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- CALCULS DE DEPLACEMENTS ISOTOPIQUES ET STRUCTURES HYPERFINES AU DEUXIEME ORDRE.

- FONCTIONS GENERATRICES DES COEFFICIENTS DE COUPLAGE - RECOUPLAGE DE SU (2).

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INTRODUCTION

Le travail que nous présentons comporte deux parties et se rattache à deux domaines très différents mais complémentaires de la théorie de la structure atomique. Le premier domaine est celui des techniques angulaires qui ont pour fondement l'invariance par rotation de l'hamiltonien atomique. Le deuxième est celui du modèle à particules indépendantes et des corrections d'ordre supérieur. L'opposition et la complémentarité de ces domaines peuvent être résumées par la formule : angulaire/radial.

L'une des parties de ce travail décrit l'obtention de la fonction génératrice d'un coefficient de couplage-recouplage arbitraire de SU(2) . Des fonctions génératrices des coefficients 3j , 6j et 9j ont été obtenues par Schwinger (1952) à l'aide d'opérateurs annihilation-création. En utilisant des espaces de fonctions entières, Bargmann (1962) a retrouvé les fonctions génératrices pour les coefficients 3j et 6j . Par des calculs compliqués, Wu (1972) et Huang (1974) ont obtenu les fonctions génératrices pour des 9j , 12 j et 15 j . La formule générale que nous avons découverte pour un coefficient de couplage-recouplage arbitraire s'exprime géométriquement à l'aide de sommes sur deux ensembles finis de sous-graphes du graphe du coefficient.

La fonction génératrice est utilisée pour obtenir une nouvelle formule explicite des coefficients, des relations de récurrence et aussi pour discuter les symétries des coefficients.

Pour l'autre partie de ce travail, le point de départ était le calcul précis de déplacements isotopiques spécifiques de transitions optiques. Les mesures de déplacements isotopiques étant devenues plus précises grâce aux nouvelles techniques spectroscopiques et à l'utilisation d'isotopes enrichis, il devient nécessaire de savoir séparer l'effet de masse de l'effet de volume qui permet d'évaluer des paramètres nucléaires. La détermination a priori du déplacement isotopique spécifique, qui avec le déplacement isotopique normal facile à déterminer forme l'effet de masse, est d'autant plus intéressante que la séparation expérimentale des effets de masse et de volume utilisant les transitions X ou les atomes muoniques est encore trop imprécise. Le déplacement isotopique spécifique s'obtient à l'aide d'un opérateur biélectronique noté Σ . Nous avons développé une méthode de calcul consistant à utiliser des fonctions d'onde compactes adaptées au calcul du deuxième ordre $\Sigma \times Q$ (Q désignant l'opérateur d'énergie électrostatique). On choisit d'abord la forme de la fonction d'onde par des considérations angulaires et ensuite on détermine les orbitales radiales. Cette méthode pratique est très voisine de la méthode Hartree-Fock multiconfigurationnelle. Nous avons choisi de l'appliquer aux cas de l'hélium, pour lequel existent des résultats théoriques très précis, et au cas du magnésium pour des termes analogues à ceux de l'hélium.

Nous constatons alors les insuffisances de la méthode, qui nous ont amené d'une part à considérer les effets d'ordres supérieurs au deuxième et, d'autre part, à l'appliquer aux calculs de valeurs moyennes, non plus d'un opérateur biélectronique Σ , mais d'opérateurs monoélectroniques de structure hyperfine. Nous avons étudié les valeurs des paramètres $\langle r^{-3}\rangle$ dans les termes ^1P et ^3P du magnésium : valeurs qui sont expérimentalement très différentes dans les deux termes. L'étude du scandium et du titane visait à déterminer le rapport $\langle r^{-3}\rangle_{\ell}/\langle r^{-3}\rangle_{sC^2}$ pour expliquer les différences entre l'expérience et la théorie de C. Bauche-Arnoult.

Nous nous sommes également intéressés à un autre aspect des déplacements isotopiques, les déplacements isotopiques pair-impair anormaux (appelés encore écarts à la droite de King). Ces effets, dus au deuxième ordre de structure hyperfine noté hfs × hfs , sont étudiés à partir de méthodes empiriques et non plus a priori (comme c'était le cas pour les calculs des effets de deuxième ordre $\Sigma \times Q$ et hfs $\times Q$) dans le samarium et le mercure, pour lesquels les expériences mettent en évidence des anomalies.

L'exposé qui suit est un commentaire des articles présentés en annexe. Dans la première partie, nous rappelons d'abord les principales approches des effets d'ordre supérieur et décrivons ensuite les méthodes employées (Chapitre 1). Nos études a priori se trouvent au Chapitre 2 et les études empiriques au Chapitre 3. Dans la deuxième partie, nous présentons brièvement la fonction génératrice des coefficients de couplage-recouplage, après avoir rappelé les propriétés générales des fonctions génératrices et la représentation graphique de l'algèbre des moments angulaires.

1ère Partie

CALCULS de DEPLACEMENTS ISOTOPIQUES et de STRUCTURES HYPERFINES au DEUXIEME ORDRE.

CHAPITRE 1

PRINCIPALES APPROCHES DES EFFETS D'ORDRE SUPERIEUR

La description théorique des états liés des atomes à N électrons en mécanique quantique non relativiste passe par la résolution d'une équation de Schrödinger indépendante du temps :

$$H\Psi = E\Psi \qquad (1)$$

pour la fonction d'onde $\Psi(x_1,x_2...x_N)$ où x_i représente les coordonnées d'espace et de spin de l'électron i $(1 \leqslant i \leqslant N)$. Nous considérerons d'abord les études empiriques (§.1.1). Pour les études a priori (§.1.2), après avoir rappelé (§.1.2.1) les diverses méthodes, nous décrivons la méthode que nous avons développée (§§.1.2.2 et 1.2.3).

1.1 METHODES EMPIRIQUES.

La méthode empirique (ou paramétrique) d'interprétation des énergies est très utilisée en Spectroscopie Atomique depuis les travaux de Condon et Shortley (1935) et de Racah (1950). Dans cette méthode on diagonalise la restriction H_R de l'hamiltonien H (contenant habituellement seulement les interactions électrostatique et spin-orbite) à un sous-espace fini engendré par des fonctions d'onde de type configurationnel. Les parties angulaires des éléments de matrice de l'hamiltonien sont calculables une fois choisi le sous-espace. Quant aux parties radiales, elles servent de paramètres et sont ajustées de façon que les valeurs propres de H_R reproduisent les énergies expérimentales le mieux possible. Les vecteurs propres de H_R décrivent les niveaux atomiques, mais de façon très incomplète, car la partie radiale des fonctions est inconnue. Le calcul d'observables autres que l'énergie et les facteurs de Landé nécessite l'introduction d'autres paramètres. Cette méthode qui est bien adaptée à l'étude d'un grand nombre de niveaux nous a permis d'étudier les atomes Hg et Sm (Chapitre 3, où nous préciserons les variantes de la méthode que nous avons utilisées).

La méthode empirique tient compte des effets d'ordres supérieurs par rapport à l'approximation du champ central et présente les caractéristiques des méthodes utilisant une diagonalisation ou un principe variationnel : les fonctions d'onde angulaires obtenues sont les meilleures possibles dans un sous-espace donné ; elles contiennent donc tous les effets perturbationnels dans ce sous-espace. Les effets sur l'énergie extérieurs à ce sous-espace peuvent être introduits en modifiant l'hamiltonien à l'aide d'opérateurs effectifs. Notons à ce propos que la méthode empirique tient compte des effets de tout opérateur effectif d'énergie qui a même forme angulaire que l'un des opérateurs de H_R correspondant à un paramètre donné.

1.2 METHODES A PRIORI.

1.2.1 Classification des méthodes. Corrélation.

Lorsqu'on applique les méthodes a priori aux atomes légers, il est justifié en première approche de négliger les interactions magnétiques. L'hamiltonien H s'écrit alors en unités atomiques (u a) :

$$H = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{Z}{r_i}\right) + \sum_{1\leqslant i<j\leqslant N} \frac{1}{r_{ij}} \qquad (2)$$

où Z est le numéro atomique de l'élément. Pour $N\neq 1$, l'équation (1) ne peut être résolue que de façon approchée.

Une solution approchée de l'équation (1) est celle que l'on obtient dans la méthode Hartree-Fock (HF). Pour des états à couches fermées, l'approximation Ψ_{HF} de la fonction d'onde est un déterminant de Slater. Pour des couches ouvertes il est en général nécessaire d'utiliser une somme de déterminants pour former un vecteur propre de L^2 , L_z , S^2 et S_z . L'erreur faite lorsqu'on remplace Ψ par Ψ_{HF} est désignée sous le nom général de "corrélation". Notons cependant que, pour certains états de spin, dans l'approximation HF (et le modèle du champ central, d'ailleurs) les mouvements des électrons sont déjà quelque peu corrélés par suite de l'antisymétrie de Ψ_{HF} .

Le calcul précis de grandeurs atomiques, comme par exemple les constantes de structure hyperfine, exige une évaluation des effets de la corrélation. Les méthodes de calcul des effets de la corrélation ont fortement progressé ces dix dernières années par suite des perfectionnements des méthodes numériques et de l'intérêt que leur portent les physiciens et les chimistes. Ces méthodes peuvent être divisées en 3 classes : perturbationnelles, variationnelles par le procédé de Hylleraas (Hy) ou par superposition de configurations (SOC). Des recouvrements entre ces classes ne sont toutefois pas rares. Ces méthodes donnent les premiers termes d'un développement en série de la solution exacte Ψ et permettent de l'approcher, du moins en principe, autant que l'on veut (Löwdin, 1955 ; Szasz, 1962).

a) Dans les méthodes perturbationnelles on sépare l'Hamiltonien H en $H_0 + V$ en introduisant un Hamiltonien soluble H_0 (qui souvent est choisi pour donner Ψ_{HF} comme vecteur propre) et une perturbation V . Notons que la contribution d'ordre n du développement perturbationnel dépend du choix de H_0 . Dans nos calculs a priori l'appellation "deuxième ordre" est utilisée par référence à HF .

La théorie des perturbations peut être mise en oeuvre en classant les divers termes de la fonction d'onde en excitations à 1, 2, 3 ..., N électrons par rapport à Ψ_{HF} . Les équations de Bethe Goldstone (1957) d'ordre n déterminent la fonction d'onde limitée aux excitations à n

ou moins de n électrons. Chacune de ces équations détermine les contributions dues à l'excitation de n orbitales données de Ψ_{HF} et a la forme d'une équation de Schrödinger à n particules, la fonction d'onde devant satisfaire à des contraintes d'orthogonalité avec les orbitales non excitées de Ψ_{HF} . Cette méthode a été développée par Nesbet (1965, 1967, 1969) et est pratique pour $n=2$ (ce qui correspond aux équations de paires), les calculs devenant très longs dès $n=3$. Dans la méthode de Nesbet les orbitales sont développées sur une base finie de fonctions de Slater et la fonction d'onde d'ordre n est obtenue par un calcul variationnel, ce qui est équivalent à la résolution des équations de Bethe-Goldstone.

La méthode de Sinanoğlu (1961, 1969) est assez proche de la précédente (pour $n=2$). Elle est aussi du type perturbationnel-variationnel et donne des équations permettant de déterminer des fonctions de paires. Les diverses excitations sont classées en internes $(ij \to k\ell)$, semi-internes $(ij \to k\alpha)$ et externes $(ij \to \alpha\beta)$ où i, j, k et ℓ désignent des orbitales de la "mer" HF et α, β des orbitales virtuelles. Les excitations internes et semi-internes ne jouent un rôle que dans les atomes à couches ouvertes (le nombre d'orbitales de la mer HF étant alors plus grand que N).

