \rho^2} \left(g^{\frac{1}{4}} \left(g^{\rho\rho} \right)^{\frac{1}{2}} \right) &= \frac{m_1^{\frac{1}{2}}}{2} \frac{\partial}{\partial \rho} \left[\frac{\cos\theta}{\sin^{\frac{1}{2}} \theta} R_4^{\frac{1}{4}} + \sin^{\frac{1}{2}} \theta \frac{R_4'}{R_4^{\frac{3}{4}}} \right] \\ &= \frac{m_1^{\frac{1}{2}}}{2} \sin^{\frac{1}{2}} \theta R_4^{\frac{1}{4}} \frac{1}{4} \cdot \left[\frac{1 + \sin^2\theta}{\sin^2\theta} + \frac{1}{2} \frac{\cos\theta}{\sin\theta} \frac{R_4'}{R_4} + \frac{4 R_4'' R_4 - 3 (R_4')^2}{R_4^2} \right] \end{aligned} \tag{B-77}$$

We will analyze the last two terms from the second derivative of $g^{\frac{1}{4}} \left(g^{\rho\rho} \right)^{\frac{1}{2}}$, near $\rho \to 0$:

$$\begin{aligned} \frac{1}{2} \frac{\cos\theta}{\sin\theta} \frac{R_4'}{R_4} |_{\rho \to 0} &\approx -\frac{1}{4} \frac{p+1}{2p} \approx const. \\ \frac{4 R_4'' R_4 - 3 (R_4')^2}{R_4^2} &\approx -\frac{1}{8} \frac{p-1}{p} \approx const. \end{aligned} \tag{B-78}$$

The previous relations (B-78) show that the dominant term is the first one in (B-79)and for this reason, we can approximate:

$$\left(g^{-\frac{1}{4}} \left(g^{\rho\rho} \right)^{-\frac{1}{2}} \right) \frac{\partial^2}{\partial \rho^2} \left(g^{\frac{1}{4}} \left(g^{\rho\rho} \right)^{\frac{1}{2}} \right) \approx \frac{1}{16} \frac{1 + \sin^2\theta}{\sin^2\theta} \approx \frac{1}{4} \frac{1}{\rho} \tag{B-79}$$

B.8 Taylor Series Expansion of the Contravariant Metric Tensor Elements as Function of the Stretching Coordinates

We use for the contravariant metric tensor the symbol: $\mu = g^{-1}$ and for the elements:

$$\mu_{\alpha\beta} = g^{\alpha\beta} = \left(g_{\alpha\beta} \right)^{-1}$$

The expansion in series of the metric tensor elements has the following expression:

$$g_{\alpha\beta} = g^0_{\alpha\beta} + \sum_r a^{\alpha\beta}_r S^r + \sum_{rs} a^{\alpha\beta}_{rs} S^r S^s \tag{B-80}$$

where

$$a^{\alpha\beta}_r = \left(\frac{\partial g_{\alpha\beta}}{\partial S^r}\right)_0 \quad , \quad a^{\alpha\beta}_{rs} = \left(\frac{\partial^2 g_{\alpha\beta}}{\partial S^r \partial S^s}\right)_0$$

We note the sums from the expansion, by G_s, respectively G_{ss}:

$$\begin{aligned} G_s &= \left[\sum_r a^{\alpha\beta}_r S^r\right] \sim S^r \\ G_{ss} &= \left[\sum_{rs} a^{\alpha\beta}_{rs} S^r S^s\right] \sim S^r S^s \sim (S^r)^2 \end{aligned} \tag{B-81}$$

We introduce the expansion in power series in the formula of μ and we obtain:

$$\begin{aligned} \mu &= (g^0 + G_s + G_{ss})^{-1} \\ &= \left[(g^0)^{\frac{1}{2}} E (g^0)^{\frac{1}{2}} + (g^0)^{\frac{1}{2}} (g^0)^{-\frac{1}{2}} G_s (g^0)^{-\frac{1}{2}} (g^0)^{\frac{1}{2}} + (g^0)^{\frac{1}{2}} (g^0)^{-\frac{1}{2}} G_{ss} (g^0)^{-\frac{1}{2}} (g^0)^{\frac{1}{2}}\right]^{-1} \\ &= (g^0)^{-\frac{1}{2}} \left[E + (g^0)^{-\frac{1}{2}} G_s (g^0)^{-\frac{1}{2}} + (g^0)^{-\frac{1}{2}} G_{ss} (g^0)^{-\frac{1}{2}}\right]^{-1} (g^0)^{-\frac{1}{2}} \\ &\simeq (g^0)^{-\frac{1}{2}} \left[E - (g^0)^{-\frac{1}{2}} G_s (g^0)^{-\frac{1}{2}} - (g^0)^{-\frac{1}{2}} G_{ss} (g^0)^{-\frac{1}{2}}\right. \\ &+ \left. (g^0)^{-\frac{1}{2}} G_s (g^0)^{-\frac{1}{2}} (g^0)^{-\frac{1}{2}} G_s (g^0)^{-\frac{1}{2}} + \mathcal{O}(S^3)\right] (g^0)^{-\frac{1}{2}} \\ &= (g^0)^{-1} - (g^0)^{-1} G_s (g^0)^{-1} - (g^0)^{-1} G_{ss} (g^0)^{-1} + (g^0)^{-1} G_s (g^0)^{-1} G_s (g^0)^{-1} \end{aligned} \tag{B-82}$$

Then, the matrix elements of μ are the following:

$$\begin{aligned} \mu_{\alpha\beta}(\rho, S^r) &= \mu^0_{\alpha\beta} - \sum_r \sum_{\delta\gamma} \mu^0_{\alpha\delta} a^{\delta\gamma}_r \mu^0_{\gamma\beta} S^r \\ &+ \sum_{rs} \left[-\sum_{\delta\gamma} \mu^0_{\alpha\delta} a^{\delta\gamma}_{rs} \mu^0_{\gamma\beta} + \sum_{\delta\gamma\epsilon\eta} \mu^0_{\alpha\delta} a^{\delta\gamma}_r \mu^0_{\gamma\epsilon} a^{\epsilon\eta}_s \mu^0_{\eta\beta}\right] S^r S^s \end{aligned} \tag{B-83}$$

The values of $\mu^0_{\alpha\beta}$ from (§B.4) are:

$$\mu_{\alpha\beta} = \delta_{\alpha\beta} \mu^0_{\alpha\alpha}$$

The final formula for the contravariant metric tensor elements is:

$$\begin{aligned} \mu_{\alpha\beta}(\rho, S^r) &= \mu^0_{\alpha\alpha} \delta_{\alpha\beta} - \sum_r \mu^0_{\alpha\alpha} a^{\alpha\beta}_r \mu^0_{\beta\beta} S^r \\ &+ \sum_{rs} \left[-\mu^0_{\alpha\alpha} a^{\alpha\beta}_{rs} \mu^0_{\beta\beta} + \sum_\gamma \mu^0_{\alpha\alpha} a^{\alpha\gamma}_r \mu^0_{\gamma\gamma} a^{\gamma\beta}_s \mu^0_{\beta\beta}\right] S^r S^s \end{aligned} \tag{B-84}$$

The above formula is similar with [6, eq.(4.24)], but here it is not a $\frac{3}{4}$ factor to the quadratic terms, due to a different choice of our stretching coordinates. In our formula was considered the second derivative of the metric tensor elements, to have a consistent magnitude of terms in our expansion.

We must emphasis the expansion for the diagonal terms μ^{ss}_{aa}. From (§B.4), eq.(B-43) and eq.(B-47), taking into account the metric tensor formulas from (§B.3):

$$\begin{array}{ll} g_{\rho s} \propto S^s & \text{from eq.(B-26)} \\ g_{\rho a} \propto S^a & \text{from eq.(B-28)} \\ g_{ss} \not= f(S^s, S^a) & \text{from eq.(B-18)} \\ g_{aa} \not= f(S^s, S^a) & \text{from eq.(B-20)} \end{array} \tag{B-85}$$

the expansion up to quadratic terms is:

$$\begin{aligned}
\mu_{aa}^{ss} &\simeq \frac{\alpha_1\left[1+\beta_1 S^s+\mathcal{O}_1\left((S^s)^2,(S^a)^2\right)\right]}{\alpha_2\left[1+\beta_1 S^s+\mathcal{O}_2\left((S^s)^2,(S^a)^2\right)\right]} \\
&\simeq \frac{\alpha_1}{\alpha_2}\left[1+\beta_1 S^s+\mathcal{O}_1\left((S^s)^2,(S^a)^2\right)\right]\left[1-\beta_1 S^s+\mathcal{O}_2\left((S^s)^2,(S^a)^2\right)\right] \\
&= \frac{\alpha_1}{\alpha_2}\left[1+\mathcal{O}_2\left((S^s)^2,(S^a)^2\right)\right] \qquad \text{(B-86)}
\end{aligned}$$

We can observe from (B-86) that there aren't terms linear in S^s or S^a.

B.9 Expansion in Taylor Series of the Pseudo-Potential Term from the Kinetic Energy: $\frac{1}{2}(g_0)^{-\frac{1}{4}}\left[P_\rho, g^{\rho\rho}(g_0)^{\frac{1}{2}}\left[P_\rho,(g_0)^{-\frac{1}{4}}\right]\right]$, as Function of the Stretching Coordinates

We consider the definition of μ from (§B.8) and the terms $\frac{1}{2}(g_0)^{-\frac{1}{4}}\left[P_\rho, g^{\rho\rho}(g_0)^{\frac{1}{2}}\left[P_\rho,(g_0)^{-\frac{1}{4}}\right]\right]$ become, with eq.(B-84):

$$\begin{aligned}
&(\mu^0)^{\frac{1}{4}}\left[P_\rho,\mu_{\rho\rho}(\mu^0)^{-\frac{1}{2}}\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right]\right] \qquad \text{(B-87)} \\
=\ &\mu_{\rho\rho}(\mu^0)^{\frac{1}{4}}\left[P_\rho,(\mu^0)^{\frac{1}{4}}\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right]\right]+(\mu^0)^{-\frac{1}{4}}\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right][P_\rho,\mu_{\rho\rho}]_0 \\
\approx\ &\mu^0_{\rho\rho}(\mu^0)^{\frac{1}{4}}\left[P_\rho,(\mu^0)^{\frac{1}{4}},\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right]\right]-(\mu^0)^{\frac{1}{4}}\left[P_\rho,(\mu^0)^{\frac{1}{4}},\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right]\right]\times \\
&\left\{\frac{1}{2}\sum_r \mu^0_{\rho\rho}a_r^{\rho\rho}\mu^0_{\rho\rho}S^r-\sum_{rs}\left[-\sum_{\delta\gamma}\mu^0_{\rho\delta}a_{rs}^{\delta\gamma}\mu^0_{\gamma\rho}+\sum_{\delta\gamma\epsilon\eta}\mu^0_{\rho\delta}a_r^{\delta\gamma}\mu^0_{\gamma\epsilon}a_s^{\epsilon\eta}\mu^0_{\eta\rho}\right]S^rS^s\right\} \\
+\ &(\mu^0)^{-\frac{1}{4}}\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right][P_\rho,\mu_{\rho\rho}]_0 \\
\approx\ &(\mu^0)^{\frac{1}{4}}\left[P_\rho,\mu^0_{\rho\rho}(\mu^0)^{-\frac{1}{2}}\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right]\right]-(\mu^0)^{\frac{1}{4}}\left[P_\rho,(\mu^0)^{\frac{1}{4}},\left[P_\rho,(\mu^0)^{\frac{1}{4}}\right]\right]\times \\
&\left\{\sum_r \mu^0_{\rho\rho}a_r^{\rho\rho}\mu^0_{\rho\rho}S^r-\sum_{rs}\left[-\mu^0_{\rho\rho}a_{rs}^{\rho\rho}\mu^0_{\rho\rho}+\sum_\delta \mu^0_{\rho\rho}a_r^{\rho\delta}\mu^0_{\delta\delta}a_s^{\delta\rho}\mu^0_{\rho\rho}\right]S^rS^s\right\}
\end{aligned}$$

In equation (B-87) we have made the approximation:

$$[P_\rho,\mu_{\rho\rho}]_0 \approx [P_\rho,\mu^0_{\rho\rho}] \qquad \text{(B-88)}$$

If we introduce the functions $f_1^r(\rho)$ and $f_2^{rt}(\rho)$:

$$\begin{aligned}
f_1^r(\rho) &= -\frac{1}{2}\sum_r \mu^0_{\rho\rho}a_r^{\rho\rho}\mu^0_{\rho\rho} \\
f_2^{rt}(\rho) &= -\sum_{\delta\gamma}\mu^0_{\rho\delta}a_{rs}^{\delta\gamma}\mu^0_{\gamma\rho}+\sum_{\delta\gamma\epsilon\eta}\mu^0_{\rho\delta}a_r^{\delta\gamma}\mu^0_{\gamma\epsilon}a_s^{\epsilon\eta}\mu^0_{\eta\rho} \qquad \text{(B-89)}
\end{aligned}$$

the eq.(B-87) is the same as (3.48).

B.10 The Kinetic Energy Formula in the Case of the Stretch-Bender Model

From (§B.4) and (§B.8) we have the following useful relations(with the notations from §B.8):

$$
\begin{array}{ll}
(g^0) = g_{ss}g_{aa}g_{\rho\rho}g_{\varphi\varphi} & \text{from eq.(B-49)} \\
[P_s\,,g^{s\rho}] = -\,(g^{ss})^0\,[P_s\,,g_{s\rho}]\,(g^{\rho\rho})^0 & \text{from (B-35), (B-26) and } g^{\alpha\beta} \text{ in (B-84)} \\
[P_a\,,g^{a\rho}] = -\,(g^{aa})^0\,[P_a\,,g_{a\rho}]\,(g^{\rho\rho})^0 & \text{from (B-37), (B-28) and } g^{\alpha\beta} \text{ in (B-84)} \\
a_s^{\rho\rho} = \frac{\partial}{\partial S^s}\,(g_{\rho\rho})_0 \not= 0 & \text{from (B-15)} \\
a_a^{\rho\rho} = \frac{\partial}{\partial S^a}\,(g_{\rho\rho})_0 = 0 & \text{because } S^a \text{ is as a square in (B-15)} \\
a_{ss}^{\rho\rho} = \frac{\partial^2}{\partial (S^s)^2}\,(g_{\rho\rho})_0 \not= 0 & \text{from eq.(B-15)} \\
a_{as}^{\rho\rho} = \frac{\partial^2}{\partial (S^s)\partial (S^a)}\,(g_{\rho\rho})_0 = 0 & \text{because } S^a \text{ is as a square in (B-15)} \\
a_{aa}^{\rho\rho} = \frac{\partial^2}{\partial (S^a)^2}\,(g_{\rho\rho})_0 \not= 0 & \text{from (B-15)} \\
a_s^{s\rho} = \frac{\partial}{\partial S^s}\,(g_{s\rho})_0 \not= 0 & \text{from (B-26)} \\
a_a^{a\rho} = \frac{\partial}{\partial S^a}\,(g_{a\rho})_0 \not= 0 & \text{from (B-28)}
\end{array}
\qquad \text{(B-90)}
$$

If we consider the formula (B-53) together with the expression of the contravariant tensor elements from (§B.8), we obtain with (B-90),

$$
\begin{aligned}
T \;=\;& T_{br}^0 + T_{str} + \frac{1}{2} g_0^{-\frac{1}{4}}\, g_0^{ss}\left[P_s\,,g^{\frac{1}{2}}\left[P_s\,,g^{-\frac{1}{4}}\right]\right]_0 \\
+\;& \frac{1}{2} g_0^{\frac{1}{4}}\, g_0^{aa}\left[P_a\,,\left[P_a\,,g^{-\frac{1}{4}}\right]\right]_0 - \frac{1}{2}\left[g_0^{ss}\,[P_s\,,g_{s\rho}]_0 + g_0^{aa}\,[P_a\,,g_{a\rho}]_0\right](g_0^{\rho\rho})\; g_0^{\frac{1}{4}}\left[P_\rho\,,g_0^{-\frac{1}{4}}\right] \\
+\;& \frac{1}{2} g_0^{-\frac{1}{4}}\left[P_\rho\,,g_0^{\frac{1}{2}}\left[P_\rho\,,g_0^{-\frac{1}{4}}\right]\right](g_0^{\rho\rho})^2 \cdot \left\{-a_s^{\rho\rho}\,S^s + \left[-a_{ss}^{\rho\rho} + (a_s^{\rho s} g_0^{ss} a_s^{\rho s} + a_s^{\rho\rho} g_0^{\rho\rho} a_s^{\rho\rho})\right](S^s)^2\right. \\
& \left. + \left[-a_{aa}^{\rho\rho} + (a_a^{\rho a}\, g_0^{aa} a_a^{\rho a} + a_a^{\rho\rho}\, g_0^{\rho\rho}\, a_a^{\rho\rho})\right](S^a)^2 + a_a^{\rho\rho} g_0^{\rho\rho} a_s^{\rho\rho}\, S^s\, S^a\right\}
\end{aligned}
\qquad \text{(B-91)}
$$

where

$$
\begin{aligned}
T_{rb}^0 \;&=\; \frac{1}{2}(g_0^{\rho\rho})\,P_\rho^2 + \frac{1}{2}[P_\rho\,,g_0^{\rho\rho}]\,P_\rho + \frac{1}{2} g_0^{-\frac{1}{4}}\left[P_\rho\,,g_0^{\rho\rho}\;(g_0)^{\frac{1}{2}}\left[P_\rho\,,g_0^{-\frac{1}{4}}\right]\right] \\
T_{str} \;&=\; \frac{1}{2} g_0^{ss} P_s^2 + \frac{1}{2} g_0^{aa} P_a^2
\end{aligned}
\qquad \text{(B-92)}
$$

Obs. If we consider the minimum condition ($S^s = S^a = 0$), before the derivation, some terms will vanish:

$$\left[P_s\,,(g_0)^{-\frac{1}{4}}\right] = 0 \quad \left[P_a\,,(g_0)^{-\frac{1}{4}}\right] = 0$$

$$[P_s\,,g_0^{s\rho}] = 0 \qquad [P_a\,,g_0^{a\rho}] = 0$$

B.11 The Behavior of the Pseudo-Potential Function $f(\rho)$ from the Bending Kinetic Energy near $\rho \to 0$

The pseudo-potential for the bending kinetic energy, from eq.(3.50) and formula below eq.(3.51), page 72, is:

$$
\begin{aligned}
f(\rho) \;=\;& f_0(\rho) + \left(\frac{\hbar^2}{2}\right)^{-1} (g_0^{\rho\rho})^{-1} \times \\
& \left\{\frac{1}{2}(g_0)^{-\frac{1}{4}}\, g_0^{ss}\left[P_s\,,g^{\frac{1}{2}}\left[P_s\,,g^{-\frac{1}{4}}\right]\right]_0 + \frac{1}{2}(g_0)^{\frac{1}{4}}\, g_0^{aa}\left[P_a\,,\left[P_a\,,g^{-\frac{1}{4}}\right]\right]_0\right. \\
& \left. -\frac{1}{2} g_0^{\rho\rho}\,(g_0)^{\frac{1}{4}}\left[P_\rho\,,(g_0)^{-\frac{1}{4}}\right]\left(g_0^{ss}\,[P_s\,,g_{s\rho}]_0 + g_0^{aa}\,[P_a\,,g_{a\rho}]_0\right)\right\}
\end{aligned}
\qquad \text{(B-93)}
$$

The first line is the term $f_0(\rho)$, with the behavior described in eq.(3.46) and (§B.7). We are interested in the last two rows of equation (B-93). From eq.(B-31), we have,

$$\begin{aligned}
\left(\frac{\partial g}{\partial \rho}\right)_{\substack{\rho\to 0\\ S^s\to 0\\ S^a\to 0}} &\simeq \frac{m_1 r_4}{p}\left(\frac{\rho}{2}\right)^2\cdot\sqrt{2}\frac{p}{r} = \sqrt{2}m_1 r^3\left(\frac{\rho}{2}\right)^2 \sim \left(\frac{\rho}{2}\right)^2\\
\left(\frac{\partial^2 g}{\partial (S^s)^2}\right)_{\substack{\rho\to 0\\ S^s\to 0\\ S^a\to 0}} &\simeq \frac{m_1 r_4}{p}\left(\frac{\rho}{2}\right)^2\cdot\frac{p^2}{2r^2} = \frac{p\,m_1 r^2}{2}\left(\frac{\rho}{2}\right)^2 \sim \left(\frac{\rho}{2}\right)^2\\
\left(\frac{\partial^2 g}{\partial (S^a)^2}\right)_{\substack{\rho\to 0\\ S^s\to 0\\ S^a\to 0}} &\simeq \frac{m_1 r_4}{p}\left(\frac{\rho}{2}\right)^2\cdot\frac{p^2}{2r^2} = \frac{p\,m_1 r^2}{2}\left(\frac{\rho}{2}\right)^2 \sim \left(\frac{\rho}{2}\right)^2\\
g_{a\rho} &\sim \rho S^a r\\
g_{s\rho} &\sim \rho S^s
\end{aligned} \tag{B-94}$$

The pseudo-potential terms are:

$$\begin{aligned}
g_0^{-\frac{1}{4}} g_0^{ss}\left[P_s, g_0^{\frac{1}{2}}\left[P_s, g_0^{-\frac{1}{4}}\right]\right] &\sim \left(\frac{\partial^2 g}{\partial (S^s)^2}\right)\frac{1}{g_0} - \frac{3}{4}\frac{1}{g^2}\frac{\partial g}{\partial S^s} \sim \frac{\left(\frac{\rho}{2}\right)^2}{\left(\frac{\rho}{2}\right)^2} - \frac{3}{4}\frac{\left[\left(\frac{\rho}{2}\right)^2\right]}{\left[\left(\frac{\rho}{2}\right)^2\right]} \sim const\\
\frac{1}{2}(g_0)^{\frac{1}{4}} g_0^{aa}\left[P_a, \left[P_a, g^{-\frac{1}{4}}\right]\right]_0 &\sim \left(\frac{\partial^2 g}{\partial (S^a)^2}\right)\frac{1}{g_0} \sim \frac{\left(\frac{\rho}{2}\right)^2}{\left(\frac{\rho}{2}\right)^2} \sim const
\end{aligned} \tag{B-95}$$

$$\begin{aligned}
\frac{1}{2} g_0^{\rho\rho}(g_0)^{\frac{1}{4}}\left[P_\rho, (g_0)^{-\frac{1}{4}}\right]\left(g_0^{ss}\left[P_s, g_{s\rho}\right]_0 + g_0^{aa}\left[P_a, g_{a\rho}\right]_0\right) &\sim \frac{g_0}{g_0'}\left[\frac{\partial}{\partial S^s}(g_{s\rho}) + \frac{\partial}{\partial S^a}(g_{a\rho})\right]\\
&\sim \frac{\left(\frac{\rho}{2}\right)}{\left(\frac{\rho}{2}\right)^2}[\rho+\rho] \sim const
\end{aligned} \tag{B-96}$$

As it can be seen from the above relations, the terms don't change proportional to $\left(\frac{1}{\rho^2}\right)$, near $\rho \to 0$; they are constants and for this reason we consider that they can be neglected.

Appendix C

Potential energy

C.1 The Compuation of the ρ Dependence for the Bond Length

We consider the internal generalized coordinates for stretching (3.19):

$$\begin{aligned} \Delta r_{12} &= \frac{1}{\sqrt{2}}\left(R_1\, S^s + R_5\, S^a\right) + \mathcal{R}\left(\rho\right) = r_{12} - r_{12}^0 \\ \Delta r_{23} &= \frac{1}{\sqrt{2}}\left(R_1\, S^s - R_5\, S^a\right) + \mathcal{R}\left(\rho\right) = r_{23} - r_{23}^0 \end{aligned} \tag{C-1}$$

The change from internal generalized coordinates to symmetric generalized coordinates for stretching displacements is:

$$\begin{array}{l} \Delta r_{12} = \frac{1}{\sqrt{2}}\left(\Delta r_s + \Delta r_a\right) \\ \Delta r_{23} = \frac{1}{\sqrt{2}}\left(\Delta r_s - \Delta r_a\right) \end{array} \quad \rightarrow \quad \begin{array}{l} \Delta r_s = \frac{1}{\sqrt{2}}\left(\Delta r_{12} + \Delta r_{23}\right) = R_1\, S^s + \sqrt{2}\mathcal{R}\left(\rho\right) \\ \Delta r_a = \frac{1}{\sqrt{2}}\left(\Delta r_{12} - \Delta r_{23}\right) = R_5\, S^a \end{array} \tag{C-2}$$

The generalized potential has the expression, with the definition of the constants from [46]:

$$V_{gen} = \frac{1}{2} f_{11}\left(\Delta r_{12}^2 + \Delta r_{23}^2\right) + f_{13}\,\Delta r_{12}\,\Delta r_{23} + F_{122}\left(\Delta r_{12} + \Delta r_{23}\right)\left(\rho - \rho_e\right)^2 \tag{C-3}$$

From the above expression, the generalized potential become in symmetric generalized coordinates:

$$V_{gen} = \frac{1}{2}\left(f_{11} + f_{13}\right)\Delta r_s^2 + \frac{1}{2}\left(f_{11} - f_{13}\right)\Delta r_a^2 + \sqrt{2} F_{122}\Delta r_s\,\left(\rho - \rho_e\right)^2 \tag{C-4}$$

The dependence of the bond length from the angle is:

$$\begin{array}{l} \frac{\partial V}{\partial(\Delta r_s)}|_{S^s=S^a=0} = 0 \quad \rightarrow \quad \left(f_{11} + f_{13}\right)\Delta r_s|_{S^s=0} + \sqrt{2} F_{122}\,\left(\rho - \rho_e\right)^2 = 0 \\ \frac{\partial V}{\partial(\Delta r_a)}|_{S^s=S^a=0} = 0 \quad \rightarrow \quad \left(f_{11} - f_{13}\right)\Delta r_a|_{S^a=0} = \left(f_{11} - f_{13}\right) R_5\, S^a|_{S^a=0} = 0 \end{array} \tag{C-5}$$

If we consider the relations (C-2) and (C-5) we obtain:

$$\Delta r_s|_{S^s=0} = \sqrt{2}\mathcal{R}\,\left(\rho - \rho_e\right) \quad \Rightarrow \quad \left(f_{11} + f_{13}\right)\mathcal{R}\,\left(\rho\right) + F_{122}\,\left(\rho - \rho_e\right)^2 = 0 \tag{C-6}$$

The dependence of the bond length from the angle become:

$$\mathcal{R}\,\left(\rho\right) = -\frac{F_{122}(\rho-\rho_e)^2}{f_{11}+f_{13}} + \mathcal{O}(\rho^4) \quad \text{or} \quad F_{122} = -\frac{(f_{11}+f_{13})\mathcal{R}\,(\rho)}{(\rho-\rho_e)^2} \tag{C-7}$$

The eq. (C-7) shows that the dependence of the bond length to angle is connected to the F_{122} anharmonic potential factor. Then, the semirigid bender model assumed implicitly anharmonic potential force constant, for the Fermi interaction.

Obs. In the case of a bent molecule, the term F_{2i}, with $i = 1, 3$ is non-zero. Then, in the eq. (C-4) we must add the term $\sqrt{2}F_{12}\Delta r_s\,\left(\rho - \rho_e\right)$. In this case, the equation (C-7) will have the form,

$$\mathcal{R}\,\left(\rho\right) = -\frac{F_{12}\left(\rho - \rho_e\right)}{f_{11} + f_{13}} - \frac{F_{122}\left(\rho - \rho_e\right)^2}{f_{11} + f_{13}} + \mathcal{O}(\rho^4)$$

C.2 Stretching Potential in Curvilinear Coordinates

If we introduce the relations (C-2) and (C-7) into the relation of the generalized potential, (C-4),its expression become:

$$\begin{aligned} V_{gen} &= \frac{1}{2}(f_{11}+f_{13})\cdot\left[R_1 S^s+\sqrt{2}\mathcal{R}(\rho)\right]^2+\frac{1}{2}(f_{11}-f_{13})R_5^2(S^a)^2 \\ &- \sqrt{2}\frac{(f_{11}+f_{13})\mathcal{R}(\rho)}{(\rho-\rho_e)^2}\left[R_1 S^s+\sqrt{2}\mathcal{R}(\rho)\right](\rho-\rho_e)^2 \\ &= \frac{1}{2}(f_{11}+f_{13})(R_1 S^s)^2+\frac{1}{2}(f_{11}-f_{13})(R_5 S^a)^2-(f_{11}+f_{13})\mathcal{R}^2(\rho) \end{aligned} \tag{C-8}$$

The formula for the potential in curvilinear coordinates is:

$$V^{curv}=\frac{1}{2}f_{rr}^s(S^s)^2+\frac{1}{2}f_{rr}^a(S^a)^2-(f_{11}+f_{13})\mathcal{R}^2(\rho) \tag{C-9}$$

where

$$f_{rr}^s=(f_{11}+f_{13})\cdot R_1^2(S^s)^2 \quad \text{and} \quad f_{rr}^a=(f_{11}-f_{13})\cdot R_5^2(S^a)^2 \tag{C-10}$$

The third term from the eq. (C-9) will be introduced into the bending potential because it not depends on the stretching coordinates. This imply that we can consider for the stretching potential only the first two terms:

$$V^{curv}\simeq\frac{1}{2}f_{rr}^s(S^s)^2+\frac{1}{2}f_{rr}^a(S^a)^2 \tag{C-11}$$

This relation represents the value of the potential relative to the "zero" potential (which has as reference point $f(\rho)$).

C.3 General Stretching Potential and Calculus of $f(\rho)$ Dependence of the Bond Length

We consider the expression of the potential until cubic order terms, with the potential force constants from [46]:

$$V=\sum_{i\le j}F_{ij}\cdot\mathbf{R}^i\,\mathbf{R}^j+\sum_{i\le j\le k}F_{ijk}\cdot\mathbf{R}^i\,\mathbf{R}^j\,\mathbf{R}^k \tag{C-12}$$

In the previous equation, we have $i,j,k=1,3$. The potential expansion in power series of S_1 and S_3, or S^s and S^a, respectively, for each value of ρ is [6, 17]:

$$V=V_0(\rho)+\sum_i\bar{F}_i(\rho)\mathbf{R}^i+\sum_{i\le j}\bar{F}_{ij}(\rho)\cdot\mathbf{R}^i\,\mathbf{R}^j+\sum_{i\le j\le k}\bar{F}_{ijk}(\rho)\cdot\mathbf{R}^i\,\mathbf{R}^j\,\mathbf{R}^k \tag{C-13}$$

where $V_0(\rho)$ is the bending potential. We will use some notations [46]:

$$\begin{array}{ll} \bar{F}_i(\rho)=\bar{f}_i(\rho) & 2\bar{F}_{ii}(\rho)=\bar{f}_{ii}(\rho) \\ \bar{F}_{ij}(\rho)=\bar{f}_{ij}(\rho) & 6\bar{F}_{iii}(\rho)=\bar{f}_{iii}(\rho) \\ 2\bar{F}_{iij}(\rho)=\bar{f}_{iij}(\rho) & \bar{F}_{ijk}(\rho)=\bar{f}_{ijk}(\rho) \end{array} \tag{C-14}$$

By using the above relations we will obtain the expression for the bending potential:

$$V_0(\rho)=F_{22}(\rho_e-\bar{\rho})^2+F_{222}(\rho_e-\bar{\rho})^3+F_{2222}(\rho_e-\bar{\rho})^4 \tag{C-15}$$

and after identifications of the power of the stretching coordinate in (C-12):

$$\begin{aligned} \bar{F}_i(\rho) &= F_{i2}(\rho_e-\bar{\rho})+F_{i22}(\rho_e-\bar{\rho})^2+F_{i222}(\rho_e-\bar{\rho})^3 \\ \bar{F}_{ij}(\rho) &= F_{ij}+F_{ij2}(\rho_e-\bar{\rho})+F_{ij22}(\rho_e-\bar{\rho})^2 \\ \bar{F}_{ijk}(\rho) &= F_{ijk}+F_{ijk2}(\rho_e-\bar{\rho}) \end{aligned} \tag{C-16}$$

The semirigid bender conditions is, as in (§C.1):

$$\left[\frac{\partial V^{as}}{\partial(\mathbf{R}^i)}\right]_0 = \left[\frac{\partial V}{\partial(\mathbf{R}^i)}\right]_0 = 0 \tag{C-17}$$

If we consider the semirigid bender condition for the potential the following relation will be obtained:

$$\begin{aligned} & \bar{F}_i(\rho) + \sum_{\substack{i \\ i \le j}} \bar{F}_{ij}(\rho)\mathbf{R}^j|_{\delta_{ij}} + \sum_{\substack{ik \\ i \le j \le k}} \bar{F}_{ijk}(\rho)\left(\mathbf{R}^j\,\mathbf{R}^k\right)|_{\substack{\delta_{ij} \\ \delta_{ki}}} \\ = \;& \bar{F}_i(\rho) + 2F_{ii}(\rho)\mathbf{R}^i + 3\bar{F}_{iii}(\rho)(\mathbf{R}^i)^2 = 0 \end{aligned} \tag{C-18}$$

The variation of the bond length is:

$$\mathbf{R}^i|_0 = (\Delta r)_0 \approx \mathcal{R}(\rho) \tag{C-19}$$

If we introduce the semirigid bender condition (C-19) into the relation (C-18), the expression for the variation of the bond length become:

$$\mathbf{R}^i|_0 = \frac{-\bar{F}_{ii} + \sqrt{(\bar{F}_{ii})^2 - 3\bar{F}_{iii}\cdot\bar{F}_i}}{3\bar{F}_{iii}} = -\frac{\bar{F}_{ii}}{3\bar{F}_{iii}} + \frac{\bar{F}_{ii}}{3\bar{F}_{iii}}\sqrt{1 - \frac{3\bar{F}_{iii}\cdot\bar{F}_i}{(\bar{F}_{ii})^2}} \simeq -\frac{\bar{F}_i(\rho)}{\bar{f}_{ii}(\rho)} \tag{C-20}$$

Obs. The difference between the relation (C-20) and [14, eq.(20)] is the different level of approximation, connected with the presence of $\bar{F}_{ii}$ factor outside of square root, instead of $\bar{f}_{ii}$ factor. But the above formula is the same with the corrected formula of [14, eq.(20)], as it is given in [74, eq.(21)-(23)]. In the case of a linear molecule the two formulas are equal.