Les méthodes perturbationnelles que nous venons de considérer sont classées par le nombre d'électrons excités et deviennent exactes lorsque $n=N$. Examinons maintenant les développements perturbationnels suivant les puissances du potentiel perturbateur V . La théorie des perturbations à N corps (MBPT) du type Brueckner-Goldstone (Brueckner, 1955a,b, 1959 ; Goldstone, 1957) a été appliquée en physique atomique par Kelly (1963) et développée par de nombreux auteurs. Les termes de la série perturbationnelle sont représentés par des graphes de Feynman : chaque graphe apporte une contribution de la forme d'une somme de produits d'intégrales radiales par une partie angulaire qui est un coefficient de couplage-recouplage dont la représentation graphique coïncide avec le graphe de Feynman. La description graphique de MBPT est donc non seulement une visualisation des effets de la corrélation, mais aussi un moyen pratique de calcul. La méthode a été très employée pour des calculs jusqu'au troisième ordre (et en tenant compte des ordres supérieurs par des méthodes de resommation du type équation de Dyson) . Citons quelques articles qui comportent une description très détaillée de la méthode : Freed (1968), Dutta et al. (1969), Ray et al. (1973), Garpman et al. (1975) et Wilson et Silver (1976).

Dans les calculs du type de ceux de Kelly la partie radiale est évaluée par sommations sur un ensemble complet d'orbitales virtuelles. Une variante importante consiste à remplacer ces sommations par la résolution d'équations différentielles inhomogènes. Un graphe de Feynman contenant une seule ligne excitée peut ainsi être calculé à l'aide d'une orbitale perturbée vérifiant une telle équation (Morrison, 1972) et un graphe à 2 lignes excitées à l'aide d'une fonction perturbée à 2 variables solution d'une équation inhomogène aux dérivées partielles (Garpman et al., 1975). Ces équations sont similaires aux équations donnant les corrections à la fonction d'onde dans la théorie des perturbations de Schrödinger-Rayleigh (Sternheimer, 1950, 1967 ; Dalgarno, 1961).

b) Les deux méthodes variationnelles SOC et Hy ont été d'abord introduites par Hylleras (1928, 1929) afin d'étudier l'atome He . Dans la méthode Hy les fonctions variationnelles d'essai font intervenir explicitement les coordonnées interélectroniques $r_{ij} = |\vec{r_i} - \vec{r_j}|$. Ainsi pour les atomes à deux électrons les fonctions variationnelles sont formées à l'aide de monomes $r_{12}^{\alpha} (r_1 + r_2)^{\beta} (r_1 - r_2)^{\gamma}$. Dans la méthode originelle α, β, γ sont positifs ou nuls. L'utilisation de valeurs négatives (Kinoshita, 1957 ; Pekeris, 1958) a permis l'obtention de fonctions d'onde à 2 électrons très précises. En particulier, les fonctions d'onde de Schiff, Lifson, Pekeris et Rabinowitz (1965) pour l'hélium qui peuvent être considérées comme exactes nous serviront pour mettre à l'épreuve nos calculs de déplacements isotopiques présentés plus loin. Les applications les plus récentes de la méthode Hy concernent l'atome à quatre électrons (Szasz et Byrne, 1967 ; Sims et Hagstrom, 1971). Notons que des applications de la méthode Hy à des atomes plus complexes ont été faites en conjonction avec des fonctions de paires dans des calculs de type Bethe-Goldstone (Szasz et McGinn, 1972), ce qui nous permet de rappeler que notre classification (perturbations, SOC, Hy) ne doit pas être utilisée avec trop de rigidité.

Les méthodes SOC présentent l'avantage sur la méthode Hy de ne pas sacrifier le concept d'orbitales (monoélectroniques). De plus, elles ne font pas intervenir le continuum, dont l'introduction dans la théorie des perturbations est plus un artifice mathématique qu'une réalité physique lorsqu'on s'intéresse seulement à des états liés. Les méthodes SOC semblent aussi être avantageuses sur MBPT lorsqu'il s'agit de faire le tri des excitations à conserver et à négliger. Elles utilisent une fonction d'onde Φ , approximation de Ψ , de la forme :

$$|\Phi\rangle = \alpha|f\rangle + \beta_1|e_1\rangle + \beta_2|e_2\rangle + \ldots \qquad (3)$$

où $|f\rangle$, $|e_1\rangle$, $|e_2\rangle$ ... sont des termes Russell-Saunders (RS) ayant les mêmes valeurs SL . Certains auteurs désignent ces termes RS par l'appellation de configurations. Bien sûr une configuration (au sens spectroscopique habituel) peut donner plusieurs termes RS dans le développement (3). Les orbitales apparaissant dans $|f\rangle$ seront désignées sous le nom d'orbitales du coeur, celles qui apparaissent seulement dans les $|e_i\rangle$ sous le nom d'orbitales virtuelles ou excitées.

Deux sortes de procédés SOC peuvent être distingués.

Le premier procédé SOC est la méthode d'interaction de configurations (CI) (Hylleraas, 1929) dans laquelle, partant d'orbitales données à l'avance, on obtient les poids des configurations par diagonalisation de la matrice de l'énergie. En pratique, les divers auteurs optimisent d'une manière ou d'une autre les orbitales de départ.

Le deuxième procédé est la méthode Hartree-Fock multiconfigurationnelle (MCHF) (Hartree et al., 1939). La forme optimale des orbitales apparaissant dans la fonction d'onde est déterminée par itération jusqu'à convergence d'un système d'équations. Les orbitales sont obtenues sous forme numérique point par point (Froese-Fischer, 1969) ou sous forme analytique (Sabelli et Hinze, 1969).

Pour des calculs très précis, dans la méthode CI les termes RS prolifèrent et dans la méthode MCHF ce sont les orbitales qui deviennent très nombreuses. Dans les deux cas l'interprétation physique de Hartree-Fock simple est perdue. Citons par exemple pour l'état fondamental $1s^2 2s^2$ du Be le calcul MCHF de Froese-Fischer et Saxena (1974) comportant 13 orbitales s , 16p , 12d , 4f et 3g (et qui, de plus, sont non orthogonales) et 52 termes RS , qui est légèrement moins précis que le calcul CI de Bunge (1976), utilisant 10 orbitales orthogonales s , 9p , 8d , 7f , 5g , 3h et 1i et 650 termes RS.

L'introduction d'orbitales naturelles (Löwdin, 1955) permet de réduire le nombre de termes RS utilisés dans les calculs CI . Ainsi, par exemple, $\alpha\ 1s^2 + \beta\ 1s2s + \gamma\ 2s^2$ peut être remplacé par $\alpha' 1s'^2 + \beta' 2s'^2$ en modifiant les orbitales de départ. Les orbitales déterminées dans les calculs MCHF , n'étant pas fixées à l'avance, sont aussi des orbitales naturelles. Cela explique que le nombre de termes RS est moindre dans les calculs MCHF que dans les calculs CI de précision comparable.

Pour des calculs d'une moins haute précision la méthode MCHF nous paraît beaucoup plus satisfaisante : on peut en effet se limiter à peu d'orbitales et peu de configurations qui, ainsi, ont encore un sens physique intuitif. Il n'en est évidemment pas de même pour la méthode CI . C'est justement dans ce cadre que se place notre travail. Nous cherchons à évaluer des grandeurs physiques pour des atomes complexes (le plus complexe ici est l'atome de titane à 22 électrons), aussi devons-nous limiter nos prétentions pour la précision atteinte. Nous allons donc maintenant décrire notre méthode (§.1.2.2 pour les questions angulaires et §.1.2.3 pour les questions radiales) ; les applications à des calculs physiques sont décrites dans le prochain chapitre (§.2) .

1.2.2 Choix des termes excités.

Nous choisissons les termes du développement (3) selon le problème physique étudié. Supposons que nous voulions calculer la valeur moyenne de l'opérateur A . Au deuxième ordre (on suppose $|\beta_j| << \alpha$ dans (3)), les seuls termes $|e_j\rangle$ qui sont utiles dans (3) sont ceux tels que :

$$\langle f|H|e_j\rangle \langle e_j|A|f\rangle \neq 0 \quad . \qquad (4)$$

Ainsi donc dans (3) nous ne garderons que des termes satisfaisant à (4). Il est clair que $|e_j\rangle$ diffère de $|f\rangle$ par au plus deux orbitales (H est biélectronique). Si A est un opérateur monoélectronique, comme par exemple un opérateur de structure hyperfine, $|e_j\rangle$ diffère de $|f\rangle$ par une seule orbitale.

De plus, pour une configuration excitée donnée (obtenue par une bi- ou monoexcitation de $|f\rangle$), il est possible de choisir une base des termes RS de la configuration

$$|e_1\rangle , |e_2\rangle \dots |e_k\rangle , |e'_1\rangle \dots |e'_\ell\rangle \qquad (5)$$

telle que les k premiers termes $|e_j\rangle$ $(1 \leqslant j \leqslant k)$ vérifient (4), tandis que les ℓ derniers termes $|e'_j\rangle$ $(1 \leqslant j \leqslant \ell)$ ne vérifient pas (4) , c'est-à-dire ne contribuent pas au deuxième ordre de A . Un tel choix peut être fait par des considérations angulaires seulement et est alors indépendant de la partie radiale des orbitales. Dans notre article (annexe A) nous décrivons en détail comment on peut construire la base (5) en la réduisant pour que k soit minimal. Le principe de la méthode est fondé sur le fait que le coefficient angulaire de l'élément de matrice $\langle f|O_p^X|e_j\rangle$ (O_p^X ($p = 1, 2 \ldots$) désignant les composantes de $X = H$ ou A de forme angulaire définie) est égal à la projection du vecteur $|e_j\rangle$ sur un certain vecteur $|a_p^X\rangle$. Les termes cherchés $|e_1\rangle \ldots |e_k\rangle$ (avec k minimal) forment une base de l'intersection des espaces vectoriels E^H et E^A où E^X désigne l'espace engendré par les $|a_p^X\rangle$ ($p = 1, 2 \ldots$). Par exemple, lorsque A est un opérateur de structure hyperfine, la valeur minimale de k est 1. Autrement dit, dans le développement de la fonction d'onde Φ, on ne garde qu'un terme par configuration excitée, ce qui est à rapprocher du fait que dans les interprétations empiriques il n'y a qu'un paramètre non diagonal de structure hyperfine (pour un opérateur donné) par configuration excitée. Lorsque A est l'opérateur de déplacement isotopique spécifique, la valeur minimale de k est 1 en général (ou exceptionnellement 2).

Nous avons écrit un programme EXCGH (annexe C) qui construit les termes excités $|e_j\rangle$ et calcule la partie angulaire des éléments de matrices de l'énergie et des opérateurs A intéressants. Comme entrée de ce programme on donne l'état fondamental $|f\rangle$ sous la forme d'une somme pondérée de déterminants de Slater et les configurations excitées désirées sous la forme d'excitations $ab \rightarrow cd$ faites à partir de $|f\rangle$. L'opérateur A pour lequel on effectue la réduction peut être H , l'opérateur de déplacement isotopique spécifique Σ (défini plus loin §.2.1), un quelconque des opérateurs de structure hyperfine (s , ℓ , sC^2 , C^2) ou la réunion de ces 4 types, l'opérateur spin-orbite $\sum_i \vec{s}_i\,\vec{\ell}_i$ ou l'opérateur dipolaire C^1 . Ce dernier cas utilise des possibilités supplémentaires du programme EXCGH (plusieurs fondamentaux) que nous ne décrirons pas ici, mais qui sont exposées en détail dans l'annexe C. L'utilisation du programme EXCGH est facilitée par le programme TERM (décrit dans l'annexe B) qui permet d'obtenir par la méthode des opérateurs de projection le développement en déterminants de Slater de l'état $|f\rangle$ écrit dans la notation spectroscopique.