C.4 Relations between the Internal Generalized Coordinates and the Curvilinear Symmetrized Coordinates

- From (§A.10) for $R_1(\rho)$ and $R_5(\rho)$ auxiliary functions, and equation (3.14) and (3.21) for the bending angle, the relation between generalized and curvilinear coordinates (3.19) become:

$$\begin{aligned} \mathbf{R}^1|_{\rho\to 0} &\simeq \frac{1}{\sqrt{2}}\left\{S^s\left[1 + R_1^\rho\left(\frac{\rho}{2}\right)^2\right] + S^a\left[p - R_1^\rho\left(\frac{\rho}{2}\right)^2\right]\right\} + d\rho^2 \\ \mathbf{R}^3|_{\rho\to 0} &\simeq \frac{1}{\sqrt{2}}\left\{S^s\left[1 + R_1^\rho\left(\frac{\rho}{2}\right)^2\right] - S^a\left[p - R_1^\rho\left(\frac{\rho}{2}\right)^2\right]\right\} + d\rho^2 \end{aligned} \tag{C-21}$$

$$\gamma = \bar{\rho} = \rho\left[1 + \frac{A_\rho}{\sqrt{2}r}S^s\right] \tag{C-22}$$

Obs. The approximation of eq.(C-22) with eq.(3.12) may be justified for values near $\rho_e \to 0$, as follows: in first approximation we neglect the ρ_e value as being small, and we consider only the ρ value,

$$(\rho - \rho_e)\,|_{\rho_e\to 0} \simeq \rho \tag{C-23}$$

This approximation is done only in the formula:

$$(\bar{S}^s - S^s) \simeq \left(\frac{\partial S^s}{\partial \rho}\right)_{\bar{S}^s = S^s}(\rho - \rho_e)\,|_{\rho_e\to 0} \simeq \left(\frac{\partial S^s}{\partial \rho}\right)_{\bar{S}^s = S^s}\rho \tag{C-24}$$

From the eq. (C-21) we obtain:

$$\begin{aligned} \mathbf{R}^1|_{\rho\to 0} &\simeq \frac{1}{\sqrt{2}}\left[S^s\left(1 + A_a\rho^2\right) + S^a\left(p - A_a\rho^2\right)\right] + d\rho^2 \\ \mathbf{R}^3|_{\rho\to 0} &\simeq \frac{1}{\sqrt{2}}\left[S^s\left(1 + A_a\rho^2\right) - S^a\left(p - A_a\rho^2\right)\right] + d\rho^2 \end{aligned} \tag{C-25}$$

where there are the following notations, with the dependance of the bond length with angle like in (3.84):

$$\begin{aligned} R_1^\rho &= (p-1)(1-8\frac{d}{r}) \\ A_\rho &= R_2^\rho = (p-1) - 8\frac{d}{r} \\ A_s &= \frac{1}{4}R_1^\rho - 2\frac{d}{r}A_\rho = A_a - 2\frac{d}{r}A_\rho \\ A_a &= \frac{1}{4}R_1^\rho \end{aligned} \tag{C-26}$$

- The potential constants are changing when the coordinates transformation occur and in order to obtain their relations we consider the following derivatives, *which are different from zero* [46, eq.(4)-(6)]:

$$\begin{array}{llll} \left(\frac{\partial\gamma}{\partial\rho}\right)_0 = 1 & \left(\frac{\partial^2\gamma}{\partial\rho\partial S^s}\right)_0 = \frac{A_\rho}{\sqrt{2}r} & \left(\frac{\partial\mathbf{R}^1}{\partial S^s}\right)_0 = \frac{1}{\sqrt{2}} & \left(\frac{\partial^3\mathbf{R}^1}{\partial S^s\partial\rho^2}\right)_0 = 2\frac{A_a}{\sqrt{2}} \\ \left(\frac{\partial\mathbf{R}^1}{\partial S^a}\right)_0 = \frac{p}{\sqrt{2}} & \left(\frac{\partial^3\mathbf{R}^1}{\partial S^a\partial\rho^2}\right)_0 = -2\frac{A_a}{\sqrt{2}} & \left(\frac{\partial^2\mathbf{R}^1}{\partial\rho^2}\right)_0 = 2d & \left(\frac{\partial\mathbf{R}^3}{\partial S^s}\right)_0 = \frac{1}{\sqrt{2}} \\ \left(\frac{\partial^3\mathbf{R}^3}{\partial S^s\partial\rho^2}\right)_0 = 2\frac{A_a}{\sqrt{2}} & \left(\frac{\partial\mathbf{R}^3}{\partial S^a}\right)_0 = -\frac{p}{\sqrt{2}} & \left(\frac{\partial^3\mathbf{R}^3}{\partial S^a\partial\rho^2}\right)_0 = 2\frac{A_a}{\sqrt{2}} & \left(\frac{\partial^2\mathbf{R}^3}{\partial\rho^2}\right)_0 = 2d \end{array} \tag{C-27}$$

- With the previous relations, the potential constant are the following:
  - The non vanishing derivatives:

$$b_s^1 = \frac{1}{\sqrt{2}} \quad b_s^3 = \frac{1}{\sqrt{2}} \tag{C-28}$$

The quadratic symmetric stretching potential constant:

$$\begin{aligned} f_{ss} &= f_{11}\,b_s^1\,b_s^1 + f_{33}\,b_s^1\,b_s^1 + 2\,f_{13}\,b_s^1\,b_s^3 \\ &= \left[\frac{1}{2}\,(f_{11}+f_{33}) + f_{13}\right]_{f_{11}=f_{33}} = f_{11} + f_{13} \end{aligned} \tag{C-29}$$

  - The non vanishing derivatives:

$$b_s^1 = \frac{1}{\sqrt{2}} \quad b_a^1 = \frac{p}{\sqrt{2}} \quad b_s^3 = \frac{1}{\sqrt{2}} \quad b_a^3 = \frac{p}{\sqrt{2}} \tag{C-30}$$

The mixed quadratic stretching constant vanish, as it should be:

$$\begin{aligned} f_{as} &= f_{11}\,b_s^1\,b_a^1 + f_{33}\,b_s^3\,b_a^3 + f_{13}\,b_s^1\,b_a^3 + f_{31}\,b_s^3\,b_a^1 \\ &= \frac{p}{2}\,(f_{11} - f_{33}) + \frac{p}{2}\,(-f_{13} + f_{31}) = 0 \end{aligned} \tag{C-31}$$

  - The non vanishing derivatives:

$$b_s^1 = \frac{1}{\sqrt{2}} \quad b_s^3 = \frac{1}{\sqrt{2}} \quad b_\rho^2 = 1 \tag{C-32}$$

The mixed quadratic symmetric stretch-bending constant vanish, as it should be:

$$f_{\rho s} = f_{12}\,b_s^1\,b_\rho^2 + 2f_{21}\,b_\rho^1\,b_s^2 + f_{32}\,b_s^3\,b_\rho^2 = \frac{1}{\sqrt{2}}\,(f_{12}+f_{32})\,|_{f_{12}=f_{32}} = \sqrt{2}\,f_{12} = 0 \tag{C-33}$$

  - The non vanishing derivatives:

$$b_a^1 = p \quad b_a^3 = -p \tag{C-34}$$

The quadratic antisymmetric stretching constant:

$$\begin{aligned} f_{aa} &= f_{11}\,b_a^1\,b_a^1 + f_{33}\,b_a^3\,b_a^3 + 2f_{13}\,b_a^1\,b_a^3 \\ &= \left[\frac{p^2}{2}\,(f_{11}+f_{33}) - 2\frac{p^2}{2}f_{13}\right]_{f_{11}=f_{33}} = (f_{11} - f_{13})\,p^2 \end{aligned} \tag{C-35}$$

– The non vanishing derivatives:

$$b_\rho^2 = 1 \tag{C-36}$$

The quadratic bending constant:

$$f_{\rho\rho} = f_{22}\, b_\rho^2\, b_\rho^2 = f_{22} \tag{C-37}$$

– The non vanishing derivatives:

$$b_a^1 = \tfrac{p}{\sqrt{2}} \quad b_a^3 = -\tfrac{p}{\sqrt{2}} \quad b_\rho^2 = 1 \tag{C-38}$$

The mixed quadratic antisymmetric stretch-bending constant vanish, as it should be:

$$f_{a\rho} = f_{12}\, b_a^1\, b_\rho^2 + f_{32}\, b_a^3\, b_\rho^2 = \frac{p}{\sqrt{2}}\,(f_{12} - f_{32}) = 0 \tag{C-39}$$

– The non vanishing derivatives:

$$\begin{array}{lll} b_s^1 = \frac{1}{\sqrt{2}} & b_s^3 = \frac{1}{\sqrt{2}} & b_{\rho\rho}^1 = 2d \\ b_{\rho\rho}^3 = 2d & b_\rho^2 = 1 & b_{\rho s}^2 = \frac{A_\rho}{\sqrt{2}r} \end{array} \tag{C-40}$$

The anharmonic cubic potential constant:

$$\begin{aligned} f_{s\rho\rho} &= f_{122}\, b_s^1\, b_\rho^2\, b_\rho^2 + f_{322}\, b_\rho^3\, b_\rho^2\, b_\rho^2 + f_{11}\left(b_s^1\, b_{\rho\rho}^1 + 2b_\rho^1\, b_{\rho s}^1\right) + f_{33}\left(b_s^3\, b_{\rho\rho}^3 + 2b_\rho^3\, b_{\rho s}^3\right) \\ &\quad + f_{13}\left(b_s^1\, b_{\rho\rho}^3 + 2b_\rho^1\, b_{\rho s}^3\right) + f_{31}\left(b_s^3\, b_{\rho\rho}^1 + 2b_\rho^3\, b_{\rho s}^1\right) + f_{22}\left(b_s^2\, b_{\rho\rho}^2 + 2b_\rho^2\, b_{\rho s}^2\right) \\ &= \left[f_{122}\,\frac{1}{\sqrt{2}} + f_{322}\,\frac{1}{\sqrt{2}} + 2f_{11}\,\frac{2d}{\sqrt{2}} + 2f_{13}\,\frac{2d}{\sqrt{2}} + 2f_{22}\,\frac{A_\rho}{\sqrt{2}r}\right]_{\substack{f_{122}=f_{322} \\ f_{11}=f_{33}}} \\ &= \sqrt{2}f_{122} + 2\sqrt{2}\,(f_{11} + f_{13})\; d + \sqrt{2}f_{22}\frac{A_\rho}{r} \\ &= \underbrace{\sqrt{2}\,[f_{122} + 2d\,(f_{11} + f_{13})]}_{\sim 0\ from\ eq.(3.56)} + \sqrt{2}\, f_{22}\frac{A_\rho}{r} \end{aligned} \tag{C-41}$$

The effective anharmonic cubic potential constant, with (3.56) can be computed in the case we use d^{th} defined in (3.56). When d is computed in with other methods (rotational constants), we must add to the previous formula:

$$2\sqrt{2}\,\frac{(g_D - 1)}{g_D}\; d\;\,(f_{11} + f_{13})$$

and the formula will be,

$$F_{s\rho\rho} = \frac{1}{2} f_{s\rho\rho} = f_{22}\frac{A_\rho}{\sqrt{2}r} + \sqrt{2}\,\frac{(g_D - 1)}{g_D}\; d\;\,(f_{11} + f_{13}) \tag{C-42}$$

– The non vanishing derivatives:

$$b_\rho^2 = 1 \quad b_{\rho\rho}^1 = 2d \quad b_{\rho\rho}^3 = 2d \tag{C-43}$$

The quartic bending constant,

$$\begin{aligned} f_{\rho\rho\rho\rho} &= f_{2222}\, b_\rho^2\, b_\rho^2\, b_\rho^2\, b_\rho^2 + 2f_{122}\left(b_{\rho\rho}^1\, b_\rho^2\, b_\rho^2 \cdot 6\right) \\ &\quad + \left[f_{11}\left(b_{\rho\rho}^1\, b_{\rho\rho}^1 \cdot 3\right) + f_{33}\left(b_{\rho\rho}^3\, b_{\rho\rho}^3 \cdot 3\right) + 2f_{13}\left(b_{\rho\rho}^1\, b_{\rho\rho}^3 \cdot 3\right)\right] \\ &= f_{2222} + 24d\, f_{122} + 24d^2\,(f_{11} + f_{13}) \end{aligned} \tag{C-44}$$

The effective quartic bending constant:

$$F_{\rho\rho\rho\rho} = \frac{1}{24} f_{\rho\rho\rho\rho} = F_{2222} + 2dF_{122} + d^2\,(f_{11} + f_{13}) \tag{C-45}$$

C.5 Connection between Curvilinear Symmetrized Coordinates and Internal Generalized Coordinates

- We consider the following relations for the coordinates transformation (from eq.(3.82) and (3.83)):

$$\begin{aligned}
\mathbf{R}^1|_{\rho\to 0} &\simeq \frac{1}{\sqrt{2}}\left[S^s + \frac{1}{4}R_1^\rho\,\rho^2\,S^s + pS^a - \frac{1}{4}R_1^\rho\,\rho^2\,S^a\right] + d\rho^2 + \mathcal{O}((S^s)^2\rho^2) \\
&= \frac{1}{\sqrt{2}}\left[S^s + A_a\rho^2 S^s + pS^a - A_a\rho^2 S^a\right] + d\rho^2 \\
\mathbf{R}^3|_{\rho\to 0} &\simeq \frac{1}{\sqrt{2}}\left[S^s + A_a\rho^2 S^s - pS^a + A_a\rho^2 S^a\right] + d\rho^2
\end{aligned} \tag{C-46}$$

We will consider the difference and the summation, of the previous equations,

$$\begin{aligned}
\mathbf{R}^1 - \mathbf{R}^3 &= \sqrt{2}\left[p - A_a\rho^2\right]S^a \\
\mathbf{R}^1 + \mathbf{R}^3 &= \sqrt{2}\left[1 + A_a\rho^2\right]S^s + 2d\,\rho^2
\end{aligned} \tag{C-47}$$

The relation for the bending angle is (we have the notation: $\gamma \equiv \bar{\rho}$):

$$\rho = \frac{\gamma}{\left[1 + \frac{A_\rho}{\sqrt{2}r}S^s\right]} \simeq \gamma\left[1 - \frac{A_\rho}{\sqrt{2}r}S^s\right] \tag{C-48}$$

If we introduce ρ relation into the eq.(C-47) we obtain:

$$\begin{aligned}
\frac{1}{\sqrt{2}}\left(\mathbf{R}^1 - \mathbf{R}^3\right) &\simeq \left(p - A_a\gamma^2\right)S^a \\
\frac{1}{\sqrt{2}}\left(\mathbf{R}^1 + \mathbf{R}^3\right) &\simeq \left(1 + A_a\gamma^2\right)S^s + \sqrt{2}d\,\gamma^2\left(1 - \sqrt{2}\frac{A_\rho}{r}S^s\right) \\
&= \left(1 + A_s\gamma^2\right)S^s + \sqrt{2}d\,\gamma^2
\end{aligned} \tag{C-49}$$

By using the above relations we get the curvilinear coordinates as function of internal generalized coordinates:

$$\begin{aligned}
S^a &= \frac{1}{\sqrt{2}}\frac{\mathbf{R}^1 - \mathbf{R}^3}{p - A_a\gamma_2} \simeq \frac{1}{\sqrt{2}p}(\mathbf{R}^1 - \mathbf{R}^3)\left(1 + \frac{A_a}{p}\gamma^2\right) \\
S^s &= \frac{1}{\sqrt{2}}\frac{(\mathbf{R}^1 - \mathbf{R}^3) - 2d\gamma^2}{1 + A_s\gamma_2} \simeq \frac{1}{\sqrt{2}}(\mathbf{R}^1 + \mathbf{R}^3)\left(1 - A_s\gamma^2\right) - \sqrt{2}d\gamma^2 + \mathcal{O}(\gamma^4)
\end{aligned} \tag{C-50}$$

The relation of ρ when we introduce the relations (C-50) become:

$$\begin{aligned}
\rho &\simeq \gamma\left\{1 - \frac{A_\rho}{\sqrt{2}r}\left[\frac{1}{\sqrt{2}}(\mathbf{R}^1 + \mathbf{R}^3)\left(1 - A_a\gamma^2\right) - \sqrt{2}d\gamma^2\right]\right\} \\
&\simeq \gamma\left[1 - \frac{A_\rho}{2r}(\mathbf{R}^1 + \mathbf{R}^3)\right] + \frac{d}{r}A_\rho\,\gamma^3 + \mathcal{O}(\gamma^3\mathbf{R}^1) \simeq \gamma\left[1 - \frac{A_\rho}{2r}(\mathbf{R}^1 + \mathbf{R}^3)\right] + \frac{d}{r}A_\rho\,\gamma^3
\end{aligned} \tag{C-51}$$

- The relations for the potential constants transformations when we pass from the curvilinear symmetrized coordinates to the generalized coordinates can be obtained by considering first the following derivatives, *which are different from zero* [46, eq.(4)-(6)]:

$$\begin{aligned}
&\left(\frac{\partial\rho}{\partial\gamma}\right)_0 = 1 && \left(\frac{\partial^2\rho}{\partial\gamma\partial(\mathbf{R}^1)}\right)_0 = \left(\frac{\partial^2\rho}{\partial\gamma\partial(\mathbf{R}^3)}\right)_0 = -\frac{A_\rho}{2r} \\
&\left(\frac{\partial^3\rho}{\partial\gamma^3}\right)_0 = 6\frac{d}{r}A_\rho && \left(\frac{\partial S^s}{\partial(\mathbf{R}^1)}\right)_0 = \left(\frac{\partial S^s}{\partial(\mathbf{R}^3)}\right)_0 = \frac{1}{\sqrt{2}} \\
&\left(\frac{\partial^3 S^s}{\partial(\mathbf{R}^1)\partial\gamma^2}\right)_0 = \left(\frac{\partial^3 S^s}{\partial(\mathbf{R}^3)\partial\gamma^2}\right)_0 = -\sqrt{2}A_s && \left(\frac{\partial^2 S^s}{\partial\gamma^2}\right)_0 = -2\sqrt{2}d \\
&\left(\frac{\partial S^a}{\partial(\mathbf{R}^1)}\right)_0 = -\left(\frac{\partial S^a}{\partial(\mathbf{R}^3)}\right)_0 = \frac{1}{\sqrt{2}p} && \left(\frac{\partial^3 S^a}{\partial(\mathbf{R}^1)\partial\gamma^2}\right)_0 = -\left(\frac{\partial^3 S^a}{\partial(\mathbf{R}^3)\partial\gamma^2}\right)_0 = \frac{\sqrt{2}}{p^2}A_a
\end{aligned} \tag{C-52}$$

Using the previous derivatives, the potential constants are the following:

– The non vanishing derivatives:

$$b_1^s = \frac{1}{\sqrt{2}} \quad b_1^a = \frac{1}{\sqrt{2}p} \tag{C-53}$$

The stretching quadratic potential constant:

$$f_{11} = f_{ss}\, b_1^s\, b_1^s + f_{aa}\, b_1^a\, b_1^a = \frac{1}{2} f_{ss} + \frac{1}{2p^2} f_{aa} = \frac{1}{2}\left(f_{ss} + \frac{f_{aa}}{p^2}\right) \tag{C-54}$$

– The non vanishing derivatives:

$$b_2^\rho = 1 \tag{C-55}$$

The bending quadratic constant:

$$f_{22} = f_{\rho\rho}\, b_2^\rho\, b_2^\rho = f_{\rho\rho} \tag{C-56}$$

– The non vanishing derivatives:

$$b_3^s = \frac{1}{\sqrt{2}} \quad b_3^a = -\frac{1}{\sqrt{2}p} \tag{C-57}$$

The stretching antisymmetric quadratic constant:

$$f_{33} = f_{ss}\, b_3^s\, b_3^s + f_{aa}\, b_3^a\, b_3^a = \frac{1}{2}\left(f_{ss} + \frac{f_{aa}}{p^2}\right) \tag{C-58}$$

– The non vanishing derivatives:

$$\begin{array}{ll} b_1^s = \frac{1}{\sqrt{2}} & b_3^s = \frac{1}{\sqrt{2}} \\ b_1^a = \frac{1}{\sqrt{2}p} & b_3^a = -\frac{1}{\sqrt{2}p} \end{array} \tag{C-59}$$

The mixed stretching quadratic constant:

$$f_{13} = f_{ss}\, b_1^s\, b_3^s + f_{aa}\, b_1^a\, b_3^a = \frac{1}{2}\left(f_{ss} - \frac{f_{aa}}{p^2}\right) \tag{C-60}$$

– The non vanishing derivatives:

$$\begin{array}{lll} b_1^s = \frac{1}{\sqrt{2}} & b_1^a = \frac{1}{\sqrt{2}p} & b_{22}^s = -2\sqrt{2}d \\ b_2^\rho = 1 & b_{12}^\rho = -\frac{A_\rho}{2r} & \end{array} \tag{C-61}$$

The anharmonic cubic term:

$$\begin{aligned} f_{122} &= f_{s\rho\rho}\, b_1^s\, b_2^\rho\, b_2^\rho + f_{ss}\,(b_1^s\, b_{22}^s + 2 b_2^s\, b_{12}^s) + f_{\rho\rho}\,(b_1^\rho\, b_{22}^\rho + 2 b_2^\rho\, b_{12}^\rho) \\ &= \frac{1}{\sqrt{2}} f_{s\rho\rho} - 2d\, f_{ss} - \frac{A_\rho}{r} f_{\rho\rho} \end{aligned} \tag{C-62}$$

The effective cubic potential constant:

$$F_{122} = \frac{1}{\sqrt{2}} F_{s\rho\rho} - d f_{ss} - \frac{A_\rho}{2r} f_{\rho\rho} \tag{C-63}$$

– The non vanishing derivatives:

$$b_2^\rho = 1 \quad b_{222}^\rho = 6\tfrac{d}{r} A_\rho \quad b_{22}^s = -2\sqrt{2}d \tag{C-64}$$

The quartic potential constant:

$$\begin{aligned} f_{2222} &= f_{\rho\rho\rho\rho}\, b_2^\rho\, b_2^\rho\, b_2^\rho\, b_2^\rho + f_{s\rho\rho}\,(b_{22}^s\, b_2^\rho\, b_2^\rho \cdot 6) + [f_{ss}\,(b_{22}^s\, b_{22}^s \cdot 3) + f_{\rho\rho}\,(b_2^\rho\, b_{222}^\rho \cdot 4)] \\ &= f_{\rho\rho\rho\rho} + 6(-2\sqrt{2}d) f_{s\rho\rho} + 4(6\frac{d}{r} A_\rho) f_{\rho\rho} + 3\left(2\sqrt{2}d\right)^2 f_{\rho\rho} \\ &= f_{\rho\rho\rho\rho} - 12\sqrt{2}\, d\, f_{s\rho\rho} + 24 d^2 f_{\rho\rho} + 24\frac{d}{r} A_\rho f_{\rho\rho} \end{aligned} \tag{C-65}$$

The effective quartic constant:

$$F_{2222} = \frac{1}{24} f_{2222} = F_{\rho\rho\rho\rho} - \sqrt{2} d F_{s\rho\rho} + d^2 f_{ss} + \frac{d}{r} A_\rho\, f_{\rho\rho} \tag{C-66}$$

C.6 Relations between the Linearized Internal Generalized Coordinates and the Curvilinear Symmetrized Coordinates

- From the relations between the generalized and linearized coordinates [3, eq.(6)-(8)] and [4, eq.(8)] we can find (here we have the notation $q \equiv \mathbf{R}^1$ and $q' \equiv \mathbf{R}^3$):

$$\begin{aligned} q_0^1 &\simeq \mathbf{R}^1\left(1-\frac{1}{8}\gamma^2\right)-\frac{1}{8}\mathbf{R}^3\gamma^2-\frac{r}{8}\gamma^2 \\ q_0^3 &\simeq \mathbf{R}^3\left(1-\frac{1}{8}\gamma^2\right)-\frac{1}{8}\mathbf{R}^1\gamma^2-\frac{r}{8}\gamma^2 \end{aligned} \tag{C-67}$$

If we introduce the relations (3.82) the previous relations become,

$$\begin{aligned} q_0^1 &\simeq \frac{1}{\sqrt{2}}S^s\left(1+A_a\rho^2\right)-\frac{1}{8\sqrt{2}}S^s\rho^2+\frac{1}{\sqrt{2}}S^a\left(p-A_a\rho^2\right)+d\rho^2 \\ &- \frac{1}{8\sqrt{2}}S^s\rho^2-\frac{r}{8}\rho^2-\frac{A_\rho}{4\sqrt{2}}S^s\rho^2+\mathcal{O}(\rho^2(S^s)^2,\ \rho^4,\ \rho^4S^s) \\ &\simeq \frac{1}{\sqrt{2}}S^s\left[1+\rho^2\left(A_a-\frac{1}{4}-\frac{A_\rho}{4}\right)\right]+\frac{S^a}{\sqrt{2}}\left(p-A_a\rho^2\right)-\frac{r}{8}\left(1-8\frac{d}{r}\right)\rho^2 \\ &= \frac{1}{\sqrt{2}}S^s\left\{1+\left[A_a-\frac{1}{4}\left(A_\rho+1\right)\right]\rho^2\right\}+\frac{S^a}{\sqrt{2}}\left(p-A_a\rho^2\right)-\frac{r}{8}\left(1-8\frac{d}{r}\right)\rho^2 \end{aligned} \tag{C-68}$$

In a similar way we obtain for q_0^3:

$$\begin{aligned} q_0^3 &\simeq \frac{1}{\sqrt{2}}S^s\left(1+A_a\rho^2\right)-\frac{1}{8\sqrt{2}}S^s\rho^2-\frac{1}{\sqrt{2}}S^a\left(p-A_a\rho^2\right)+d\rho^2 \\ &- \frac{1}{8\sqrt{2}}S^s\rho^2-\frac{r}{8}\rho^2-\frac{A_\rho}{4\sqrt{2}}S^s\rho^2+\mathcal{O}(\rho^2(S^s)^2,\ \rho^4) \\ &\simeq \frac{1}{\sqrt{2}}S^s\left\{1+\rho^2\left[A_a-\frac{1}{4}-\frac{A_\rho}{4}\right]\right\}-\frac{1}{\sqrt{2}}S^a\left(p-A_a\rho^2\right)-\frac{r}{8}\left(1-8\frac{d}{r}\right)\rho^2 \\ &= \frac{1}{\sqrt{2}}S^s\left\{1+\left[A_a-\frac{1}{4}\left(A_\rho+1\right)\right]\rho^2\right\}-\frac{1}{\sqrt{2}}S^a\left(p-A_a\rho^2\right)-\frac{r}{8}\left(1-8\frac{d}{r}\right)\rho^2 \end{aligned} \tag{C-69}$$

From the relations derived by Pliva [3, 4], we find for the bending coordinate:

$$\begin{aligned} \gamma_0 &\simeq \gamma\left(1+\frac{\mathbf{R}^1+\mathbf{R}^3}{2r}\right)-\frac{1}{24}\gamma^3=\rho\left\{1+S^s\left[\frac{A_\rho}{\sqrt{2}r}+\frac{1}{\sqrt{2}r}\right]\right\}+\rho^3\left[\frac{d}{r}-\frac{1}{24}\right]+\mathcal{O}(\rho^3S^s) \\ &\simeq \rho\left[1+\frac{1}{\sqrt{2}r}\left(A_\rho+1\right)S^s\right]-\frac{1}{24}\left(1-24\frac{d}{r}\right)\rho^3 \end{aligned} \tag{C-70}$$

- The potential constants are changing when the coordinates transformation occur and in order to obtain their relations we consider the following derivatives, *which are different from zero* [46, eq.(4)-(6)]:

$$\begin{array}{lll} \left(\frac{\partial\gamma_0}{\partial\rho}\right)_0=1 & \left(\frac{\partial^2\gamma_0}{\partial\rho\partial S^s}\right)_0=\frac{A_\rho+1}{\sqrt{2}\,r} & \left(\frac{\partial^3\gamma_0}{\partial\rho^3}\right)_0=-\frac{1}{4}\left(1-24\frac{d}{r}\right) \\ \left(\frac{\partial q_0^1}{\partial S^s}\right)_0=\frac{1}{\sqrt{2}} & \left(\frac{\partial^2 q_0^1}{\partial\rho^2}\right)_0=-\frac{r}{4}\left(1-8\frac{d}{r}\right) & \left(\frac{\partial^3 q_0^1}{\partial S^s\partial\rho^2}\right)_0=\sqrt{2}\left[A_a-\frac{1}{4}\left(A_\rho+1\right)\right] \\ \left(\frac{\partial q_0^1}{\partial S^a}\right)_0=\frac{p}{\sqrt{2}} & & \left(\frac{\partial^3 q_0^1}{\partial S^a\partial\rho^2}\right)_0=-\sqrt{2}A_a \\ \left(\frac{\partial q_0^3}{\partial S^s}\right)=\frac{1}{\sqrt{2}} & \left(\frac{\partial^2 q_0^3}{\partial\rho^2}\right)_0=-\frac{r}{4}\left(1-8\frac{d}{r}\right) & \left(\frac{\partial^3 q_0^3}{\partial S^s\partial\rho^2}\right)_0=\sqrt{2}\left[A_a-\frac{1}{4}\left(A_\rho+1\right)\right] \\ \left(\frac{\partial q_0^3}{\partial S^a}\right)=-\frac{p}{\sqrt{2}} & & \left(\frac{\partial^3 q_0^3}{\partial S^a\partial\rho^2}\right)_0=\sqrt{2}A_a \end{array} \tag{C-71}$$

With the previous relations, using the relations between potential constants from [46, eq.(4)-(6)] we find:

– The non vanishing derivatives:

$$b_s^1 = \tfrac{1}{\sqrt{2}} \quad b_s^3 = \tfrac{1}{\sqrt{2}} \tag{C-72}$$

The quadratic symmetric stretching potential constant:

$$\begin{aligned} f_{ss} &= f_{11}^0\, b_s^1\, b_s^1 + f_{33}^0\, b_s^3\, b_s^3 + 2 f_{13}^0\, b_s^1\, b_s^3 = \left[\frac{1}{2}\left(f_{11}^0 + f_{33}^0\right) + f_{13}^0\right]_{f_{11}^0 = f_{33}^0} \\ &= f_{11}^0 + f_{33}^0 \end{aligned} \tag{C-73}$$

– The non vanishing derivatives:

$$b_a^1 = \tfrac{p}{\sqrt{2}} \quad b_a^3 = -\tfrac{p}{\sqrt{2}} \tag{C-74}$$

The quadratic antisymmetric stretching constant:

$$\begin{aligned} f_{aa} &= f_{11}^0\, b_a^1\, b_a^1 + f_{33}^0\, b_a^3\, b_a^3 + 2 f_{13}^0\, b_a^1\, b_a^3 = \left[\frac{p^2}{2}\left(f_{11}^0 + f_{33}^0\right) - p^2 f_{13}^0\right]_{f_{11}^0 = f_{33}^0} \\ &= p^2\left(f_{11}^0 - f_{13}^0\right) \end{aligned} \tag{C-75}$$

– The non vanishing derivatives:

$$b_\rho^2 = 1 \tag{C-76}$$

The quadratic bending constant:

$$f_{\rho\rho} = f_{22}^0\, b_\rho^2\, b_\rho^2 = f_{22}^0 \tag{C-77}$$

– The non vanishing derivatives:

$$\begin{aligned} &b_s^1 = \tfrac{1}{\sqrt{2}} \qquad b_s^3 = \tfrac{1}{\sqrt{2}} \quad b_{\rho\rho}^1 = \tfrac{r}{4}\left(1 - 8\tfrac{d}{r}\right) \\ &b_{\rho\rho}^3 = -\tfrac{r}{4}\left(1 - 8\tfrac{d}{r}\right) \quad b_\rho^2 = 1 \quad b_{S^s\rho}^2 = \tfrac{A_\rho + 1}{\sqrt{2} r} \end{aligned} \tag{C-78}$$

The anharmonic cubic potential constant:

$$\begin{aligned} f_{s\rho\rho} &= f_{122}^0\, b_s^1\, b_\rho^2\, b_\rho^2 + f_{322}^0\, b_s^3\, b_\rho^2\, b_\rho^2 + \left[f_{11}^0\left(b_s^1\, b_{\rho\rho}^1 + 2 b_\rho^1\, b_{S^s\rho}^1\right) + f_{33}^0\left(b_s^3\, b_{\rho\rho}^3 + 2 b_\rho^3\, b_{S^s\rho}^3\right)\right. \\ &\quad \left. + f_{13}^0\left(b_s^1\, b_{\rho\rho}^3 + 2 b_\rho^1\, b_{S^s\rho}^3\right) + f_{31}^0\left(b_s^3\, b_{\rho\rho}^1 + 2 b_\rho^3\, b_{S^s\rho}^1\right) + f_{22}^0\left(b_s^2\, b_{\rho\rho}^2 + 2 b_\rho^2\, b_{S^s\rho}^2\right)\right] \\ &= \sqrt{2} f_{122} + \sqrt{2}\left[-\frac{r}{4}\left(1 - 8\frac{d}{r}\right)\right]\left(f_{11}^0 + f_{13}^0\right) + \sqrt{2}\frac{A_\rho + 1}{r} f_{22}^0 \end{aligned} \tag{C-79}$$

The effective anharmonic cubic potential constant:

$$\begin{aligned} F_{s\rho\rho} &= \frac{1}{2} f_{s\rho\rho} \\ &= \frac{1}{\sqrt{2}}\left[f_{122}^0 - \frac{r}{4}\left(1 - 8\frac{d}{r}\right)\left(f_{11}^0 + f_{13}^0\right)\right] + \frac{A_\rho + 1}{\sqrt{2} r} f_{22}^0 \\ &= \sqrt{2} F_{122}^0 - \frac{r}{4\sqrt{2}}\left(1 - 8\frac{d}{r}\right)\left(f_{11}^0 + f_{13}^0\right) + \frac{A_\rho + 1}{\sqrt{2} r} f_{22}^0 \end{aligned} \tag{C-80}$$

– The non vanishing derivatives:

$$b_\rho^2 = 1 \quad b_{\rho\rho\rho}^2 = -\tfrac{1}{4}\left(1 - 24\tfrac{d}{r}\right) \quad b_{\rho\rho}^1 = -\tfrac{r}{4}\left(1 - 8\tfrac{d}{r}\right) \quad b_{\rho\rho}^3 = -\tfrac{r}{4}\left(1 - 8\tfrac{d}{r}\right) \tag{C-81}$$

The quartic bending constant,

$$\begin{aligned} f_{\rho\rho\rho\rho} &= f_{2222}^0\, b_\rho^2\, b_\rho^2\, b_\rho^2\, b_\rho^2 + 2 f_{122}^0\left(b_{\rho\rho}^1\, b_\rho^2\, b_\rho^2 \cdot 6\right) \\ &\quad + \left[2 f_{11}^0\left(b_{\rho\rho}^1\, b_{\rho\rho}^1 \cdot 3\right) + 2 f_{13}^0\left(b_{\rho\rho}^1\, b_{\rho\rho}^3 \cdot 3\right) + 2 f_{22}^0\left(b_\rho^2\, b_{\rho\rho\rho}^2 \cdot 4\right)\right] \\ &= f_{2222}^0 - 3r\left(1 - 8\frac{d}{r}\right) f_{122}^0 + \frac{3}{8} r^2\left(1 - 8\frac{d}{r}\right)^2\left(f_{11}^0 + f_{13}^0\right) - \left(1 - 24\frac{d}{r}\right) f_{22}^0 \end{aligned} \tag{C-82}$$

The effective quartic bending constant:

$$\begin{aligned} F_{\rho\rho\rho\rho} &= \frac{1}{24} f_{\rho\rho\rho\rho} = F_{2222}^0 - \frac{r}{4}\left(1 - 8\frac{d}{r}\right) F_{122}^0 \\ &+ \frac{r^2}{64}\left(1 - 8\frac{d}{r}\right)^2\left(f_{11}^0 + f_{13}^0\right) - \frac{1}{24}\left(1 - 24\frac{d}{r}\right) f_{22}^0 \end{aligned} \tag{C-83}$$

C.7 Connection between Curvilinear Symmetrized Coordinates and Linearized Internal Generalized Coordinates

- We consider the equation (C-50) or (3.86), and the relations between the generalized and linearized coordinates [3, eq.(6)-(8)] and [4, eq.(8)] and we find:

$$\begin{aligned}
S^s &= \frac{1}{\sqrt{2}}\left(\mathbf{R}^1+\mathbf{R}^3\right)\left(1-A_s\,\gamma^2\right)-\sqrt{2}d\gamma^2+\mathcal{O}(\gamma_0^4,\gamma_0^2q^2)\\
&\simeq \frac{1}{\sqrt{2}}\left(q_0^1+q_0^3+\frac{r}{4}\gamma_0^2\right)\left\{1-A_s\gamma_0^2\left[1-\frac{1}{2r}\underbrace{\left(q_0^1+q_0^3\right)}_{\sim 0}\right]^2\right\}\\
&- \sqrt{2}d\gamma_0^2\left[1-\frac{1}{2r}\left(q_0^1+q_0^3\right)\right]^2+\mathcal{O}(\gamma_0^4,\gamma_0^2q^2)\\
&= \frac{1}{\sqrt{2}}\left(q_0^1+q_0^3\right)\left(1-A_s\,\gamma^2\right)+\frac{r}{4\sqrt{2}}\gamma_0^2-\sqrt{2}d\gamma_0^2+\sqrt{2}\frac{d}{r}\left(q_0^1+q_0^3\right)\gamma_0^2+\mathcal{O}(\gamma_0^4,\gamma_0^2q^2)\\
&\simeq \frac{1}{\sqrt{2}}\left(q_0^1+q_0^3\right)\left[1-\left(A_s-2\frac{d}{r}\right)\gamma_0^2\right]+\frac{r}{4\sqrt{2}}\left(1-8\frac{d}{r}\right)\gamma_0^2
\end{aligned}\tag{C-84}$$

$$\begin{aligned}
S^a &= \frac{1}{\sqrt{2}p}\left(\mathbf{R}^1-\mathbf{R}^3\right)\left(1+\frac{A_\rho}{p}\,\gamma^2\right)\simeq\frac{1}{\sqrt{2}p}\left(q_0^1-q_0^3\right)\left\{1+\frac{A_a}{p}\gamma_0^2\left[1-\frac{1}{2r}\underbrace{\left(q+q'\right)}_{\sim 0}\right]^2\right\}\\
&\simeq \frac{1}{\sqrt{2}p}\left(q_0^1-q_0^3\right)\left(1+\frac{A_a}{p}\gamma_0^2\right)
\end{aligned}\tag{C-85}$$

$$\begin{aligned}
\rho &= \gamma\left[1-\frac{A_\rho}{2r}\left(\mathbf{R}^1+\mathbf{R}^3\right)\right]+\frac{d}{r}A_\rho\gamma^3\\
&\simeq \gamma_0\left[1-\frac{1}{2r}\left(q_0^1+q_0^3\right)-\frac{1}{12}\gamma_0^2\right]\left[1-\frac{A_\rho}{2r}\left(q_0^1+q_0^3+\frac{r}{4}\gamma_0^2\right)\right]+\frac{d}{r}A_\rho\gamma^3\\
&\simeq \gamma_0\left[1-\frac{A_\rho+1}{2r}\left(q_0^1+q_0^3\right)\right]-\left[\frac{1}{12}+\frac{A_\rho}{8}\left(1-8\frac{d}{r}\right)\right]\gamma_0^3
\end{aligned}\tag{C-86}$$

- The relations for the potential constants transformations when we pass from the curvilinear symmetrized coordinates to the generalized coordinates can be obtained by considering first the following derivatives, *which are different from zero* [46, eq.(4)-(6)]:

$$\begin{array}{ll}
\left(\frac{\partial\rho}{\partial\gamma_0}\right)_0=1 & \left(\frac{\partial^2\rho}{\partial\gamma_0\partial(q_0^1)}\right)=\left(\frac{\partial^2\rho}{\partial\gamma_0\partial(q_0^3)}\right)=-\frac{A_\rho+1}{2r}\\
\left(\frac{\partial^3\rho}{\partial\gamma_0^3}\right)_0=-6\frac{A_\rho}{8}\left(1-8\frac{d}{r}\right)-\frac{1}{2} & \left(\frac{\partial S^s}{\partial(q_0^1)}\right)_0=\left(\frac{\partial S^s}{\partial(q_0^3)}\right)_0=\frac{1}{\sqrt{2}}\\
\left(\frac{\partial^2 S^s}{\partial\gamma_0^2}\right)_0=\frac{r}{2\sqrt{2}}\left(1-8\frac{d}{r}\right) & \left(\frac{\partial^3 S^s}{\partial(q_0^1)\partial\gamma_0^2}\right)_0=\left(\frac{\partial^3 S^s}{\partial(q_0^3)\partial\gamma_0^2}\right)_0=-\sqrt{2}\left(A_s-2\frac{d}{r}\right)\\
\left(\frac{\partial S^a}{\partial(q_0^1)}\right)_0=-\left(\frac{\partial S^a}{\partial(q_0^3)}\right)_0=\frac{1}{\sqrt{2}p} & \left(\frac{\partial^3 S^s}{\partial(q_0^1)\partial\gamma_0^2}\right)_0=\left(\frac{\partial^3 S^s}{\partial(q_0^3)\partial\gamma_0^2}\right)_0=\frac{\sqrt{2}A_a}{p^2}
\end{array}\tag{C-87}$$

  With the previous relations, using the relations between potential constants from [46, eq.(4)-(6)] we find:

  - The non vanishing derivatives:

$$b_1^s=\frac{1}{\sqrt{2}}\quad b_1^a=\frac{1}{\sqrt{2}p}\tag{C-88}$$

    The quadratic stretching potential constant:

$$f_{11}^0=f_{ss}\,b_1^s\,b_1^s+f_{aa}\,b_1^a\,b_1^a=\frac{1}{2}\left(f_{ss}+\frac{f_{aa}}{p^2}\right)\tag{C-89}$$

– The non vanishing derivatives:

$$b_3^s = \tfrac{1}{\sqrt{2}} \quad b_3^a = -\tfrac{1}{\sqrt{2p}} \tag{C-90}$$

The quadratic stretching potential constant:

$$f_{33}^0 = f_{ss}\, b_3^s\, b_3^s + f_{aa}\, b_3^a\, b_3^a = \frac{1}{2}\left(f_{ss} + \frac{f_{aa}}{p^2}\right) \tag{C-91}$$

– The non vanishing derivatives:

$$b_1^s = \tfrac{1}{\sqrt{2}} \quad b_3^s = \tfrac{1}{\sqrt{2}} \quad b_1^a = \tfrac{1}{\sqrt{2p}} \quad b_3^a = -\tfrac{1}{\sqrt{2p}} \tag{C-92}$$

The quadratic mixed stretching constant:

$$f_{13}^0 = f_{ss}\, b_1^s\, b_3^s + f_{aa}\, b_1^a\, b_3^a = \frac{1}{2}\left(f_{ss} - \frac{f_{aa}}{p^2}\right) \tag{C-93}$$

– The non vanishing derivatives:

$$b_2^\rho = 1 \tag{C-94}$$

The quadratic bending constant:

$$f_{22}^0 = f_{\rho\rho}\, b_2^\rho\, b_2^\rho = f_{\rho\rho} \tag{C-95}$$

– The non vanishing derivatives:

$$\begin{array}{lll} b_1^s = \tfrac{1}{\sqrt{2}} & b_1^a = \tfrac{1}{\sqrt{2p}} & b_{22}^s = \tfrac{r}{2\sqrt{2}}\left(1 - 8\tfrac{d}{r}\right) \\ b_2^\rho = 1 & b_{12}^\rho = -\tfrac{A_\rho + 1}{2r} & \end{array} \tag{C-96}$$

The anharmonic cubic potential constant:

$$\begin{aligned} f_{122}^0 &= f_{s\rho\rho}\, b_1^s\, b_2^\rho\, b_2^\rho + f_{ss}\,(b_1^s\, b_{22}^s + 2 b_2^s\, b_{12}^s) + f_{aa}\,(b_1^s\, b_{22}^s + 2 b_2^s\, b_{12}^s) \\ &+ f_{\rho\rho}\,(b_1^\rho\, b_{22}^\rho + 2 b_2^\rho\, b_{12}^\rho) = \frac{1}{\sqrt{2}} f_{s\rho\rho} + f_{ss}\,\frac{r}{4}\left(1 - 8\frac{d}{r}\right) - \frac{A_\rho + 1}{r} f_{\rho\rho} \end{aligned} \tag{C-97}$$

The effective anharmonic cubic potential constant:

$$F_{122}^0 = \frac{1}{2} f_{122}^0 = \frac{1}{\sqrt{2}} F_{s\rho\rho} + \frac{r}{8}\left(1 - 8\frac{d}{r}\right) f_{ss} - \frac{A_\rho + 1}{2r} f_{\rho\rho} \tag{C-98}$$

– The non vanishing derivatives:

$$b_2^\rho = 1 \quad b_{222}^\rho = -\tfrac{3}{4} A_\rho \left(1 - 8\tfrac{d}{r}\right) \quad b_{22}^s = \tfrac{r}{2\sqrt{2}}\left(1 - 8\tfrac{d}{r}\right) \tag{C-99}$$

The quartic bending constant,

$$\begin{aligned} f_{2222}^0 &= f_{\rho\rho\rho\rho}\, b_2^\rho\, b_2^\rho\, b_2^\rho\, b_2^\rho + f_{s\rho\rho}\,(b_{22}^s\, b_2^\rho\, b_2^\rho \cdot 6) + [f_{ss}\,(b_{22}^s\, b_{22}^s \cdot 3) + f_{\rho\rho}\,(b_2^\rho\, b_{222}^\rho \cdot 4)] \\ &= f_{\rho\rho\rho\rho} + \frac{3}{\sqrt{2}} r\left(1 - 8\frac{d}{r}\right) f_{s\rho\rho} + \frac{3}{8} r^2 \left(1 - 8\frac{d}{r}\right)^2 f_{ss} \\ &- \left[2 + 3A_\rho\left(1 - 8\frac{d}{r}\right)\right] f_{\rho\rho} \end{aligned} \tag{C-100}$$

The effective quartic bending constant:

$$\begin{aligned} F_{2222}^0 &= \frac{1}{24} f_{\rho\rho\rho\rho} = F_{\rho\rho\rho\rho} + \frac{r}{4\sqrt{2}}\left(1 - 8\frac{d}{r}\right) F_{s\rho\rho} \\ &+ \frac{r^2}{64}\left(1 - 8\frac{d}{r}\right)^2 f_{ss} - \left[\frac{1}{12} + \frac{1}{8} A_\rho\left(1 - 8\frac{d}{r}\right)\right] f_{\rho\rho} \end{aligned} \tag{C-101}$$

Appendix D

Solving the Eigenvalue Problem

D.1 Obtainment of Coupled Equations and Anharmonic Terms in K and l Basis Formalism

We consider the wavefunction in Born-Oppenheimer approximation:

$$\psi^{(i)}_{BO}(\nu,\varphi,\rho,S^s) = \frac{1}{\sqrt{2\pi}} e^{iK\varphi}\,\psi^{(i)}_{el}(\nu-\varphi,\rho)\,\chi_s(S^s;\rho)\,\psi^{(i)}_{b,K}(\rho) \tag{D-1}$$

where the electronic wavefunction is, with $i = +,-$:

$$\psi^{(\pm)}_{el}(\nu-\varphi,\rho) = \frac{1}{\sqrt{4\pi}}\left[e^{i\Lambda(\nu-\varphi)} \pm e^{-i\Lambda(\nu-\varphi)}\right] \tag{D-2}$$

The Schrodinger equation is:

$$\left[H_b(\rho) + H_s(S^s) + H^z_{rot}(\nu,\varphi;\rho) + V^{(i)}(\rho,S^s) - E\right]\psi^i(\nu,\varphi,\rho,S^s) = 0 \tag{D-3}$$

where the kinetic energy for rotation along the linear Oz axis, as well as the symmetric stretching energy are,

$$\begin{aligned} H^z_{rot}(\nu,\varphi;\rho) &= \frac{g^{\varphi\varphi}}{2}\,(N_z - L_z) = -\frac{\hbar^2}{2}\,g^{\varphi\varphi}\left[\frac{\partial}{\partial\varphi} - \frac{\partial}{\partial(\nu-\varphi)}\right]^2 \\ H_s(S^s) &= -\frac{\hbar^2}{2}\,g^{ss}(\rho,r^0)\,\frac{\partial^2}{\partial {S^s}^2} \simeq -\frac{\hbar^2}{2}\,g^{ss}(\rho)\,\frac{\partial^2}{\partial {S^s}^2} \end{aligned} \tag{D-4}$$

and the potential energy from eq.(3.64) and(3.72) is,

$$V^{(i)}(\rho,S^s) = V(\rho)^{(i)} - \left(\frac{\partial V_0}{\partial\rho}\right)_0 \frac{R_2(r_\rho,\rho)}{r_\rho}\,S^s + \left(\frac{\partial V}{\partial S^s}\right)\left(\frac{\partial S^s}{\partial\rho}\right)\rho + \frac{1}{2}\underbrace{\left[f_{ss}(\rho)\,S_1^2(R_\rho,\rho)\right]}_{f^s_{eff}(\rho)}\,{S^s}^2 \tag{D-5}$$

- We neglect the dependence of ρ as function of S^s and in this case the equation in S^s represents the equation of the harmonic oscillator which has ρ as parameter.
- We consider: $r_\rho = r_\rho|_{S^s=0} = r^0$.
- We consider during the calculus only the electronic coordinate $(\nu-\varphi)$, defined in Fig.2.3.

If we introduce the Born-Oppenheimer wavefunction into the Schrodinger equation we get:

$$\begin{aligned} &\left[H_b(\rho) + H^z_{rot}(\nu,\varphi;\rho) + V^{(i)}(\rho) - \left(\frac{\partial V_0}{\partial\rho}\right)_0 \frac{R_2(r_\rho,\rho)}{r_\rho}\,S^s + \hbar\omega^{(i)}_s(\rho)\left(v_s+\frac{1}{2}\right) - E\right]\times \\ &\frac{1}{\sqrt{2\pi}}\,e^{iK\varphi}\,\psi^{(i)}_{el}(\nu-\varphi,\rho)\,\chi_s(S^s;\rho)\,\psi_{b,K}(\rho) = 0 \end{aligned} \tag{D-6}$$

We consider two wavefunctions, corresponding to the two states:+ and − and we take a linear combination of them to have the B.O wavefunction:

$$\psi(\nu,\varphi,\rho,S^s) = \psi^+_{B.O}(\nu,\varphi,\rho,S^s) + \psi^-_{B.O}(\nu,\varphi,\rho,S^s) \tag{D-7}$$

We will integrate over the electronic coordinate $(\nu-\varphi)$ and we get:

$$\begin{aligned}&\left[H_b(\rho)+V^+(\rho)+\hbar\omega_s^+(\rho)\left(v_s+\frac{1}{2}\right)-\left(\frac{\partial V_0}{\partial\rho}\right)_0\frac{R_2(r_\rho,\rho)}{r_\rho}S^s+f_{eff}^s(\rho)\left(\frac{\partial S^s}{\partial\rho}\right)S^s\,\rho\right.\\&\left.+\frac{\hbar^2}{2}g^{\varphi\varphi}(\rho)\left(K^2+\Lambda^2\right)-E\right]\frac{1}{\sqrt{2\pi}}e^{iK\varphi}\,\chi_s^+(S^s;\rho)\,\psi_{b,K}^+(\rho)\\=\;&\frac{\hbar^2}{\sqrt{2\pi}}g^{\varphi\varphi}(\rho)\,K\,\Lambda\,e^{iK\varphi}\,\chi_s^-(S^s;\rho)\,\psi_{b,K}^-(\rho)\end{aligned}\tag{D-8}$$

- $K\Lambda$ is used in order to characterize the passage from the ψ_{el}^+ to ψ_{el}^- and in the inverse one, too.
- When we integrate over φ all the elements with K_1 /=K_2 vanish because none of the matrix elements depend on φ and

$$\frac{1}{2\pi}\int_0^{2\pi}e^{-iK_1\varphi}\,e^{iK_2\varphi}\,d\varphi=\delta_{K_1,K_2}$$

If we take into account the previous points we get:

$$\begin{aligned}&\left[H_b(\rho)+V^+(\rho)+\hbar\omega_s^+(\rho)\left(v_s+\frac{1}{2}\right)-\left(\frac{\partial V_0}{\partial\rho}\right)_0\frac{R_2(r_\rho,\rho)}{r_\rho}S^s+f_{eff}^s(\rho)\left(\frac{\partial S^s}{\partial\rho}\right)S^s\,\rho\right.\\&\left.+\frac{\hbar^2}{2}g^{\varphi\varphi}(\rho)\left(K^2+\Lambda^2\right)-E\right]\chi_s^+(S^s;\rho)\,\psi_{b,K}^+(\rho)\\=\;&\hbar^2g^{\varphi\varphi}(\rho)\,K\,\Lambda\,\chi_s^-(S^s;\rho)\,\psi_{b,K}^-(\rho)\end{aligned}\tag{D-9}$$

Because $\chi_s^\pm(S^s;\rho)$ function depend parametricaly on ρ, the derivative part of $H_b(\rho)$ will act on the stretching function too, and we have:

$$\begin{aligned}&\chi_s^+(S^s;\rho)\left[H_b(\rho)+V^+(\rho)+\hbar\omega_s^+(\rho)\left(v_s+\frac{1}{2}\right)+\frac{\hbar^2}{2}g^{\varphi\varphi}(\rho)\left(K^2+\Lambda^2\right)\right]\psi_{b,K}^+(\rho)\\&+\psi_{b,K}^+(\rho)\left[-\left(\frac{\partial V_0}{\partial\rho}\right)_0\frac{R_2}{r_\rho}S^s+f_{eff}^s(\rho)\left(\frac{\partial S^s}{\partial\rho}\right)S^s\,\rho\right]\chi_s^+(S^s;\rho)\\&-\frac{\hbar^2}{2}g^{\rho\rho}(\rho)\,\psi_{b,K}^+(\rho)\frac{\partial^2}{\partial\rho^2}\chi_s^+(S^s;\rho)-\hbar^2g^{\rho\rho}(\rho)\frac{\partial}{\partial\rho}\psi_s^+(S^s;\rho)\frac{\partial}{\partial\rho}\chi_s^+(S^s;\rho)\\=\;&\hbar^2g^{\varphi\varphi}(\rho)\,K\,\Lambda\,\chi_s^-(S^s;\rho)\,\psi_{b,K}^-(\rho)\end{aligned}\tag{D-10}$$

We integrate over $\chi_s^+(S^s;\rho)$ and we obtain:

$$\begin{aligned}&\delta_{s,s'}\left[H_b(\rho)+V^+(\rho)+\hbar\omega_s^+(\rho)\left(v_s+\frac{1}{2}\right)+\frac{\hbar^2}{2}g^{\varphi\varphi}(\rho)\left(K^2+\Lambda^2\right)\right]\psi_{b,K}^+(\rho)\\&+\psi_{b,K}^+(\rho)\left[-\left(\frac{\partial V_0}{\partial\rho}\right)_0\frac{R_2}{r_\rho}S^s+f_{eff}^s(\rho)\left(\frac{\partial S^s}{\partial\rho}\right)S^s\,\rho\right]\underbrace{\langle\chi_{s'}|S^s|\chi_s\rangle}_{H^{01}\delta_{s,s'\pm1}}\\&-\frac{\hbar^2}{2}g^{\rho\rho}(\rho)\,\psi_{b,K}^+(\rho)\underbrace{\langle\chi_{s'}|\frac{\partial^2}{\partial\rho^2}|\chi_s\rangle}_{\substack{H^{00}(\rho)\delta_{s,s'}+H_1^{02}\delta_{s,s'\pm2}\\+H^{04}(\rho)\delta_{s,s'\pm4}}}-\hbar^2g^{\rho\rho}(\rho)\frac{\partial}{\partial\rho}\psi_{b,K}^+(\rho)\underbrace{\langle\chi_{s'}|\frac{\partial}{\partial\rho}|\chi_s\rangle}_{H_2^{02}\delta_{s,s'\pm2}}\\=\;&\delta_{s,s'}\hbar^2g^{\varphi\varphi}(\rho)\,K\,\Lambda\,\psi_{b,K}^-(\rho)\end{aligned}\tag{D-11}$$

If we consider the wavefunction in the l basis (eq. (3.94) and (3.95)),with l defined in eq.(3.96), we have:

$$\begin{aligned}\psi_{el}^+\,\psi_{b,l}^+(\rho)&=\frac{1}{\sqrt{2}}\left[\left(\psi_{el}^+\right)_{B.O}\,\psi_{b,K}^+(\rho)+\left(\psi_{el}^-\right)_{B.O}\,\psi_{b,K}^-(\rho)\right]\\\psi_{el}^-\,\psi_{b,l}^-(\rho)&=\frac{1}{\sqrt{2}}\left[\left(\psi_{el}^+\right)_{B.O}\,\psi_{b,K}^+(\rho)-\left(\psi_{el}^-\right)_{B.O}\,\psi_{b,K}^-(\rho)\right]\end{aligned}\tag{D-12}$$

The wavefunction is taken as a linear combination of the previous wavefunctions:

$$\psi=\psi^+(\nu,\varphi,\rho,S^s)+\psi^-(\nu,\varphi,\rho,S^s)=\psi_{B.O}^+(\nu,\varphi,\rho,S^s)\tag{D-13}$$

We rebuild wavefunctions in order to solve the Schrodinger equation in l basis and get:

$$\begin{aligned}
&\left\{H_b(\rho)+\frac{1}{2}\left[\bar{V}^+(\rho)+\bar{V}^-(\rho)\right]+\frac{1}{2}g^{\varphi\varphi}(K^2+\Lambda^2)\right\}\left[\left(\psi^+_{el}\right)_{B.O}+\left(\psi^-_{el}\right)_{B.O}\right]\\
-\;& g^{\varphi\varphi}K\,\Lambda\left[\left(\psi^+_{el}\right)_{B.O}+\left(\psi^-_{el}\right)_{B.O}\right]+\frac{1}{2}\left(\bar{V}^+-\bar{V}^-\right)\left[\left(\psi^+_{el}\right)_{B.O}-\left(\psi^-_{el}\right)_{B.O}\right]\\
=\;& E\left[\left(\psi^+_{el}\right)_{B.O}+\left(\psi^-_{el}\right)_{B.O}\right] \qquad \text{(D-14)}
\end{aligned}$$

where the following notations were used:

$$\begin{aligned}
\bar{V}^+(\rho) &= V^+(\rho)+\hbar\omega^+_s(\rho)\left(v_s+\frac{1}{2}\right)-\left(\frac{\partial V^+_0}{\partial\rho}\right)_0\frac{R_2(r_\rho,\rho)}{r_\rho}S^s+\left(\frac{\partial V^+_0}{\partial S^s}\right)\left(\frac{\partial S^s}{\partial\rho}\right)\rho\\
\bar{V}^-(\rho) &= V^-(\rho)+\hbar\omega^-_s(\rho)\left(v_s+\frac{1}{2}\right)-\left(\frac{\partial V^-_0}{\partial\rho}\right)_0\frac{R_2(r_\rho,\rho)}{r_\rho}S^s+\left(\frac{\partial V^-_0}{\partial S^s}\right)\left(\frac{\partial S^s}{\partial\rho}\right)\rho \qquad \text{(D-15)}
\end{aligned}$$

If we introduce the wavefunctions (D-12) in (D-14), with $l=K-\Lambda$ and $l'=K+\Lambda$, (D-15) we get:

$$\begin{aligned}
&\left\{H_b(\rho)+\frac{1}{2}g^{\varphi\varphi}(K-\Lambda)^2+\frac{1}{2}\left[\bar{V}^+(\rho)+\bar{V}^-(\rho)\right]+\frac{1}{2}\hbar\left[\omega^+_s(\rho)+\omega^-_s(\rho)\right]\left(v_s+\frac{1}{2}\right)\right.\\
-\;&\left.\frac{1}{2}\left[\frac{\partial V^+_0}{\partial\rho}+\frac{\partial V^-_0}{\partial\rho}\right]\frac{R_2(r_\rho,\rho)}{r_\rho}S^s+\frac{1}{2}\left[\left(f^s_{eff}\right)^+\left(\frac{\partial S^s}{\partial\rho}\right)+\left(f^s_{eff}\right)^-\left(\frac{\partial S^s}{\partial\rho}\right)\right]S^s\,\rho-E\right\}\\
\times\;&\frac{1}{2\pi}e^{il\varphi}\,e^{i\Lambda\nu}\,\chi_s(S^s;\rho)\,\psi^+_{b,l}(\rho)\\
+\;&\frac{1}{2}\left\{\left[V^+(\rho)-V^-(\rho)\right]+\hbar\left[\omega^+_s(\rho)-\omega^-_s(\rho)\right]\left(v_s+\frac{1}{2}\right)-\left(\frac{\partial V^+}{\partial\rho}-\frac{\partial V^-}{\partial\rho}\right)\frac{R_2(r_\rho,\rho)}{r_\rho}S^s\right.\\
+\;&\left.\left[\left(f^s_{eff}\right)^+\left(\frac{\partial S^s}{\partial\rho}\right)-\left(f^s_{eff}\right)^-\left(\frac{\partial S^s}{\partial\rho}\right)\right]S^s\,\rho\right\}\\
\times\;&\frac{1}{2\pi}e^{il'\varphi}\,e^{-i\Lambda\nu}\chi_s(S^s;\rho)\,\psi^-_{b,l'}(\rho) \;=\; 0 \qquad \text{(D-16)}
\end{aligned}$$

If we integrate over ν and φ as in the previous equations,the terms will be separated:

$$\begin{aligned}
&\chi_s(S^s;\rho)\left\{H_b(\rho)+\frac{1}{2}g^{\varphi\varphi}(K-\Lambda)^2+\frac{1}{2}\left[\bar{V}^+(\rho)+\bar{V}^-(\rho)\right]\right.\\
+\;&\frac{1}{2}\hbar\left[\omega^+_s(\rho)+\omega^-_s(\rho)\right]\left(v_s+\frac{1}{2}\right)-\frac{1}{2}\left[\frac{\partial V^+_0}{\partial\rho}+\frac{\partial V^-_0}{\partial\rho}\right]\frac{R_2(r_\rho,\rho)}{r_\rho}S^s\\
+\;&\left.\frac{1}{2}\left[\left(f^s_{eff}\right)^+\left(\frac{\partial S^s}{\partial\rho}\right)+\left(f^s_{eff}\right)^-\left(\frac{\partial S^s}{\partial\rho}\right)\right]S^s\,\rho-E\right\}\psi^+_{b,l}(\rho)\\
-\;&\frac{\hbar^2}{2}g^{\rho\rho}(\rho)\,\psi^+_{b,K}(\rho)\,\frac{\partial^2}{\partial\rho^2}\chi_s(S^s;\rho)-\hbar^2\,g^{\rho\rho}(\rho)\,\frac{\partial}{\partial\rho}\psi^+_s(S^s;\rho)\,\frac{\partial}{\partial\rho}\chi_s(S^s;\rho)\\
+\;&\chi_s(S^s;\rho)\,\psi^-_{b,l'}(\rho)\,\frac{1}{2}\left\{\left[V^+(\rho)-V^-(\rho)\right]+\hbar\left[\omega^+_s(\rho)-\omega^-_s(\rho)\right]\left(v_s+\frac{1}{2}\right)\right. \qquad \text{(D-17)}\\
-\;&\left.\left.\left(\frac{\partial V^+}{\partial\rho}-\frac{\partial V^-}{\partial\rho}\right)\frac{R_2(r_\rho,\rho)}{r_\rho}S^s+\left[\left(f^s_{eff}\right)^+\left(\frac{\partial S^s}{\partial\rho}\right)-\left(f^s_{eff}\right)^-\left(\frac{\partial S^s}{\partial\rho}\right)\right]S^s\,\rho\right\}\;=\;0
\end{aligned}$$

If we integrate as in the case of eq.(D-11) over $\chi_s(S^s;\rho)$ functions, we find:

$$\begin{aligned}
&\delta_{s,s'}\left\{H_b(\rho)+\frac{1}{2}g^{\varphi\varphi}(K-\Lambda)^2+\frac{1}{2}\left[\bar{V}^+(\rho)+\bar{V}^-(\rho)\right]\right.\\
&\left.+\frac{1}{2}\hbar\left[\omega^+_s(\rho)+\omega^-_s(\rho)\right]\left(v_s+\frac{1}{2}\right)-E\right\}\psi^+_{b,l}(\rho)\\
+\;&\psi^+_{b,l}(\rho)\left\{-\frac{1}{2}\left[\frac{\partial V^+_0}{\partial\rho}+\frac{\partial V^-_0}{\partial\rho}\right]\frac{R_2(r_\rho,\rho)}{r_\rho}+\frac{1}{2}\left[\left(f^s_{eff}\right)^+\left(\frac{\partial S^s}{\partial\rho}\right)+\left(f^s_{eff}\right)^-\left(\frac{\partial S^s}{\partial\rho}\right)\right]\rho\right\}
\end{aligned}$$

$$
\begin{aligned}
&\times \underbrace{\langle \chi_{s'}|S^s|\chi_s\rangle}_{H^{01}\delta_{s,s'\pm 1}} \\
&- \frac{\hbar^2}{2} g^{\rho\rho}(\rho)\,\psi^+_{b,l}(\rho) \underbrace{\langle \chi_{s'}|\frac{\partial^2}{\partial\rho^2}|\chi_s\rangle}_{\substack{H^{00}(\rho)\delta_{s,s'}+H^{02}_1\delta_{s,s'\pm 2}\\ +H^{04}(\rho)\delta_{s,s'\pm 4}}} - \hbar^2 g^{\rho\rho}(\rho)\,\frac{\partial}{\partial\rho}\psi^+_{b,l}(\rho)\underbrace{\langle \chi_{s'}|\frac{\partial}{\partial\rho}|\chi_s\rangle}_{H^{02}_2\delta_{s,s'\pm 2}} \\
&+ \delta_{s,s'}\,\psi^-_{b,l'}(\rho)\,\frac{1}{2}\left\{\left[V^+(\rho)-V^-(\rho)\right]+\hbar\left[\omega^+_s(\rho)-\omega^-_s(\rho)\right]\left(v_s+\frac{1}{2}\right)\right\} \qquad \text{(D-18)}\\
&+ \psi^-_{b,l'}(\rho)\,\frac{1}{2}\left\{-\left(\frac{\partial V^+}{\partial\rho}-\frac{\partial V^-}{\partial\rho}\right)\frac{R_2(r_\rho,\rho)}{r_\rho}+\left[(f^s_{eff})^+\left(\frac{\partial S^s}{\partial\rho}\right)-(f^s_{eff})^-\left(\frac{\partial S^s}{\partial\rho}\right)\right]\rho\right\} \\
&\times \underbrace{\langle \chi_{s'}|S^s|\chi_s\rangle}_{H^{01}\delta_{s,s'\pm 1}} = 0
\end{aligned}
$$

Obs. The equations (D-18) in the l basis can be obtained from eq.(D-11) in the K basis, with a transformation of type:

$$\mathbf{H}^l = \mathbf{S}^+\,\mathbf{H}^K\,\mathbf{S} \qquad \text{(D-19)}$$

where $\mathbf{S}$ is the transformation matrix defined in (D-12).

D.2 Calculus of Adiabatic and non-Adiabatic Integrals

The wavefunction for the stretchig motion is the harmonic oscillator function, which depend parameteicaly on the bending angle, and hence has the form:

$$\chi_n = \sqrt{\beta}\,H_n(\xi)e^{-\frac{\xi^2}{2}} \qquad \text{(D-20)}$$

where $\sqrt{\beta}$ is the square root of the inverse of volume element. H_n are Hermite polynomials and we have the following relations between the Hermite polynomials [50, 47]:

$$
\begin{aligned}
H'_n &= \sqrt{2n}\,H_{n-1} \\
\xi\,H_n &= \sqrt{\frac{n+1}{2}}\,H_{n+1}+\sqrt{\frac{n}{2}}\,H_{n-1}
\end{aligned}
\qquad \text{(D-21)}
$$

where ξ is the dimensionless coordinate used in the Hermite polynomials [212],

$$
\begin{aligned}
&\xi = \alpha x \quad \rightarrow \quad \tfrac{\partial}{\partial\rho} = \tfrac{\partial\xi}{\partial\rho}\tfrac{\partial}{\partial\xi} = \tfrac{\alpha'}{\alpha}\xi\tfrac{\partial}{\partial\xi} \\
&\qquad \text{and} \quad \alpha = \sqrt{\tfrac{\mu\omega}{\hbar}}
\end{aligned}
\qquad \text{(D-22)}
$$

The volume element (the α factor arise because the wavefunction is normalized to dx and the Hermite polynomials are normalized to $d\xi$) is considered in a more general manner, as $dV = (g^{ss})^{-1}\,\alpha\,dx$ and then the normalization ρ dependent factor and its derivatives are:

$$
\begin{aligned}
&\beta = \tfrac{\alpha}{g^{ss}} \\
&\beta' = \beta\left[\tfrac{\alpha'}{\alpha}-\tfrac{(g^{ss})'}{g^{ss}}\right]
\end{aligned}
\qquad \text{(D-23)}
$$

We consider the first and second order derivatives of the wavefunction relative to the parameter ρ:

$$
\begin{aligned}
\frac{\partial\chi_n}{\partial\rho} &= \frac{1}{2}\frac{\beta'}{\beta}\chi_n-\frac{\alpha'}{\alpha}\xi\sqrt{\frac{n+1}{2}}\,\chi_{n+1}+\frac{\alpha'}{\alpha}\xi\sqrt{\frac{n}{2}}\,\chi_{n-1} \\
&= \frac{1}{2}\left(\frac{\beta'}{\beta}-\frac{\alpha'}{\alpha}\right)\chi_n-\frac{\alpha'}{2\alpha}\sqrt{(n+1)(n+2)}\,\chi_{n+2}+\frac{\alpha'}{2\alpha}\sqrt{n(n-1)}\,\chi_{n-2} \\
\frac{\partial^2\chi_n}{\partial\rho^2} &= \frac{\partial}{\partial\rho}\left[\frac{1}{2}\left(\frac{\beta'}{\beta}-\frac{\alpha'}{\alpha}\right)\chi_n-\frac{\alpha'}{2\alpha}\sqrt{(n+1)(n+2)}\,\chi_{n+2}+\frac{\alpha'}{2\alpha}\sqrt{n(n-1)}\,\chi_{n-2}\right]
\end{aligned}
$$

$$
\begin{aligned}
&= \left[-\left(\frac{\alpha'}{2\alpha}\right)^2(2n^2+2n+2)+\frac{\beta''}{2\beta}-\left(\frac{\beta'}{2\beta}\right)^2-\frac{\alpha''}{2\alpha}+3\left(\frac{\alpha'}{2\alpha}\right)^2-2\left(\frac{\alpha'}{2\alpha}\right)\cdot\frac{\beta'}{2\beta}\right]\chi_n \\
&+ \sqrt{(n+1)(n+2)}\left[4\left(\frac{\alpha'}{2\alpha}\right)^2-2\frac{\alpha'}{2\alpha}\frac{\beta'}{2\beta}-\frac{\alpha''}{2\alpha}\right]\cdot\chi_{n+2} \\
&- \sqrt{n(n-1)}\left[4\left(\frac{\alpha'}{2\alpha}\right)^2-2\frac{\alpha'}{2\alpha}\frac{\beta'}{2\beta}-\frac{\alpha''}{2\alpha}\right]\cdot\chi_{n-2} \\
&+ \sqrt{(n+1)(n+2)(n+3)(n+4)}\left(\frac{\alpha'}{2\alpha}\right)^2\chi_{n+4} \\
&+ \sqrt{n(n-1)(n-2)(n-3)}\left(\frac{\alpha'}{2\alpha}\right)^2\cdot\chi_{n-4} \qquad \text{(D-24)}
\end{aligned}
$$

In the case when $\alpha = \beta$ (no metric tensor element involved in the volume element $\rightarrow$ no first order partial derivatives to be removed in the stretching vibration hamiltonian [5, 57]), the previous formula will be simplified:

$$
\begin{aligned}
\frac{\partial\chi_n}{\partial\rho}|_{\beta=\alpha} &= -\left(\frac{\alpha'}{2\alpha}\right)\sqrt{(n+1)(n+2)}\chi_{n+2}+\left(\frac{\alpha'}{2\alpha}\right)\sqrt{n(n-1)}\chi_{n-2} \\
\frac{\partial^2\chi_n}{\partial\rho^2}|_{\beta=\alpha} &= -\left(\frac{\alpha'}{2\alpha}\right)^2(2n^2+2n+2)\,\chi_n \\
&+ \left[2\left(\frac{\alpha'}{2\alpha}\right)^2-\left(\frac{\alpha''}{2\alpha}\right)\right]\sqrt{(n+1)(n+2)}\chi_{n+2} \\
&- \sqrt{n(n-1)}\left[2\left(\frac{\alpha'}{2\alpha}\right)^2-\frac{\alpha''}{2\alpha}\right]\chi_{n-2} \\
&+ \sqrt{(n+1)(n+2)(n+3)(n+4)}\left(\frac{\alpha'}{2\alpha}\right)^2\chi_{n+4} \\
&+ \sqrt{n(n-1)(n-2)(n-3)}\left(\frac{\alpha'}{2\alpha}\right)^2\chi_{n-4} \qquad \text{(D-25)}
\end{aligned}
$$