1.2.3 Détermination des orbitales radiales.

Ayant choisi ainsi la forme angulaire de Φ , l'étape suivante du calcul est la détermination des orbitales radiales, d'où découlera aisément le calcul de la grandeur physique. Les orbitales radiales peuvent être déterminées par la méthode MCHF à l'aide d'une version du programme de Froese-Fischer (1969) implantée par Bagus au Centre de Calcul CIRCE. Cependant, lorsque les orbitales virtuelles ont des nombres d'occupation petits, il est difficile d'obtenir la convergence de la méthode si on ne possède pas une bonne approximation de départ. C'est principalement cette raison qui nous a conduit à développer le programme ESSAI1 décrit dans l'annexe D. Il s'agit d'un programme variationnel déterminant des orbitales sous la forme paramétrée de sommes de fonctions de Slater. L'optimisation des paramètres se fait par la méthode du simplexe (Nelder, 1965), méthode qui a été popularisée au Laboratoire Aimé Cotton par les travaux de Klapisch (1971) sur le potentiel paramétrique. Comme chaque orbitale dépend de peu de paramètres (1 à 5 en général), il n'y a plus de problèmes de convergence. D'autres possibilités du programme ESSAI1 sont : a) l'introduction dans l'énergie d'intégrales I du champ central non diagonales ; b) les orbitales peuvent ne pas être orthogonales, à condition que le produit scalaire de deux termes RS ne soit pas plus compliqué que le produit de deux intégrales de recouvrements ; c) obtention d'orbitales virtuelles au sens de Sternheimer (1950, 1967). Cette obtention est réalisée par exemple en remplaçant les intégrales non diagonales de l'énergie par $(a/r^{-3}/b)$ pour la structure hyperfine.

Les possibilités a) et b) ci-dessus avaient été incluses dans le programme pour étudier le cas du magnésium qui est décrit plus loin (annexe E), car la version du programme MCHF de Froese-Fischer, déjà citée, interdit les intégrales I non diagonales et la non-orthogonalité. Notons cependant que le nouveau programme MCHF de Froese-Fischer (1977) n'a plus ces limitations.

CHAPITRE 2

CALCULS A PRIORI DE DEPLACEMENTS ISOTOPIQUES SPECIFIQUES ET DE STRUCTURES HYPERFINES.

2.1 CALCULS DE DEPLACEMENTS ISOTOPIQUES SPECIFIQUES : He, Mg .

La mesure expérimentale des déplacements isotopiques ne permet de déterminer que la somme de l'effet de volume dû à la taille finie du noyau et de l'effet de masse dû à l'entraînement du noyau par les électrons (voir par exemple Bauche et Champeau, 1976). A partir de ces seules mesures, on ne peut donc remonter aux paramètres nucléaires que par le calcul a priori de l'effet de masse, qui se décompose d'ailleurs en un effet dit normal trivial à calculer (du moins lorsqu'on néglige les corrections relativistes) et un effet spécifique qui est donné par l'opérateur biélectronique $\Sigma = \frac{1}{M} \sum_{1 \leqslant i < j \leqslant N} \vec{p}_i \cdot \vec{p}_j$ pour un noyau de masse M , $\vec{p}_i$ étant l'impulsion de l'électron i . Il nous a donc paru intéressant d'aller au-delà de l'approximation Hartree-Fock dans les calculs de déplacements isotopiques spécifiques. Nous avons choisi l'atome d'hélium, pour lequel on dispose de calculs très précis déjà cités (Schiff et al., 1955) et de celui de magnésium pour lequel on connaît les valeurs expérimentales du déplacement isotopique spécifique, l'effet de volume étant négligé dans cet atome très léger.

Nous avons restreint l'étude aux deux termes $^{1,3}P$ de la configuration sp la plus basse. Les détails de cette étude se trouvant dans l'article de l'annexe A, nous nous bornons ici à commenter les résultats (tableau 1 pour He , tableau 3 pour Mg).

Examinons d'abord les résultats du deuxième ordre pour Mg . Lorsque l'élément de matrice de l'interaction électrostatique entre le fondamental (^{1}P ou ^{3}P) et un terme excité a la même expression littérale pour ^{1}P et ^{3}P on pourrait s'attendre à ce que ce terme excité ne contribue pas au deuxième ordre de $\Delta\sigma$, différence des déplacements spécifiques de ces deux termes. Cela serait strictement vrai dans le modèle du champ central, les orbitales radiales étant les mêmes dans les deux termes fondamentaux ^{1}P et ^{3}P . Mais ici ces orbitales sont différentes, provenant de deux calculs "HF simple" séparés, et la contribution à $\Delta\sigma$ des états excités donnant la même expression littérale du 2ème ordre pour les termes ^{1}P et ^{3}P est aussi importante que celle des autres états excités (tableau 3 de l'annexe A).

Notre résultat au 2ème ordre pour Mg est très peu satisfaisant et même moins bon que le résultat obtenu par les calculs "HF simple". Le fait de négliger les effets relativistes (spin-orbite) ne semble pas être en cause. En effet le couplage LS est excellent pour la configuration 3s3p de Mg . Nous attribuons donc l'écart entre notre valeur et la valeur expérimentale à des effets d'ordres supérieurs.

Cela est confirmé par les calculs concernant He (tableau 1 de l'annexe A). Là aussi les résultats du deuxième ordre restent loin des valeurs exactes, alors que les calculs multiconfigurationnels utilisant les 4 configurations 1s2p , 2pd , sp et p'd' redonnent à 1% près les valeurs exactes du déplacement isotopique spécifique. Ces calculs, qui ont été faits à l'aide du programme ESSAI1 déjà décrit, chaque orbitale dépendant de 5 paramètres, peuvent être considérés comme étant des calculs MCHF comportant des orbitales non orthogonales (p et p' ainsi que d et d'). En comparant ces résultats avec ceux bien moins bons de calculs MCHF à orbitales orthogonales, on voit l'intérêt que présentent les calculs MCHF à orbitales non orthogonales. L'importance critique des effets d'ordres supérieurs semble venir de ce que nous calculons la valeur moyenne d'un opérateur biélectronique. Ces effets d'ordres supérieurs se font-ils moins sentir sur les valeurs moyennes d'opérateurs monoélectroniques ? Nous examinons cette question au paragraphe suivant pour la structure hyperfine.

2.2 CALCULS DES PARAMETRES $\langle r^{-3}\rangle$ DE STRUCTURE HYPERFINE DANS Mg , Sc , Ti .

Il est commode d'interpréter les résultats expérimentaux de structure hyperfine (hfs) en fonction des paramètres $|\Psi_s(0)|^2$, $\langle r^{-3}\rangle_\ell$, $\langle r^{-3}\rangle_{sC^2}$ et $\langle r^{-3}\rangle_{C^2}$ (voir par exemple Bauche-Arnoult et Bauche, 1968).

Les grandeurs $\langle r^{-3}\rangle_\ell$, $\langle r^{-3}\rangle_{sC^2}$ et $\langle r^{-3}\rangle_{C^2}$, égales dans l'approximation monoconfigurationnelle, sont différentes par suite des corrélations et de corrections relativistes. Nous nous sommes ici intéressés au calcul du deuxième ordre de ces grandeurs. Notre méthode est particulièrement bien adaptée à ce genre de calcul. En effet, nous voulons calculer la valeur moyenne d'un opérateur monoélectronique et, dans ce cas, le nombre de termes excités nécessaires est très limité. Par contre, il est théoriquement infini dans le cas des opérateurs biélectroniques car on doit considérer des séries d'excitations du type : $2p^2 \rightarrow p_I^2$, $2p^2 \rightarrow p_{II}^2$, $2p^2 \rightarrow p_{III}^2$, ... Le programme EXCGH permet de déterminer rapidement les éléments de matrice angulaires nécessaires. On peut ensuite déterminer les orbitales virtuelles, soit à l'aide du programme MCHF de Froese, soit à l'aide du programme ESSAI1 . Le recours à ce dernier programme est d'ailleurs la seule méthode que nous ayons lorsque le poids des termes excités est trop faible.

2.2.1 Cas du magnésium.

Notre première application concerne les termes $3s3p\ ^{1,3}P$ de Mg I . On a en effet la surprise de constater, en examinant les valeurs expérimentales de $\langle r^{-3}\rangle$, qu'elles sont très différentes dans les deux termes (alors qu'elles sont identiques dans l'approximation du potentiel central) : $\langle r^{-3}\rangle_{sC^2}(^3P) = 0{,}809 \pm 0{,}009$ et $\langle r^{-3}\rangle_{\ell}(^1P) = 0{,}257 \pm 0{,}021$ (en u.a.) . L'article de l'annexe E décrit comment nous avons réussi à bien interpréter ces valeurs expérimentales, et aussi à évaluer le moment quadrupolaire de ^{25}Mg . Soulignons le point suivant : L'interprétation de la valeur expérimentale $\langle r^{-3}\rangle_{\ell}(^1P)$ n'était pas possible dans le cadre de l'approximation du deuxième ordre et nous avons dû faire intervenir des effets d'ordre supérieur. Pour cela nous avons fait un calcul MCHF sur $3s3p + d_{III}3p$. Un tel calcul ne donne pas seulement les effets du deuxième ordre dus à l'excitation $3s \rightarrow d_{III}$ (ce deuxième ordre est d'ailleurs nul pour le terme ^1P), mais aussi des effets d'ordres supérieurs. Ces effets viennent principalement de la modification de l'orbitale 3p par rapport à un calcul HF et sont assez faibles pour le terme ^3P , mais très importants pour le terme ^1P . La répulsion électrostatique entre les électrons 3s et 3p est plus grande pour le terme ^1P que pour le terme ^3P dans le modèle HF . Comme l'orbitale 3s , plus interne, varie peu d'un terme à l'autre, l'orbitale 3p très extérieure, est trop extérieure pour le terme ^1P . Cela est corrigé par l'introduction de la configuration $d_{III}3p$ dans le calcul MCHF , la valeur moyenne de r^{-3} pour l'orbitale 3p étant plus que doublée pour le terme ^1P . Physiquement l'importance de la configuration $d_{III}3p$ vient de ce que la configuration 3d3p n'est expérimentalement pas très au-dessus de la configuration 3s3p dans Mg I . Notons que l'orbitale d_{III} a la forme d'une orbitale 3d . Le calcul MCHF $3s3p + d_{III}3p$ fait intervenir d'autres effets d'ordre supérieur. D'une part l'effet assez faible de la modification du poids de la configuration $3s3p$, d'autre part les effets indirects dus au fait que c'est l'orbitale $3p$ modifiée qui est utilisée pour les autres calculs du deuxième ordre. Un de ces effets indirects est que pour l'orbitale $3p$ modifiée l'excitation vers le terme de Brillouin $3p \rightarrow p_{III}$ intervient maintenant au deuxième ordre. Notons que cette excitation a été prise en compte dans le calcul "MCHF" (les guillemets indiquent que le calcul a été fait à l'aide du programme ESSAI1) : $3s3p + d_{III}3p'$ équivalent à un calcul $3s3p + d_{III}3p + 3s\ p_{III}$.

2.2.2 Cas du scandium et du titane.

Notre deuxième application, exposée en annexe F, concerne les termes de Hund de $3d^N4s^2$ pour Sc (N=1) et Ti (N=2) . C. Bauche-Arnoult (1971) a montré que dans ce cas le rapport $\alpha = \langle r^{-3} \rangle_{\ell} / \langle r^{-3} \rangle_{sC^2}$ calculé au deuxième ordre des perturbations, en négligeant l'excitation $3d \rightarrow g$, a la même expression littérale pour Sc et Ti . Or, expérimentalement, $\alpha = 1,123 \pm 0,010$ pour Sc et $\alpha = 1,03$ pour Ti . Il nous a donc paru intéressant de calculer a priori les valeurs du deuxième ordre de ce rapport α à l'aide de nos programmes. Nous avons pu ainsi examiner l'influence des légères variations des orbitales radiales lorsqu'on passe de Sc à Ti et aussi l'influence de l'excitation $3d \rightarrow g$. Là encore il reste un désaccord entre les valeurs expérimentales et les valeurs théoriques du deuxième ordre, ce qui nous avait amené à supputer que les effets d'interaction proche ou d'ordres supérieurs sont importants. Ceci a été confirmé par l'étude de Bauche et Bauche-Arnoult (1977).

2.3 REMARQUES SUR LES EFFETS D'ORDRES SUPERIEURS AU DEUXIEME.

Nous avons vu (§.B) l'importance des effets d'ordres supérieurs au deuxième pour le déplacement isotopique spécifique, importance que nous avons attribuée au caractère biélectronique de l'opérateur. En effet, en examinant le livre "La Structure Hyperfine des Atomes et des Molécules" édité par Lefebvre et Moser (1967) on se rend compte que le deuxième ordre interprète bien les paramètres de structure hyperfine (terme de contact excepté). Dans les cas que nous avons étudiés en structure hyperfine, nous avons vu apparaître des effets d'ordre supérieurs au deuxième, mais de façon moins dramatique que pour le déplacement isotopique spécifique. Cependant, ces effets d'ordres supérieurs peuvent aussi être très importants en structure hyperfine. Citons les calculs de Nesbet (1970) et ceux de Hameed et Foley (1972) du paramètre $\langle r^{-3}\rangle_{C^2}$ pour le terme $2\ ^2P$ de Li I . Ces auteurs montrent que les corrections du troisième ordre annulent pratiquement la correction du deuxième ordre (la correction Sternheimer). De tels calculs d'ordres supérieurs au deuxième sont très difficiles, même pour un atome à 3 électrons comme Li . La classification de Sinanoglu (1969) des effets de corrélation est alors certainement utile pour les atomes complexes. D'après lui les biexcitations importantes dans les calculs de valeurs moyennes d'opérateurs monoélectroniques sont les excitations internes et semi-internes.

CHAPITRE 3

INTERPRETATIONS EMPIRIQUES
DE DEPLACEMENTS ISOTOPIQUES PAIR-IMPAIR ANORMAUX.

3.1 ECARTS à LA DROITE DE KING.

Nous avons déjà indiqué qu'expérimentalement on ne pouvait pas séparer l'effet de masse de l'effet de volume dans le déplacement isotopique. De façon plus précise, la variation d'énergie d'un niveau $\Delta E(A,A')$ entre les isotopes de nombres de masse A et A' ($A'>A$, $\Delta E(A,A') = E_{A'}-E_A$) s'écrit (voir par exemple Bauche et Champeau, 1976):

$$\Delta E(A,A') = P \times C(A,A') + \left(\frac{1}{A} - \frac{1}{A'}\right) K \quad . \qquad (1)$$

Le premier terme dans le membre de droite, qui rend compte de l'effet de volume, est le produit d'une grandeur électronique P , qui ne dépend que du niveau considéré, par un facteur $C(A,A')$ dépendant seulement des propriétés nucléaires des noyaux. Le deuxième terme, qui décrit l'effet de masse, s'exprime à l'aide d'une grandeur électronique K fonction du niveau (en fait $K = \langle \frac{-1}{m_n} \left(\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2} + \sum_{N \geqslant i > j \geqslant 1} \vec{p}_i \, \vec{p}_j \right) \rangle$ où les deux sommes correspondent aux effets de masse normal et spécifique respectivement et où l'unité de masse atomique m_n vaut 1822,5 masses de l'électron).

On obtient le déplacement isotopique d'une transition $\Delta\nu(A,A')$ en prenant la différence de deux équations du type (1) :

$$(A,A') = P_t \times C(A,A') + (\frac{1}{A} - \frac{1}{A'})\ K_t \quad . \tag{2}$$

De même pour une autre transition on a :

$$\Delta\nu'(A,A') = P_{t'} \times C(A,A') + (\frac{1}{A} - \frac{1}{A'})\ K_{t'} \quad .$$

Portant sur un même graphique $x = \dfrac{\Delta\nu(A,A')}{\frac{1}{A} - \frac{1}{A'}}$ et $y = \dfrac{\Delta\nu'(A,A')}{\frac{1}{A} - \frac{1}{A'}}$

pour diverses paires d'isotopes on obtient des points situés sur la droite d'équation paramétrique (droite de King) :

$$\begin{cases} x = P_t\ u + K_t \\ y = P_{t'}\ u + K_{t'} \end{cases}$$

correspondant à diverses valeurs du paramètre $u = \dfrac{C(A,A')}{\frac{1}{A} - \frac{1}{A'}}$.

La relation (1) est très bien vérifiée expérimentalement. Cependant les droites de King publiées par Hansen et al. (1967) semblent indiquer que certains points correspondant à des couples pair-impair s'écartent de la droite, l'écart étant du même ordre de grandeur que les incertitudes expérimentales. Ces points concernent des déplacements mesurés avec une grande précision de 5 transitions optiques du samarium et du néodyme. Ce sont ces écarts que nous avons essayé d'interpréter.

3.2 CAS DU SAMARIUM.

Le déplacement isotopique d'un niveau $|\alpha J\rangle$, pour un isotope impair est obtenu en prenant la moyenne pondérée par les poids statistiques $2F+1$ sur les sous-niveaux $|\alpha JF\rangle$. Il est donc affecté par l'opérateur de structure hyperfine au deuxième ordre des perturbations. Nous avons étudié (article de l'annexe H) 127 niveaux des sous-configurations $f^6\ {}^7F\ sp$, $f^5\ {}^6H\ ds^2$ et $f^5\ {}^6F\ ds^2$ de ${}^{147}Sm$ $(I=7/2)$ et ${}^{149}Sm$ $(I=7/2)$ en utilisant la méthode classique de Woodgate (1966). Pour la partie dipolaire magnétique, la contribution du deuxième ordre a la forme du produit $\frac{I+1}{I}\mu^2$ (I spin du noyau, $\frac{\mu}{I}$ facteur de Landé nucléaire) par une quantité électronique. Cette proportionnalité à $\frac{I+1}{I}\mu^2$ est en désaccord avec les mesures expérimentales dans le samarium, puisque l'isotope de $|\mu|$ le plus faible donne le plus grand effet. Ce désaccord ne vient pas de la partie quadrupolaire électrique de l'opérateur hfs qui s'est révélée être négligeable devant la partie dipolaire. Cependant les valeurs numériques, obtenues à l'aide des fonctions d'onde de l'étude empirique de Carlier et al. (1968), étant inférieures à $0{,}1\ 10^{-3}\ cm^{-1}$ mettent en doute l'existence d'écarts observables à la droite de King, puisque le seuil d'observation est de l'ordre de $10^{-3}\ cm^{-1}$. Notons toutefois que notre calcul du deuxième ordre est incomplet car il ne fait intervenir que des niveaux perturbateurs proches.

3.3 CAS DU MERCURE.

Les configurations 6snd des isotopes impairs du mercure sont un exemple connu depuis les travaux de Schüler et Jones (1932) et de Casimir (1932) où le deuxième ordre de structure hyperfine est mesurable. Les structures fines et hyperfines y sont du même ordre de grandeur. Nous avons étudié les configurations 6snd des isotopes 199 et 201 par une variante de la méthode empirique consistant à diagonaliser l'hamiltonien comprenant l'opérateur de structure hyperfine. Cette étude est résumée dans la table VII de l'article de l'annexe G. On peut voir qu'elle permet de bien interpréter les déplacements pair-impairs anormaux en remarquant que les paramètres a_{6s} de structure hyperfine que nous avons obtenus sont les mêmes que ceux déterminés par Gerstenkorn et Vergès (1975) (ces auteurs déterminent des valeurs expérimentales des déplacements isotopiques dus au deuxième ordre de structure hyperfine par comparaison avec les déplacements isotopiques pair-pair, et ils obtiennent les paramètres a_{6s} après correction des intervalles de structure hyperfine par ce 2ème ordre).

Le phénomène physique étudié dans les cas du samarium et du mercure est le même, mais l'ordre de grandeur diffère, ce qui explique que nous ayons traité l'opérateur de structure hyperfine comme une perturbation pour Sm et à l'égal des opérateurs électrostatiques et spin-orbite pour Hg .

2ème Partie

FONCTION GENERATRICE des COEFFICIENTS de COUPLAGE-RECOUPLAGE de SU(2)

Nous rappelons des propriétés des fonctions génératrices (§.1) et des coefficients de couplage-recouplage (§.2). Notre travail est ensuite présente au §.3 .

1. DEFINITION ET UTILITE DES FONCTIONS GENERATRICES.

Lorsqu'on étudie des grandeurs f_k dépendant de l'indice $k=1,2,3...$ il est souvent avantageux d'introduire une fonction génératrice des f_k , c'est-à-dire une fonction :

$$F(x) = \sum_{k=1,2...} n_k \, f_k \, x^k \qquad (1)$$

où les n_k sont des coefficients arbitraires. La définition précédente s'étend à des grandeurs $f_{ijk...}$ dépendant de plusieurs indices prenant des valeurs entières : la fonction génératrice est alors fonction de plusieurs variables x, y, z .... Dans le cas de la fonction génératrice des coefficients de couplage-recouplage les grandeurs $f_{ijk...}$ sont des nombres, mais, dans ce paragraphe, nous allons examiner le cas plus général où ces grandeurs sont des fonctions, en nous limitant toutefois à un indice : $f_k(z)$, la fonction génératrice étant notée $F(x,z)$.

Des exemples classiques de tels $f_k(z)$ sont les polynomes d'Hermite, de Laguerre ou de Legendre. Remarquons que la liberté de choix des coefficients n_k est limitée par des raisons pratiques : $F(x,z)$ et les n_k doivent être suffisamment simples. Ainsi, pour les polynomes de Laguerre le choix le plus commun est :

$$\frac{e^{-zx/(1-x)}}{(1-x)^{a+1}} = \sum_{k=0}^{\infty} \frac{x^k}{\Gamma(k+a+1)} L_k^a(z) \quad .$$

Mais un autre choix des coefficients n_k est parfois utilisé (Morse et Feshbach (1953) p. 937) :

$$\frac{J_a(2\sqrt{xz})}{(xz)^{a/2}} e^x = \sum_{k=0}^{\infty} \frac{x^k}{[\Gamma(k+a+1)]^2} L_k^a(z) \quad .$$

On voit que $f_k(z)$ est obtenu en développant $F(x,z)$ en série de x . Si $F(x,z)$ est holomorphe en x dans un domaine de bord c contenant l'origine, on obtient pour les $f_k(z)$ des représentations intégrales :

$$n_k \, f_k(z) = \frac{1}{2\pi i} \oint_c F(x,z) \, x^{-k-1} \, dx \quad .$$

Donnons maintenant un exemple de détermination de fonction génératrice, celle des fonctions d'onde de l'oscillateur harmonique de fréquence ω ($\hbar = m = 1$) à une dimension : $f_i(z) = \langle z|i\rangle$, où l'état $|i\rangle$ s'obtient à partir de l'état fondamental $|0\rangle$ par i applications de l'opérateur création a^+ . Définissons la fonction génératrice suivante:

$$F(x,z) = \sum_{i=0}^{\infty} \frac{x^i}{\sqrt{i!}} f_i(z) = \langle z|e^{xa^+}|0\rangle \quad .$$