D.3 The Symmetry of Matrix Elements

We consider the matrix elements concerning the adiabatic and non-adiabatic terms from eq.(D-11)-third line, or (D-18)-fifth line. We analyse the symmetric position elements of the matrix,

$$
\begin{aligned}
H_{vb,v'b'} &= 2\int\varphi_b^*\frac{\partial}{\partial\rho}\varphi_{b'}\langle\chi_v|\frac{\partial}{\partial\rho}|\chi_{v'}\rangle d\rho+\int\varphi_b^*\varphi_{b'}\langle\chi_{v'}|\frac{\partial^2}{\partial\rho^2}|\chi_{v'}\rangle d\rho \\
H_{v'b',vb} &= 2\int\varphi_{b'}^*\frac{\partial}{\partial\rho}\varphi_b\langle\chi_{v'}|\frac{\partial}{\partial\rho}|\chi_v\rangle d\rho+\int\varphi_{b'}^*\varphi_b\langle\chi_{v'}|\frac{\partial^2}{\partial\rho^2}|\chi_v\rangle d\rho \qquad \text{(D-26)}
\end{aligned}
$$

We make the following shortcuts:

$$
\begin{aligned}
f_{vv'} &= \langle\chi_v|\frac{\partial}{\partial\rho}|\chi_{v'}\rangle \\
g_{v,v'} &= \langle\chi_v|\frac{\partial^2}{\partial\rho^2}|\chi_{v'}\rangle \qquad \text{(D-27)}
\end{aligned}
$$

In order to obtain the properties of $f_{v,v'}$ and $g_{v,v'}$ functions, we start by considering the orthonormalization of the stretching wavefunctions χ_v:

$$
\int\chi_v\,\chi_{v'}d\rho = \delta_{vv'} \qquad \text{(D-28)}
$$

We will do the derivative of the relation (D-28) and will get the properties of $f_{v,v'}$ function:

$$
\begin{aligned}
0 &= \frac{\partial}{\partial\rho}\left[\int\chi_v\,\chi_{v'}d\rho\right]=\int\chi_v'\,\chi_{v'}d\rho+\int\chi_v\,\chi_{v'}'d\rho \\
&= f_{vv'}+f_{v'v} \qquad \text{(D-29)}
\end{aligned}
$$

Then, from the previous equation we get,

$$f_{vv'} = -f_{v'v} \tag{D-30}$$

In order to obtain the properties for the $g_{vv'}$ function we will do the derivative two times of the relation for orthonormalization of the wavefunctions:

$$\begin{aligned} 0 &= \frac{\partial^2}{\partial\rho^2}\left[\int \chi_v\,\chi_{v'}\,d\rho\right] \\ &= \int \chi''_v\,\chi_{v'}\,d\rho + 2\int \chi'_v\,\chi'_{v'}\,d\rho + \int \chi_v\,\chi''_{v'}\,d\rho \\ &= g_{vv'} + g_{v'v} + 2\int \chi'_v\,\chi'_{v'}\,d\rho \end{aligned} \tag{D-31}$$

We will consider the derivative of $f_{v,v'}$ function:

$$\begin{aligned} f'_{vv'} &= \frac{\partial}{\partial\rho}\int \chi_v\,\chi'_{v'}\,d\rho \\ &= \int \chi'_v\,\chi'_{v'}\,d\rho + g_{vv'} \end{aligned} \tag{D-32}$$

If we take into account the relations (D-31)-(D-32) we obtain the propriety for the $g_{v,v'}$ function:

$$g_{v,v'} - g_{v',v} = 2f'_{v,v'} \tag{D-33}$$

In our case (see matrix elements from equation (D-25)) the relation between $f_{v,v'}$ and $g_{v,v'}$ functions is:

$$\left.\begin{array}{lll} g_{vv'} - g_{v'v} = 2f'_{vv'} & \text{for} & v = v' \pm 2 \\ g_{vv'} - g_{v'v} = 0 & \text{for} & \left\{\begin{array}{l} v = v' \\ v = v' \pm 4 \end{array}\right. \end{array}\right\} \quad g_{vv'} = f'_{vv'} \tag{D-34}$$

For the matrix elements from (D-26), if we apply the integration by parts and the normalization of the basis functions, we get

$$\begin{aligned} H_{bv,b'v'} &= 2\int \varphi^*_b\,\frac{\partial}{\partial\rho}\,\varphi_{b'}\,f_{vv'}\,d\rho + \int \varphi^*_b\,\varphi_{b'}\,g_{vv'}\,d\rho \\ &= 2\int \varphi^*_b\,\frac{\partial}{\partial\rho}\,\varphi_{b'}\,f_{vv'}\,d\rho - \int f_{vv'}\varphi^*_{b'}\frac{\partial}{\partial\rho}\,\varphi_b\,d\rho - \int f_{vv'}\varphi^*_b\frac{\partial}{\partial\rho}\,\varphi_{b'}\,d\rho \\ &= \int \underbrace{f_{vv'}}_{antisym.}\underbrace{\left(\varphi^*_b\,\frac{\partial}{\partial\rho}\,\varphi_{b'} - \varphi^*_{b'}\,\frac{\partial}{\partial\rho}\,\varphi_b\right)}_{antisym.}d\rho \end{aligned} \tag{D-35}$$

In the case when we consider the derivative operators $\frac{\partial^n}{\partial\rho^n}$ multiplied by a function $g^{\rho\rho}(\rho) = g(\rho)$, the symmetry change and we have:

$$\begin{aligned} H_{vb,v'b'} - H_{v'b',vb} &= 2\int g(\rho)\,\varphi_b\,\frac{\partial}{\partial\rho}\varphi_{b'}\,f_{vv'}\,d\rho + \int g(\rho)\,\varphi_b\,\varphi_{b'}\,g_{vv'}\,d\rho \\ &- 2\int g(\rho)\,\varphi_{b'}\,\frac{\partial}{\partial\rho}\varphi_b\,f_{v'v}\,d\rho - \int g(\rho)\,\varphi_b\,\varphi_{b'}\,g_{v'v}\,d\rho \\ &= 2\left[-\int g'(\rho)\,f_{vv'}(\rho)\,\varphi_b\,\varphi_{b'}\,d\rho - \int g(\rho)\,f'_{vv'}\,\varphi_b\,\varphi_{b'}\,d\rho + \int g(\rho)\,\varphi_b\,\varphi_{b'}\,f'_{vv'}\,d\rho\right] \\ &= -2\int g'(\rho) f_{vv'}(\rho)\,\varphi_b\,\varphi_{b'}\,d\rho \end{aligned} \tag{D-36}$$

Obs. In the case when the volume element is $dV = \frac{1}{g^{\rho\rho}(\rho)}d\rho$, the previous equation become symmetric, because the metric tensor element vanish.

Appendix E

Numerical Calculus Considerations

E.1 Relations between Bond Length Parameters and Rotational Constants

The rotational constants can be expressed as [210],

$$B(v) = \langle B \rangle_v \sim \left\langle \frac{1}{r_z^2} \right\rangle_v \tag{E-1}$$

In the previous equation, $\langle \cdots \rangle$ means integration over the vibrational basis, and r_z is the projection of the bond length on the linear axis of the molecule (Oz axis in this case, as in Fig.2.3 or in Fig.3.1).

In the equilibrium case, from the above formula we find the equilibrium rotational constant

$$B_e \sim \frac{1}{(r_z^0)^2} = \frac{1}{(r^0)^2 \cos^2 \frac{\rho_e}{2}} \sim \left(\frac{1}{r^0}\right)^2 \tag{E-2}$$

In the semirigid bender approach, the bond length can vary as in eq.(3.1), with a formula:

$$r(\rho) = r^0 + d\,\rho^2 \tag{E-3}$$

The rotational constant for a vibrational level v, $B(v)$ became with eq.(E-3) and (E-1), for small angles,

$$\begin{aligned}
\langle B \rangle_v &= B_e \left\langle \frac{1}{\left(\frac{r_z}{r^0}\right)^2} \right\rangle_v = B_e \left\langle \frac{1}{\left(1+\frac{d}{r^0}\rho^2\right)^2 \cos^2 \frac{\rho}{2}} \right\rangle_v \simeq B_e \left\langle \frac{1}{\left(1+\frac{d}{r^0}\rho^2\right)^2 \left[1-\left(\frac{\rho}{2}\right)^2\right]} \right\rangle_v \\
&\simeq B_e \left\langle \frac{1}{1-\left(1-\frac{8d}{r^0}\right)\left(\frac{\rho}{2}\right)^2} \right\rangle_v \simeq B_e \left\langle 1+\left(1-\frac{8d}{r^0}\right)\left(\frac{\rho}{2}\right)^2 \right\rangle_v \\
&= B_e \left[1+\frac{1}{2}\left(1-\frac{8d}{r^0}\right)\left\langle \frac{\rho^2}{2} \right\rangle_v\right] = B_e \left[1+\frac{\tilde{\omega}}{2\,\tilde{k}_{22}}\left(1-\frac{8d}{r^0}\right)\left(v+\frac{g_s}{2}\right)\right]
\end{aligned} \tag{E-4}$$

In the previous equation, g_s is a weight factor (see (2.42)), corresponding to the harmonic oscillator g_s-fold degenerate and $\tilde{\omega}$, $\tilde{k}_{22}$ are in cm^{-1}. If we define the vibration-rotation coupling term as

$$\alpha_e = -\frac{B_e\,\tilde{\omega}}{2\,\tilde{k}_{22}}\left(1-\frac{8d}{r^0}\right) \tag{E-5}$$

eq.(E-4) become the well known formula (3.148)-(3.149),

$$B(v) = B_e - \alpha_e \left(v+\frac{g_s}{2}\right) \tag{E-6}$$

For $v = -\frac{g_2}{2}$, we have from eq.(E-6) and (E-2),

$$B\left(-\frac{g_2}{2}\right) = B_e$$

and we can find the r^0 value. By a least square method we can find α_e value, and because $\alpha_e = f(d)$, from eq.(E-5), the dependence of the bond length with angle can be found.

If we consider the expression from [150, eq.(3)], the rotational constants for an AB_2 molecule are:

$$\begin{aligned} B_v &= \langle \frac{\hbar}{4\pi c\, m_1 r^2(\rho)} \cdot \frac{1}{1+\cos\rho} \rangle \\ C_v &= \langle \frac{\hbar\left(\frac{1}{2}m_2 + m_1\right)}{4\pi c\, m_1 r^2(\rho)} \cdot \frac{1}{m_2 + m_1\,(1+\cos\rho)} \rangle \end{aligned} \tag{E-7}$$

We use the following notation for "zero" rotational constant:

$$B_e = \frac{\hbar}{8\pi c\, m_1\, r_0^2} = \frac{C_{g^{\rho\rho}}}{2m_1\, r_0^2} \tag{E-8}$$

In the case of the bi-dimensional oscillator we have:

$$\langle \rho^2 \rangle = \frac{1}{\alpha_\rho}(v_2 + 1) \tag{E-9}$$

where α is the dimensional constant for the oscillator:

$$x = \alpha_\rho \rho^2 \quad \alpha_\rho = \frac{\mu r_0^2 \tilde{\omega}_2}{2C_{g^{\rho\rho}}} = \frac{\mu\omega_2}{\hbar} r_0^2 \tag{E-10}$$

We are using the following approximations :

$$\begin{aligned} \cos x &\simeq 1 - \frac{x^2}{2} + \mathcal{O}(x^4) \\ \tan^2 x &\simeq x^2 + \mathcal{O}(x^4) \end{aligned} \tag{E-11}$$

In this case we find for the bond length in the semirigid bender approach, from [147], as in (E-3):

$$r(\rho) = r_0 + d_1 \tan^2(\frac{\rho}{2}) + d_2\rho^2 \simeq r_0 + d_1\left(\frac{\rho}{2}\right)^2 + d_2\rho^2 = r_0\left(1 + \frac{d}{r_0}\rho^2\right) \tag{E-12}$$

In the case of small angles we expand in power series the rotational constants (E-7):

$$\begin{aligned} B_v &= B_e\left\langle \frac{1}{\left[1 + \frac{d}{r_0}\rho^2 + \mathcal{O}(\rho^4)\right]^2} \cdot \frac{2}{2 - \frac{\rho^2}{2} + \mathcal{O}(\rho^4)} \right\rangle \\ &\simeq B_e\left\langle \frac{1}{\left(1 + 2\frac{d}{r_0}\rho^2\right)} \cdot \frac{1}{\left(1 - \frac{\rho^2}{4}\right)} \right\rangle = B_e + B_e\left(\frac{1}{4} - \frac{2d}{r_0}\right)\langle\rho^2\rangle \end{aligned} \tag{E-13}$$

$$\begin{aligned} C_v &= B_e\left\langle \frac{1}{\left(1 + \frac{d}{r_0}\rho^2\right)^2} \cdot \frac{m_2 + 2m_1}{m_2 + m_1(1+\cos\rho)} \right\rangle \simeq \left\langle \frac{1}{\left(1 + \frac{d}{r_0}\rho^2\right)^2} \cdot \frac{m}{m_2 + m_1\left(2 - \frac{\rho^2}{2}\right) + \mathcal{O}(\rho^4)} \right\rangle \\ &\simeq B_e\left\langle \frac{1}{\left(1 + \frac{2d}{r_0}\rho^2\right)} \cdot \frac{1}{\left(1 - \frac{m_1}{m}\cdot\frac{\rho^2}{2}\right)} \right\rangle \simeq B_e\left\langle \left(1 - 2\frac{d}{r_0}\rho^2\right)\left(1 + \frac{m_1}{m}\cdot\frac{\rho^2}{2}\right) \right\rangle \\ &= B_e + \left(\frac{m_1}{2m} - \frac{2d}{r_0}\right) B_e\langle\rho^2\rangle \end{aligned}$$

The mean value of the rotational constant has the formula:

$$\begin{aligned} \bar{B}_v &= \frac{1}{2}(B_v + C_v) = \frac{1}{2}B_e\left[1 + \left(\frac{1}{4} - \frac{2d}{r_0}\right)\langle\rho^2\rangle + 1 + \left(\frac{m_1}{2m} - \frac{2d}{r_0}\right)\langle\rho^2\rangle\right] \\ &= B_e + \frac{B_e}{2}\left(\frac{1}{4} + \frac{m_1}{2m} - \frac{4d}{r_0}\right)\langle\rho^2\rangle = B_e + \frac{B_e}{2}\left(\frac{m + 2m_1}{4m} - \frac{4d}{r_)}\right)\langle\rho^2\rangle|_{osc.\ bidim.} \\ &= B_e + \frac{B_e}{2}\left(\frac{m + 2m_1}{4m} - \frac{4d}{r_0}\right)\frac{1}{\alpha_\rho}(v_2 + 1) = B_e - \alpha_e(v_2 + 1) \end{aligned} \tag{E-14}$$

where:

$$-\alpha_e = \left(\frac{m + 2m_1}{4m} - \frac{4d}{r_0}\right)\frac{C_{g^{\rho\rho}}}{\mu r_0^2} \cdot \frac{B_e}{\tilde{\omega}_2} \tag{E-15}$$

The reduced mass for the bending displacement in the case of a symmetrical molecule is:

$$\mu = \frac{m_1}{2p} \quad \text{with} \quad p = 1 + \frac{2m_1}{m_2} \tag{E-16}$$

We can find the bond length in the linear configuration from (E-8):

$$r_0 = \sqrt{\frac{C_{g\rho\rho}}{2m_1 B_e}} \text{ [Å]} \tag{E-17}$$

By taking into account the formula (E-15) we obtain for the bond length variation with the bending angle:

$$d = \sqrt{\frac{C_{g\rho\rho}}{2m_1 B_e}} \cdot \frac{1}{4}\left(\frac{m+2m_1}{4m} + \frac{\alpha_e \tilde{\omega}_2}{4pB_e^2}\right) = \sqrt{\frac{C_{g\rho\rho}}{2m_1 B_e}} \cdot \frac{1}{4}\left(\frac{2p-1}{4p} + \frac{\alpha_e \tilde{\omega}_2}{4pB_e^2}\right) \text{ [Å]} \tag{E-18}$$

If we introduce the rigid bender condition $d = 0$ we get the limit condition:

$$\alpha_e|_{lim} = -pB_e \frac{m+2m_1}{m} \frac{B_e}{\tilde{\omega}_2} = -B_e(2p-1)\frac{B_e}{\tilde{\omega}_2} \tag{E-19}$$

E.2 Relation between Bond Length Variation with the Bending Angle in the Semirigid Bender Formalism of [14] and [147]

For the "standard" semirigid bender model, the bond length variation with the angle is done in [14, eq.(20)]:

$$r_{i2} = r_{i2}^0 - \frac{f_{i2}}{f_{ii}}(\rho_e - \rho) + \left[\frac{f_{ii2}^2}{2f_{ii}fiii} - \frac{f_{iii}}{2f_{ii}}\right](\rho_e - \rho)^2 \tag{E-20}$$

The previous equation correspond to a potential defined as:

$$V^{BL} = \frac{1}{2}\sum_i f_{ii}\mathbf{R}_i^2 + \sum_{i>j} f_{ij}\mathbf{R}_i\mathbf{R}_j + \frac{1}{6}\sum_i f_{iii}\,\mathbf{R}_i^3 + \frac{1}{2}\sum_{i>j} f_{ijj}\mathbf{R}_i\mathbf{R}_j^2 + \sum_{i>j>k} f_{ijk}\mathbf{R}_i\mathbf{R}_j\mathbf{R}_k \tag{E-21}$$

In our formalism, [147, eq.(5)], the bond length variation is as in (E-12):

$$r_{i2} = r_{i2}^0 + d_1 \tan^2\left(\frac{\rho}{2}\right)^2 + d_2\rho^2 \simeq r_{i2}^0 + d\rho^2 \quad \text{with} \quad d = \frac{d_1}{4} + d_2 \tag{E-22}$$

If we write in another form (E-20) we will have:

$$r(\rho) \simeq \bar{r}_0 + D_1\rho - 2D_2\rho_e\rho + D_2\rho^2 \tag{E-23}$$

with the values $\bar{r}_0$, D_1, D_2 defined as:

$$\bar{r}_0 = r_{i2}^0 - D_1\rho_e + D_2\rho_e^2 \quad D_1 = \frac{f_{i2}}{f_{ii}} \quad D_2 = \left(\frac{f_{ii2}^2}{2f_{ii}f_{iii}} - \frac{f_{i22}}{2f_{ii}}\right) \tag{E-24}$$

If (E-22) must be equivalent with (E-23), we have (because in (E-22) there isn't linear terms):

$$D_1 - 2D_2\rho_e = 0 \tag{E-25}$$

With (E-24) in the previous condition we get:

$$f_{i2} = \left(\frac{f_{ii2}^2}{f_{iii}} - f_{i22}\right)\rho_e \tag{E-26}$$

This condition is fulfill for the linear molecules where $f_{i2} = f_{ii2} = \rho_e = 0$. In the general case, if the two formula (E-20) and (E-22) are equivalents, the condition (E-26) must be fulfilled in the limits of experimental errors. We will test the previous condition for the water molecule [39]. In this case the potential has the formula:

$$2V^{PL} = \sum_{i,j} K(q_i\, q_j)\, \mathbf{R}_i\, \mathbf{R}_j + \sum_{i\geq j\geq k} K(q_i\, q_j\, q_k)\, \mathbf{R}_i\, \mathbf{R}_j\, \mathbf{R}_k \tag{E-27}$$

The potential constants from [39] (if we consider eq.(E-21) and (E-27)) are:

$$\begin{array}{ll} K(q^2)^{PL} = 8.4526 & f_{ii} = 8.4526 \\ K(qq')^{PL} = -0.1004 & f_{ij} = -0.1004 \\ K(q\gamma)^{PL} = 0.22415 & f_{i2} = 0.22415 \\ K(q^2\gamma)^{PL} = 0.4649 & f_{ii2} = 0.4649 \\ K(q\gamma^2)^{PL} = -0.5226 & f_{i22} = -0.5226 \\ K(q^3)^{PL} = -19.749 & f_{iii} = -6.583 \end{array} \tag{E-28}$$

Equilibrium angle is done by:

$$\rho_e = \pi - \alpha_e = 3.14159 - 1.8378 = 1.16217 \tag{E-29}$$

Therefore:

$$\left(\frac{f_{ii2}^2}{f_{iii}} - f_{i22}\right)\rho_e = 0.5978 \tag{E-30}$$

The error is:

$$\Delta = \left[f_{i2} - \left(\frac{f_{ii2}^2}{f_{iii}} - f_{ii2}\right)\rho_e\right] \frac{2 \star 100}{f_{i2} + \left(\frac{f_{ii2}^2}{f_{iii}} - f_{ii2}\right)\rho_e} \simeq 91\% \tag{E-31}$$

This error indicate that either the two formalisms are not equivalents, or the power expansion in eq.(E-22) can not be done for a bent molecule.

E.3 Theoretical Formula for g_D Parameter

E.3.1 The Hamiltonian Terms in Normal Coordinates

General Formulas

The relation between the curvilinear stretching and the normal stretching co-ordinates [6] is:

$$S = L \cdot Q \tag{E-32}$$

The L matrix is defined as:

$$L^{-1}\,(G\,F)\,L = \Lambda \tag{E-33}$$

From the previous equation we find that the L matrix is diagonal, $L_{ij} = L_{ii}\,\delta_{ij}$. In the case of a symmetrical molecule, the L matrix can be determined from the normalization condition [6, eq.(3.26)]:

$$L\,L^T = G \tag{E-34}$$

From the previous equation and from the equation for G matrix [6, eq.(3.20)], we found that:

$$L_{11} = \pm\sqrt{\frac{m_2+2m_1\sin^2\frac{\rho}{2}}{m_1 m_2}} \quad L_{33} = \pm\sqrt{\frac{m_2+2m_1\cos^2\frac{\rho}{2}}{m_1 m_2}} \tag{E-35}$$

In the case of the linear molecule ($\rho = 0$) we get:

$$L_{11} = \frac{1}{\sqrt{m_1}} \quad \text{and} \quad L_{33} = \sqrt{\frac{m_2+2m_1}{m_1 m_2}} = \sqrt{\frac{m}{m_1 m_2}} = \sqrt{\frac{p}{m_1}} \tag{E-36}$$

If we use the relations between normal and dimensionless normal coordinates from [45, eq.(9) and (9a)]:

$$\begin{aligned} Q_h &= \sqrt{\frac{\hbar}{2\pi c}} \cdot \frac{1}{\sqrt{\tilde{\omega}_h}}\, q_h \quad \rightarrow \quad q_h = \sqrt{\frac{2\pi c}{\hbar}} \cdot \sqrt{\tilde{\omega}_h}\, Q_h \\ P_h &= \sqrt{\frac{2\pi c}{\hbar}} \cdot \sqrt{\tilde{\omega}_h}\, p_h \quad \rightarrow \quad p_h = \sqrt{\frac{\hbar}{2\pi c}} \cdot \frac{p_h}{\sqrt{\tilde{\omega}_h}} \end{aligned} \tag{E-37}$$

we find the zeroth H_0 Hamiltonian from [45] in the normal coordinates:

$$H_0 = \frac{1}{2}\sum_h \left[P_h^2 + \omega_h^2 Q_h^2\right] \tag{E-38}$$

The perturbational terms from the Hamiltonian [5, eq.(62)], which are interesting for the rotational constants are the following (in the normal coordinates):

$$\begin{array}{lll} a_4 q_h p_{h'} & \text{with} & a_4 = \mu^i_{yz}\, L_{ii}\, J_y \\ a'_1 q_{h'} & \text{with} & a'_1 = \frac{1}{2}\left(\mu^i_{xx} + \mu^i_{yy}\right)\, L_{ii}\, J_x^2 \\ a_5 q_{h'} q_h^2 & \text{with} & a_5 = K_{122}\, L_{ii} \\ a_{5a} q_{h'} q_h^2 & \text{with} & a_{5a} = \frac{1}{2}\mu^1_{\rho\rho}(\mu^0_{\rho\rho})^{-1}\, L_{ii} \end{array} \tag{E-39}$$

In the following section we use the notations from [45]. The terms corresponding to first order of perturbation,

$$H^{(1)}_\rho = i\left[H_0 S_\rho - S_\rho H_0\right] \tag{E-40}$$

together with the corresponding contact term S_ρ, and the diagonal contribution from the second order of perturbation term:

$$H_{2;\tau,\rho} = \frac{i}{2}\left[S_\rho H^{(1)}_\tau - H^{(1)}_\tau S_\rho\right] \tag{E-41}$$

are computed for the terms from (E-39).

- The term $\underline{a_1 q_h}$ require a contact term which has the expression [45, Table 2]:

$$S_1 = -\frac{a_1}{A}\, p_h \tag{E-42}$$

If we put $H^{(1)}_1 = a_1 q_h$, as in [45], we obtain for S_1 the formula:

$$S_1 = -\frac{a_1}{\hbar\omega_h^2}\, p_h \tag{E-43}$$

The diagonal term do not depend on q_h or p_h coordinates.

- The term $\underline{a_4 q_h p_{h'}}$ require a contact term which has the general expression (from [45, Table 2]):

$$S_4 = -\frac{a_4}{A_4}\left[B_4\, q_h q_{h'} + C_4\, p_h p_{h'}\right] \tag{E-44}$$

If we apply the algorithm as described before (E-43), we obtain for S_4 the formula:

$$S_4 = -\frac{a_4}{\hbar\left(\omega_h^2 - \omega_{h'}^2\right)} \cdot \left(\omega_{h'}^2 q_h q_{h'} + p_h p_{h'}\right) \tag{E-45}$$

The diagonal term $H_{2;4,4}$ is (similar with [45, Table 3], and using the commutation rules from [45, Table 1]):

$$H_{2;4,4} = \frac{a_4^2}{2\left(\omega_h^2 - \omega_{h'}^2\right)} \cdot \omega_{h'}^2 \left(q_h^2 - q_{h'}^2\right) \tag{E-46}$$

where we have considered that: $(p_h^2)_{ii} = \omega_h^2 (q_h^2)_{ii}$

- The term $\underline{a_5 q_{h'} q_h^2}$ require a contact term which has the expression:

$$S_5 = -\frac{a_5}{A_5}\left[B_5\, q_h^2 p_{h'} + C_5\, \left(p_h q_h + q_h p_h\right) q_{h'} + D_5\, p_h^2 p_{h'}\right] \tag{E-47}$$

As previously discussed, we obtain for S_5 the formula:

$$S_5 = -\frac{a_5}{\hbar\omega_{h'}^2\left(4\omega_h^2 - \omega_{h'}^2\right)}\left[\left(2\omega_h^2 - \omega_{h'}^2\right) q_h^2 p_{h'} + \omega_{h'}^2\left(p_h q_h + q_h p_h\right) q_{h'} + 2p_h^2 p_{h'}\right] \tag{E-48}$$

The cross term between S_5 and $H^{(1)}_1$, namely $H_{2;1,5}$, and the other one $H_{2;5,1}$ are:

$$H_{2;1,5} = -\frac{a_5 a'_1}{2\omega_{h'}^2} \cdot q_h^2 \quad H_{2;5,1} = -\frac{a_1 a'_5}{2\omega_h^2} \cdot q_{h'}^2 \tag{E-49}$$

We see that the two terms have the same form, as it must be.

- The term $\underline{a_{5a} q_{h'} p_h^2}$ require a contact term which has the expression:

$$S_{5a} = -\frac{a_{5a}}{A_{5a}} \left[B_{5a}\, p_h^2 p_{h'} + C_{5a}\, (p_h q_h + q_h p_h)\, q_{h'} + D_{5a}\, q_h^2 p_{h'} \right] \tag{E-50}$$

The term is obtained from (E-47) swapping the operators $q_h \rightleftharpoons p_h$. As previously discussed, we obtain for S_{5a} the formula:

$$S_{5a} = -\frac{a_{5a}}{\hbar \omega_{h'}^2 \left(4\omega_h^2 - \omega_{h'}^2\right)} \left[\left(2\omega_h^2 - \omega_{h'}^2\right) p_h^2 p_{h'} - \omega_h^2\, \omega_{h'}^2\, (p_h q_h + q_h p_h)\, q_{h'} + 2\omega_h^4 q_h^2 p_{h'} \right] \tag{E-51}$$

The cross term between S_{5a} and $H_1^{(1)}$, namely $H_{2;1,5a}$, and the other one $H_{2;5a,1}$ are:

$$H_{2;5a,1} = -\frac{a_{5a} a'_1}{2\omega_{h'}^2} \omega_h^2 \cdot q_h^2 \quad H_{2;1,5a} = -\frac{a_1 a'_{5a}}{2\omega_h^2} \omega_{h'}^2 \cdot q_{h'}^2 \tag{E-52}$$

We see that the two terms have the same form, as it must be.

Constants Used in the Computation

The transformation between the normal "bending" coordinate and the bending curvilinear one is [210]:

$$\begin{aligned} Q_{2x} &= \left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}} \rho \cos\chi \\ Q_{2y} &= \left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}} \rho \sin\chi \end{aligned} \tag{E-53}$$

where $Q_2^2 = Q_{2x}^2 + Q_{2y}^2$. If we use the x coordinate from Laguerre polynomials, the relation become:

$$Q_2^2 = \frac{1}{\alpha_{Q_2}} x \tag{E-54}$$

where: $\alpha_{Q_2} = \left(\frac{a\mu_{\rho\rho}^0}{\hbar}\right)$ is the dimensional constant, and we have for the square of the coordinate:

$$\langle Q_2^2 \rangle = \frac{1}{\alpha_{Q_2}} (v_2 + 1) \tag{E-55}$$

From (E-53) we find for the angular momentum:

$$\begin{aligned} P_z &= -\left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}} \rho \sin\chi\, P_{Q_{2x}} + \left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}} \rho \cos\chi\, P_{Q_{2y}} \\ P_\rho &= \left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}} \cos\chi\, P_{Q_{2x}} + \left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}} \sin\chi\, P_{Q_{2y}} \end{aligned} \tag{E-56}$$

The transformation relation between the curvilinear bending coordinate and the dimensionless Laguerre polynomials coordinate is (from (E-53)-(E-54)):

$$\rho^2 = \tfrac{1}{\alpha_\rho} x \quad \text{with} \quad \alpha_\rho = \tfrac{a}{\hbar} \tag{E-57}$$

and the equation between the two dimensional constants is:

$$\alpha_{Q_2} = \mu_{\rho\rho}^0\, \alpha_\rho \tag{E-58}$$

In the previous equation we use the constants from [5, eq.(64)-(67)] for the rotational terms involving $(v_2 + 1)$:

$$a = \sqrt{\frac{f_{22}}{\mu_{\rho\rho}^0}} = \sqrt{\frac{\omega_2^2}{\mu_{\rho\rho}^0} \cdot \frac{1}{\mu_{\rho\rho}^0}} = \left(\frac{\omega_2}{\mu_{\rho\rho}^0}\right) \tag{E-59}$$

where the force constant for the curvilinear coordinate is defined as:

$$f_{22} = \frac{\omega_2^2}{\mu_{\rho\rho}^0} = \frac{a^2}{\mu_{\rho\rho}^0} \tag{E-60}$$

Using the equation (E-8) for B_e, the constant a become:

$$a = \frac{\tilde{\omega}_2}{8\, p\, B_e} \hbar \tag{E-61}$$

with $\tilde{\omega}_2$ and B_e in cm^1. From (E-61) it is easy to see that the value

$$\left(\frac{\hbar}{a}\right)^2 = 64\,p^2\left(\frac{B_e}{\tilde{\omega}_2}\right)^2 \leq 10^{-3} \tag{E-62}$$

and in the first approximation the terms proportional with the previous constant can be neglected. In the following sections we use the constants from [5]:

$$u_1 = m_1\,(m_2+m_3)\,r_{12}^2 \quad u_3 = m_3\,(m_2+m_1)\,r_{23}^2 \quad u_{13} = m_1 m_3 r_{12}^0 r_{23}^0 \tag{E-63}$$

If we consider the ρ dependence of the bond length, the previous equation become, in the case of a symmetrical molecule:

$$u_1 = u_1^0\,\left(1+\tfrac{2\,d_1}{r^0}\rho^2\right) \quad u_3 = u_3^0\,\left(1+\tfrac{2\,d_3}{r^0}\rho^2\right) \quad u_{13} = u_{13}^0\,\left(1+\tfrac{d_1+d_3}{r^0}\rho^2\right) \tag{E-64}$$

The equation between the instantaneous bending coordinate and the curvilinear coordinate can be obtained from [5, eq.(49)-(51)], or from [6, eq.(3.14),Table 1], if we use the power expansion for the trigonometric functions up to the third order:

$$\begin{aligned}\bar{\rho} &= \rho\left\{1+\sum_i\left[\frac{u_{13}\,(u_i+u_{13})}{r_{i2}\,(u_1u_3-u_{13}^2)} - \frac{u_{13}\,(u_i+u_{13})}{r_{i2}\,(u_1u_3-u_{13}^2)}\left(\frac{1}{6}+\frac{u_{13}}{2\,(u_i+u_{13})}+\frac{u_{13}^2}{(u_1u_3-u_{13}^2)^2}\right)\rho^2\right]S_i\right\}\\ &= \rho\left\{1+\sum_i\left[G_1^\rho+G_{122}^\rho\rho^2\right]S_i\right\}\end{aligned} \tag{E-65}$$

If we use eq.(E-60) and(E-65), we find the anharmonic constants depending only of the harmonic force field in the true valence coordinates:

$$\begin{aligned}K_{i22}^{Harm} &= f_{22}\,G_i^\rho = a^2\,\mu_{\rho\rho}^0 G_i^\rho = 2\,a^2\eta_1^i\\ K_{i2222}^{Harm} &= f_{22}\,G_{i22}^\rho = a^2\,\mu_{\rho\rho}^0 G_{i22}^\rho = -2\,a^2\eta_2^i\end{aligned} \tag{E-66}$$

and the constants η_1^i, η_2^i are defined as in [5, Table VII]

The Diagonal Terms for the Rotational Constants Involving (v_2+1)

We will do the calculus of the most important contact terms from the Hamiltonian defined in [5, eq.(62)]:

- First order terms:

$$\begin{aligned}\langle n|H^{(1)}|n\rangle &= \langle n|\frac{1}{2}\left(\mu_{xx}^{22}\,J_x^2+\mu_{yy}^{22}\,J_y^2\right)\rho^2|n\rangle = \frac{1}{2}\left(\mu_{xx}^{22}+\mu_{yy}^{22}\right)\langle n|J_x^2\rho^2|n\rangle\\ &= \frac{1}{2}\left(\mu_{xx}^{22}+\mu_{yy}^{22}\right)\langle J_x^2\rangle\langle\rho^2\rangle = \frac{\hbar^2}{4}\left(\mu_{xx}^{22}+\mu_{yy}^{22}\right)J(J+1)\,\frac{1}{\alpha_\rho}\,(v_s+1)\\ &= B_0^{(1)}\cdot J(J+1)(v_2+1)\end{aligned} \tag{E-67}$$

  where:

$$B_0^{(1)} = \frac{\hbar^3}{4a}\left(\mu_{xx}^{22}+\mu_{yy}^{22}\right) \tag{E-68}$$

- Terms in the second order of perturbation:
  - The term $a_4 q_h p_{h'}$ is computed using (E-56) and the contact transformation S_4 defined above:

$$\begin{aligned}\frac{1}{2}(\rho^{-1}\mu_{yz}^i)\,S_i\,(J_yP_z+P_zJ_y) &= \rho^{-1}\mu_{yz}^i J_y\,S_i\,P_z\\ &= \mu_{yz}^i\,L_{ii}\,\left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}}\,J_y\,[-\sin\chi P_{Q_2x}+\cos\chi P_{Q_2y}]\,Q_i\end{aligned} \tag{E-69}$$

$$\begin{aligned}(\rho^{+1}\mu_{x\rho}^i)\,S_i\,\rho^{-1}P_\rho J_x &= \mu_{x\rho}^i P_\rho\,S_i\,J_x\\ &= \mu_{x\rho}^i\,L_{ii}\,\left(\mu_{\rho\rho}^0\right)^{-\frac{1}{2}}\,J_x\,[\cos\chi P_{Q_2x}+\sin\chi P_{Q_2y}]\,Q_i\end{aligned} \tag{E-70}$$

We have the constants:

$$\begin{array}{ll} a_4^{(z_1)} = -\mu_{yz}^i\, L_{ii}\, (\mu_{\rho\rho}^0)^{-\frac{1}{2}}\, J_y \sin\chi & a_4^{(z_2)} = \mu_{yz}^i\, L_{ii}\, (\mu_{\rho\rho}^0)^{-\frac{1}{2}}\, J_y \cos\chi \\ a_4^{(\rho_1)} = \mu_{x\rho}^i\, L_{ii}\, (\mu_{\rho\rho}^0)^{-\frac{1}{2}}\, J_x \cos\chi & a_4^{(\rho_2)} = \mu_{x\rho}^i\, L_{ii}\, (\mu_{\rho\rho}^0)^{-\frac{1}{2}}\, J_x \sin\chi \end{array} \tag{E-71}$$

With $\mu_{yz}^i = \mu_{x\rho}^i$, we have the diagonal term:

$$\begin{aligned} \langle n|H_{2;4,4}|n\rangle &= \frac{\left[(a_4^{(z_1)})^2 + (a_4^{(\rho_1)})^2\right] + \left[(a_4^{(z_2)})^2 + (a_4^{(\rho_2)})^2\right]}{2(\omega_i^2 - \omega_2^2)} \omega_2^2\, (Q_i^2 - Q_2^2) \\ &= B_0^{(2)} \cdot J(J+1)(v_2+1) \end{aligned} \tag{E-72}$$

where:

$$B_0^{(2)} = \frac{\hbar^3 a}{4\,(\omega_2^2 - \omega_i^2)} \cdot \left(\mu_{yz}^i\, L_{ii}\right)^2 \tag{E-73}$$

– The terms: $a_5 q_{h'} q_{h'}^2$ and $a_{5a} q_{h'} p_{h'}^2$ are computed using the contact transformation S_5 and S_{5a} defined above. The terms are computed in connection with $a_1' q_{h'}$ and the contact transformation S_1.

$$K_{122}^{harm}\, S_i \rho^2 = K_{122}^{harm} \cdot L_{ii}\, Q_i \cdot (\mu_{\rho\rho}^0)\, Q_2^2 \tag{E-74}$$

$$a_5 = K_{122}^{harm}\, L_{ii}\, \mu_{\rho\rho}^0 \tag{E-75}$$

With (E-56) and $\mu_{zz}^i = \mu_{\rho\rho}^i$, we find the constant a_{5a} as:

$$\begin{aligned} \frac{1}{2}\left\{\left(\mu_{\rho\rho} - \rho^2 \mu_{\rho\rho}^0\right) \rho^{-1} P_\rho \rho^{-1} P_\rho + \left(\mu_{zz} - \rho^{-2}\mu_{zz}\right) P_z^2\right\} &= \frac{1}{2}\mu_{\rho\rho}^1\, (\mu_{\rho\rho}^0)^{-1}\, L_{ii} Q_i P_2^2 \\ a_{5a} &= \frac{1}{2}\mu_{\rho\rho}^1\, (\mu_{\rho\rho}^0)^{-1}\, L_{ii} \end{aligned} \tag{E-76}$$

where the coordinates are: $q_{h'} = Q_i$, $q_h = Q_2$, $p_h = P_2$. The term $a_1' q_{h'}$ can be obtained as:

$$a_1' = \frac{1}{2}\left(\mu_{xx}^1 + \mu_{yy}^1\right)\, L_{ii}\, J_x^2 \tag{E-77}$$

with the coordinate $q_{h'} = Q_i$. We obtain the form of $B_0^{(3)}$ from:

$$\langle n|H_{2;1,5} + H_{2;5,1} + H_{2;1,5a} + H_{2;5a,1}|n\rangle = B_0^{(3)} \cdot J(J+1)(v_2+1) \tag{E-78}$$

where we have:

$$B_0^{(3)} = -\frac{\hbar^3}{4a} \cdot \frac{1}{\omega_i^2}\left[\left(\mu_{xx}^1 + \mu_{yy}^1\right)\, L_{ii}^2\right]\left[K_{122}^{harm} + \frac{1}{2}\omega_2^2\, (\mu_{\rho\rho}^0)^{-2}\, \mu_{\rho\rho}^1\right] \tag{E-79}$$

Taking into account that:

$$K_{122}^{harm} = f_{22}\frac{u_{13}(u_1+u_{13})}{r_{i2}(u_1 u_3 - u_{13}^2)} = a^2 \mu_{\rho\rho}^0 \frac{u_{13}(u_1+u_{13})}{r_{i2}(u_1 u_3 - u_{13}^2)} = 2a^2\eta_1^2 \tag{E-80}$$

the final form of $B_0^{(3)}$ is;

$$B_0^{(3)} = -\frac{\hbar^3 a}{2\omega_i^2}\left[\left(\mu_{xx}^1 + \mu_{yy}^1\right)\, L_{ii}\right]\left[\underbrace{\left(\eta_1^i + \frac{1}{4}\mu_{\rho\rho}^1\right)}_{\eta_3^i}\, L_{ii}\right] \tag{E-81}$$

In the case of $B_0^{(4)}$ we have the same relations, but instead of K_{122}^{harm} we put K_{122}, and we do not have the term $a_{5a} q_{h'} p_h^2$. The final form of $B_0^{(4)}$ is:

$$B_0^{(4)} = -\frac{\hbar^3}{4a} \cdot \frac{1}{\omega_i^2}\left[\left(\mu_{xx}^1 + \mu_{yy}^1\right)\, L_{ii}\right]\left[K_{122}\, L_{ii}\right] \tag{E-82}$$

E.3.2 Expansion in Power Series of the Elements of Metric Tensor

The calculus of the elements obtained from the metric tensor expansion, [5, eq.(61)] is done for the volume element [5, eq.(57)]:

$$dV = dQ_1\, dQ_3\, \rho d\rho\, \sin\theta\, d\theta\, d\varphi\, d\chi \tag{E-83}$$

μ is the inverse for:

$$I'_{\alpha\beta} = \left[I_{\alpha\beta} - Q^{tr}\, \zeta^{\alpha}\, \left(\zeta^{\beta}\right)^{tr}\right] \rho^{-(\delta_{\rho\alpha}+\delta_{\rho\beta})} \tag{E-84}$$

If we consider only the first order terms in the stretching coordinates Q_i, μ will be the inverse only of the tensor $I_{\alpha\beta}$. We consider the series expansion:

$$\mu = \left(W\, I^0\, W\right)^{-1} - \sum_{i=1,3} W^{-1}\, (I^0)^{-1}\, J^{(i)}\, (I^0)^{-1}\, W^{-1}\, S_i \tag{E-85}$$

with

$$W_{\alpha\beta} = \left[1 + \delta_{\alpha\rho}\left(\rho^{-1} - 1\right)\right] \delta_{\alpha\beta} \tag{E-86}$$

It is convenient, as in [5], to introduce the following coefficients in the power series expansion of the elements of μ:

$$\mu_{\alpha\beta} = \rho^n \left[\mu^0_{\alpha\beta} + \mu^{22}_{\alpha\beta}\, \rho^2 + \mu^{2222}_{\alpha\beta}\, \rho^4 + \cdots + \sum_i \left(\mu^i_{\alpha\beta}\, S_i + \mu^{i22}_{\alpha\beta}\, S_i \rho^2 + \cdots\right) + \cdots\right] \tag{E-87}$$

where

$$\begin{array}{lll} n = 0 \rightarrow \mu_{xx}\,,\ \mu_{yy} & n = -2 \rightarrow \mu_{zz} & n = 2 \rightarrow \mu_{\rho\rho} \\ & n = -1 \rightarrow \mu_{yz}\,, \mu_{zy} & n = 1 \rightarrow \mu_{x\rho}\,,\ \mu_{\rho x} \end{array}$$

From (E-85) and (E-86) we have:

$$\begin{aligned} \mu_{\alpha\beta} &= W_{\alpha\alpha}\, (I^0)^{-1}_{\alpha\beta}\, W_{\beta\beta} + \sum_{i=1,3} W^{-1}_{\alpha\alpha}\, (I^0)^{-1}_{\alpha\gamma} (J^{(i)})_{\gamma\delta}\, (I^0)^{-1}_{\delta\beta}\, W_{\beta\beta}\, S_i \\ &= W_{\alpha\alpha} W_{\beta\beta} \left[(I^0)^{-1}_{\alpha\beta} + \sum_{i=1,3} (I^0)^{-1}_{\alpha\gamma} (J^{(i)})_{\gamma\delta}\, (I^0)^{-1}_{\delta\beta}\, S_i\right] \end{aligned} \tag{E-88}$$

To find the tensor elements of $\mu_{\alpha\beta}$ defined above, we must compute the values for the inverse of the tensor $I_{\alpha\beta}$, defined in [5, eq.(37)]. We will use the angle dependence of the bond length as in (E-22), and the constants defined in (E-64). The bond lengths in the linear configuration are assumed equal, $r_{12} = r_{23} = r_0$, which is true for a symmetrical molecule. We have the following expansions in power series for the $\varepsilon(\rho)$ and related quantities, in the first order in ρ:

$$\begin{aligned} \varepsilon &\simeq \rho \cdot \frac{u^0_3 + u^0_{13}}{u^0_1 + u^0_3 + u^0_{13}} \\ \rho - \varepsilon &\simeq \rho \cdot \frac{u^0_1 + u^0_{13}}{u^0_1 + u^0_3 + u^0_{13}} \\ \rho - 2\varepsilon &\simeq \rho \cdot \frac{u^0_1 - u^0_3}{u^0_1 + u^0_3 + u^0_{13}} \end{aligned} \tag{E-89}$$

$$\begin{aligned} \varepsilon'(\rho) &= \frac{u_1 + u_{13}\cos\rho}{u_1 + u_3 + 2u_{13}\cos\rho} \simeq \frac{u_1 + u_{13}\left(1 - \frac{\rho^2}{2}\right)}{u_1 + u_3 + 2u_{13}\left(1 - \frac{\rho^2}{2}\right)} \\ &\simeq \frac{u^0_1 + u^0_{13}}{u^0_1 + u^0_3 + u^0_{13}} + \rho^2 \cdot \frac{u^0_{13}(u^0_1 - u^0_3)}{2(u^0_1 + u^0_3 + u^0_{13})} \end{aligned} \tag{E-90}$$

In the above equations we have taken into account the terms in the second order expansion for ρ, and in the case of a symmetrical molecule we have:

$$\frac{u_i + u_{13}}{u_1 + u_3 + u_{13}} \simeq \frac{u^0_i + u^0_{13}}{u^0_1 + u^0_3 + u^0_{13}} \quad \text{with} \quad i = 1, 3 \tag{E-91}$$

Also, in the case of the symmetric molecule we get:

$$\varepsilon = \tfrac{\rho}{2} \quad \rho - \varepsilon = \tfrac{\rho}{2} \quad \rho - 2\varepsilon = 0 \quad \varepsilon'(\rho)|_{sym} = \tfrac{1}{2} \tag{E-92}$$

With all these computational considerations, we get for the elements $(I^0_{\alpha\beta})^{-1}$:

- $$(I^0)^{-1}_{xx} = \frac{m}{u_1 + u_3 + 2u_{13}\cos\rho} = \mu^0_{xx} + \mu^{22}_{xx}\rho^2 \tag{E-93}$$

where:

$$\begin{aligned} \mu^0_{xx} &= \frac{m}{u^0_1 + u^0_3 + 2u^0_{13}} \\ \mu^{22}_{xx} &= \frac{m}{(u^0_1 + u^0_3 + 2u^0_{13})^2}\left\{u^0_{13} - \frac{2}{r_0}\left[(u^0_1 + u^0_{13})\,d_1 + (u^0_3 + u^0_{13})\,d_3\right]\right\} \end{aligned} \tag{E-94}$$

In the case of the symmetric molecule the previous equation become:

$$\begin{aligned} (\mu^0_{xx})_{|sim} &= \frac{1}{2m_1 r_0^2} \\ (\mu^{22}_{xx})_{|sim} &= \frac{1}{4m_1\, r_0^2}\left[\frac{p-1}{p} - 8\frac{d}{r_0}\right] \end{aligned} \tag{E-95}$$

with $\frac{m_1}{m_2} = \frac{p-1}{2}$, $\frac{m}{m_2} = p$ and $\frac{m}{m_1} = \frac{2p}{p-1}$. The discriminant is:

$$\begin{aligned} \Delta &= I^0_{yy} I^0_{zz} - (I^0_{yz})^2 \\ &= \frac{1}{m^2}\left[u_1\cos^2(\rho-\varepsilon) + u_3\cos^2\varepsilon + 2u_{13}\cos\varepsilon\cos(\rho-\varepsilon)\right] \\ &\star \left[u_1\sin^2(\rho-\varepsilon) + u_3\sin^2\varepsilon + 2u_{13}\sin\varepsilon\sin(\rho-\varepsilon)\right] \\ &- \frac{1}{4m^2}\left[u_1\sin 2(\rho-\varepsilon) - u_3\sin 2\varepsilon + 2u_{13}\sin(\rho-2\varepsilon)\right]^2 \\ &= \frac{1}{m^2}\left\{u_1u_3\sin^2\rho - u^2_{13}\left[\sin 2\varepsilon\sin 2(\rho-\varepsilon) + \sin^2(\rho-2\varepsilon)\right]\right\} \end{aligned} \tag{E-96}$$

After using the equation (E-64) we get:

$$\Delta = \frac{\rho^2}{m^2}\left[\Delta_0 - \frac{\Delta_2}{3}\rho^2\right] \tag{E-97}$$

where:

$$\begin{aligned} \Delta_0 &= u^0_1u^0_3 - (u^0_{13})^2\frac{4(u^0_3+u^0_{13})(u^0_1+u^0_{13}) - (u^0_1-u^0_3)^2}{(u^0_1+u^0_3+2u^0_{13})^2} \\ \Delta_2 &= u^0_1u^0_3\left[1 - 6\frac{d_1+d_3}{r_0}\right] \\ &- (u^0_{13})^2\left\{\frac{8(u^0_1+u^0_{13})(u^0_3+u^0_{13})\left[(u^0_3+u^0_{13})^2 + (u^0_1+u^0_{13})^2\right] + (u^0_1-u^0_3)^4}{(u^0_1+u^0_3+2u_{13})^4}\right. \\ &- \left. 6\frac{d_1+d_3}{r_0}\frac{\left[4(u^0_3+u^0_{13})(u^0_1+u^0_{13}) + (u^0_1-u^0_{13})^2\right]}{(u^0_1+u^0_3+2u^0_{13})^2}\right\} \end{aligned} \tag{E-98}$$

In the case of the symmetric molecule we get:

$$\begin{aligned} \Delta_0|_{sym} &= m_1^2 m_2 m\, r_0^4 \\ \Delta_2|_{sym} &= m_1^2 m_2 m\, r_0^4\left(1 - \frac{12d}{r_0}\right) \end{aligned} \tag{E-99}$$

- We consider $(I^0)^{-1}_{yy}$:

$$(I^0)^{-1}_{yy} = \frac{I^0_{zz}}{\Delta} \tag{E-100}$$

with:

$$\begin{aligned} I^0_{zz} &= \frac{1}{m}\left[u_1\sin^2(\rho-\varepsilon) + u_3\sin^2\varepsilon - 2u_{13}\sin\varepsilon\sin(\rho-\varepsilon)\right] \\ &\simeq \frac{1}{m}\left\{u_1\left[(\rho-\varepsilon)^2 - \frac{1}{3}(\rho-\varepsilon)^4\right] + u_3\left(\varepsilon^2 - \frac{1}{3}\varepsilon^4\right) - 2u_{13}\left(\varepsilon - \frac{1}{3!}\varepsilon^3\right)\left[(\rho-\varepsilon) - \frac{1}{3!}(\rho-\varepsilon)^3\right]\right\} \end{aligned} \tag{E-101}$$

After expanding all terms in power series in second order, we obtain:

$$I^0_{zz} = \frac{\rho^2}{m}\left(A_0 - \frac{1}{3}A_2\rho^2\right) \tag{E-102}$$

with:

$$A_0 = \frac{u^0_1(u^0_1+u^0_{13})^2 + u^0_3(u^0_3+u^0_{13})^2 - 2u^0_{13}(u^0_1+u^0_{13})(u^0_3+u^0_{13})}{(u^0_1+u^0_3+2u^0_{13})^2} \tag{E-103}$$

$$A_2 = \frac{u^0_1(u^0_1+u^0_{13})^4 + u^0_3(u^0_3+u^0_{13})^4 - u^0_{13}(u^0_1+u^0_{13})(u^0_3+u^0_{13})\left[(u^0_1+u^0_{13})^2+(u^0_3+u^0_{13})^2\right]}{(u^0_1+u^0_3+2u^0_{13})^4}$$
$$- \frac{6}{r_0}\cdot\frac{d_1u^0_1(u^0_1+u^0_{13})^2 + d_3u^0_3(u^0_3+u^0_{13})^2 - (d_1+d_3)(u^0_1+u^0_{13})(u^0_3+u^0_{13})u^0_{13}}{(u^0_1+u^0_3+2u^0_{13})^2}$$

In the case of the symmetric molecule we have:

$$\begin{aligned} A_0|_{sym} &= \frac{1}{2}m_1m_2r_0^2 \\ A_2|_{sym} &= \frac{1}{8}m_1m_2r_0^2\left(1-24\frac{d}{r_0}\right) \end{aligned} \tag{E-104}$$

The final form of $(I^0)^{-1}_{yy}$ is:

$$\begin{aligned} (I^0)^{-1}_{yy} &= m\frac{A_0\left(1-\frac{A_2}{3A_0}\rho^2\right)}{\Delta_0\left(1-\frac{\Delta_2}{3\Delta_0}\rho^2\right)} \\ &\simeq m\frac{A_0}{\Delta_0}\left(1-\frac{A_2}{3A_0}\rho^2\right)\left(1+\frac{\Delta_2}{3\Delta_0}\rho^2\right) = m\frac{A_0}{\Delta_0} + m\frac{A_0}{3\Delta_0}\left(\frac{\Delta_2}{\Delta_0}-\frac{A_2}{A_0}\right)\rho^2 \\ &= \mu^0_{yy} + \mu^{22}_{yy}\rho^2 \end{aligned} \tag{E-105}$$

In the case of the symmetric molecule we obtain:

$$\begin{aligned} (\mu^0_{yy})_{|sym} &= m\frac{A_0}{\Delta_0} = \frac{1}{2m_1r_0^2} \\ (\mu^{22}_{yy})_{|sym} &= m\frac{A_0}{3\Delta_0}\left(\frac{\Delta_2}{\Delta_0}-\frac{A_2}{A_0}\right) = \frac{1}{8m_1r_0^2}\left(1-\frac{8d}{r_0}\right) \end{aligned} \tag{E-106}$$

- In the same way we consider $(I^0)^{-1}_{zz}$, which has the form:

$$(I^0)^{-1}_{zz} = \frac{I^0_{yy}}{\Delta} \tag{E-107}$$

with the tensor element:

$$\begin{aligned} I^0_{yy} &= \frac{1}{m}\left[u_1\cos^2(\rho-\varepsilon) + u_3\cos^2\varepsilon + 2u_{13}\cos\varepsilon\cos(\rho-\varepsilon)\right] \\ &= \frac{1}{m}\left(B_0 - B_2\rho^2\right) \end{aligned} \tag{E-108}$$

with:

$$\begin{aligned} B_0 &= u^0_1 + u^0_3 + 2u^0_{13} \\ B_2 &= \frac{u^0_1(u^0_1+u^0_{13})^2 + u^0_3(u^0_3+u^0_{13})^2 + u^0_{13}\left[(u^0_1+u^0_{13})^2+(u^0_3+u^0_{13})^2\right]}{(u^0_1+u^0_3+2u^0_{13})^2} \\ &- \frac{2}{r_0}\left[u^0_1d_1 + u^0_3d_3 + u^0_{13}(d_1+d_3)\right] \end{aligned} \tag{E-109}$$

In the case of the symmetric molecule we have:

$$\begin{aligned} B_0|_{sym} &= 2m_1\, m\, r_0^2 \\ B_2|_{sym} &= \frac{1}{2}m_1\, m\, r_0^2\left(1-\frac{8d}{r_0}\right) \end{aligned} \tag{E-110}$$

The final form of $(I^0)^{-1}_{zz}$ is:

$$\begin{aligned}(I^0)^{-1}_{zz} &= \frac{B_0 - B_2\rho^2}{\frac{\rho^2}{m}\left(\Delta_0 - \frac{1}{3}\Delta_2\rho^2\right)} \\ &\simeq \frac{m}{\rho^2}\frac{B_0}{\Delta_0}\left(1 - \frac{B_2}{B_0}\rho^2\right)\left(1 + \frac{1}{3}\frac{\Delta_2}{\Delta_0}\rho^2\right) = \frac{1}{\rho^2}\left[\mu^0_{zz} + \mu^{22}_{zz}\right]\end{aligned} \tag{E-111}$$

where:

$$\begin{aligned}\mu^0_{zz} &= m\frac{B_0}{\Delta_0} \\ \mu^{22}_{zz} &= m\frac{B_0}{\Delta_0}\left(\frac{1}{3}\frac{\Delta_2}{\Delta_0} - \frac{B_2}{B_0}\right)\end{aligned} \tag{E-112}$$

In the case of the symmetric molecule we get:

$$\begin{aligned}(\mu^0_{zz})_{|sym} &= \frac{2p}{m_1 r_0^2} \\ (\mu^{22}_{zz})_{|sym} &= \frac{1}{6}\frac{p}{m_1 r_0^2}\left(1 - \frac{24d}{r_0}\right)\end{aligned} \tag{E-113}$$

- We compute $(I^0)^{-1}_{yz}$ and we start with:

$$(I^0)^{-1}_{yz} = -\frac{I^0_{yz}}{\Delta} \tag{E-114}$$

with:

$$I^0_{yz} = \frac{1}{2m}\left[u_1 \sin 2(\rho - \varepsilon) - u_3 \sin 2\varepsilon + 2u_{13}\sin(\rho - 2\varepsilon)\right] \tag{E-115}$$

After the calculus we obtain:

$$I^0_{yz} = \frac{\rho}{2m}\left(C_0 + \frac{C_2}{3}\rho^2\right) \tag{E-116}$$

where:

$$\begin{aligned}C_0 &= 2\frac{u^0_1(u^0_1 + u^0_{13}) - u^0_3(u^0_3 + u^0_{13}) + 2u^0_{13}(u^0_1 - u^0_3)}{u^0_1 + u^0_3 + 2u^0_{13}} \\ C_2 &= \frac{4\left[u^0_3(u^0_3 + u^0_{13})^3 - u^0_1(u^0_1 + u^0_{13})^3\right] - u^0_{13}(u^0_1 - u^0_3)^3}{(u^0_1 + u^0_3 + 2u^0_{13})^3} \\ &+ 6\frac{2\left[u^0_3 d_3(u^0_3 + u^0_{13}) - u^0_1 d_1(u^0_1 + u^0_{13})\right] - u^0_{13}(d_1 + d_3)(u^0_1 - u^0_3)}{r_0(u^0_1 + u^0_3 + 2u^0_{13})}\end{aligned} \tag{E-117}$$

In the case of the symmetric molecule we get:

$$\begin{aligned}C_0|_{sym} &= 0 \\ C_2|_{sym} &= 0\end{aligned} \tag{E-118}$$

The final form of $(I^0)^{-1}_{yz}$ is:

$$(I^0)^{-1}_{yz} = \rho^{-1}\left(\mu^0_{yz} + \mu^{22}_{yz}\rho^2\right) \tag{E-119}$$

In the case of the symmetric molecule we have:

$$\begin{aligned}(\mu^0_{yz})_{|sym} &= m\frac{C_0}{2\,\Delta_0} = 0 \\ (\mu^{22}_{yz})_{|sym} &= \frac{mC_0}{6\Delta_0}\left(\frac{C_2}{C_0} + \frac{\Delta_2}{\Delta_0}\right) = 0\end{aligned} \tag{E-120}$$

- We have to calculate $(I^0)^{-1}_{\rho\rho}$ as:

$$(I^0)^{-1}_{\rho\rho} = \frac{m}{u_1(1-\varepsilon')^2 + u_3(\varepsilon')^2 - 2u_{13}\varepsilon'(1-\varepsilon')\cos\rho} \tag{E-121}$$

After calculus we obtain:

$$(I^0)^{-1}_{\rho\rho} = \mu^0_{\rho\rho} + \mu^{22}_{\rho\rho}\rho^2 \tag{E-122}$$

where:

$$\begin{aligned}
\mu^0_{\rho\rho} &= \frac{m(u^0_1 + u^0_3 + 2u^0_{13})}{u^0_1 u^0_3 - (u^0_{13})^2} \\
\mu^{22}_{\rho\rho} &= -m\left(\frac{u^0_1 + u^0_3 + 2u^0_{13}}{u^0_1 u^0_3 - (u^0_{13})^2}\right)^2 \left[\frac{u^0_{13}(u^0_1 + u^0_{13})(u^0_3 + u^0_{13})}{(u^0_1 + u^0_3 + 2u^0_{13})^2} - \frac{3(u^0_{13})^2(u^0_1 - u^0_3)^2}{(u^0_1 + u^0_3 + 2u^0_{13})^3}\right. \\
&+ \left.\frac{[d_1(u^0_1 + u^0_{13}) + d_3(u^0_3 + u^0_{13})]\,[u^0_1 u^0_3 - (u^0_{13})^2] - (d_1 + d_3)u^0_{13}(u^0_1 + u^0_{13})(u^0_3 + u^0_{13})}{r_0(u^0_1 + u^0_3 + 2u_{13^0})^2}\right]
\end{aligned} \tag{E-123}$$

In the case of the symmetric molecule we obtain:

$$\begin{aligned}
(\mu^0_{\rho\rho})|_{sym} &= \frac{2p}{m_1 r_0^2} \\
(\mu^{22}_{\rho\rho})|_{sym} &= -\frac{p}{2m_1 r_0^2}\left[(p-1) - \frac{2d}{r_0}(p-3)\right]
\end{aligned} \tag{E-124}$$

We will calculate the $J^{(i)}_{\alpha\beta}$ elements from [5, Tab.VI], expanding in power series with respect to the ρ angle, and we will drop the terms after the second order. Because $\varepsilon'|_{sym} = \frac{1}{2}$ for a symmetrical molecule, we have:

$$|J^{(1)}_{\alpha\beta}| = |J^{(3)}_{\alpha\beta}| \tag{E-125}$$

The nonvanishing derivatives $J^{(i)}_{\alpha\beta}$ of the $\alpha\beta$ component of the moment of inertia tensor $I_{\alpha\beta}$ for a symmetrical molecule, taken with respect to the symmetry coordinate S_i are:

-

$$\begin{aligned}
J^{(i)}_{xx}|_{sym} &\simeq \frac{p-1}{m_1 p}\left[1 - \frac{(p-1)^2}{4p}\rho^2\right]\frac{1}{r_0\left(1 + \frac{d}{r_0}\rho^2\right)} \\
&\star \left[u^0_1\left(1 + \frac{2d}{r_0}\rho^2\right) + u^0_{13}\left(1 + \frac{2d}{r_0}\rho^2\right)\left(1 - \frac{\rho^2}{2}\right)\right] \\
&\simeq 2m_1 r_0\left\{1 + \left[\frac{d}{r_0} - \frac{(p-1)}{4}\right]\rho^2\right\}
\end{aligned} \tag{E-126}$$

-

$$\begin{aligned}
J^{(i)}_{yy}|_{sym} &\simeq J^{(i)}_{xx}\cos^2\left(\frac{\rho^2}{2}\right) \simeq J^{(i)}_{xx}\left[1 - \frac{1}{2}(\frac{\rho^2}{2})\right] \\
&= 2m_1 r_0\left\{1 + \left[\frac{d}{r_0} - \frac{2p-1}{8}\right]\rho^2\right\}
\end{aligned} \tag{E-127}$$

-

$$\begin{aligned}
J^{(i)}_{zz}|_{sym} &\simeq J^{(i)}_{xx}\sin^2\left(\frac{\rho^2}{2}\right) \simeq J^{(i)}_{xx}(\frac{\rho^2}{2})^2 \\
&= \frac{1}{2}\rho^2 m_1 r_0\left\{1 + \left[\frac{d}{r_0} - \frac{p-1}{4}\right]\rho^2\right\} \simeq \frac{1}{2}m_1 r_0\rho^2 + \mathcal{O}(\rho^4)
\end{aligned} \tag{E-128}$$

- $$J^{(i)}_{\rho\rho}|_{sym} \simeq J^{(i)}_{xx}(\varepsilon')^2 \simeq J^{(i)}_{xx}\frac{1}{4} = \frac{1}{2}m_1 r_0\left\{1 + \left[\frac{d}{r_0} - \frac{p-1}{4}\right]\rho^2\right\} \tag{E-129}$$

- $$J_{yz}^{(1)}|_{sym} = -J_{yz}^{(3)}|_{sym} = \frac{p-1}{m_1 p}\left[1 - \frac{(p-1)^2}{4p}\rho^2\right][u_1 \sin\rho - u_{13}\cos\rho\sin\rho]\frac{1}{2r} \tag{E-130}$$

After calculus we obtain:

$$J_{yz}^{(1)}|_{sym} = \rho\frac{m_1 r_0}{p}\left\{1 + \rho^2\left[\frac{d}{r_0} + \frac{(p-1)}{4p}\right]\right\} \tag{E-131}$$

- $$J_{\rho x}^{(1)}|_{sym} = -J_{\rho x}^{(3)}|_{sym} = \frac{p-1}{m_1 p}\left[1 - \frac{(p-1)^2}{4p}\rho^2\right][u_1 - u_{13}\cos\rho]\frac{1}{2r} \tag{E-132}$$

After calculus we obtain:

$$J_{\rho x}^{(1)}|_{sym} = \frac{m_1 r_0}{p}\left\{1 + \rho^2\left[\frac{d}{r_0} + \frac{(p-1)}{4p}\right]\right\} \tag{E-133}$$

Now, we can compute the μ tensor elements (E-87), with the equation (E-88):

-
$$\begin{aligned}(\mu_{xx})_{|sym} &= (I^0)^{-1}_{xx} - \sum_{i=1,3}\left[(I^0)^{-1}_{xx} J^{(i)}_{xx}(I^0)^{-1}_{xx}\right]_{|_{J^{(1)}_{xx}=J^{(3)}_{xx}}} S_i \\ &= (I^0)^{-1}_{xx} - \left[(I^0)^{-1}_{xx} J^{(1)}_{xx}(I^0)^{-1}_{xx}\right](S_1+S_3) \\ &= \mu^0_{xx} + \mu^{22}_{xx}\rho^2 + \mu^1_{xx}(S_1+S_3) + \mu^{122}_{xx}(S_1+S_3)\rho^2\end{aligned} \tag{E-134}$$

where the expansion coefficients for the bending coordinate are done in (E-95) and for the stretching coordinates there are:

$$\begin{aligned}(\mu^1_{xx})_{|sym} &= -\frac{1}{2m_1 r_0^3} \\ (\mu^{122}_{xx})_{|sym} &= \frac{1}{2m_1 r_0^3}\left[\frac{3d}{r_0} + \frac{(p-1)(p-2)}{4p}\right]\end{aligned} \tag{E-135}$$

-
$$\begin{aligned}(\mu_{yy})_{|sym} &= (I^0)^{-1}_{yy} - \left[(I^0)^{-1}_{yy} J^{(i)}_{yy}(I^0)^{-1}_{yy}\right](S_1+S_3) \\ &= \mu^0_{yy} + \mu^{22}_{yy}\rho^2 + \mu^1_{yy}(S_1+S_3) + \mu^{122}_{yy}(S_1+S_3)\rho^2\end{aligned} \tag{E-136}$$

where the coefficients for the ρ coordinate are from (E-106), and for the stretching coordinates we have:

$$\begin{aligned}(\mu^1_{yy})_{|sym} &= -\frac{1}{2m_1 r_0^3} \\ (\mu^{122}_{yy})_{|sym} &= \frac{1}{2m_1 r_0^3}\left[\frac{3d}{r_0} + \frac{2p-5}{8}\right]\end{aligned} \tag{E-137}$$

-
$$\begin{aligned}(\mu_{zz})_{|sym} &= (I^0)^{-1}_{zz} - \sum_{i=1,3}\left[(I^0)^{-1}_{zz} J^{(i)}_{zz}(I^0)^{-1}_{zz}\right]_{|_{J^{(1)}_{zz}=J^{(3)}_{zz}}} S_i \\ &= \rho^{-2}\left[\mu^0_{zz} + \mu^{22}_{zz}\rho^2 + \mu^1_{zz}(S_1+S_3) + \mu^{122}_{zz}(S_1+S_3)\rho^2\right]\end{aligned} \tag{E-138}$$

where the terms for the bending coordinate are defined in (E-113), and for the stretching we get:

$$\begin{aligned}(\mu^1_{zz})_{|sym} &= -\frac{2p^2}{m_1 r_0^3} \\ (\mu^{122}_{zz})_{|sym} &= \frac{2p^2}{m_1 r_0^3}\left[\frac{3d}{r_0} + \frac{2p-5}{12}\right]\end{aligned} \tag{E-139}$$

•

$$
\begin{aligned}
(\mu_{yz})_{|sym} &= (\mu_{zy})_{|sym} = -\sum_{i=1,3}\left[(I^0)^{-1}_{yy} J^{(i)}_{yz} (I^0)^{-1}_{zz}\right]_{|_{J^{(1)}_{yz}=-J^{(3)}_{yz}}} S_i \\
&= \rho^{-1}\left[\mu^1_{yz}(S_1 - S_3) - \mu^{122}_{yz}(S_1 - S_3)\rho^2\right]
\end{aligned}
\tag{E-140}
$$

where for the bending coordinate the coefficients vanish as in (E-120), and for the stretching coordinate we have:

$$
\begin{aligned}
(\mu^1_{yz})_{|sym} &= -\frac{1}{m_1 r_0^3} \\
(\mu^{122}_{yz})_{|sym} &= -\frac{1}{m_1 r_0^3}\left[\frac{7p-4}{12p} - \frac{3d}{r_0}\right]
\end{aligned}
\tag{E-141}
$$

•

$$
\begin{aligned}
(\mu_{\rho\rho})_{|sym} &= \rho^2\left\{(I^0)^{-1}_{\rho\rho} - \sum_{i=1,3}\left[(I^0)^{-1}_{\rho\rho} J^{(i)}_{\rho\rho} (I^0)^{-1}_{\rho\rho}\right] S_i\right\} \\
&= \rho^2\left[\mu^0_{\rho\rho} + \mu^{22}_{\rho\rho} + \mu^1_{\rho\rho}(S_1 + S_3) + \mu^{122}_{\rho\rho}(S_1 + S_3)\rho^2\right]
\end{aligned}
\tag{E-142}
$$

where for bending we have (E-124), and the remaining coefficients are:

$$
\begin{aligned}
(\mu^1_{\rho\rho})_{|sym} &= -\frac{2p^2}{m_1 r_0^3} \\
(\mu^{122}_{\rho\rho})_{|sym} &= \frac{2p^2}{m_1 r_0^3}\left[\frac{3(p-1)}{4} - \frac{d}{r_0}(2p-5)\right]
\end{aligned}
\tag{E-143}
$$

•

$$
\begin{aligned}
(\mu_{\rho x})_{|sym} &= (\mu_{x\rho})_{|sym} = \rho\left\{-\sum_{i=1,3}\left[(I^0)^{-1}_{\rho\rho} J^{(i)}_{\rho x} (I^0)^{-1}_{xx}\right] S_i\right\} \\
&= \rho\left[\mu^1_{\rho x}(S_1 - S_3) + \mu^{122}_{\rho x}(S_1 - S_3)\rho^2\right]
\end{aligned}
\tag{E-144}
$$

where the coefficients are:

$$
\begin{aligned}
(\mu^1_{\rho x})_{|sym} &= -\frac{1}{m_1 r_0^3} \\
(\mu^{122}_{\rho x})_{|sym} &= \frac{1}{m_1 r_0^3}\left[\frac{(p-1)(p-2)}{4p} - \frac{d}{2r_0}(5-p)\right]
\end{aligned}
\tag{E-145}
$$

As in [5] we have the relations between coefficients;

$$
\begin{aligned}
&\mu^0_{yz} = \mu^0_{\rho x} = \mu^{22}_{\rho x} = 0 \quad \mu^1_{\rho x} = \mu^1_{yz} \quad \mu^1_{\rho\rho} = \mu^1_{zz} \\
&\text{and} \\
&\mu^0_{xx} = \mu^0_{yy} \quad \mu^0_{zz} = \mu^0_{\rho\rho} \quad \mu^1_{xx} = \mu^1_{yy} \\
&\mu^1_{\rho x} = -\mu^3_{\rho x} \quad \mu^1_{yz} = -\mu^3_{yz} \quad \mu^{122}_{\rho x} = -\mu^{322}_{\rho x} \quad \mu^{122}_{yz} = -\mu^{322}_{yz}
\end{aligned}
\tag{E-146}
$$

E.3.3 Calculus of the g_D Factor from the Rotational Constant Expressed in the Two Formalisms of [5] and [147]

In the equations [5, eq.(64)-(67)] concerning the terms from rotational constants involving $(v_2 + 1)$ dependence, in the first approximation, only the first terms of each equation for $B^{(i)}$ are considered. This is marked by the subscript "$_0$" for the terms $B^{(i)} \to B^{(i)}_0$. This is due to the fact that the other terms in these equations are multiplied with $\left(\frac{\hbar}{a}\right)^2$, which is a small factor, as shown in (E-62). In the demonstration below we will use the constants and factors previously defined in (E-59), (E-60), (E-61), (E-8), (E-35),(E-36). The terms $B^{(i)}_0$ are multiplied by $(v_2 + 1)$, against $B^{(i)}$ from [5], which include $(v_2 + 1)$.