En utilisant $\langle z|a^+|\Psi\rangle = \left(\sqrt{\frac{\omega}{2}}\, z - \frac{1}{\sqrt{2\omega}} \frac{\partial}{\partial z}\right) \langle z|\Psi\rangle$, on voit qu'elle vérifie l'équation :

$$\frac{\partial F(x,z)}{\partial x} = \left(\sqrt{\frac{\omega}{2}}\, z - \frac{1}{\sqrt{2\omega}}\frac{\partial}{\partial z}\right) F(x,z) \quad .$$

Cette équation, avec la condition initiale :

$F(0,z) = f_0(z) = (\frac{\omega}{\pi})^{1/4}\ e^{-\omega z^2/2}$, suffit pour déterminer $F(x,z)$:

$$F(x,z) = (\frac{\omega}{\pi})^{1/4}\ e^{-(\omega z^2+x^2)/2+\sqrt{2\omega}\, xz} \quad .$$

Cette fonction génératrice est d'ailleurs la fonction génératrice habituellement utilisée des polynomes d'Hermite car :

$$f_i(z) = (\frac{\omega}{\pi})^{1/4}\ \frac{1}{\sqrt{2^i\ i!}}\ e^{-\omega z^2/2}\ H_i(z\sqrt{\omega}) \quad .$$

L'exemple précédent est une application de la technique d'obtention de fonction génératrice basée sur la représentation d'algèbres de Lie par des opérateurs différentiels. Ici l'algèbre engendrée par a (opérateur annihilation), a^+ et 1 est réalisée par les opérateurs $\sqrt{\frac{\omega}{2}}\, z \pm \frac{1}{\sqrt{2\omega}}\frac{\partial}{\partial z}$ et 1 . L'introduction de l'opérateur a permet de déterminer $f_0(z)$ par la condition $\left(\sqrt{\frac{\omega}{2}}\, z + \frac{1}{\sqrt{2\omega}}\frac{\partial}{\partial z}\right) f_0(z) = 0$. Cette technique a été appliquée par Miller (1968) aux algèbres de dimension 3 (donnant les fonctions génératrices des polynomes d'Hermite, de Laguerre et de Legendre). Une application plus complexe, celle de Kyriakopoulos (1974), concernant les fonctions hypergéométriques utilise une algèbre de dimension 6.

Les fonctions génératrices permettent d'obtenir simplement un grand nombre de propriétés des $f_i(z)$. Nous avons déjà vu comment elles fournissaient des représentations intégrales. En dérivant $F(x,z)$ par rapport à x et z on obtient des relations de récurrence entre les

$f_i(z)$. Une autre application est le calcul d'intégrales contenant les $f_i(z)$: citons par exemple le calcul des grandeurs atomiques des états liés de l'atome d'hydrogène qui peut être fait à l'aide de la fonction génératrice des polynomes de Laguerre (Condon et Shortley, p. 115).

Les fonctions génératrices peuvent aussi intervenir dans la résolution de certaines équations intégrales (Morse et Feshbach (1953), p. 935). Considérons le cas où les $f_i(z)$ forment une base orthonormée pour le produit scalaire $(f,g) = \int f(z)\, g(z)\, d\mu(z)$.

L'équation intégrale en φ : $A(x) = \int F(x,z)\, \varphi(z)\, d\mu(z)$ peut alors être résolue en développant $\varphi(z)$ sur la base $f_i(z)$:

$\varphi(z) = \Sigma\, a_i\, f_i(z)$. L'équation intégrale devient alors :

$A(x) = \sum_i n_i\, a_i\, x^i$ et l'obtention des inconnues a_i se ramène au développement en série de $A(x)$.

2. REPRESENTATION GRAPHIQUE DES COEFFICIENTS DE COUPLAGE-RECOUPLAGE.

Les couplages et recouplages de moments cinétiques s'expriment à l'aide des coefficients de Clebsch-Gordan (ou des symboles 3j). Les méthodes de Racah permettent d'exprimer la partie angulaire des éléments de matrice de grandeurs atomiques en termes de coefficients de couplage-recouplage. Les cas les plus simples donnent des formules contenant un petit nombre de symboles 3j , 6j ou 9j , mais dans les cas complexes où un grand nombre de moments cinétiques intervient, il devient utile d'utiliser la représentation graphique des coefficients de couplage-recouplage. Cette représentation graphique permet non seulement de visualiser les coefficients de couplage-recouplage, mais aussi de fournir des méthodes de calcul par réduction aux symboles 3j et 6j . La représentation graphique des 3j et les méthodes de calculs de sommes de produits de 3j ayant été inventées par Levinson (1956 a et b, 1957), c'est à tort que nous avons utilisé dans notre article (annexe I) l'appellation de graphes de Jucys (les modifications introduites par Jucys, lignes de deux épaisseurs, sont surtout d'ordre pratique). Des exposés complets de ce traitement graphique se trouvent dans les livres de Jucys et al. (1965) et de El Baz et al. (1969).

Indiquons maintenant le principe de la représentation graphique.

Le coefficient 3j est représenté par une étoile à 3 branches (voir figure 1 de l'annexe I) . Un produit de 3j est représenté par la réunion des graphes des 3j du produit. Une sommation sur un nombre quantique magnétique m : $\sum_{m} (-)^{j-m} \begin{pmatrix} \cdot & \cdot & j \\ \cdot & \cdot & m \end{pmatrix} \begin{pmatrix} \cdot & \cdot & j \\ \cdot & \cdot & -m \end{pmatrix}$ d'un tel produit est représentée en reliant les branches j (voir figure 5 de l'annexe I). Les graphes des coefficients 6j et 9j qui s'obtiennent par sommations sur tous les nombres quantiques magnétiques de produits de 4 ou 6 coefficients 3j sont représentés sur les figures 12 et 13 de l'annexe I.

Bien que les règles de réduction des graphes aient une importance pratique considérable, nous ne les décrirons pas ici car nous ne les avons pas utilisées.

3. FONCTION GENERATRICE DES COEFFICIENTS DE COUPLAGE-RECOUPLAGE.

3.1 Fonction génératrice des 3j .

Au lieu des 6 indices j_1, m_1 , j_2, m_2 , j_3, m_3 liés par la relation $m_1 + m_2 + m_3 = 0$ du 3j on peut introduire les 9 indices suivants :

$$k_1 = -j_1 + j_2 + j_3$$

$$k_2 = j_1 - j_2 + j_3$$

$$k_3 = j_1 + j_2 - j_3$$

$$K_i = j_i + m_i \quad , \quad \lambda_i = j_i - m_i \quad (i = 1,2,3) \quad .$$

La condition triangulaire sur j_1, j_2, j_3 et le fait que les j_i soient entiers ou demi-entiers sont alors équivalents à ce que les k_i soient des entiers non négatifs. La condition que m_i soit projection de j_i est équivalente à la condition que K_i et λ_i soient des entiers non négatifs. Notons toutefois que les neuf nouveaux indices ne sont pas indépendants. En posant :

$$L = \begin{pmatrix} k_1 & k_2 & k_3 \\ K_1 & K_2 & K_3 \\ \lambda_1 & \lambda_2 & \lambda_3 \end{pmatrix} \quad , \text{ les conditions de dépendance}$$

s'expriment par le fait que L est un carré magique (la somme des lignes et des colonnes est constante).

En représentant par G_L la valeur du 3j $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ si L est magique et en posant $G_L = 0$ sinon, on peut définir une fonction génératrice des coefficients 3j sous la forme :

$$\Phi_{3j}(\tau_1,\tau_2,\tau_3,\xi_1,\xi_2,\xi_3,\eta_1,\eta_2,\eta_3)$$
$$= \Sigma\ N_L\, G_L\, \tau_1^{k_1}\ \tau_2^{k_2}\ \tau_3^{k_3}\ \xi_1^{K_1}\ \xi_2^{K_2}\ \xi_3^{K_3}\ \eta_1^{\lambda_1}\ \eta_2^{\lambda_2}\ \eta_3^{\lambda_3}$$

où la somme porte sur les entiers non négatifs $k_1,k_2 \ldots \lambda_3$. Schwinger (1952) a montré qu'en choisissant pour valeur de N_L :

$$N_L = \sqrt{\frac{(k_1+k_2+k_3+1)!}{k_1!\ k_2!\ k_3!\ K_1!\ K_2!\ K_3!\ \lambda_1!\ \lambda_2!\ \lambda_3!}}$$

la fonction génératrice Φ_{3j} prend l'expression simple :

$$\Phi_{3j} = \exp\left(\begin{vmatrix} \tau_1 & \tau_2 & \tau_3 \\ \xi_1 & \xi_2 & \xi_3 \\ \eta_1 & \eta_2 & \eta_3 \end{vmatrix}\right) .$$

De là découlent les propriétés de symétrie de Regge (1958) des 3j : G_L est invariant au signe près par les permutations de lignes ou de colonnes et par transposition (72 symétries)

3.2 Fonction génératrice d'un coefficient de couplage-recouplage arbitraire.

Nous avons déterminé une fonction génératrice d'un coefficient de couplage-recouplage arbitraire en faisant intervenir les propriétés géométriques du graphe du coefficient. Considérons d'abord le cas du 3j . On peut dessiner sur son graphe 6 diagrammes ouverts joignant deux extrémités du graphe (voir figure 1 de l'annexe I). A chaque diagramme ouvert T nous associons un monome M(T) en τ_i,ξ_i,η_i par des règles simples décrites au §.5 de l'annexe I. Avec ces définitions la fonction génératrice du $3j$ s'écrit $\Phi_{3j} = \exp(-\Sigma\, M(T))$ où la somme est sur les diagrammes ouverts du $3j$. Considérons ensuite le cas d'un produit de $3j$. On peut définir sa fonction génératrice par le produit des fonctions génératrices des $3j$, écrites avec des variables différentes. Les diagrammes ouverts du graphe G' du produit de $3j$ sont ceux des divers $3j$. La fonction génératrice est donc donnée par la même formule que pour le $3j$:

$$\Phi_{G'} = \exp\,(-\Sigma\, M(T))$$

la somme étant sur les diagrammes ouverts de G'.

Examinons enfin le cas général d'un graphe G représentant une somme sur divers m d'un produit de $3j$. Chaque sommation sur m_i fait disparaître l'indice m_i, ou de façon équivalente les indices K_i, λ_i. Nous montrons dans l'annexe I qu'il est possible de définir une fonction génératrice Φ_G du coefficient de couplage-recouplage qui s'obtient à partir de $\Phi_{G'}$, fonction génératrice du produit de $3j$, par une simple intégration. En effectuant cette intégration nous exprimons Φ_G à l'aide du déterminant et de l'inverse d'une matrice. Nous interprétons ensuite ce déterminant et cet inverse en termes géométriques. Cela nous amène à généraliser la définition des diagrammes ouverts à un graphe quelconque, et à introduire des diagrammes fermés (car en général on peut tracer des circuits sur G). La fonction génératrice Φ_G prend alors une forme remarquablement simple :

$$\Phi_G = \frac{\exp\left(\dfrac{-\sum\limits_{T\in\Omega} M(T)}{1+\sum\limits_{D\in K} M(D)}\right)}{\left[1+\sum\limits_{D\in K} M(D)\right]^2}$$

où Ω et K sont les ensembles de diagrammes ouverts et fermés respectivement du graphe G . Ces ensembles sont finis et faciles à construire. Par exemple, pour les coefficients 6j et 9j , il n'y a pas de diagrammes ouverts et il y a 7 et 15 diagrammes fermés respectivement. Notons par contre que l'obtention de Φ_G se fait à l'aide de calculs graphiques faisant intervenir des ensembles infinis de diagrammes. L'expression de Φ_G est moins étonnante lorsqu'on se rend compte qu'il est possible de façon générale d'exprimer le déterminant et l'inverse d'une matrice à l'aide d'une méthode graphique. Dans l'article de l'annexe J , nous dérivons cette expression et nous montrons son utilité dans des calculs analytiques à l'aide d'un exemple donné en détail. Signalons aussi un autre cas dans lequel un déterminant et un inverse sont transcrits en utilisant des idées de théorie des graphes. Il s'agit de la méthode de Nakanishi (1971) qui permet d'exprimer les intégrales de Feynman à l'aide des graphes de Feynman correspondants.