In the "semirigid bender" formalism of [14], the bond length dependence of the bending angle is defined for a linear molecule as:

$$d_{(i)}^{BL} = -\frac{f_{i22}}{2\,f_{ii}} = -\frac{K_{i22}}{f_{ii}} \tag{E-147}$$

In our formalism the same dependence is defined by the equation (E-12), as in [147]. The formula (E-15) for the α_e factor in the rotational constant can be rewritten as:

$$B^{ChJ} = -\alpha_e^{ChJ} = B_e 4p \left(\frac{B_e}{\tilde{\omega}_2}\right)\left(\frac{2p-1}{4p} - \frac{4d^{ChJ}}{r_0}\right) = B_e p \left(\frac{B_e}{\tilde{\omega}_2}\right)\left(\frac{2p-1}{p} - \frac{4d_1^{ChJ}}{r_0}\right) \tag{E-148}$$

where B_e is defined in (E-8) and d_1^{ChJ} in (E-12). The factor g_D is defined as,

$$g_D = \frac{d_1^{ChJ}}{d_1^{BL}} \quad \text{where} \quad d_1^{BL} = \frac{d^{BL}}{4} \tag{E-149}$$

and can be found from the equation:

$$B^{ChJ} = B_0^{(1)} + B_0^{(2)} + B_0^{(3)} + B_0^{(4)} \tag{E-150}$$

The quantities on the right of the previous equation represent respectively [5]:

- $B_0^{(1)}$: first order contribution from terms quadratic in J_x and J_y, corresponding to α_2^{harm} in the traditional formalism. The equation for this term, in the case of a symmetrical molecule is, from [5, eq.(64)] and(E-68), with (E-95), (E-106):

$$B_0^{(1)} = \frac{\hbar^3}{4a}\frac{1}{hc}\left(\mu_{xx}^{22} + \mu_{yy}^{22}\right) = B_e\, p \left(\frac{B_e}{\tilde{\omega}_2}\right)\left(\frac{2p-1}{p} - \frac{4d_1^{BL}}{r_0}\right) \tag{E-151}$$

- $B_0^{(2)}$: second order contribution from terms linear in J_x and J_y, corresponding to α_2^{Cor}. In the case of a symmetrical molecule, using [5, eq.(65)] and(E-73), with (E-141) is:

$$\begin{aligned} B_0^{(2)} &= \sum_i \frac{\hbar^3 a}{4}\frac{1}{hc}\left(\omega_2^2 - \omega_i^2\right)^{-1}\left[\mu_{yz}^i L_{ii}\right]^2 = \frac{\hbar^3 a}{4}\frac{1}{hc}\left(\mu_{yz}^1\right)^2\left[\frac{L_{11}^2}{\omega_2^2-\omega_1^2} + \frac{L_{33}^2}{\omega_2^2-\omega_3^2}\right] \\ &= B_e\, p \left(\frac{B_e}{\tilde{\omega}_2}\right)\frac{2\tilde{\omega}_2^2}{p^2}\left[\frac{1}{\tilde{\omega}_2^2-\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_2^2-\tilde{\omega}_3^2}\right] \end{aligned} \tag{E-152}$$

- $(B_0^{(3)} + B_0^{(4)})$: second order contribution from products of a term quadratic in J_x and J_y and a term independent of J_x and J_y, corresponding to α_2^{anh}, respectively. Before analyzing the $B_0^{(3)}$ term, we must find the corresponding quantities from [5, Table VII], using (E-65), (E-66), (E-80):

$$\begin{aligned} \eta_1^1 &= \eta_1^3 = \frac{1}{2}\mu_{\rho\rho}^0 G_1^\rho = \frac{p(p-1)}{2m_1 r_0^3} \\ \eta_2^1 &= \eta_2^3 = -\frac{1}{2}\mu_{\rho\rho}^0 G_{122}^\rho = \frac{p(p-1)(3p-1)}{24m_1 r_0^3} \\ \eta_3^1 &= \eta_3^3 = \eta_1^1 + \frac{1}{4}\mu_{\rho\rho}^1 = -\frac{p}{2m_1 r_0^3} \\ \eta_6^1 &= \eta_6^3 = 4G_1^\rho = \frac{2(p-1)}{r_0} \end{aligned} \tag{E-153}$$

In the case of a symmetric molecule, from [5, eq.(66)] and(E-81), using (E-66), (E-80), (E-153) and (E-135), (E-137), we find for $B_0^{(3)}$:

$$\begin{aligned} B_0^{(3)} &= \sum_i -\frac{\hbar^3 a}{2\omega_i^2}\frac{1}{hc}\left[(\mu_{xx}^i + \mu_{yy}^i)\eta_3^i L_{ii}^2\right] = -\frac{\hbar^3 a}{2hc}\left[(\mu_{xx}^1 + \mu_{yy}^1)\eta_3^1\right]\left[\frac{L_{11}^2}{\omega_1^2} + \frac{L_{33}^2}{\omega_3^2}\right] \\ &= -B_e\, p \left(\frac{B_e}{\tilde{\omega}_2}\right)\frac{2\tilde{\omega}_2^2}{p}\left[\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2}\right] \end{aligned} \tag{E-154}$$

In the case of the stretching potential constants, using (3.28), (3.38), (3.41), (3.42) and (E-35), (E-36), the formula similar with (E-60), for the stretching coordinates in the formalism of [5, 6], is:

$$f_{ii} = \frac{\omega_i^2}{L_{ii}^2} \quad \text{where the effective stretching mass is:} \quad m_{Q_i} = (L_{ii})^{-2} \tag{E-155}$$

With the previous relation and with (E-147) we have the important relation in the case of the "semirigid bender" approach:

$$\sum_{i=1,3} [\omega_i^{-2} K_{i22} (L_{ii})^2] = -\left(\sum_{i=1,3} d_{(i)}^{BL} \right)_{|_{sym}} = -2d^{BL} = -\frac{1}{2} d_1^{BL} \tag{E-156}$$

The above equation is not quite the equation which define the angle dependence of the bond length, as in [14, eq.(20)], but a mean value, closer to our definition of this dependence, as it is in (3.56) and(3.220). The factor d^{BL} is function of both stretching frequencies, and it is equal with the formula of [14] only in the limit case, for small angles, when, from (E-155),

$$\frac{\tilde{\omega}_3}{\tilde{\omega}_1} = \sqrt{p}$$

With [5, eq.(67)] and (E-82), using (E-135), (E-137) and (E-156) we calculate $B_0^{(4)}$ as:

$$\begin{aligned} B_0^{(4)} &= \sum_i -\frac{\hbar^3}{4a} \omega_i^{-2} \frac{1}{hc} [(\mu_{xx}^i + \mu_{yy}^i) K_{i22} L_{ii}^2] = -\frac{\hbar^3}{4a\, hc} [(\mu_{xx}^1 + \mu_{yy}^1) K_{122}] \left[\frac{L_{11}^2}{\omega_1^2} + \frac{L_{33}^2}{\omega_3^2} \right] \\ &= B_e\, p \left(\frac{B_e}{\tilde{\omega}_2} \right) \cdot 32 B_e (r_0 \tilde{K}_{122}) \left[\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2} \right] = -B_e\, p \left(\frac{B_e}{\tilde{\omega}_2} \right) \cdot \frac{4 d_1^{BL}}{r^0} \end{aligned} \tag{E-157}$$

Obs. There is a **very important** observation to be done: we can not use in the same time the d_1^{BL} term from $B_0^{(1)}$ and the $B_0^{(4)}$. This is due to the fact that in the case of the "semirigid bender", the term K_{i22} vanish and is replaced by the d^{BL} factor, as pointed out in the equations (3.56), (3.57) and in (§C.2). Therefore, we can use the two similar approaches:

- "Rigid bender" approach: we use all the terms $B_0^{(1)} - B_0^{(4)}$, but $B_0^{(1)-Rigid}$ has the formula:

$$B_0^{(1)-Rigid} = B_e\, p \left(\frac{B_e}{\tilde{\omega}_2} \right) \frac{2p-1}{p}$$

  which is issued if we have $d^{BL} = 0$ in (E-151). The previous formula is identical with (E-19).
- "Semirigid bender" approach: we use only $B_0^{(1)} - B_0^{(3)}$, because in that case $K_{i22} = 0$.

We see from (E-151) and (E-157) that the terms mutual exclusive are equals, and therefore the results will be identical.

From the equation (E-150) with the above formulas for the B^{ChJ} and $B^{(i)}$, $i = \overline{1,4}$, we find the final formula concerning the g_D factor:

$$\begin{aligned} g_D &= 1 + \frac{r_0}{4 d_1^{BL}} \left\{ -\frac{2\tilde{\omega}_2^2}{p^2} \left[\frac{1}{\tilde{\omega}_2^2 - \tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_2^2 - \tilde{\omega}_3^2} \right] + \frac{2\tilde{\omega}_2^2}{p} \left[\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2} \right] \right\} \\ &= 1 + \frac{r_0}{4 d_1^{BL}} \frac{2\tilde{\omega}_2^2}{p} \left\{ -\frac{1}{p} \left[\frac{1}{\tilde{\omega}_2^2 - \tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_2^2 - \tilde{\omega}_3^2} \right] + \left[\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2} \right] \right\} \end{aligned} \tag{E-158}$$

It must be emphasized that the factor d^{BL} does not vanish, due to (E-147), because always $K_{i22} \neq 0$ in the true valence coordinate system. The equation (E-156), in the case of a symmetric molecule, can be put into another form, more useful, with (E-8) and (E-168):

$$\sum_{i=1,3} [\omega_i^{-2} K_{i22} (L_{ii})^2] = 4 B_e r_0 (r_0 \tilde{K}_{122}) \left[\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2} \right] \tag{E-159}$$

With the above equation and with (E-156), the final equation (E-158) can be put into another form, depending only on spectroscopic and potential constants,

$$g_D = 1 + \frac{\tilde{\omega}_2^2}{16 p B_e (-r_0 \tilde{K}_{122})} \left[1 - \frac{1}{p \left(\frac{1}{\tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_3^2} \right)} \left(\frac{1}{\tilde{\omega}_2^2 - \tilde{\omega}_1^2} + \frac{p}{\tilde{\omega}_2^2 - \tilde{\omega}_3^2} \right) \right] \tag{E-160}$$

E.4 Phase of the STU Matrix from Jungen and Merer [15] Used in the Stretch-Bender Model

The waves functions in Jungen approach [33, 15], in connection with (3.174), are:

$$\begin{array}{rclcl} |\psi^{ChJ}\rangle & = & |\psi^{Renner}\rangle\langle\psi^{Renner}|\psi^{ChJ}\rangle & = & |\psi^{Renner}\rangle(S^l) \\ \langle\psi^{ChJ}| & = & \langle\psi^{ChJ}|\psi^{Renner}\rangle\langle\psi^{Renner}| & = & (S^l)^+\langle\psi^{Renner}| \end{array} \tag{E-161}$$

We define the matrix:

$$(S^l)_{n,m} = (-1)^{n-1}\,\delta_{n,m} \tag{E-162}$$

where $n, m = \overline{1, N}$. The wavefunction vector $|\psi^{Renner}\rangle$ is formed by wavefunctions $\Phi^i_{v_2,l}$ defined in (3.95), where $v = \overline{0, N_v}$ and the counting into the matrix begin from 1. We consider the matrix change as:

$$\begin{array}{rcl} S^{ChJ} & = & \langle\psi^{ChJ}|\begin{array}{c}\cos\theta\\ \sin\theta\end{array}|\psi^{ChJ}\rangle = (S^l)^+\langle\psi^{Renner}|\begin{array}{c}\cos\theta\\ \sin\theta\end{array}|\psi^{Renner}\rangle(S^l) = (S^l)^+\,S\,(S^l) \\ T^{ChJ} & = & \langle\psi^{ChJ,-}|\psi^{ChJ,+}\rangle = (S^l)^+\langle\psi^{Renner,-}|\psi^{Renner,+}\rangle(S^l) = (S^l)^+\,T\,(S^l) \end{array} \tag{E-163}$$

The matrix S^{ChJ} and T^{ChJ}, as well as U^{ChJ} are defined in [15]. The U matrix is linked to the U^{ChJ} matrix as below:

$$U = (S^l)\,(U^{ChJ}) \quad \text{and} \quad U^{ChJ} = (S^l)^+\,U \tag{E-164}$$

From the previous relations (E-163), (E-164) let us to obtain the total matrix:

$$\begin{array}{rcl} (STU)^{ChJ} & = & S^{ChJ}\,T^{ChJ}\,U^{ChJ} \\ & = & \underbrace{(S^l)^+\,S\,(S^l)}_{S^{ChJ}}\underbrace{(S^l)^+\,T\,(S^l)}_{T^{ChJ}}\underbrace{(S^l)^+\,U}_{U^{ChJ}} = (S^l)^+\,(S\,T\,U) \end{array} \tag{E-165}$$

E.5 Constant Values Used in Numerical Calculus

The constant which enter in the dimensionless factor from Hermite polynomials variable is [212]:

$$\begin{array}{rcl} \alpha & = & \sqrt{\dfrac{\mu\,[\mathrm{g}]\;\omega\,[s^{-1}]}{\hbar\,[erg\cdot s]}} \\ & = & \sqrt{\dfrac{\mu\,[amu]\cdot 1\,amu\,[\mathrm{g}]\;2\pi c\tilde{\omega}\,[cm^{-1}]}{h\,[erg\cdot s]\,\frac{1}{2\pi}}} \\ & = & \sqrt{\mu\,[amu]\;\tilde{\omega}\,[cm^{-1}]}\cdot\underbrace{2\pi\sqrt{\dfrac{1amu\,[\mathrm{g}]\,c\,[\frac{cm}{s}]}{h\,[erg\cdot s]}}}_{\mathcal{C}_1} \end{array} \tag{E-166}$$

where

$$\mathcal{C}_1 = 17.222085\cdot 10^6\ cm^{-1} \tag{E-167}$$

The constant $\mathbf{C}_\alpha$ from eq.(3.191) is

$$\mathbf{C}_\alpha = \mathcal{C}_1\cdot 10^{-8}$$

due to the multiplication with $1\text{Å} = 10^{-8}cm$.

The dimensional factor from the adiabatic and non-adiabatic integrals (3.192) is:

$$\begin{array}{rcl} & & \dfrac{1}{2}\dfrac{\hbar^2}{hc}\,(g^{\rho\rho}\,[\mathrm{g}^{-1}\cdot cm^{-2}]) \\ & = & g^{\rho\rho}\,[(amu)^{-1}\cdot\text{Å}^{-2}]\cdot\underbrace{\dfrac{\hbar^2\,[erg\cdot s]}{2\,h\,[erg\cdot s]\,c\,[cm\cdot s^{-1}]\cdot 1amu\,[\mathrm{g}]\cdot 10^{-16}}}_{\mathbf{C}_{g^{\rho\rho}}} \end{array} \tag{E-168}$$

where $\mathbf{C}_{g^{\rho\rho}} = 16.85771\ cm^{-1}$

The adiabatic and non-adiabatic integrals from (3.192) have to be multiplied by the constant $\mathcal{C}_{g^{\rho\rho}}$.

Appendix F

Extension of the Formalism for non-Symmetric Molecules

F.1 Displacements for the Stretching Coordinates

The total mass of the molecule, m is: $m = m_1 + m_2 + m_3$. The conditions for the displacement involving only r_{12} bond, are (see Fig.F.1, (a)):

$$q_{3x} = 0 \quad q_{3y} = 0 \quad q_{3z} = 0 \tag{F-1}$$

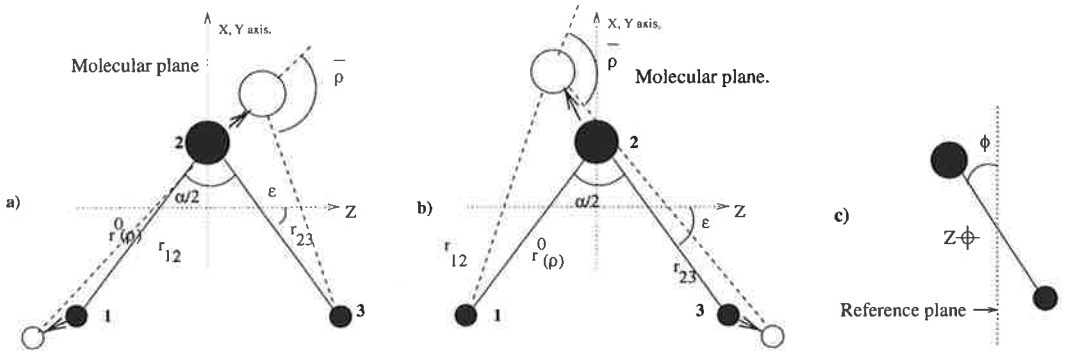


Figure F.1: The definition of the molecule-fixed stretch-bender coordinate system and the displacement coordinates used for a triatomic molecule with an a symmetrical equilibrum configuration.**a)** Bond r_{12} stretching; **b)** Bond r_{23} stretching; **c)** Azimuthal angle φ. The displacements in figure are much greater than in reality.

The coordinates of the first atom relative to the second atom are defined as,

$$\begin{aligned} x_1^0 &= x_2^0 - r_{12}\sin(\rho-\varepsilon)\cos\varphi \\ y_1^0 &= y_2^0 + r_{12}\sin(\rho-\varepsilon)\sin\varphi \\ z_1^0 &= z_2^0 - r_{12}\cos(\rho-\varepsilon) \end{aligned} \tag{F-2}$$

Similar, the coordinates of the third atom relative to the second atom are,

$$\begin{aligned} x_3^0 &= x_2^0 - r_{12}\sin\varepsilon\cos\varphi \\ y_3^0 &= y_2^0 + r_{12}\sin\varepsilon\sin\varphi \\ z_3^0 &= z_2^0 + r_{12}\cos\varepsilon \end{aligned} \tag{F-3}$$

The condition for the center of mass is:

$$\begin{aligned} m_1x_1^0 + m_2x_2^0 + m_3x_3^0 &= 0 \\ m_1y_1^0 + m_2y_2^0 + m_3y_3^0 &= 0 \\ m_1z_1^0 + m_2z_2^0 + m_3z_3^0 &= 0 \end{aligned} \tag{F-4}$$

From previous equations we find the coordinates for the Ox axis,

$$\begin{aligned} x_2^0 &= [m_1 r_{12}\sin(\rho-\varepsilon) + m_3 r_{23}\sin\varepsilon]\frac{\cos\varphi}{m} \\ x_1^0 &= [-(m_2+m_3) r_{12}\sin(\rho-\varepsilon) + m_3 r_{23}\sin\varepsilon]\frac{\cos\varphi}{m} \\ x_3^0 &= [m_1 r_{12}\sin(\rho-\varepsilon) - (m_1+m_2) r_{23}\sin\varepsilon]\frac{\cos\varphi}{m} \end{aligned} \tag{F-5}$$

Analogous as in [5, eq.(2)], we find for the second axis,

$$\begin{aligned} y_2^0 &= -[m_1 r_{12}\sin(\rho-\varepsilon) + m_3 r_{23}\sin\varepsilon]\frac{\sin\varphi}{m} \\ y_1^0 &= [(m_2+m_3) r_{12}\sin(\rho-\varepsilon) - m_3 r_{23}\sin\varepsilon]\frac{\sin\varphi}{m} \\ y_3^0 &= [-m_1 r_{12}\sin(\rho-\varepsilon) + (m_1+m_2) r_{23}\sin\varepsilon]\frac{\sin\varphi}{m} \end{aligned} \tag{F-6}$$

and for the third axis:

$$\begin{aligned} z_2^0 &= \frac{1}{m}[m_1 r_{12}\cos(\rho-\varepsilon) - m_3 r_{23}\cos\varepsilon] \\ z_1^0 &= \frac{1}{m}[-(m_2+m_3) r_{12}\cos(\rho-\varepsilon) - m_3 r_{23}\cos\varepsilon] \\ z_3^0 &= \frac{1}{m}[m_1 r_{12}\cos(\rho-\varepsilon) + (m_1+m_2) r_{23}\cos\varepsilon] \end{aligned} \tag{F-7}$$

From the conditions for the center of mass [5, eq.(7a)] results for the displacements the following relations:

$$q_{1x} = -\tfrac{m_2}{m_1} q_{2x} \quad q_{1y} = -\tfrac{m_2}{m_1} q_{2y} \quad q_{1z} = -\tfrac{m_2}{m_1} q_{2z} \tag{F-8}$$

Taking the direction of $\vec{k}$ versor along the Oz axis, the displacement in the molecular plane is:

$$\frac{q_{1y}}{q_{1x}} = \frac{y_1^0 - y_2^0}{x_1^0 - x_2^0} = -\tan\varphi \tag{F-9}$$

Before using the Sayvetz condition from HBJ [5, eq.(7c)], we must compute the derivatives of the coordinates with the bending angle:

$$\begin{aligned} \frac{\partial x_1^0}{\partial\rho} - \frac{\partial x_2^0}{\partial\rho} &= -r_{12}\cos\varphi\left[\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon) + (1-\varepsilon')\cos(\rho-\varepsilon)\right] \\ \frac{\partial y_1^0}{\partial\rho} - \frac{\partial y_2^0}{\partial\rho} &= r_{12}\sin\varphi\left[\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon) + (1-\varepsilon')\cos(\rho-\varepsilon)\right] \\ \frac{\partial z_1^0}{\partial\rho} - \frac{\partial z_2^0}{\partial\rho} &= -r_{12}\left[\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon) - (1-\varepsilon')\sin(\rho-\varepsilon)\right] \end{aligned} \tag{F-10}$$

The condition [5, eq.(7c)] together with (F-8) and (F-10) give:

$$m_1\left(\frac{\partial x_1^0}{\partial\rho} - \frac{\partial x_2^0}{\partial\rho}\right) q_{1x} + m_1\left(\frac{\partial y_1^0}{\partial\rho} - \frac{\partial y_2^0}{\partial\rho}\right) q_{1y} + m_1\left(\frac{\partial z_1^0}{\partial\rho} - \frac{\partial z_2^0}{\partial\rho}\right) q_{1z} = 0 \tag{F-11}$$

The solutions are the following:

$$\begin{aligned} q_{1x} &= -S_3\cos\varphi\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right] \\ q_{1y} &= S_3\sin\varphi\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right] \\ q_{1z} &= S_3\left[\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon)\right] \end{aligned} \tag{F-12}$$

The relations (F-12) are consequence of the Sayvetz condition. If we consider the equations (F-2) together with (F-12), as well as the (F-3) with (F-12), we get:

$$\begin{array}{lll} x_1 = x_1^0 + q_{1x} & x_2 = x_2^0 + q_{2x} & x_3 = x_3^0 \\ y_1 = y_1^0 + q_{1y} & y_2 = y_2^0 + q_{2y} & y_3 = y_3^0 \\ z_1 = z_1^0 + q_{1z} & z_2 = z_2^0 + q_{2z} & z_3 = z_3^0 \end{array} \tag{F-13}$$

When we introduce the relations (F-12) explicitly, the relations (F-13) are given by the equations:

$$
\begin{aligned}
x_1 &= -\left\{\frac{(m_2+m_3)}{m} r_{12}\sin(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\sin\varepsilon + S_1\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right]\right\}\cos\varphi \\
x_2 &= \left\{\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) + \frac{m_3}{m} r_{23}\sin\varepsilon + S_1\frac{m_1}{m_2}\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right]\right\}\cos\varphi \\
x_3 &= \left[\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) - \frac{(m_1+m_2)}{m} r_{23}\sin\varepsilon\right]\cos\varphi \\
y_1 &= \left\{\frac{(m_2+m_3)}{m} r_{12}\sin(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\sin\varepsilon + S_1\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right]\right\}\sin\varphi \\
y_2 &= -\left\{\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) + \frac{m_3}{m} r_{23}\sin\varepsilon + S_1\frac{m_1}{m_2}\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right]\right\}\sin\varphi \\
y_3 &= \left[-\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) + \frac{(m_1+m_2)}{m} r_{23}\sin\varepsilon\right]\sin\varphi \qquad \text{(F-14)} \\
z_1 &= -\frac{(m_2+m_3)}{m} r_{12}\cos(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\cos\varepsilon - S_1\left[\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon)\right] \\
z_2 &= \frac{m_1}{m} r_{12}\cos(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\cos\varepsilon + S_1\frac{m_1}{m_2}\left[\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon)\right] \\
z_3 &= \frac{m_1}{m} r_{12}\cos(\rho-\varepsilon) + \frac{(m_1+m_2)}{m} r_{23}\cos\varepsilon
\end{aligned}
$$

The calculus for the stretching of the bond 2-3 is similar to that of the stretching for the bond 1-2, just discussed previously (see Fig.F.1, (b)).

$$q_{1x} = 0 \quad q_{1y} = 0 \quad q_{1z} = 0 \qquad \text{(F-15)}$$

From the conditions for the center of mass [5, eq.(7a)] results for the displacements:

$$q_{3x} = -\tfrac{m_2}{m_3} q_{2x} \quad q_{3y} = -\tfrac{m_2}{m_3} q_{2y} \quad q_{3z} = -\tfrac{m_2}{m_3} q_{2z} \qquad \text{(F-16)}$$

Taking the direction of $\vec{k}$ versor along the Oz axis, the displacement in the molecular plane is:

$$\frac{q_{3y}}{q_{3x}} = \frac{y_3^0 - y_2^0}{x_3^0 - x_2^0} = -\tan\varphi \qquad \text{(F-17)}$$

As above, before using the Sayvetz condition from HBJ [5, eq.(7c)], we must compute the derivatives of the coordinates with the bending angle:

$$
\begin{aligned}
\frac{\partial x_3^0}{\partial\rho} - \frac{\partial x_2^0}{\partial\rho} &= -r_{23}\cos\varphi\left[\frac{r'_{23}}{r_{23}}\sin\varepsilon + \varepsilon'\cos\varepsilon\right] \\
\frac{\partial y_3^0}{\partial\rho} - \frac{\partial y_2^0}{\partial\rho} &= r_{23}\sin\varphi\left[\frac{r'_{23}}{r_{23}}\sin\varepsilon + \varepsilon'\cos\varepsilon\right] \qquad \text{(F-18)} \\
\frac{\partial z_3^0}{\partial\rho} - \frac{\partial z_2^0}{\partial\rho} &= -r_{23}\left[\frac{r'_{23}}{r_{23}}\cos\varepsilon - \varepsilon'\sin\varepsilon\right]
\end{aligned}
$$

(F-19)

The condition [5, eq.(7c)] together with (F-16) and (F-18) give the Sayvetz condition in our case:

$$m_3\left(\frac{\partial x_3^0}{\partial\rho} - \frac{\partial x_2^0}{\partial\rho}\right) q_{3x} + m_3\left(\frac{\partial y_3^0}{\partial\rho} - \frac{\partial y_2^0}{\partial\rho}\right) q_{3y} + m_3\left(\frac{\partial z_3^0}{\partial\rho} - \frac{\partial z_2^0}{\partial\rho}\right) q_{3z} = 0 \qquad \text{(F-20)}$$

The solutions due to Sayvetz condition are the following:

$$
\begin{aligned}
q_{3x} &= -S_3\cos\varphi\left[\sin\varepsilon - \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\varepsilon\right] \\
q_{3y} &= S_3\sin\varphi\left[\sin\varepsilon - \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\varepsilon\right] \\
q_{3z} &= S_3\left[\cos\varepsilon + \frac{1}{\varepsilon}\frac{r'_{23}}{r_{23}}\sin\varepsilon\right] \qquad \text{(F-21)}
\end{aligned}
$$

If we consider the equations similar to (F-2) together with (F-21), as well as the (F-16) with (F-21), we get:

$$\begin{array}{lll} x_1 = x_1^0 & x_2 = x_2^0 + q_{2x} & x_3 = x_3^0 + q_{3x} \\ y_1 = y_1^0 & y_2 = y_2^0 + q_{2y} & y_3 = y_3^0 + q_{3y} \\ z_1 = z_1^0 & z_2 = z_2^0 + q_{2z} & z_3 = z_3^0 + q_{3z} \end{array} \tag{F-22}$$

When we introduce the relations (F-21) explicitly, the relations (F-22) become

$$\begin{aligned}
x_1 &= -\left[\frac{(m_2+m_3)}{m} r_{12}\sin(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\sin\varepsilon\right]\cos\varphi \\
x_2 &= \left\{\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) + \frac{m_3}{m} r_{23}\sin\varepsilon + S_3\frac{m_3}{m_2}\left[\sin\varepsilon - \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\varepsilon\right]\right\}\cos\varphi \\
x_3 &= \left\{\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) - \frac{(m_1+m_2)}{m} r_{23}\sin\varepsilon - S_3\left[\sin\varepsilon - \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\varepsilon\right]\right\}\cos\varphi \\
y_1 &= \left[\frac{(m_2+m_3)}{m} r_{12}\sin(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\sin\varepsilon\right]\sin\varphi \\
y_2 &= -\left\{\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) + \frac{m_3}{m} r_{23}\sin\varepsilon + S_3\frac{m_3}{m_2}\left[\sin\varepsilon - \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\varepsilon\right]\right\}\sin\varphi \\
y_3 &= \left\{-\frac{m_1}{m} r_{12}\sin(\rho-\varepsilon) + \frac{(m_1+m_2)}{m} r_{23}\sin\varepsilon + S_3\left[\sin\varepsilon - \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\varepsilon\right]\right\}\sin\varphi \\
z_1 &= -\frac{(m_2+m_3)}{m} r_{12}\cos(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\cos\varepsilon \\
z_2 &= \frac{m_1}{m} r_{12}\cos(\rho-\varepsilon) - \frac{m_3}{m} r_{23}\cos\varepsilon - S_3\frac{m_3}{m_2}\left[\cos\varepsilon + \frac{1}{\varepsilon}\frac{r'_{23}}{r_{23}}\sin\varepsilon\right] \\
z_3 &= \frac{m_1}{m} r_{12}\cos(\rho-\varepsilon) + \frac{(m_1+m_2)}{m} r_{23}\cos\varepsilon + S_3\left[\cos\varepsilon + \frac{1}{\varepsilon}\frac{r'_{23}}{r_{23}}\sin\varepsilon\right]
\end{aligned} \tag{F-23}$$

(F-24)

F.2 The Derivative of the Bending Angle to the Stretching Coordinates

The derivative of the angle ρ as function of the stretching coordinate, using equations (F-13) and (F-8), is:

$$\begin{aligned}
\left(\frac{\partial\rho}{\partial S_1}\right)_0 &= \left(\frac{\partial\rho}{\partial x_1}\cdot\frac{\partial x_1}{\partial S_1} + \frac{\partial\rho}{\partial x_2}\cdot\frac{\partial x_2}{\partial S_1} + \frac{\partial\rho}{\partial x_3}\cdot\frac{\partial x_3}{\partial S_1} + \frac{\partial\rho}{\partial y_1}\cdot\frac{\partial y_1}{\partial S_1}\right. \\
&+ \left.\frac{\partial\rho}{\partial y_2}\cdot\frac{\partial y_2}{\partial S_1} + \frac{\partial\rho}{\partial z_2}\cdot\frac{\partial z_2}{\partial S_1}\right)_0 \\
&= \left[\frac{\partial\rho}{\partial x_1} - \frac{m_1}{m_2}\frac{\partial\rho}{\partial x_2}\right]_0\left(\frac{\partial x_1}{\partial S_1}\right)_0 + \left[\frac{\partial\rho}{\partial y_1} - \frac{m_1}{m_2}\frac{\partial\rho}{\partial y_2}\right]_0\left(\frac{\partial y_1}{\partial S_1}\right)_0 \\
&+ \left[\frac{\partial\rho}{\partial z_1} - \frac{m_1}{m_2}\frac{\partial\rho}{\partial z_2}\right]_0\left(\frac{\partial z_1}{\partial S_1}\right)_0
\end{aligned} \tag{F-25}$$

As we see in Fig.(A.2) and from eq.(A-23), the angle ρ can be written as:

$$\rho = -\arctan\frac{\sqrt{(x_1-x_2)^2+(y_1-y_2)^2}}{(z_1-z_2)} + \arctan\frac{\sqrt{(x_3-x_2)^2+(y_3-y_2)^2}}{(z_3-z_2)} \tag{F-26}$$

We consider first the derivatives of the angle ρ to the Cartesian coordinates, from the previous equation and eq.(F-5)-(F-7):

$$\left(\frac{\partial\rho}{\partial x_1}\right)_0 = -\frac{1}{r_{12}}\cos(\rho-\varepsilon)\cos\varphi$$

$$
\begin{aligned}
\left(\frac{\partial\rho}{\partial x_2}\right)_0 &= \frac{1}{r_{12}}\cos(\rho-\varepsilon)\,\cos\varphi+\frac{1}{r_{32}}\cos\varepsilon\,\cos\varphi\\
\left(\frac{\partial\rho}{\partial y_1}\right)_0 &= \frac{1}{r_{12}}\cos(\rho-\varepsilon)\,\sin\varphi\\
\left(\frac{\partial\rho}{\partial y_2}\right)_0 &= -\frac{1}{r_{12}}\cos(\rho-\varepsilon)\,\sin\varphi-\frac{1}{r_{32}}\cos\varepsilon\,\sin\varphi\\
\left(\frac{\partial\rho}{\partial z_1}\right)_0 &= \frac{1}{r_{12}}\sin(\rho-\varepsilon)\\
\left(\frac{\partial\rho}{\partial z_2}\right)_0 &= -\frac{1}{r_{12}}\sin(\rho-\varepsilon)+\frac{1}{r_{23}}\sin\varepsilon
\end{aligned}
\tag{F-27}
$$

We consider now the derivatives of the Cartesian coordinates as function of the stretching coordinate from eq.(F-14):

$$
\begin{aligned}
\left(\frac{\partial x_1}{\partial S_1}\right)_0 &= -\cos\varphi\left[\sin(\rho-\varepsilon)-\frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right]\\
\left(\frac{\partial y_1}{\partial S_1}\right)_0 &= \sin\varphi\left[\sin(\rho-\varepsilon)-\frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\cos(\rho-\varepsilon)\right]\\
\left(\frac{\partial z_1}{\partial S_1}\right)_0 &= -\cos(\rho-\varepsilon)+\frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon)
\end{aligned}
\tag{F-28}
$$

If we introduce the relations ((F-27)-(F-28)) in (F-25) we obtain:

$$
\begin{aligned}
\left(\frac{\partial\rho}{\partial S_1}\right)_0 =\ & \\
&-\left[-\frac{\cos(\rho-\varepsilon)}{r_{12}}-\frac{m_1}{m_2}\left(\frac{\cos(\rho-\varepsilon)}{r_{12}}+\frac{\cos\varepsilon}{r_{23}}\right)\right]\left[\sin(\rho-\varepsilon)-\frac{1}{(1-\varepsilon')}\cos(\rho-\varepsilon)\right]\cos^2\varphi\\
&+\left[\frac{\cos(\rho-\varepsilon)}{r_{12}}-\frac{m_1}{m_2}\left(\frac{-\cos(\rho-\varepsilon)}{r_{12}}-\frac{\cos\varepsilon}{r_{23}}\right)\right]\left[\sin(\rho-\varepsilon)-\frac{1}{(1-\varepsilon')}\cos(\rho-\varepsilon)\right]\sin^2\varphi\\
&-\left[\frac{\sin(\rho-\varepsilon)}{r_{12}}-\frac{m_1}{m_2}\left(\frac{-\sin(\rho-\varepsilon)}{r_{12}}+\frac{\sin\varepsilon}{r_{23}}\right)\right]\left[\cos(\rho-\varepsilon)+\frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin(\rho-\varepsilon)\right]
\end{aligned}
\tag{F-29}
$$

After algebraic calculus, the above expression become:

$$
\left(\frac{\partial\rho}{\partial S_1}\right)_0 = -\left[\frac{1}{r_{12}}\left(1+\frac{m_1}{m_2}\right)\frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}-\frac{m_1}{m_2}\frac{1}{r_{23}}\sin\rho+\frac{m_1}{m_2}\frac{1}{r_{23}}\frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\cos\rho\right] \tag{F-30}
$$

In order to obtain the derivative of the angle ρ as function of the coordinate S_3 we will do a similar calculus as above. First of all we will analyze from eq.(F-25), (F-14), (F-22), the following corespondence for the signs of the derivatives as function of Cartesian coordinates:

$$
\begin{cases}
\frac{\partial\rho}{\partial x_3}\leftrightarrow\frac{\partial\rho}{\partial x_1}\\
\frac{\partial\rho}{\partial y_3}\leftrightarrow\frac{\partial\rho}{\partial y_1}\\
\frac{\partial\rho}{\partial z_3}\leftrightarrow-\frac{\partial\rho}{\partial z_1}
\end{cases}
\quad\text{and}\quad
\begin{cases}
\frac{\partial x_1}{\partial S_1}\leftrightarrow\frac{\partial x_3}{\partial S_3}\\
\frac{\partial y_1}{\partial S_1}\leftrightarrow\frac{\partial y_3}{\partial S_3}\\
\frac{\partial z_1}{\partial S_1}\leftrightarrow-\frac{\partial z_3}{\partial S_3}
\end{cases}
\tag{F-31}
$$

After algebraic calculus we get the final form of the derivative of the ρ angle as function of the S_3 coordinate:

$$
\left(\frac{\partial\rho}{\partial S_3}\right)_0 = -\left[\frac{1}{r_{23}}\left(1+\frac{m_3}{m_2}\right)\frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}-\frac{1}{r_{12}}\frac{m_3}{m_2}\sin\rho+\frac{1}{r_{12}}\frac{m_3}{m_2}\frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\cos\rho\right] \tag{F-32}
$$

F.3 The Change of the Bond Length from the Reference Configuration as Function of the Stretching Coordinates

The bond length between atoms 1 and 2 is:

$$
r_{12}=\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2} \tag{F-33}
$$

If we introduce the relations (F-14) the bond length become:

$$\begin{aligned} r_{12} &= \left\{\left[-r_{12}^0\sin(\rho-\varepsilon) - S_1\left(1+\frac{m_1}{m_2}\right)\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\right]^2\cos^2\varphi\right. \\ &+ \left[r_{12}^0\sin(\rho-\varepsilon) + S_1\left(1+\frac{m_1}{m_2}\right)\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\right]^2\sin^2\varphi \\ &+ \left.\left[-r_{12}^0\cos(\rho-\varepsilon) - S_1\left(1+\frac{m_1}{m_2}\right)\left[\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin(\rho-\varepsilon)\right]\right]^2\right\}^{\frac{1}{2}} \end{aligned} \tag{F-34}$$

For small S_1 we can neglect the squares of the S_1 and in this case the previous relation become, when expanding in power series:

$$\begin{aligned} r_{12} &\simeq \left\{(r_{12}^0)^2\sin^2(\rho-\varepsilon)\cos^2\varphi + r_{12}^2\sin^2(\rho-\varepsilon)\sin^2\varphi\right. \\ &+ 2r_{12}^0S_1\sin(\rho-\varepsilon)\left(1+\frac{m_1}{m_2}\right)\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\cos^2\varphi \\ &+ 2r_{12}^0S_1\sin(\rho-\varepsilon)\left(1+\frac{m_1}{m_2}\right)\left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\sin^2\varphi \\ &+ \left.r_{12}^2\cos^2(\rho-\varepsilon) + 2r_{12}^0S_1\cos(\rho-\varepsilon)\left(1+\frac{m_1}{m_2}\right)\left[\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin(\rho-\varepsilon)\right]\right\}^{\frac{1}{2}} \\ &= \sqrt{r_{12}^2 + 2r_{12}^0S_1\left(1+\frac{m_1}{m_2}\right)} \simeq r_{12}^0\left[1+\frac{S_1}{(r_{12}^0)}\left(1+\frac{m_1}{m_2}\right)\right] \end{aligned} \tag{F-35}$$

The bond length between atoms 2 and 3 is:

$$r_{23} = \sqrt{(x_3-x_2)^2 + (y_3-y_2)^2 + (z_3-z_2)^2} \tag{F-36}$$

If we introduce the relations (F-23) the bond length become:

$$\begin{aligned} r_{23} &= \left\{\left[-r_{23}^0\sin\varepsilon - S_1\frac{m_1}{m_2}\left(\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right)\right]^2\cos^2\varphi\right. \\ &+ \left[r_{23}^0\sin\varepsilon + S_1\frac{m_1}{m_2}\left(\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right)\right]^2\sin^2\varphi \\ &+ \left.\left[r_{23}^0\cos\varepsilon - S_1\frac{m_1}{m_2}\left(\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin(\rho-\varepsilon)\right)\right]^2\right\}^{\frac{1}{2}} \end{aligned} \tag{F-37}$$

For small S_1 we can neglect the squares of the S_1 and in this case after expanding in power series, the previous relation become:

$$\begin{aligned} r_{23} &\simeq \left\{(r_{23}^0)^2 + 2r_{23}^0S_1\frac{m_1}{m_2}\left[\sin\varepsilon\left(\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right)\right.\right. \\ &\quad \left.\left. - \cos\varepsilon\left(\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin(\rho-\varepsilon)\right)\right]\right\}^{\frac{1}{2}} \\ &= r_{23}^0\sqrt{1 - \frac{2S_1}{r_{23}^0}\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin\rho\right]} \\ &\simeq r_{23}^0\left[1 - \frac{S_1}{r_{23}^0}\frac{m_1}{m_2}\left(\cos\rho + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin\rho\right)\right] \end{aligned} \tag{F-38}$$

In a similar manner we can obtain the bond length as function of the stretching coordinate S_3:

$$\begin{aligned} r_{12} &\simeq r_{12}^0 - S_3\frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{r_{23}^0}{r_{23}^0}\sin\rho\right] \\ r_{23} &\simeq r_{23}^0 + S_3\left(1+\frac{m_3}{m_2}\right) \end{aligned} \tag{F-39}$$

With eq.((F-35),(F-38),(F-39)), the variation of the displacement as function of the S_1 and S_3 coordinates can be expressed as:

$$\begin{aligned}
\Delta r_1^{S_1} &= r_{12} - r_{12}^0(\rho) = \left(1 + \frac{m_1}{m_2}\right) S_1 \\
\Delta r_3^{S_1} &= -\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin\rho\right] S_1
\end{aligned} \tag{F-40}$$

$$\begin{aligned}
\Delta r_1^{S_3} &= -\frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right] S_3 \\
\Delta r_3^{S_3} &= \left(1 + \frac{m_3}{m_2}\right) S_3
\end{aligned} \tag{F-41}$$

F.4 The Derivative of the Stretching Coordinates in the Reference Frame

If we express from eq.(3.1), the change of the bond length as function of the bond angle function $\mathcal{R}_{i2}$, with $i = 1, 3$, we have:

$$\begin{aligned}
\Delta r_1 &= r_{12} - r_{12}^0(\rho_0) = r_{12}^e + \mathcal{R}_{12}(\rho_0 + d\rho) - [r_{12}^e + \mathcal{R}_{12}(\rho_0)] \\
\Delta r_3 &= r_{23} - r_{23}^0(\rho_0) = r_{23}^e + \mathcal{R}_{23}(\rho_0 + d\rho) - [r_{23}^e + \mathcal{R}_{23}(\rho_0)]
\end{aligned} \tag{F-42}$$

If we use the equations (F-40),(F-41), the change is:

$$\begin{aligned}
\Delta r_1 &= \mathcal{R}_{12}(\rho_0 + d\rho) - \mathcal{R}_{12}(\rho_0) = \mathcal{R}'_{12}(\rho_0)d\rho \\
&= \left(1 + \frac{m_1}{m_2}\right) dS_1 - \frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right] dS_3 \\
\Delta r_3 &= \mathcal{R}_{23}(\rho_0 + d\rho) - \mathcal{R}_{23}(\rho_0) = \mathcal{R}'_{23}(\rho_0)d\rho \\
&= -\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin\rho\right] dS_1 + \left(1 + \frac{m_3}{m_2}\right) dS_3
\end{aligned} \tag{F-43}$$

Adding and substracting each other the two equations from (F-43), and dividing with $d\rho$ we have,

$$\begin{aligned}
\mathcal{R}'_{12}(\rho_0) - \mathcal{R}'_{23}(\rho_0) &= \left\{\left(1 + \frac{m_1}{m_2}\right) + \frac{m_1}{m_2}\left[\cos\rho + \frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin\rho\right]\right\}\frac{\partial S_1}{\partial\rho} \\
&- \left\{\left(1 + \frac{m_3}{m_2}\right) + \frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right]\right\}\frac{\partial S_3}{\partial\rho} \\
\mathcal{R}'_{12}(\rho_0) + \mathcal{R}'_{23}(\rho_0) &= \left\{\left(1 + \frac{m_1}{m_2}\right) - \frac{m_1}{m_2}\left[\cos\rho + \frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin\rho\right]\right\}\frac{\partial S_1}{\partial\rho} \\
&+ \left\{\left(1 + \frac{m_3}{m_2}\right) - \frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right]\right\}\frac{\partial S_3}{\partial\rho}
\end{aligned} \tag{F-44}$$

To find the derivatives from the previous system, we calculate the discriminant Δ of the system:

$$\begin{aligned}
\Delta &= \left\{1 + \frac{m_1}{m_2} + \frac{m_1}{m_2}\left[\cos\rho + \frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin\rho\right]\right\}\left\{1 + \frac{m_3}{m_2} - \frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right]\right\} \\
&+ \left\{1 + \frac{m_1}{m_2} - \frac{m_1}{m_2}\left[\cos\rho + \frac{1}{(1-\varepsilon')}\frac{r'_{12}}{r_{12}}\sin\rho\right]\right\}\left\{1 + \frac{m_3}{m_2} + \frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right]\right\}
\end{aligned} \tag{F-45}$$

From (F-44), the partial derivatives are found with Cramer rule:

$$\begin{aligned}
\frac{\partial S_1}{\partial\rho} &= \frac{1}{\Delta}\left\{[\mathcal{R}'_{12} - \mathcal{R}'_{23}]\left[1 + \frac{m_3}{m_2} - \frac{m_3}{m_2}\left(\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right)\right]\right. \\
&+ \left.[\mathcal{R}'_{12} + \mathcal{R}'_{23}]\left[1 + \frac{m_3}{m_2} + \frac{m_3}{m_2}\left(\cos\rho + \frac{1}{\varepsilon'}\frac{r'_{23}}{r_{23}}\sin\rho\right)\right]\right\} \\
\frac{\partial S_3}{\partial\rho} &= \frac{1}{\Delta}\left\{[\mathcal{R}'_{12} + \mathcal{R}'_{23}]\left[1 + \frac{m_1}{m_2} + \frac{m_1}{m_2}\left(\cos\rho + \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\sin\rho\right)\right]\right. \\
&- \left.[\mathcal{R}'_{12} - \mathcal{R}'_{23}]\left[1 + \frac{m_1}{m_2} - \frac{m_1}{m_2}\left(\cos\rho + \frac{1}{1-\varepsilon'}\frac{r'_{12}}{r_{12}}\sin\rho\right)\right]\right\}
\end{aligned} \tag{F-46}$$

F.5 Metric Tensor Elements in the Stretch-Bender Model for Asymmetric Molecules

The derivatives of the Cartesian coordinates to time, from eq. (F-14), when only the stretching coordinate S_1 is taken into account, and $S_1 = 0$ is put after derivation, are the following:

♣

$$\begin{aligned}
\dot{x}_1|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{ -\frac{m_2+m_3}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon) + (r_{12}^0)'\sin(\rho-\varepsilon)\right]\right.\\
&\quad \left. + \frac{m_3}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon + (r_{23}^0)'\sin\varepsilon\right]\right\}\cos\varphi\,\dot{\rho}\\
&- \left[-\frac{m_2+m_3}{m}r_{12}^0\sin(\rho-\varepsilon) + \frac{m_3}{m}r_{23}^0\sin\varepsilon\right]\sin\varphi\,\dot{\varphi}\\
&- \left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\cos\varphi\,\dot{S}_1
\end{aligned} \tag{F-47}$$

$$\begin{aligned}
\dot{y}_1|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{ \frac{m_2+m_3}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon) + (r_{12}^0)'\sin(\rho-\varepsilon)\right]\right.\\
&\quad \left. - \frac{m_3}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon + (r_{23}^0)'\sin\varepsilon\right]\right\}\sin\varphi\,\dot{\rho}\\
&+ \left[\frac{m_2+m_3}{m}r_{12}^0\sin(\rho-\varepsilon) - \frac{m_3}{m}r_{23}^0\sin\varepsilon\right]\cos\varphi\,\dot{\varphi}\\
&+ \left[\sin(\rho-\varepsilon) - \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\sin\varphi\,\dot{S}_1
\end{aligned} \tag{F-48}$$

$$\begin{aligned}
\dot{z}_1|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{ \frac{m_2+m_3}{m}\left[r_{12}^0(1-\varepsilon')\sin(\rho-\varepsilon) - (r_{12}^0)'\cos(\rho-\varepsilon)\right]\right. \qquad \text{(F-49)}\\
&+ \left.\frac{m_3}{m}\left[\varepsilon' r_{23}^0\sin\varepsilon - (r_{23}^0)'\cos\varepsilon\right]\right\}\dot{\rho} - \left[\cos(\rho-\varepsilon) + \frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin(\rho-\varepsilon)\right]\dot{S}_1
\end{aligned}$$

♣

$$\begin{aligned}
\dot{x}_3|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{ \frac{m_1}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon) + (r_{12}^0)'\sin(\rho-\varepsilon)\right]\right.\\
&\quad \left. - \frac{m_1+m_2}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon + (r_{23}^0)'\sin\varepsilon\right]\right\}\cos\varphi\,\dot{\rho}\\
&- \left[\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon) - \frac{m_1+m_2}{m}r_{23}^0\sin\varepsilon\right]\sin\varphi\,\dot{\varphi}
\end{aligned} \tag{F-50}$$

$$\begin{aligned}
\dot{y}_3|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{ -\frac{m_1}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon) + (r_{12}^0)'\sin(\rho-\varepsilon)\right]\right.\\
&\quad \left. + \frac{m_1+m_2}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon + (r_{23}^0)'\sin\varepsilon\right]\right\}\sin\varphi\,\dot{\rho}\\
&- \left[\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon) - \frac{m_1+m_2}{m}r_{23}^0\sin\varepsilon\right]\cos\varphi\,\dot{\varphi}
\end{aligned} \tag{F-51}$$

$$\begin{aligned}
\dot{z}_3|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{ \frac{m_1}{m}\left[-r_{12}^0(1-\varepsilon')\sin(\rho-\varepsilon) + (r_{12}^0)'\cos(\rho-\varepsilon)\right]\right.\\
&\quad \left. + \frac{m_1+m_2}{m}\left[-\varepsilon' r_{23}^0\sin\varepsilon + (r_{23}^0)'\cos\varepsilon\right]\right\}\dot{\rho}
\end{aligned} \tag{F-52}$$

♣

$$\begin{aligned}
\dot{x}_2\big|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{\frac{m_1}{m}\left[r_{12}^0\,(1-\varepsilon')\cos(\rho-\varepsilon)+(r_{12}^0)'\sin(\rho-\varepsilon)\right]\right.\\
&\quad \left.+\frac{m_3}{m}\left[\varepsilon'\,r_{23}^0\cos\varepsilon+(r_{23}^0)'\sin\varepsilon\right]\right\}\cos\varphi\dot{\rho}\\
&- \left[\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon)+\frac{m_3}{m}r_{23}^0\sin\varepsilon\right]\sin\varphi\,\dot{\varphi}\\
&+ \frac{m_1}{m_2}\left[\sin(\rho-\varepsilon)-\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\cos\varphi\,\dot{S}_1
\end{aligned}\tag{F-53}$$

$$\begin{aligned}
\dot{y}_2\big|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{-\frac{m_1}{m}\left[r_{12}^0\,(1-\varepsilon')\cos(\rho-\varepsilon)+(r_{12}^0)'\sin(\rho-\varepsilon)\right]\right.\\
&\quad \left.-\frac{m_3}{m}\left[\varepsilon'\,r_{23}^0\cos\varepsilon+(r_{23}^0)'\sin\varepsilon\right]\right\}\sin\varphi\dot{\rho}\\
&+ \left[-\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon)-\frac{m_3}{m}r_{23}^0\sin\varepsilon\right]\cos\varphi\,\dot{\varphi}\\
&- \frac{m_1}{m_2}\left[\sin(\rho-\varepsilon)-\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\sin\varphi\,\dot{S}_1
\end{aligned}\tag{F-54}$$

$$\begin{aligned}
\dot{z}_2\big|_{\substack{S_1=0\\ S_3=\dot{S}_3=0}} &= \left\{\frac{m_1}{m}\left[-r_{12}^0\,(1-\varepsilon')\sin(\rho-\varepsilon)+(r_{12}^0)'\cos(\rho-\varepsilon)\right]\right.\\
&\quad \left.-\frac{m_3}{m}\left[-\varepsilon'\,r_{23}^0\sin\varepsilon+(r_{23}^0)'\cos\varepsilon\right]\right\}\dot{\rho}+\frac{m_1}{m_2}\left[\cos(\rho-\varepsilon)+\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin(\rho-\varepsilon)\right]\dot{S}_1
\end{aligned}\tag{F-55}$$

The kinetic energy when only the S_1 stretching coordinate is considered, is:

$$2T = m_1\left(\dot{x}_1^2+\dot{y}_1^2+\dot{z}_1^2\right)+m_2\left(\dot{x}_2^2+\dot{y}_2^2+\dot{z}_2^2\right)+m_3\left(\dot{x}_3^2+\dot{y}_3^2+\dot{z}_3^2\right)\tag{F-56}$$

We make some abbreviations, similar with [5, eq.(5)]:

$$\begin{aligned}
u_1 &= (r_{12}^0)^2\,m_1\,(m_2+m_3)\\
u_3 &= (r_{23}^0)^2\,m_3\,(m_2+m_1)\\
u_{13} &= r_{12}^0\,r_{23}^0\,m_1\,m_3
\end{aligned}\tag{F-57}$$

If we introduce the previous derivatives and abbreviations into the formula for the kinetic energy, we get for the bending angle, rotation around the linear axis and S_1 stretching coordinates:

$$\begin{aligned}
2T &= \frac{1}{m}\left\{(1-\varepsilon')^2\left[1+\frac{1}{(1-\varepsilon')^2}\left(\frac{(r_{12}^0)'}{r_{12}^0}\right)^2\right]u_1+(\varepsilon')^2\left[1+\frac{1}{(\varepsilon')^2}\left(\frac{(r_{23}^0)'}{r_{23}^0}\right)^2\right]u_3\right.\\
&\quad \left.-2u_{13}(1-\varepsilon')\varepsilon'\left[\left(1-\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\right)\cos\rho+\left(\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}+\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\right)\sin\rho\right]\right\}\dot{\rho}^2\\
&+ \frac{1}{m}\left[u_1\sin^2(\rho-\varepsilon)+u_3\sin^2\varepsilon-2u_{13}\sin(\rho-\varepsilon)\sin\varepsilon\right]\dot{\varphi}^2\\
&+ m_1\left(1+\frac{m_1}{m_2}\right)\left[1+\frac{1}{(1-\varepsilon')^2}\left(\frac{(r_{12}^0)'}{r_{12}^0}\right)^2\right]\dot{S}_1^2
\end{aligned}\tag{F-58}$$

where, as in [14, eq.(23)]:

$$\varepsilon' = \frac{u_1+u_{13}\cos\rho+u_{13}\sin\rho\left[\left(\frac{(r_{12}^0)'}{r_{12}^0}\right)-\left(\frac{(r_{23}^0)'}{r_{23}^0}\right)\right]}{u_1+u_3+2u_{13}\cos\rho}\tag{F-59}$$

and

$$1-\varepsilon' = \frac{u_3+u_{13}\cos\rho+u_{13}\sin\rho\left[\left(\frac{(r_{23}^0)'}{r_{23}^0}\right)-\left(\frac{(r_{12}^0)'}{r_{12}^0}\right)\right]}{u_1+u_3+2u_{13}\cos\rho}\tag{F-60}$$

We consider the classical momenta associated to coordinates:

$$
\begin{aligned}
p_\rho &= \frac{\partial T}{\partial \dot\rho} = \dot\rho \Bigg\{ u_1 \left[1 + \frac{1}{(1-\varepsilon')^2} \left(\frac{(r_{12}^0)'}{r_{12}^0} \right)^2 \right] + \left(\frac{\varepsilon'}{1-\varepsilon'} \right)^2 \left[1 + \frac{1}{(\varepsilon')^2} \left(\frac{(r_{23}^0)'}{r_{23}^0} \right)^2 \right] u_3 \\
&- 2u_{13} \frac{\varepsilon'}{1-\varepsilon'} \left[\left(1 - \frac{1}{(1-\varepsilon')\varepsilon'} \left(\frac{(r_{12}^0)'}{r_{12}^0} \right) \left(\frac{(r_{23}^0)'}{r_{23}^0} \right) \right) \cos\rho \right. \\
&\left. + \left(\frac{1}{\varepsilon'} \frac{(r_{23}^0)'}{r_{23}^0} + \frac{1}{1-\varepsilon'} \frac{(r_{12}^0)'}{r_{12}^0} \right) \sin\rho \right] \Bigg\} \frac{(1-\varepsilon')^2}{m} \\
p_\varphi &= \frac{\partial T}{\partial \dot\varphi} = \dot\varphi \left[u_1 \sin^2(\rho-\varepsilon) + u_3 \sin^2\varepsilon - 2u_{13} \sin(\rho-\varepsilon)\sin\varepsilon \right] \frac{1}{m} \\
p_1 &= \frac{\partial T}{\partial \dot S_1} = \dot S_1 m_1 \left(1 + \frac{m_1}{m_2} \right) \left[1 + \frac{1}{(1-\varepsilon')^2} \left(\frac{(r_{12}^0)'}{r_{12}^0} \right)^2 \right]
\end{aligned}
\tag{F-61}
$$

We can express the kinetic energy as function of momenta and we obtain:

$$
2T = g^{\rho\rho} p_\rho^2 + g^{\varphi\varphi} p_\varphi^2 + g^{S_1 S_1} p_{S_1}^2 \tag{F-62}
$$

with the contravariant metric tensor elements for the coordinates (S_1, ρ, φ):

$$
\begin{aligned}
g^{\rho\rho} &= \Bigg\{ u_1 \left[1 + \frac{1}{(1-\varepsilon')^2} \left(\frac{(r_{12}^0)'}{r_{12}^0} \right)^2 \right] + \left(\frac{\varepsilon'}{1-\varepsilon'} \right)^2 \left[1 + \frac{1}{(\varepsilon')^2} \left(\frac{(r_{23}^0)'}{r_{23}^0} \right)^2 \right] u_3 \\
&- 2u_{13} \frac{\varepsilon'}{(1-\varepsilon')} \left[\left(1 - \frac{1}{(1-\varepsilon')\varepsilon'} \frac{(r_{12}^0)'}{r_{12}^0} \frac{(r_{23}^0)'}{r_{23}^0} \right) \cos\rho \right. \\
&\left. + \left(\frac{1}{\varepsilon'} \frac{(r_{23}^0)'}{r_{23}^0} + \frac{1}{(1-\varepsilon')} \frac{(r_{12}^0)'}{r_{12}^0} \right) \sin\rho \right] \Bigg\}^{-1} \frac{m}{(1-\varepsilon')^2} \\
\text{Obs:} \quad & g^{\rho\rho}|_{(r_{12}^0)'=(r_{23}^0)'=0} \equiv \text{[5, eq.(37)]} \\
g^{\varphi\varphi} &= \frac{m}{u_1 \sin^2(\rho-\varepsilon) + u_3 \sin^2\varepsilon - 2u_{13}\sin(\rho-\varepsilon)\sin\varepsilon} \\
g^{11} &= \frac{1}{m_1 \left(1 + \frac{m_1}{m_2} \right) \left[1 + \frac{1}{(1-\varepsilon')^2} \left(\frac{(r_{12}^0)'}{r_{12}^0} \right)^2 \right]}
\end{aligned}
\tag{F-63}
$$

The derivatives of the Cartesian coordinates from eq. (F-23), when only the stretching coordinate S_3 is taken into account, and $S_3 = 0$ is put after derivation, are the following:

$\diamondsuit$

$$
\begin{aligned}
\dot x_1|_{\substack{S_1=\dot S_1=0 \\ S_3=0}} &= \Bigg\{ -\frac{m_2+m_3}{m} \left[r_{12}^0 (1-\varepsilon') \cos(\rho-\varepsilon) + (r_{12}^0)' \sin(\rho-\varepsilon) \right] \\
&+ \frac{m_3}{m} \left[\varepsilon' r_{23}^0 \cos\varepsilon + (r_{23}^0)' \sin\varepsilon \right] \Bigg\} \cos\varphi\, \dot\rho \\
&- \left[-\frac{m_2+m_3}{m} r_{12}^0 \sin(\rho-\varepsilon) + \frac{m_3}{m} r_{23}^0 \sin\varepsilon \right] \sin\varphi\, \dot\varphi
\end{aligned}
\tag{F-64}
$$

$$
\begin{aligned}
\dot y_1|_{\substack{S_1=\dot S_1=0 \\ S_3=0}} &= \Bigg\{ \frac{m_2+m_3}{m} \left[r_{12}^0 (1-\varepsilon') \cos(\rho-\varepsilon) + (r_{12}^0)' \sin(\rho-\varepsilon) \right] \\
&- \frac{m_3}{m} \left[\varepsilon' r_{23}^0 \cos\varepsilon + (r_{23}^0)' \sin\varepsilon \right] \Bigg\} \sin\varphi\, \dot\rho \\
&+ \left[\frac{m_2+m_3}{m} r_{12}^0 \sin(\rho-\varepsilon) - \frac{m_3}{m} r_{23}^0 \sin\varepsilon \right] \cos\varphi\, \dot\varphi
\end{aligned}
\tag{F-65}
$$

$$\dot{z}_1|_{\substack{S_1=\dot{S}_1=0\\S_3=0}} = \left\{\frac{m_2+m_3}{m}\left[r_{12}^0(1-\varepsilon')\sin(\rho-\varepsilon)-(r_{12}^0)'\cos(\rho-\varepsilon)\right]\right.$$
$$\left. + \frac{m_3}{m}\left[\varepsilon' r_{23}^0\sin\varepsilon-(r_{23}^0)'\cos\varepsilon\right]\right\}\dot{\rho} \tag{F-66}$$

$\diamondsuit$

$$\dot{x}_2|_{\substack{S_1=\dot{S}_1=0\\S_3=0}} = \left\{\frac{m_1}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon)+(r_{12}^0)'\sin(\rho-\varepsilon)\right]\right. \tag{F-67}$$
$$\left. + \frac{m_3}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon+(r_{23}^0)'\sin\varepsilon\right]\right\}\cos\varphi\dot{\rho}$$
$$- \left[\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon)+\frac{m_3}{m}r_{23}^0\sin\varepsilon\right]\sin\varphi\,\dot{\varphi}+\frac{m_3}{m_2}\left[\sin\varepsilon-\frac{1}{\varepsilon}\frac{(r_{23}^0)'}{r_{23}^0}\cos\varepsilon\right]\cos\varphi\,\dot{S}_3$$

$$\dot{y}_2|_{\substack{S_1=\dot{S}_1=0\\S_3=0}} = \left\{-\frac{m_1}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon)+(r_{12}^0)'\sin(\rho-\varepsilon)\right]\right. \tag{F-68}$$
$$\left. - \frac{m_3}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon+(r_{23}^0)'\sin\varepsilon\right]\right\}\sin\varphi\dot{\rho}$$
$$- \left[\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon)+\frac{m_3}{m}r_{23}^0\sin\varepsilon\right]\cos\varphi\,\dot{\varphi}-\frac{m_3}{m_2}\left[\sin\varepsilon-\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\cos\varepsilon\right]\sin\varphi\,\dot{S}_3$$

$$\dot{z}_2|_{\substack{S_1=\dot{S}_1=0\\S_3=0}} = \left\{\frac{m_1}{m}\left[-r_{12}^0(1-\varepsilon')\sin(\rho-\varepsilon)+(r_{12}^0)'\cos(\rho-\varepsilon)\right]\right. \tag{F-69}$$
$$\left. - \frac{m_3}{m}\left[-\varepsilon' r_{23}^0\sin\varepsilon+(r_{23}^0)'\cos\varepsilon\right]\right\}\dot{\rho}-\frac{m_3}{m_2}\left[\cos\varepsilon+\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\sin\varepsilon\right]\dot{S}_3$$

$\diamondsuit$

$$\dot{x}_3|_{\substack{S_1=\dot{S}_1=0\\S_3=0}} = \left\{\frac{m_1}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon)+(r_{12}^0)'\sin(\rho-\varepsilon)\right]\right. \tag{F-70}$$
$$\left. - \frac{m_1+m_2}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon+(r_{23}^0)'\sin\varepsilon\right]\right\}\cos\varphi\,\dot{\rho}$$
$$- \left[\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon)-\frac{m_1+m_2}{m}r_{23}^0\sin\varepsilon\right]\sin\varphi\,\dot{\varphi}-\left[\sin\varepsilon-\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\cos\varepsilon\right]\cos\varphi\,\dot{S}_3$$

$$\dot{y}_3|_{\substack{S_1=\dot{S}_1=0\\S_3=0}} = \left\{-\frac{m_1}{m}\left[r_{12}^0(1-\varepsilon')\cos(\rho-\varepsilon)+(r_{12}^0)'\sin(\rho-\varepsilon)\right]\right. \tag{F-71}$$
$$\left. + \frac{m_1+m_2}{m}\left[\varepsilon' r_{23}^0\cos\varepsilon+(r_{23}^0)'\sin\varepsilon\right]\right\}\sin\varphi\,\dot{\rho}$$
$$+ \left[-\frac{m_1}{m}r_{12}^0\sin(\rho-\varepsilon)+\frac{m_1+m_2}{m}r_{23}^0\sin\varepsilon\right]\cos\varphi\,\dot{\varphi}+\left[\sin\varepsilon-\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\cos\varepsilon\right]\sin\varphi\,\dot{S}_3$$

$$\dot{z}_3|_{\substack{S_1=\dot{S}_1=0\\S_3=0}} = \left\{\frac{m_1}{m}\left[-r_{12}^0(1-\varepsilon')\sin(\rho-\varepsilon)+(r_{12}^0)'\cos(\rho-\varepsilon)\right]\right. \tag{F-72}$$
$$\left. + \frac{m_1+m_2}{m}\left[-\varepsilon' r_{23}^0\sin\varepsilon+(r_{23}^0)'\cos\varepsilon\right]\right\}\dot{\rho}+\left[\cos\varepsilon+\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\sin\varepsilon\right]\dot{S}_3$$

As in the case of the S_1 vibration, using the above formulas, the kinetic energy when only the S_3 stretching coordinate is considered is:

$$2T = \frac{1}{m}\left\{(1-\varepsilon')^2\left[1+\frac{1}{(1-\varepsilon')^2}\left(\frac{(r_{12}^0)'}{r_{12}^0}\right)^2\right]u_1+(\varepsilon')^2\left[1+\frac{1}{(\varepsilon')^2}\left(\frac{(r_{23}^0)'}{r_{23}^0}\right)^2\right]u_3\right.$$

$$
\begin{aligned}
&- 2u_{13}(1-\varepsilon')\varepsilon'\left[\left(1-\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\right)\cos\rho+\left(\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}+\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\right)\sin\rho\right]\Bigg\}\dot{\rho}^2\\
&+\quad\frac{1}{m}\left\{u_1\sin^2(\rho-\varepsilon)+u_3\sin^2\varepsilon-2u_{13}\sin(\rho-\varepsilon)\sin\varepsilon\right]\dot{\varphi}^2\\
&+\quad m_3\left(1+\frac{m_3}{m_2}\right)\left[1+\frac{1}{(\varepsilon')^2}\left(\frac{(r_{23}^0)'}{r_{23}^0}\right)^2\right]\dot{S}_3^2
\end{aligned}
\tag{F-73}
$$

In the case of the asymmetric molecule, if the two stretching coordinates are considered together, the following observations can be made:

- in $\dot{x}_1\,,\dot{y}_1\,,\dot{z}_1$ enter only $\dot{S}_1$ and consequently the square of the derivatives do not have $\dot{S}_1\dot{S}_3$
- in $\dot{x}_3\,,\dot{y}_3\,,\dot{z}_3$ enter only $\dot{S}_3$ and consequently the square of the derivatives do not have $\dot{S}_1\dot{S}_3$
- in $\dot{x}_2\,,\dot{y}_2\,,\dot{z}_2$ enter $\dot{S}_1$ and $\dot{S}_3$ and consequently the square of the derivatives contain $\dot{S}_1\dot{S}_3$
- in kinetic energy formula enter $\dot{S}_1\dot{S}_3$ and the term in $\dot{S}_1\dot{S}_3$ is:

$$
\begin{aligned}
&\frac{2m_1m_3}{m_2}\left\{\left[\sin(\rho-\varepsilon)-\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\cos(\rho-\varepsilon)\right]\times\left[\sin\varepsilon-\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\cos\varepsilon\right]\right.\\
&\left.-\left[\cos(\rho-\varepsilon)+\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin(\rho-\varepsilon)\right]\left[\cos\varepsilon+\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\sin\varepsilon\right]\right\}\\
=\;&-\frac{2m_1m_2}{m_2}\left[\cos\rho+\frac{1}{1-\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\sin\rho+\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}\sin\rho-\frac{1}{(1-\varepsilon')\varepsilon'}\left(\frac{(r_{12}^0)'}{r_{12}^0}\right)\left(\frac{(r_{23}^0)'}{r_{23}^0}\right)\cos\rho\right]
\end{aligned}
\tag{F-74}
$$