3.3 Applications.

La fonction génératrice des coefficients de couplage-recouplage nous permet d'obtenir une nouvelle expression générale des coefficients. Cette expression, qui généralise les formules de Racah pour les 3j et 6j , n'est pas efficace pour les calculs numériques car elle ne présente aucune factorisation. Par exemple pour le 9j notre formule se présente sous la forme d'une somme sur 6 variables (15 variables liées par 9 relations). La formule exprimant le 9j comme somme d'un produit de trois 6j est alors plus efficace puisqu'elle équivaut à une somme sur 4 variables (dont une par 6j) et est de plus factorisée.

La fonction génératrice des coefficients de couplage-recouplage fournit un moyen commode d'étude des symétries des coefficients. Nous avons déjà vu qu'elle donne de suite les symétries de Regge du symbole 3j . Il en est de même pour le 6j . Nous l'utilisons pour montrer que les symétries des coefficients 3j , 6j et 9j obtenues à l'aide de transformations linéaires inversibles des indices des coefficients sont uniquement les symétries connues.

Une autre utilité des fonctions génératrices est qu'elles permettent d'obtenir des relations de récurrence : nous donnons un exemple dans l'article de l'annexe I.

CONCLUSION

Résumons maintenant l'essentiel du contenu des études présentées et rappelons les conclusions principales de chaque étude.

1ère Partie.

1) Le calcul a priori des déplacements isotopiques spécifiques (He et Mg §.2.1), dont nous avons souligné l'intérêt pour l'interprétation de la partie nucléaire de l'effet de volume, est un problème compliqué pour lequel le traitement au deuxième ordre de perturbation dans le modèle de HF s'est révélé décevant. La situation ressemble à celle du calcul a priori des énergies des niveaux, ce qu'on peut rapprocher du fait que l'opérateur de déplacement isotopique ressemble à la partie $C^1 \cdot C^1$ de l'interaction électrostatique. Nous avons montré l'importance des effets d'ordres supérieurs au deuxième dans le cas très simple de l'hélium. Nous avons vu à ce propos tout l'avantage des calculs MCHF à orbitales non orthogonales (méthode qui a été depuis appliquée systématiquement par C. Froese-Fischer) : un calcul utilisant 4 configurations redonne à 1 % près les valeurs du déplacement isotopique spécifique du calcul très précis de Pekeris.

Dans le cas des termes ^1P et ^3P du magnésium l'insuffisance au deuxième ordre apparaît même avant la comparaison à l'expérience : la variation des orbitales radiales entre le singulet et triplet a un effet très important. Le résultat au deuxième ordre est très peu satisfaisant et même moins bon que le résultat obtenu par des calculs "HF simple".

2) Dans nos calculs a priori de structures hyperfines (§.2.2) nous avons interprété correctement les valeurs expérimentales très différentes $\langle r^{-3}\rangle_{sC^2}(^3P) = 0,809$ et $\langle r^{-3}\rangle_{\ell}(^1P) = 0,257$ concernant les termes $3s3p\ ^{1,3}P$ de l'atome de magnésium. Là encore les effets d'ordres supérieurs au deuxième sont importants, mais nous avons pu les évaluer.

Dans les cas des termes de Hund des configurations $3d^N4s^2$ du scandium et du titane, nos calculs ont confirmé le résultat de C. Bauche-Arnoult selon lequel la valeur du rapport $\langle r^{-3}\rangle_{\ell}/\langle r^{-3}\rangle_{sC^2}$ ne doit pratiquement pas changer du premier élément au second.

3) Nos calculs du deuxième ordre véritable de structure hyperfine (hfs × hfs) pour le samarium, basés sur une interprétation paramétrique, mettent en doute l'existence dans ce spectre d'écarts observables à la droite de King (§.3.2).

Par contre dans le mercure, où de tels écarts sont connus depuis longtemps sous le nom de déplacements pair-impairs anormaux, nous les avons interprétés correctement par une étude phénoménologique (§.3.3).

4) Les calculs décrits aux paragraphes 1) et 2) ci-dessus peuvent être appelés calculs de second ordre croisé (notés respectivement $\Sigma \times Q$ et $hfs \times Q$) dans la mesure où ils visent à atteindre une précision bien meilleure que la méthode de Hartree-Fock simple ("premier ordre"). Pour les réaliser nous avons développé une méthode (§§. 1.2.2-3) consistant à utiliser des fonctions d'onde compactes adaptées au deuxième ordre croisé. Cette méthode peut permettre d'obtenir un grand nombre de résultats en physique atomique du type de ceux présentés ici (auxquels on peut ajouter le cas $dipole \times Q$) ou encore du type Sternheimer par détermination d'orbitales virtuelles. Elle est très facile à mettre en oeuvre car nos programmes, qui forment une chaîne à trois maillons, nécessitent un nombre minimal de données et de plus vérifient des données de façon extensive. Rappelons aussi leur utilité dans les calculs MCHF , soit pour obtenir des approximations initiales, soit pour traiter des excitations de poids trop faibles. Dans la ligne de cette méthode l'extension au cas relativiste semble un sujet d'étude intéressant car il est certain que le besoin d'orbitales relativistes se fera de plus en plus sentir.

2ème Partie.

Nous avons découvert une formule générale pour la fonction génératrice d'un coefficient de couplage-recouplage dans SU(2) . Cette formule est la généralisation à un nombre de moments angulaires quelconque des résultats obtenus par Schwinger et Bargman. Pour l'obtenir nous effectuons des calculs graphiques ; le résultat s'exprime géométriquement à l'aide de deux ensembles finis de sous-graphes du graphe du coefficient de couplage-recouplage.

Cette formule nous a permis d'obtenir, entre autres, une nouvelle formule explicite des coefficients, des formules de récurrence et la propriété que les seules symétries inversibles des 3j , 6j et 9j sont celles connues.

La généralisation de notre résultat à SU(n) semble très complexe. La représentation graphique se généralise (compliquée par la multiplicité dans la série de Kronecker) mais les calculs, dès SU(3) , sont intervenir des intégrales très difficiles à calculer. De plus, les fonctions génératrices des états (polynomes bosoniques) sont connus explicitement uniquement pour les représentations de la forme m_1 m_2 0 0 0 ... (Henrich, 1974).

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ANNEXE A

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Correlation effects on specific isotope shifts

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Abstract. A practical method of obtaining compact atomic non-relativistic wavefunctions adapted to the 2nd order calculation of expectation values of mono- and bi-electronic operators is described. Specific isotope shifts are thus calculated: as a test for the method, in He I 1s2p for which the exact values are known; in Mg I for the virtual transition 3s3p ^1P–^3P.

1. Introduction

One way of improving the *ab initio* monoconfigurational wavefunction $|f)$ of a Russell–Saunders (RS) term, such as might be obtained by the simple restricted Hartree–Fock (HF) method, is to look for an expansion:

$$|\Phi) = |f)+\beta_1|e_1)+\beta_2|e_2)+\dots \tag{1}$$

where the $|e_i)$ are RS terms of the required LS values in excited configurations.

We denote excitations from the fundamental configuration (we thus call the configuration of $|f)$) by symbols like $a \rightarrow b$ (for monoexcitations) or $ab \rightarrow cd$ (for biexcitations) where $a \equiv nl$, etc .... We shall have to consider series of excitations $ab \rightarrow cd$, $ab \rightarrow c'd' \dots$ such that the resulting configurations differ only by radial orbitals.

In order to reach high accuracy one should allow the excited terms $|e_i)$ to span a space as large as possible. In the configuration interaction (CI) method this is attained by piling up large numbers of terms with orbitals chosen beforehand, the weights being obtained by diagonalizing the energy matrix. In the multiconfigurational Hartree–Fock (MCHF) method, in which the orbitals are optimized, the number of terms is reduced but expansion (1) still ought to include, for each excited configuration retained, all RS terms with proper LS values. This can give very cumbersome expansions. For example considering the term $4s^23d^8\ {}^3P$ of Ni I we find in the excited configuration $4s^23d^6f^2$ (corresponding to the excitation $3d^2 \rightarrow f^2$) 35 RS terms with the 3P symmetry.

Compact non-relativistic wavefunctions have usually been obtained by adapting them to the physical problem under way. Thus the perturbed function method has been used to study the influence of the quadrupole moment of the nucleus (Sternheimer 1950, 1951, 1954, 1957, 1967). It has also been used in combination with Feynman graphical method to study the Coulomb configuration interaction in rather heavy atoms (Morrison 1972). Lately MCHF calculations have been made producing very compact wavefunctions adapted to the study of the hyperfine structure of 2p atoms (Bauche and Bagus 1973). Another means of obtaining compact wavefunctions is to use natural orbitals (Löwdin 1955, 1956) which can be obtained from CI wavefunctions. First order wavefunctions (Schaefer III *et al* 1968) of 2p atoms have thus been analysed in terms of natural spin orbitals (Larsson *et al* 1972).

In this paper we describe a practical method of obtaining compact wavefunctions approximating the eigenvector of lowest energy (for given L and S) of an atomic non-relativistic hamiltonian H and adapted to the calculation of the mean value of an operator A up to the second order of perturbation. The method consists in contracting the wavefunction in two ways. (i) The first contraction is accomplished by choosing peculiar angular couplings in the excited terms. This choice, which is described in § 2, is made by angular reasons, not assuming previous knowledge of the radial orbitals and heeding the fact we are interested in the mean value of A. (ii) To a given angular coupling, such as obtained in (i) corresponds a series of excited terms differing by the radial orbitals. This series can be reduced to one term in the case of monoexcitations. For biexcitations, it can be simplified by the use of natural orbitals (Löwdin 1955, Weiss 1967). This point is described in § 3.

2. Choice of the excited terms

In this section we describe a method of choosing the angular couplings of the RS terms entering into expansion (1) with the aim of making it as concise as possible. Such an expansion would be suited to calculations in the MCHF scheme. The method is based on the fact that we adapt the wavefunction to the computation or the mean value of an hermitian operator A up to the second order of perturbation. Considering the hamiltonian

$$H_1 = H + A = H_0 + Q + A \quad \text{with} \quad H_0 = \sum_i \left(\frac{1}{2m} p_i^2 + V(r_i) \right)$$

we only retain in expansion (1) the RS term $|e_i)$ when it contributes to the crossed second order energy of Q and A for $|f)$. The condition is $(f/Q/e_i)(e_i/A/f)/\Delta E \neq 0$ and we split it in two:

$$(f/H/e_i) \neq 0 \tag{2}$$

$$(f/A/e_i) \neq 0 \tag{3}$$

where we used $(f/H_0/e_i) = 0$. Clearly we have to keep to excited configurations that possess terms such that (2) and (3) hold. From (2) it follows that these differ from $|f)$ by only one or two orbitals. Moreover when A is a monoelectronic operator (eg a hyperfine structure operator), from (3) it follows that the excited configurations are obtained by monoexcitations of $|f)$.

The states $|e_1)$, $|e_2) \ldots |e_l)$, here not necessarily RS terms, are supposed to form an orthonormal basis of an excited configuration E. We want to find a new orthonormal basis $|e'_1)$, $|e'_2) \ldots |e'_k)$, $|e''_{k+1}) \ldots |e''_l)$ having the property that (2) and (3) are both satisfied only for the first k states $|e'_1) \ldots |e'_k)$, so that for each $|e''_i)$ $(i > k)$ at least one of the two off diagonal matrix elements $(f|H|e''_i)$ or $(f|A|e''_i)$ vanishes. Furthermore we want the solution to be obtained by angular considerations, so that it will be independent of the radial part of the orbitals. Since the compact wavefunction we are looking for only contains $|e'_i)$ states we have to make k as small as possible. Second order values can be calculated as well from the $|e_i)$ as from the whole configuration. These values can be expressed in terms of second order parameters, so that there are as many $|e_i)$ as independent parameters though, as we shall see later, the solution $|e'_i)$ is not unique in general. To find a solution of this reduction problem we proceed in two steps.

Step 1

We rotate the $|e_i)$ states to obtain a new orthonormal basis $|e_1^{(1)}), \dots |e_{k_1}^{(1)}), |e_{k_1+1}^{(2)}), \dots |e_l^{(2)})$ of E, satisfying, for angular reasons, the relations $(f|H|e_i^{(1)}) \neq 0$ and $(f|H|e_j^{(2)}) = 0$. In fact we are only interested in the $|e_i^{(1)})$. For every $|x)$ in E we write the matrix element $(f|H|x)$ as $(f|H|x) = \Sigma_k\, \alpha_k(x)\mathscr{T}_k$, where each $\mathscr{T}_k$ is a radial integral (a Slater integral F, G or R or possibly a central field integral $I_{nl-n'l}$ in the case of a monoexcitation $nl \to n'l$), and each $\alpha_k(x)$ is an angular coefficient which does not depend on the radial orbitals. For each k $\alpha_k(x)$ is a linear form on E and can be written as $\alpha_k(x) = (a_k|x)$ where $|a_k)$ is a vector in E.

Now if we call E' the span of the vectors $|a_k)$ and construct a basis $|e_1^{(1)}), \dots |e_{k_1}^{(1)})$ of E' we get the terms we were looking for, since

$$(f|H|x) = \sum_k (a_k|x)\mathscr{T}_k$$

is zero when $|x)$ is perpendicular to E'. We note that it is not possible to find less than k_1 $(= \dim E')$ terms $|e_i^{(1)})$ when the knowledge of the radial part of the orbitals is not assumed.

One way of building a set $|e_i^{(1)})$ is to apply the Schmidt orthogonalization process to the vectors $|a_k)$; the matrix elements of H are then of the form:

$$\begin{aligned}
(f|H|e_1^{(1)}) &= a_1\mathscr{T}_1 + a_2\mathscr{T}_2 + \dots + a_n\mathscr{T}_n \\
(f|H|e_2^{(1)}) &= b_2\mathscr{T}_2 + \dots + b_n\mathscr{T}_n \\
&\vdots \\
(f|H|e_{k_1}^{(1)}) &= q_n\mathscr{T}_n
\end{aligned} \tag{4}$$

It is to be noticed that the radial integral $\mathscr{T}_1$ only appears in the first matrix element.

One important property of the $|e_i^{(1)})$ is that they are Russell–Saunders terms with the same SL values as $|f)$.

Step 2

We rotate the $|e_1^{(1)}) \dots |e_{k_1}^{(1)})$ to obtain a new basis of E': $|e'_1) \dots |e'_k)|e''_{k+1}) \dots |e''_{k_1})$ such that $(f|A|e'_i) \neq 0$ and $(f|A|e''_i) = 0$. Clearly this step is like the first one, but with H replaced by A and with different initial states. Of course the radial integrals $\mathscr{T}_k$ are also different. Finally the $|e'_i)$ are a solution to our problem.

When the operator A is any of the hyperfine structure (hfs) operators (sC^2, C^2, L, contact operator) or the specific isotope shift operator Σ we are left in the end of the reduction with one term $|e'_1)$ (or exceptionally 2 terms), in agreement with the fact that there is one second order parameter (or exceptionally 2). In these cases expansion (1) is greatly simplified. When the reduction can be made to only one term $|e'_1)$, it is easy to obtain an equation for $|e'_1)$. We write, as in step 1, for every $|x)$ in the excited configuration E:

$$(f/H/x) = \sum_{k=1}^{n} (a_k/x)\mathscr{T}_k \quad \text{and} \quad (x/A/f) = (x/b)\mathscr{T}'$$

where $|a_k)$ and $|b)$ are vectors in E.

Expressing that the second order values calculated from only $|e'_1)$ is equal to the value calculated from the whole excited configuration E we get for $|e'_1)$, assumed normalized, the equations:

$$(a_k/e'_1)(e'_1/b) = (a_k/b) \qquad (1 \leqslant k \leqslant n).$$

In general the solution is not unique. An advantage of the procedure we use is that the obtained $|e'_i)$ have the same SL values as $|f)$.

We now consider the case when A is the specific isotope shift operator

$$\Sigma = \frac{1}{M}\sum_{i>j} p_i p_j$$

for a nucleus of mass M. If

$$(f|H|e_i) = \alpha R^1(nl, n''l', n'\overline{l-1}, n'''\overline{l'-1}) + \ldots$$

then

$$(f|\Sigma|e_i) = \lambda\epsilon\alpha J(nl, n'\overline{l-1})J(n''l', n'''\overline{l'-1})$$

where λ is a numerical factor ($= 2m/M$ Ryd), ϵ is ± 1, α is the same as the coefficient of the Slater integral R^1 in $(f|H|e_i)$ and

$$J(nl\,n'\overline{l-1}) = \int_0^\infty R_{nl}\left(\frac{\mathrm{d}R_{n'l-1}}{\mathrm{d}r} - \frac{l-1}{r}R_{n'l-1}\right)r^2\,\mathrm{d}r$$

is a radial integral (R_{nl} is normalized by $\int_0^\infty R^2r^2\,\mathrm{d}r = 1$) (Stone 1959).

In that case the method of finding $|e'_i)$ can be somewhat simplified. If in step 1 of the reduction we label the radial integrals in order that $\mathscr{T}_1 = R^1$ only $|e'_1)$ contains the integral R^1 and hence is the only term in the excited configuration to possess a non-zero specific isotope shift matrix element with $|f)$. Steps 1 and 2 of the reduction are thus made in a single step. In some excitations, such as $2p3p \rightarrow d^2$ one may come across two integrals R^1 and $R^{1'}$; we then choose $\mathscr{T}_2 = R^{1'}$ in equation (4) and finally obtain two terms $|e'_1)$ and $|e'_2)$ which cannot be reduced any further. We can note that for Σ the reduction to $|e'_1)$ (or to $|e'_1)$ and $|e'_2)$) is unique (but for a rotation of the $|e'_i)$ states) in opposition to the general case.

A computer program has been written to effectuate the reduction when A is any of the mentioned operators, and to calculate the angular matrix elements of H and A. Further details about it are given in Appendix A.

3. Determination of orbitals and of mixing coefficients

3.1. Series of excitations

Series of excited terms differing by the radial orbitals ought to be introduced in wavefunction (1), but when a method of optimization of the radial orbitals, such as MCHF, is used, the number of terms can be reduced according to the following considerations:

(i) The series of monoexcitations $n_0l_0 \rightarrow n^{(1)}l$, $n_0l_0 \rightarrow n^{(2)}l$, $n_0l_0 \rightarrow n^{(3)}l \ldots$ (including also continuum type orbitals) can be reduced to one monoexcitation $n_0l_0 \rightarrow nl$. Moreover when the monoexcitation $n_0l \rightarrow nl$ is considered the X term defined by Bauche and Klapisch (1972), which satisfies Brillouin's theorem, can be suppressed. When the excitation $n_0l \rightarrow nl$ contains only the X term the excitation is then suppressed altogether.

(ii) The reduction of a series of biexcitations cannot be as drastic as for a monoexcitation, and one needs in principle an infinite series. For example the set of biexcitations of He I $1s^2\ {}^1S$: $1s^2 \rightarrow p_I^2$, $1s^2 \rightarrow p_{II}^2$, $1s^2 \rightarrow p_I p_{II}$, $1s^2 \rightarrow p_{III}^2$, $1s^2 \rightarrow p_I p_{III}$, $1s^2 \rightarrow p_{II} p_{III}$ can be reduced to the 3 excitations $1s^2 \rightarrow p_I'^2$, $1s^2 \rightarrow p_{II}'^2$, $1s^2 \rightarrow p_{III}'^2$ as shown by Löwdin (1955) (p_I', p_{II}', p_{III}' are approximately the natural orbitals). A number of biexcitations can be reduced in this way. Thus for the excitations of $3s3p\ {}^{1,3}P$ of the type $3s3p \rightarrow pd$ it is sufficient to consider the series $3s3p \rightarrow p_1d_1$, $3s3p \rightarrow p_2d_2$, $3s3p \rightarrow p_3d_3 \ldots$ where the radial orbitals 3p, $p_1, p_2, p_3 \ldots$ as well as $d_1, d_2, d_3 \ldots$ are orthogonal. A more complicated reduction is considered in the last paragraph of Appendix A. For practical reasons in this work the series were limited, the number of terms taken being usually 3, 2 or even just 1.

One important feature of the method is that there is no need to introduce orbitals of the continuum type.

3.2. *Optimization of the radial orbitals*

Having chosen the excited terms and expressed the energy matrix with Slater integrals, the orbitals and the weights of the excited terms can be determined by means of the MCHF method. A program written by Froese (1969) and modified by Bagus was at our disposal to carry out these calculations. Unfortunately the use of the program was limited by difficulties in the convergence of calculations espcially when orbitals have small occupation numbers. This convergence difficulty has led us to write an analytical program to determine the radial part of the orbitals. The principle is very simple: the orbitals are made to depend on a few parameters and these parameters are optimized so as to minimize the energy. The program is described in Appendix B.

4. Calculations of specific isotope shifts

We applied the method just described to study the influence of configuration mixing on specific isotope shifts. We restricted the study to spectroscopic terms belonging to the same configuration, expecting to lessen the number of excitations needed to interpret the relative shifts within that configuration. When the matrix element of H between one excited state and the fundamental has the same formal expression for every intial term in the considered configuration (the same property is then also true for Σ), then the excited state contributes by the same quantity to the various shifts if the same radial orbitals are used for the whole fundamental configuration. Rather than the same radial orbitals we used different simple HF wavefunctions for each initial term, so that these excited states also contribute to the relative shifts, but in an appreciable way only when external shells are excited.

4.1. *He I 1s2p* $^{1,3}P$

For He I $1s2p\ {}^{1,3}P$ very accurate theoretical values of the specific isotope shifts were published (Schiff *et al* 1965). To test our method, we calculated second order expectation values σ of the operator Σ by considering the monoexcitation $1s \rightarrow d$ and the two series of excitations, limited to the first two excitations: $1s2p \rightarrow s_1p_1$, $1s2p \rightarrow s_2p_2$ and $1s2p \rightarrow p_1'd_1'$, $1s2p \rightarrow p_2'd_2'$. Excitations like $1s2p \rightarrow df$, not contributing to the second order expectation value of Σ, were left aside. We treated the excited terms separately, each virtual orbital being made to depend on 5 parameters and determined as explained in § 3. From this first order wavefunction we obtained the values of the energy E and of σ given in table 1, on the line '2nd order', in atomic units, without the nuclear factor m/M for the isotope shifts. We also give the results obtained in the same way by using only the 3 excitations 1s → d, 1s2p → sp, 1s2p → p'd' ('simplified second order'). It can be seen that the values of σ are very close in the two calculations.

To account for higher order effects we made genuine multiconfigurational calculations including the 3 excited terms 2pd, sp and p'd'. The oribtals p and p' or d and d' were not taken orthogonal and the core 1s and 2p functions were also parametrized. We used a 5 parameter description of each orbital, the initial values of which, for 1s and 2p, were obtained by comparison with the numerical simple HF orbitals. The main effect when the core functions are allowed to relax from their simple HF shapes is to slightly draw in the 2p orbital. The weight of the excited 2pd term then increases at the expense of the sp term and the values of the specific isotope shifts are then in good agreement with the exact values (table 1). Each of the obtained 4 configuration wavefunctions can be retained as good, as long as the specific shifts is concerned, and still easy to picture.