The covariant metric tensor elements corresponding to both stretching coordinates are:

$$
\begin{aligned}
g_{S_1S_3}&=-\frac{m_1m_3}{m_2}\left\{\left[1-\frac{1}{(1-\varepsilon')\varepsilon'}\frac{(r_{12}^0)'}{r_{12}^0}\frac{(r_{23}^0)'}{r_{23}^0}\right]\cos\rho+\left[\frac{1}{\varepsilon'}\frac{(r_{23}^0)'}{r_{23}^0}+\frac{1}{(1-\varepsilon')}\frac{(r_{12}^0)'}{r_{12}^0}\right]\sin\rho\right\}\\
g_{S_1S_1}&=\frac{m_1(m_1+m_2)}{m_2}\left[1+\frac{1}{(1-\varepsilon')^2}\left(\frac{(r_{12}^0)'}{r_{12}^0}\right)^2\right]\\
g_{S_3S_3}&=\frac{m_3(m_3+m_2)}{m_2}\left[1+\frac{1}{(\varepsilon')^2}\left(\frac{(r_{23}^0)'}{r_{23}^0}\right)^2\right]
\end{aligned}
\tag{F-75}
$$

F.6 The non Vanishing Terms of the Kinetic Hamiltonian

The kinetic energy, with Podolsky formula [187] is:

$$
2T=\mu^{\frac{1}{4}}\sum P_\alpha\,\mu_{\alpha\beta}\,\mu^{-\frac{1}{2}}\,P_\beta\,\mu^{\frac{1}{4}}
\tag{F-76}
$$

where $\mu_{\alpha\beta}=g^{\alpha\beta}$ is the inverse of the metric tensor element $g_{\alpha\beta}$, and μ is the inverse of the Jacobian. We consider the derivatives in "zero" point (no stretching vibrations, $S_1=S_3=0$):

$$
\begin{aligned}
\mu_{\alpha\beta}\quad&\begin{cases}=f(\rho)\\ \not=f(S_1\,,S_3\,,\varphi)\end{cases}\\
\mu\quad&\begin{cases}=f(\rho)\\ \not=f(S_1\,,S_3\,,\varphi)\end{cases}
\end{aligned}
\tag{F-77}
$$

In this case we obtain for the intermediate terms from (F-76):

$$
\begin{aligned}
&\left[P_\gamma\,,g^{\alpha\beta}\right]=0\\
&\left[P_\gamma\,,\left[P_\gamma\,,g^{\alpha\beta}\right]\right]=0\\
&\left[P_\gamma\,,g^n\right]=0
\end{aligned}
\qquad
\begin{cases}
\alpha\,,\beta=\rho\,,\varphi\,,S_1\,,S_3\\
\gamma=\varphi\,,S_1\,,S_3\\
n-\text{ real number}\\
g^0_{\rho,\gamma}=0\qquad g_0^{\rho,\gamma}=g_0^{\varphi,\gamma}=0
\end{cases}
\tag{F-78}
$$

With approximations from (F-78), the energy from (F-76) become:

$$
2T=\underbrace{\mu_0^{\frac{1}{4}}\,P_\rho\,g_0^{\rho\rho}\,\mu_0^{-\frac{1}{2}}\,P_\rho\,\mu_0^{\frac{1}{4}}}_{H_{bend}\equiv[5,\,14]}+\underbrace{g_0^{\varphi\varphi}\,P_\varphi^2}_{H_{rot}}+\underbrace{g_0^{11}\,P_1^2+g_0^{33}\,P_3^2+2g_0^{13}\,P_1\,P_3}_{H_{str}}
\tag{F-79}
$$

The change of coordinates defined in (3.209), by a unitary transformation, in order to diagonalize the stretching part of the kinetic Hamiltonian, can be done with a matrix of type:

$$\mathbf{R} = \begin{pmatrix} \sin\zeta & \cos\zeta \\ \cos\zeta & -\sin\zeta \end{pmatrix} \tag{F-80}$$

The metric tensor for the stretching part change as:

$$g_{ab}^{(\tilde{S})} = \sum_{i,j} \left(\frac{\partial S_i}{\partial \tilde{S}_a}\right) \left(\frac{\partial S_j}{\partial \tilde{S}_b}\right) g_{ij}^{(S)} \tag{F-81}$$

From eq.(F-81), the tensor elements are:

$$\begin{aligned} g_{\tilde{1}\tilde{1}} &= g_{11}\sin^2\zeta + g_{33}\cos^2\zeta + g_{13}\sin 2\zeta \\ g_{\tilde{3}\tilde{3}} &= g_{11}\cos^2\zeta + g_{33}\sin^2\zeta - g_{13}\sin 2\zeta \\ g_{\tilde{1}\tilde{3}} &= \frac{1}{2}(g_{11} - g_{33})\sin 2\zeta + g_{13}\cos 2\zeta \end{aligned} \tag{F-82}$$

To diagonalize the stretching metric tensor, we must have $g_{\tilde{1}\tilde{3}} = 0$, and we find the equation (3.210).

F.7 Stretching Potential in Curvilinear Coordinates

We consider the equation similar with (3.13) for the symmetric molecule:

$$\begin{aligned} \Delta r_1 &= r_{12} - r_{12}(\rho) = R_{\tilde{1}}^{(1)}\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}\,\tilde{S}_3 \\ \Delta r_3 &= r_{23} - r_{23}(\rho) = R_{\tilde{1}}^{(3)}\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}\,\tilde{S}_3 \end{aligned} \tag{F-83}$$

where there are defined the auxiliary functions similar with (3.16):

$$\begin{aligned} R_{\tilde{1}}^{(1)} &= \frac{m_1+m_2}{m_2}\sin\zeta - \cos\zeta\frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\left(\frac{r'_{23}}{r_{23}}\right)\sin\rho\right] \\ R_{\tilde{1}}^{(3)} &= \frac{m_3+m_2}{m_2}\cos\zeta - \sin\zeta\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{1-\varepsilon'}\left(\frac{r'_{12}}{r_{12}}\right)\sin\rho\right] \\ R_{\tilde{5}}^{(1)} &= \frac{m_1+m_2}{m_2}\cos\zeta + \sin\zeta\frac{m_3}{m_2}\left[\cos\rho + \frac{1}{\varepsilon'}\left(\frac{r'_{23}}{r_{23}}\right)\sin\rho\right] \\ R_{\tilde{5}}^{(3)} &= \frac{m_3+m_2}{m_2}\sin\zeta + \cos\zeta\frac{m_1}{m_2}\left[\cos\rho + \frac{1}{1-\varepsilon'}\left(\frac{r'_{12}}{r_{12}}\right)\sin\rho\right] \end{aligned} \tag{F-84}$$

The equation (F-83) can be written in the reference configuration (similar with (3.18)),

$$\begin{aligned} \Delta r_{12} &= \Delta r_1 + \mathcal{R}_1(\rho) \\ \Delta r_{32} &= \Delta r_3 + \mathcal{R}_3(\rho) \end{aligned} \tag{F-85}$$

Also, the generalized potential with the Fermi term can be express as (see eq.(3.55)):

$$V^{gen} = \frac{1}{2}f_{11}\Delta r_{12}^2 + \frac{1}{2}f_{33}\Delta r_{23}^2 + f_{13}\Delta r_{12}\Delta r_{23} + F_{122}\Delta r_{12}\,\rho^2 + F_{322}\Delta r_{23}\rho^2 \tag{F-86}$$

To find the dependence of the bond length from the angle, the minimum conditions for the bond length must be considered:

$$\left(\frac{\partial V^{gen}}{\partial \Delta r_{12}}\right)_{\tilde{S}_1=\tilde{S}_3=0} = 0 \quad \text{and} \quad \left(\frac{\partial V^{gen}}{\partial \Delta r_{32}}\right)_{\tilde{S}_1=\tilde{S}_3=0} = 0 \tag{F-87}$$

If we make the derivative of the V^{gen} as function of Δr_{12} and Δr_{23}, we get:

$$\begin{aligned} \left(\frac{\partial V^{gen}}{\partial \Delta r_{12}}\right)_0 &= \left[f_{11}\Delta r_{12} + f_{13}\Delta r_{23} + F_{122}\rho^2\right]_{\tilde{S}_1=\tilde{S}_3=0} = f_{11}\mathcal{R}_1 + f_{13}\mathcal{R}_3 + F_{122}\rho^2 = 0 \\ \left(\frac{\partial V^{gen}}{\partial \Delta r_{32}}\right)_0 &= \left[f_{33}\Delta r_{23} + f_{13}\Delta r_{12} + F_{322}\rho^2\right]_{\tilde{S}_1=\tilde{S}_3=0} = f_{33}\mathcal{R}_3 + f_{13}\mathcal{R}_1 + F_{322}\rho^2 = 0 \end{aligned} \tag{F-88}$$

The previous relations can be written in a system of equations, as:

$$\begin{aligned} f_{11}\mathcal{R}_1 + f_{13}\mathcal{R}_3 &= -F_{122}\rho^2 \\ f_{33}\mathcal{R}_3 + f_{13}\mathcal{R}_1 &= -F_{322}\rho^2 \end{aligned} \tag{F-89}$$

We can obtain the variation of the bond length with angle, $\mathcal{R}_1$ and $\mathcal{R}_3$:

$$\begin{aligned} \mathcal{R}_1 &= -\frac{f_{33}F_{122} - f_{13}F_{322}}{f_{11}f_{33} - f_{13}^2}\rho^2 \\ \mathcal{R}_3 &= -\frac{f_{11}F_{322} - f_{13}F_{122}}{f_{11}f_{33} - f_{13}^2}\rho^2 \end{aligned} \tag{F-90}$$

With the previous formulas (F-83), (F-83) and (F-90) introduced in (F-86), the potential for the minimum condition is:

$$\begin{aligned} V^{gen} &= \frac{1}{2}f_{11}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3 + \mathcal{R}_1\right]^2 + \frac{1}{2}f_{33}\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3 + \mathcal{R}_3\right]^2 \\ &+ f_{13}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3 + \mathcal{R}_1\right]\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3 + \mathcal{R}_3\right] \\ &+ F_{122}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3 + \mathcal{R}_1\right]\rho^2 + F_{322}\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3 + \mathcal{R}_3\right]\rho^2 \\ &= \frac{1}{2}f_{11}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3\right]^2 + f_{11}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3\right]\mathcal{R}_1 \\ &+ \mathcal{O}(\mathcal{R}_1^2) \\ &+ \frac{1}{2}f_{33}\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3\right]^2 + f_{33}\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3\right]\mathcal{R}_3 \\ &+ \mathcal{O}(\mathcal{R}_3^2) \\ &+ f_{13}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3\right]\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3\right] \\ &+ f_{13}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3\right]\mathcal{R}_3 + f_{13}\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3\right]\mathcal{R}_1 \\ &+ \mathcal{O}(\mathcal{R}_1\mathcal{R}_3) \\ &+ F_{122}\left[R_{\tilde{1}}^{(1)}(r,\rho)\,\tilde{S}_1 + R_{\tilde{5}}^{(1)}(r,\rho)\,\tilde{S}_3\right]\rho^2 + \mathcal{O}(\mathcal{R}_1\rho^2) \\ &+ F_{322}\left[R_{\tilde{1}}^{(3)}(r,\rho)\,\tilde{S}_1 - R_{\tilde{5}}^{(3)}(r,\rho)\,\tilde{S}_3\right]\rho^2 + \mathcal{O}(\mathcal{R}_3\rho^2) \\ &= \frac{1}{2}\left\{f_{11}\left[R_{\tilde{1}}^{(1)}(r,\rho)\right]^2 + f_{33}\left[R_{\tilde{1}}^{(3)}(r,\rho)\right]^2 + 2f_{13}R_{\tilde{1}}^{(1)}(r,\rho)R_{\tilde{1}}^{(3)}(r,\rho)\right\}\tilde{S}_1^2 \\ &+ \frac{1}{2}\left\{f_{11}\left[R_{\tilde{5}}^{(1)}(r,\rho)\right]^2 + f_{33}\left[R_{\tilde{5}}^{(3)}(r,\rho)\right]^2 - 2f_{13}R_{\tilde{5}}^{(1)}(r,\rho)R_{\tilde{5}}^{(3)}(r,\rho)\right\}\tilde{S}_3^2 \\ &+ \left\{f_{11}R_{\tilde{1}}^{(1)}(r,\rho)R_{\tilde{5}}^{(1)}(r,\rho) - f_{33}R_{\tilde{1}}^{(3)}(r,\rho)R_{\tilde{5}}^{(3)}(r,\rho)\right. \\ &+ \left. f_{13}\left[R_{\tilde{1}}^{(3)}(r,\rho)R_{\tilde{5}}^{(1)}(r,\rho) - R_{\tilde{1}}^{(1)}(r,\rho)R_{\tilde{5}}^{(3)}(r,\rho)\right]\right\}\tilde{S}_1\tilde{S}_3 \end{aligned} \tag{F-91}$$

We get the curvilinear potential form from the previous equation, as:

$$V^{curv} = \frac{1}{2}f_{\tilde{1}\tilde{1}}(\rho)\,\tilde{S}_1^2 + \frac{1}{2}f_{\tilde{3}\tilde{3}}(\rho)\,\tilde{S}_3^2 + f_{\tilde{1}\tilde{3}}(\rho)\,\tilde{S}_1\tilde{S}_3 \tag{F-92}$$

with the force constants defined like in eq.(3.66):

$$\begin{aligned} f_{\tilde{1}\tilde{1}}(\rho) &= f_{11}\left[R_{\tilde{1}}^{(1)}(r,\rho)\right]^2 + f_{33}\left[R_{\tilde{1}}^{(3)}(r,\rho)\right]^2 + 2f_{13}R_{\tilde{1}}^{(1)}(r,\rho)R_{\tilde{1}}^{(3)}(r,\rho) \\ f_{\tilde{3}\tilde{3}}(\rho) &= f_{11}\left[R_{\tilde{5}}^{(1)}(r,\rho)\right]^2 + f_{33}\left[R_{\tilde{5}}^{(3)}(r,\rho)\right]^2 - 2f_{13}R_{\tilde{5}}^{(1)}(r,\rho)R_{\tilde{5}}^{(3)}(r,\rho) \\ f_{\tilde{1}\tilde{3}}(\rho) &= f_{11}R_{\tilde{1}}^{(1)}(r,\rho)R_{\tilde{5}}^{(1)}(r,\rho) - f_{33}R_{\tilde{1}}^{(3)}(r,\rho)R_{\tilde{5}}^{(3)}(r,\rho) \\ &+ f_{13}\left[R_{\tilde{1}}^{(3)}(r,\rho)R_{\tilde{5}}^{(1)}(r,\rho) - R_{\tilde{1}}^{(1)}(r,\rho)R_{\tilde{5}}^{(3)}(r,\rho)\right] \end{aligned} \tag{F-93}$$

F.8 Comparison between ABC and AB_2 Molecule Formalism

In the case of the symmetric molecule the symmetric and antisymmetric coordinates are defined as in (3.22), for small amplitude:

$$S^s = \tfrac{1}{2}(S_1 + S_3) \quad S^a = \tfrac{1}{2}(S_1 - S_3) \tag{F-94}$$

If the molecule is symmetric, in these conditions the following simplifications are to be considered in the formulas:

$$\begin{array}{ll} r_{12} = r_{23} = r & \varepsilon' = \frac{1}{2} \quad \text{(see [5, 14])} \\ m_1 = m_3 & \cos\zeta = \sin\zeta = \frac{1}{\sqrt{2}} \quad \text{because} \quad \zeta = \frac{\pi}{4} \\ 1 + \frac{m_1}{m_2} = 1 + \frac{m_3}{m_2} = \frac{p+1}{2} & \frac{m_1}{m_2} = \frac{m_3}{m_2} = \frac{p-1}{2} \end{array} \tag{F-95}$$

In the equation for the auxiliary functions (F-84), we make the simplifications from (F-95) and the equation (F-83) is recomputed. The displacements from (3.217) become (3.13), as shown in the next formula:

$$\begin{aligned} \Delta r_{12} &= \frac{p+1}{2}\frac{(S^s + S^a)}{\sqrt{2}} - \frac{p-1}{2}\left[\cos\rho + \frac{2r'}{r}\sin\rho\right]\frac{(S^s - S^a)}{\sqrt{2}} \\ &= \frac{S^s}{2\sqrt{2}}\left[(p+1) - (p-1)(\cos\rho + b\sin\rho)\right] + \frac{S^a}{2\sqrt{2}}\left[(p+1) + (p-1)(\cos\rho + b\sin\rho)\right] \\ &= \frac{1}{\sqrt{2}}S^s \underbrace{\left[(\cos^2\theta + p\sin^2\theta) - (p-1)b\sin\theta\cos\theta\right]}_{R_1(\rho)} \\ &+ \frac{1}{\sqrt{2}}S^a \underbrace{\left[(\sin^2\theta + p\cos^2\theta) + (p-1)b\sin\theta\cos\theta\right]}_{R_5(\rho)} \end{aligned} \tag{F-96}$$

$$\begin{aligned} \Delta r_{23} &= \frac{p-1}{2}\frac{(S^s - S^a)}{\sqrt{2}} - \frac{p-1}{2}\left[\cos\rho + \frac{2r'}{r}\sin\rho\right]\frac{(S^s - S^a)}{\sqrt{2}} \\ &= \frac{S^s}{2\sqrt{2}}\left[(p+1) - (p-1)(\cos\rho + b\sin\rho)\right] - \frac{S^a}{2\sqrt{2}}\left[(p+1) + (p-1)(\cos\rho + b\sin\rho)\right] \\ &= \frac{1}{\sqrt{2}}S^s \underbrace{\left[(\cos^2\theta + p\sin^2\theta) - (p-1)b\sin\theta\cos\theta\right]}_{R_1(\rho)} \\ &- \frac{1}{\sqrt{2}}S^a \underbrace{\left[(\sin^2\theta + p\cos^2\theta) + (p-1)b\sin\theta\cos\theta\right]}_{R_5(\rho)} \end{aligned} \tag{F-97}$$

The derivatives of bending angle to the stretching coordinates, using the usual formulas are:

$$\begin{aligned} \left(\frac{\partial\rho}{\partial S^s}\right)_0 &= \left(\frac{\partial\rho}{\partial S_1}\right)\left(\frac{\partial S_1}{\partial S^s}\right) + \left(\frac{\partial\rho}{\partial S_3}\right)\left(\frac{\partial S_3}{\partial S^s}\right) \\ \left(\frac{\partial\rho}{\partial S^a}\right)_0 &= \left(\frac{\partial\rho}{\partial S_1}\right)\left(\frac{\partial S_1}{\partial S^a}\right) + \left(\frac{\partial\rho}{\partial S_3}\right)\left(\frac{\partial S_3}{\partial S^a}\right) \end{aligned} \tag{F-98}$$

If we use the derivatives of the implicit functions (F-94) we have:

$$\begin{array}{ll} \left(\frac{\partial S_1}{\partial S^s}\right) = \frac{1}{\sqrt{2}} & \left(\frac{\partial S_3}{\partial S^s}\right) = \frac{1}{\sqrt{2}} \\ \left(\frac{\partial S_1}{\partial S^a}\right) = \frac{1}{\sqrt{2}} & \left(\frac{\partial S_3}{\partial S^a}\right) = -\frac{1}{\sqrt{2}} \end{array} \tag{F-99}$$

From (F-98) we get the derivatives of the bend angle as function of the stretching coordinates:

$$\begin{aligned} \left(\frac{\partial\rho}{\partial S^s}\right)_0 &= \left[\left(\frac{\partial\rho}{\partial S_1}\right)_{sim} + \left(\frac{\partial\rho}{\partial S_3}\right)_{sim}\right] = 2\left(\frac{\partial\rho}{\partial S_1}\right) \\ \left(\frac{\partial\rho}{\partial S^a}\right)_0 &= \left[\left(\frac{\partial\rho}{\partial S_1}\right)_{sim} - \left(\frac{\partial\rho}{\partial S_3}\right)_{sim}\right] = 0 \end{aligned} \tag{F-100}$$

The discriminant (F-45) corresponding to the eq.(3.200) is, with b defined in eq.(3.9) and with eq.(F-95):

$$\begin{aligned}\Delta_{\substack{r_{12}=r_{23}=r\\ m_1=m_3\\ \varepsilon'=\frac{1}{2}}} &= 2\left[\left(1+\frac{m_1}{m_2}\right)^2-\left(\frac{m_1}{m_2}\right)^2(\cos\rho+b\sin\rho)^2\right] \qquad \text{(F-101)}\\ &= \frac{1}{2}\left[(p+1)+(p-1)(\cos\rho+b\sin\rho)\right]\left[(p+1)-(p-1)(\cos\rho+b\sin\rho)\right]\\ &= 2R_1(\rho,r^0)\,R_5(\rho,r^0) \qquad \text{(F-102)}\end{aligned}$$

With this value, the derivatives of the stretching symmetric coordinates to the bending angle, with (F-46), are (similar with (3.199)):

$$\begin{aligned}\left(\frac{\partial S^s}{\partial\rho}\right) &= \frac{1}{\sqrt{2}}\left[\left(\frac{\partial S_1}{\partial\rho}\right)+\left(\frac{\partial S_3}{\partial\rho}\right)\right]\\ &= \frac{1}{\sqrt{2}\Delta}\left\{(\mathcal{R}'_{12}+\mathcal{R}'_{23})\left[\left(2+\frac{m_1+m_3}{m_2}\right)+\left(\frac{m_1+m_3}{m_2}\right)\cos\rho\right.\right.\\ &+ \left.\frac{\sin\rho}{m_2}\left(\frac{m_1}{1-\varepsilon'}\cdot\frac{r'_{12}}{r_{12}}+\frac{m_3}{\varepsilon'}\cdot\frac{r'_{23}}{r_{23}}\right)\right] \qquad \text{(F-103)}\\ &+ \left.(\mathcal{R}'_{12}-\mathcal{R}'_{23})\left[\frac{m_3-m_1}{m_2}-\left(\frac{m_3-m_1}{m_2}\right)\cos\rho-\frac{\sin\rho}{m_2}\left(\frac{m_3}{\varepsilon'}\cdot\frac{r'_{23}}{r_{23}}-\frac{m_1}{1-\varepsilon'}\cdot\frac{r'_{12}}{r_{12}}\right)\right]\right\}\\ \left(\frac{\partial S^a}{\partial\rho}\right) &= \frac{1}{\sqrt{2}}\left[\left(\frac{\partial S_1}{\partial\rho}\right)-\left(\frac{\partial S_3}{\partial\rho}\right)\right]\\ &= \frac{1}{\sqrt{2}\Delta}\left\{(\mathcal{R}'_{12}-\mathcal{R}'_{23})\left[\left(2+\frac{m_1+m_3}{m_2}\right)-\left(\frac{m_1+m_3}{m_2}\right)\cos\rho\right.\right.\\ &- \left.\frac{\sin\rho}{m_2}\left(\frac{m_3}{\varepsilon'}\cdot\frac{r'_{23}}{r_{23}}+\frac{m_1}{1-\varepsilon'}\cdot\frac{r'_{12}}{r_{12}}\right)\right] \qquad \text{(F-104)}\\ &+ \left.(\mathcal{R}'_{12}+\mathcal{R}'_{23})\left[\frac{m_3-m_1}{m_2}+\left(\frac{m_3-m_1}{m_2}\right)\cos\rho+\frac{\sin\rho}{m_2}\left(\frac{m_3}{\varepsilon'}\cdot\frac{r'_{23}}{r_{23}}-\frac{m_1}{1-\varepsilon'}\cdot\frac{r'_{12}}{r_{12}}\right)\right]\right\}\end{aligned}$$

In the case of the symmetric molecule $\mathcal{R}'_{12}=\mathcal{R}'_{23}$ and the previous derivatives become the equations (3.15):

$$\begin{aligned}\left(\frac{\partial S^s}{\partial\rho}\right)_{sym} &= \frac{4}{\sqrt{2}\Delta}\mathcal{R}'\left[\left(1+\frac{m_1}{m_2}\right)+\frac{m_1}{m_2}\cos\rho+\frac{2m_1}{m_2}\frac{r'}{r}\sin\rho\right] = \sqrt{2}\frac{\mathcal{R}'}{R_1(\rho)}\\ \left(\frac{\partial S^a}{\partial\rho}\right)_{sym} &= 0 \qquad \text{(F-105)}\end{aligned}$$

The auxiliary functions defined in (F-84) can be used in order to obtain the derivatives of the bending angle as function of the new stretching coordinates. In the below formula (identical with (3.217)), we use the transformation defined in (3.209), with the transformation matrix (F-80), applied in eq.(F-83):

$$\begin{aligned}\Delta r_1 &= \left(1+\frac{m_1}{m_2}\right)S_1-\frac{m_3}{m_2}\left[\cos\rho+\frac{1}{\varepsilon'}\left(\frac{r'_{23}}{r_{23}}\right)\sin\rho\right]S_3=R^{(1)}_{\tilde{1}}\tilde{S}_1+R^{(1)}_{\tilde{5}}\tilde{S}_3\\ \Delta r_3 &= \left(1+\frac{m_3}{m_2}\right)S_3-\frac{m_1}{m_2}\left[\cos\rho+\frac{1}{1-\varepsilon'}\left(\frac{r'_{12}}{r_{12}}\right)\sin\rho\right]S_1=R^{(3)}_{\tilde{1}}\tilde{S}_1-R^{(3)}_{\tilde{5}}\tilde{S}_3 \qquad \text{(F-106)}\end{aligned}$$

In the case of the symmetric molecule from (F-94) and by taking into account all the previous simplifications, the new coordinates are:

$$\tilde{S}_1\equiv S^s \quad \tilde{S}_3\equiv S^a \qquad \text{(F-107)}$$

The auxiliary functions from (F-84) becomes those for the symmetric molecules, defined in (3.16),

$$\begin{aligned}R^{(1)}_{\tilde{1}} &= R^{(3)}_{\tilde{1}}=\frac{1}{\sqrt{2}}\left[\left(1+\frac{m_1}{m_2}\right)-\frac{m_1}{m_2}(\cos\rho+b\sin\rho)\right]\\ &= \frac{1}{\sqrt{2}}\left[(p\sin^2\theta+\cos^2\theta)-(p-1)b\sin\theta\cos\theta\right]=\frac{1}{\sqrt{2}}R_1(r,\rho)\\ R^{(1)}_{\tilde{5}} &= R^{(3)}_{\tilde{5}}=\frac{1}{\sqrt{2}}\left[\left(1+\frac{m_1}{m_2}\right)+\frac{m_1}{m_2}(\cos\rho+b\sin\rho)\right] \qquad \text{(F-108)}\\ &= \frac{1}{\sqrt{2}}\left[(p\cos^2\theta+\sin^2\theta)+(p-1)b\sin\theta\cos\theta\right]=\frac{1}{\sqrt{2}}R_5(r,\rho)\end{aligned}$$

The metric tensor defined in formula (3.204) has the following elements for the symmetric molecule:

$$\left.\begin{array}{l} g^0_{11}|_{sim} = m_1 \frac{p+1}{2}\left[1+\left(\frac{2r'}{r}\right)^2\right] = m_1 \frac{p+1}{2}\left(1+b^2\right) \\ g^0_{33}|_{sim} = m_1 \frac{p+1}{2}\left[1+\left(\frac{2r'}{r}\right)^2\right] = m_1 \frac{p+1}{2}\left(1+b^2\right) \end{array}\right\} \quad g^0_{11} = g^0_{33} \tag{F-109}$$

$$\begin{aligned} g^0_{13} &= -m_1 \frac{p-1}{2}\left\{\left[1-\left(\frac{2r'}{r}\right)^2\right]\cos\rho + 2\left(\frac{2r'}{r}\right)\sin\rho\right\} \\ &= -m_1 \frac{p-1}{2}\left[\left(\cos^2\theta - \sin^2\theta\right) + 2b\sin\rho - b^2\left(\cos^2\theta - \sin\theta^2\right)\right] \end{aligned} \tag{F-110}$$

The tensor elements defined in (3.216) for the changed stretching coordinates, become for a symmetric molecule:

$$\begin{aligned} g^0_{\tilde{1}\tilde{1}} &= \frac{1}{2}g^0_{11} + \frac{1}{2}g^0_{33} + g^0_{13} = m_1\left[\left(p\sin^2\theta + \cos^2\theta\right) - 2b(p-1)\sin\theta\cos\theta + b^2\left(p\cos^2\theta + \sin^2\theta\right)\right] \\ &= m_1 R_3(r,\rho) \\ g^0_{\tilde{3}\tilde{3}} &= \frac{1}{2}g^0_{11} + \frac{1}{2}g^0_{33} - g^0_{13} = m_1\left[\left(p\cos^2\theta + \sin^2\theta\right) + 2b(p-1)\sin\theta\cos\theta + b^2\left(p\sin^2\theta - \cos^2\theta\right)\right] \\ &= m_1 R_4(r,\rho) \end{aligned} \tag{F-111}$$

The contravariant metric tensor elements of (F-111) are:

$$\begin{aligned} g_0^{\tilde{1}\tilde{1}} &= \frac{1}{2}g_0^{11} + \frac{1}{2}g_0^{33} + g_0^{13} = \frac{m_1 R_4}{m_1^2 R_3 R_4} = \frac{1}{m_1 R_3} \\ g_0^{\tilde{3}\tilde{3}} &= \frac{1}{2}g_0^{11} + \frac{1}{2}g_0^{33} - g_0^{13} = \frac{m_1 R_3}{m_1^2 R_3 R_4} = \frac{1}{m_1 R_4} \end{aligned} \tag{F-112}$$

In the case of the symmetric molecule, the potential force constants are equal, and then eq.(3.220) become (3.56):

$$\left.\begin{array}{l} f_{11} = f_{33} \\ F_{122} = F_{322} \end{array}\right\} \quad \mathcal{R}_1|_{sim} = -\frac{F_{122}(f_{11}-f_{13})\rho^2}{f_{11}^2 - f_{13}^2} = -\frac{F_{122}}{f_{11}+f_{13}}\rho^2 = \mathcal{R}_3|_{sim} \tag{F-113}$$

From (F-108), we find the identity between formulas (3.222) and (3.66) for a symmetric molecule,

$$\left.\begin{array}{l} R^{(1)}_{\tilde{1}} = R^{(3)}_{\tilde{1}} = \frac{1}{\sqrt{2}}R_1 \\ R^{(1)}_{\tilde{5}} = R^{(3)}_{\tilde{5}} = \frac{1}{\sqrt{2}}R_5 \end{array}\right\} \rightarrow \left\{\begin{array}{l} f_{\tilde{1}\tilde{1}} = \frac{1}{2}\left(f_{11}+f_{33}\right)R_1^2 + f_{13}R_1^2 = \left(f_{11}+f_{13}\right)R_1^2 \\ f_{\tilde{3}\tilde{3}} = \frac{1}{2}\left(f_{11}+f_{33}\right)R_5^2 - f_{13}R_5^2 = \left(f_{11}-f_{13}\right)R_5^2 \\ f_{\tilde{1}\tilde{3}} = \left(f_{11}-f_{33}\right)\frac{R_1R_5}{2} + f_{13}\left(\frac{R_1R_5}{2} - \frac{R_1R_5}{2}\right) = 0 \end{array}\right. \tag{F-114}$$

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Titre: Une Nouvelle Approche au Traitement Théorique des Vibrations d'une Molécule Triatomique et de leurs Couplages. Application à CO_2 et CO_2^+

Résumé: Dans cette étude nous avons formulé une approche au traitement de la vibration-rotation d'une molécule triatomique symétrique, qui permet de prendre en compte le mouvement de déformation de grande amplitude de la molécule ainsi que son couplage avec le mouvement d'élongation. Le but de la présente étude n'est pas de concurrencer les approches variationelles, très générales, qui sont disponibles depuis quelques années, mais de proposer une alternative qui est plus légère dans la mise en oeuvre tout en s'appliquant à des nombreux cas réels. L' Hamiltonien est basé sur un systéme de référence qui suit le minimum d'énergie potentielle lorsque la molécule se plie. Cette nouvelle approche utilise la methode de Jungen et Merer pour tenir compte du couplage Renner-Teller, dans le but d'obtenir les niveaux énergétiques d'une molécule symétrique linéaire dans un état électronique dégénéré. Un paramètre, g_D, introduit ici pour la première fois, permet d'obtenir le lien entre le système de référence variable et les moments d'inertie qui interviennent dans la rotation moléculaire. L'extension du formalisme pour des molecules asymétriques a été également formulé. Le modèle a été appliqué aux molécules linéaires CO_2 et CO_2^+.
La molécule CO_2 est un exemple de couplage Fermi pur. On montre que la variation de la longueur de liaison avec l'angle de déformation contribue à la variation de la constante de rotation avec l'état vibrationnel, et elle est également responsable des perturbations Fermi. Il n'est donc pas nécessaire d'introduire un paramètre d'interaction Fermi spécifique. Les niveaux d'énergie observés de CO_2 sont bien reproduits par un ensemble restreint de paramètres d'énergie potentielle. Nous avons utilisé seulement 6 parameters, tandis que les meilleures valeurs dans la litérature, ont été obtenus en utilisant 12 paramètres (Pariseau *et al*, *J. Chem. Phys.*, **42**, 2335 (1965)). La molécule de CO_2^+ est un exemple plus complexe où l'effet Renner-Teller existe et se superpose aux perturbations Fermi. Dans ce cas également, la nouvelle approche réussit à représenter la structure énergétique des niveaux perturbés en termes de deux surfaces d'énergie potentielle de forme simple.

Title: Symmetric Stretch-Bender: a New Approach to Vibration Coupled Modes for Symmetric Triatomic Molecules

Abstract: In this work we have derived a vibration-rotation Hamiltonian for a triatomic symmetric molecule, the Stretch-Bender model, which allows for large amplitude bending motion and its coupling to the stretching motion. The Hamiltonian is based on the use of a specific stretch-bender reference frame, chosen so that as the molecule bends the reference geometry follows the minimum in the potential energy surface. This new Stretch-Bender Hamiltonian has been combined with the Jungen and Merer method of solving the Renner-Teller coupling problem in order to find the energies for a symmetrical molecule possessing a degenerate electronic state when linear. A key role in the understanding of the combined stretching - bending motions is played by the g_D term, introduced here for the first time, which relates the end-over-end rotational motion to the angle-dependent reference geometry. The Fermi coupling arises naturally from the change of the configuration during vibrational motion. The extension of the approach to asymmetric molecules is outlined. The model has been applied to the CO_2 and CO_2^+ molecules.
The CO_2 molecule is the prototype example for a pure Fermi interaction. It is shown that the variation of the bond lengths with bending angle is responsible for the vibrational variation of the rotational constants as well as of the Fermi perturbations and therefore no specific Fermi interaction parameter is necessary. The energy levels of the molecule are very well reproduced by a minimal set of potential parameters. The CO_2^+ molecule is an example where orbital angular momentum coupling occurs combined with the Fermi perturbations, but the Stretch - Bender model again succeeds in representing the perturbed level structure in terms of a simple potential surface.

Mots clés: Physique moléculaire; Spectroscopie infrarouge; Théorie des vibrations moléculaires; Interactions intramoléculaires