Table 1. He ^1P and ^3P: values of the specific isotope shift in sundry calculations (atomic units).

	He ^1P		He ^3P	
	E	σ	E	σ
exact value†	−2·123843	0·04531	−2·133164	−0·06356
simple HF	−2·122454	0·03515	−2·131437	−0·06611
2nd order	−2·122749	0·04267	−2·131596	−0·06079
simplified 2nd order‡	−2·122726	0·04279	−2·131552	−0·06054
4C parametrized core	−2·123647	0·04585	−2·133028	−0·06363
4C' (by Froese's program)	−2·123513	0·04413	−2·132969	−0·06532

† Schiff *et al* (1965).

‡ Without doubled excitations.

We also considered what could be done with Froese's multiconfigurational HF program. Since it is not possible to introduce non-orthogonal orbitals, and since in the second order treatment the virtual orbitals p and p' on the one hand and d and d' on the other hand are very similar, it is tempting to use the excitations 1s → d, 1s2p → sp and 1s2p → pd. However such a study is not possible with Froese's program because the energy matrix element between the first and third excited configurations contains the integral I_{2p-p}. The best choice in a 4 configuration treatment compatible with the limits of the program was found to be 1s → d, 1s2p → sp and 1s2p → pd' with the restriction d ⊥ d'. The resulting d' function is very much like the first order one, in agreement with the fact that the third excited configuration gives the most important contribution to the energy. But now the d function has to be orthonormal to d': it is then strongly modified and looks like a 4d function; as a backlash the weight of the excited 2pd configuration is dramatically decreased. These facts explain the not too good values of the specific isotope shifts (table 1).

4.2. Mg I $3s3p^{1,3}P$

In the case of Mg I 3s3p, the aim was to obtain a 2nd order value for the specific isotope shift $\sigma_{^3P-^1P}$ of the (virtual) transition ^1P–^3P. The excitations given in table 2 are those which possess different formal non-diagonal matrix elements for the energy in ^1P and ^3P. The values for the specific isotope shifts calculated from these excitations, in the same way as for He I and with the use of reduced terms constructed with the process of § 2, are given as 'partial second order' in table 3. The remaining 44 excitations contributing to the specific isotope shifts in the second order have the same formal matrix elements but in spite of it contribute largely to $\sigma_{^3P-^1P}$ because we start from different HF orbitals for ^1P and ^3P. The results obtained by considering all these excitations are given on the line 'total second order' in table 3 and compared to the experimental (Landolt Boernstein 1952) and Hartree–Fock (Bauche 1969) values. As in the case of He I, the present calculations were made by treating the excited terms separately and adding the second order contributions to the HF values, each virtual orbital determined depending on 5 parameters. The excitations giving the largest contributions to $\sigma_{^3P-^1P}$ were seen to involve at least one of the external orbitals 3s or 3p, and to contain a virtual d orbital. The presence of a virtual d orbital can be understood by the fact that s and p virtual orbitals are rather wriggly, being orthogonal to 1s, 2s and 3s (or 2p and 3p) and usually produce poor correlations and also smaller J integrals in the isotope shift.

Table 2. Mg I: list of excitations having different formal matrix elements in ^1P and ^3P

1s or 2s → s	1s2p or 2s2p → 3s3p	2p3p → s3s
2p → 3p	1s3s or 2s3s → p3p	2p3p → 3sd
2p → p	2p3s → s3p	3s3p → sp
3s → d	1s3p or 2s3p → 3sp	3s3p → pd

Table 3. Mg ^3P and ^1P: comparison of experimental and theoretical values for σ (atomic units)

	$\sigma_{^3P}$	$\sigma_{^1P}$	$\sigma_{^3P-^1P}$
experiment†			−0·1410
simple HF‡	−27·7177	−27·5565	−0·1612
partial 2nd order	−27·6362	−27·5029	−0·1333
total 2nd order	−22·2283	−22·0648	−0·1635

† Landolt Boernstein (1952).
‡ Bauche (1969).

Series of excitations were also introduced when the first excitation was important. One striking feature appeared in the series $2p3p \rightarrow d_A^2$, $2p3p \rightarrow d_B^2 \ldots$: the second excitation, though having a smaller mixing coefficient, is more important than the first for isotope shifts. This curious phenomenon, already observed by Keller (1972) is linked with the trouble encountered by the virtual d orbital in correlating at the same time the widely spaced 2p and 3p functions (we have $\langle r_{2p} \rangle = 0{\cdot}683$ and $\langle r_{3p} \rangle = 4{\cdot}069$ au).

5. Conclusion

The calculations of second order expectation values of a bielectronic operator, the specific isotope shifts, made on He and Mg show the critical importance of higher order effects. We were able to take these effects into account in the case of He I by MCHF calculations. In Mg I, where *LS* coupling is very good for 3s3p, we attribute the poorness of our second order value to higher order correlation effects. We also saw that it would be desirable to perform non-orthogonal MCHF calculations (which are equivalent to orthogonal MCHF calculations with non-diagonal central field integrals allowed (Froese 1973)).

The application of first order wavefunctions to calculations of expectation values of monoelectronic operators is quite simple since the number of excitations is very small. In the case of hyperfine structure operators (contact term excepted) good results were obtained by Bauche and Bagus (1973) in the 2p atoms and by Bauche *et al* (1973) in Mg I. But higher order effects (in particular near-degeneracy effects) may have to be considered. Thus in Li ^{2}P, Nesbet (1970) shows that the two-particle correlations of 1s2p are very important.

Acknowledgment

The author would like to express his gratitude to J Bauche for suggesting the problem and for helpful discussions during the course of this work.

Appendix A. Details of the reduction program

The initial $|e_i)$ states are taken to be Slater determinants of given $M_S M_L$ values and matrix elements are computed in floating point form from the $c^k(lm\,l'm')$ coefficients.

As an example let us go back to the excitation $3d^2 \rightarrow f^2$ of $4s^2 3d^8\ {}^3P$ which possesses 35 terms of symmetry ^{3}P. The number of excited determinants is 225. The off diagonal matrix elements are expressed in terms of the three Slater integrals $G^k(3d, f)$ ($k = 1, 3, 5$). When the specific isotope shift is studied we only retain term $|e_1')$, the only one to contain G^1. This term can be characterized by its matrix element

$$(f|H|e_1) = 1{\cdot}943487G^1 - 0{\cdot}050964G^3 - 0{\cdot}245019G^5.$$

Construction of 'allowed' and 'forbidden' terms

When studying excitations in Ne, Keller (1972) came across cases in which the reduction of a series of biexcitations is not as straightforward as in the cases considered in § 3.1. If E_i(d) for example is a certain term in the excitation AB → d^2 we have, replacing the radial orbital d by αd + βd′,

$$E_i(\alpha \mathrm{d}+\beta \mathrm{d}') = \alpha^2 E_i(d) + 2^{1/2}\alpha\beta S_i(\mathrm{d}, \mathrm{d}') + \beta^2 E_i(\mathrm{d}').$$

This equation defines a term S_i(d, d′) which can be shown to be a normalized term in the excitation AB → dd′. Furthermore it enables us to carry out a reduction by the method of Löwdin as in the examples of § 3.1: the set $E_i(\mathrm{d_I})$, $E_i(\mathrm{d_{II}})$, $E_i(\mathrm{d_{III}})$, $S_i(\mathrm{d_I}, \mathrm{d_{II}})$, $S_i(\mathrm{d_{II}}, \mathrm{d_{III}})$, $S_i(\mathrm{d_I}, \mathrm{d_{III}})$ can be reduced to a new set $E_i(\mathrm{d_I'})$, $E_i(\mathrm{d_{II}'})$, $E_i(\mathrm{d_{III}'})$. Thus the terms S_i(d, d′) are not useful. But the excitation AB → dd′ may not be exhausted by terms of the form S_i(dd′)

and contain useful terms $A_j(\mathrm{d}, \mathrm{d}')$. The program permits separation of the 'forbidden' S_i and 'allowed' A_j terms (only the A_j are being retained) by making use of the property expressed in the following relations:

$$(f|H|S_i) = \sum \alpha_k R^k_+ \quad \text{and} \quad (f|H|A_i) = \sum \beta_k R^k$$

where

$$R^k_\pm = R^k(\mathrm{A, B, dd'}) \pm R^k(\mathrm{A, B, d'd}).$$

Appendix B. Details of the optimization program

Radial part of orbitals

When simple and multiconfigurational Hartree–Fock orbitals are compared it is to be noticed that some orbitals vary very little from one calculation to the other. For this reason we allow orbitals to be determined once and for all (obtained for example from a simple HF calculation). The other orbitals are taken in a parametrized form. We first define an order for the orthonormalization of these orbitals. Then following this order for each orbital we compute

$$S = \sum_{i=1}^{q} a_i N_{\alpha_i k_i} r^{k_i} \,\mathrm{e}^{-\alpha_i r}. \tag{B1}$$

This is a sum of q Slater functions with the fixed integer exponents k_i. The parameters are the coefficients a_i (except a_1 which is made equal to 1) and the numbers α_i in the exponents. $N_{\alpha_i k_i}$ is a normalizing constant: $N_{\alpha k} = (2\alpha)^{k+1/2}/[(2k)!]^{1/2}$. Then the radial orbital P is taken to be

$$P = \frac{S - \Sigma_i (S|P_i)P_i}{[(S|S) - \Sigma_i (S|P_i)^2]^{1/2}}$$

where the P_i are the orthonormal radial orbitals preceding the one under calculation and to which P must be orthogonal. The scalar product is here $(P/P') = \int_0^\infty P(r)P'(r)\,\mathrm{d}r$. We have obviously $(P/P_i) = 0$ and $(P/P) = 1$. In this way we achieve a description of the orbitals with a small number of parameters (a sum of three Slater functions—that is five parameters—usually gives a very good description of the function) and it is possible to introduce non-orthogonal functions of the same l value.

Calculation of the energy

Once we have the orbitals we can calculate the mixing coefficients and the energy in two ways:

(i) Second order treatment. We need the matrix elements $(f|H|f)$, $(f|H|e_i)$ and $(e_i|H|e_i)$. The (unnormalized) wavefunction is then given by

$$|\Phi) = |f) - \sum_i \frac{H_{if}}{H_{ii} - H_{ff}} |e_i)$$

and the energy is

$$E = H_{ff} - \sum_i \frac{H_{if}^2}{H_{ii} - H_{ff}}.$$

(ii) Exact treatment. By diagonalizing the whole energy matrix we obtain the best weights for the given orbitals.

These calculations are made by using a numerical representation of the radial part of the orbitals: the value of the function is computed at the points $r_i = r_0\, e^{ih}$ and a four term expansion is used near the origin. The necessary Slater and central field integrals, and maybe overlaps of orbitals are then calculated numerically.

Optimization of the parameters

We have just seen how the energy can be computed in terms of the parameters defining the orbitals. According to the variational principle we have to minimize the energy. We use for that the simplex method described by Klapisch (1969) which only necessitates the knowledge of the function to be minimized. There is a drawback to the simplicity of the method: the energy has to be computed a great number of times; the speed of computation depends mainly on the time of computation of each integral (the time spent, for functions defined on 150 points is between 9 and 15 ms on the Univac 1108 computer).

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ANNEXE B

Generator of determinantal non-relativistic atomic states from spectroscopic notation. Computation of matrix elements.

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Short title : Generator of determinantal states.

Classification : Atomic Physics. Structure.

Program Summary.

Title of program : TERM .

Computer : UNIVAC 1110 ; Installation : Université d'Orsay, France.

Operating system : UNIVAC 1110 EXEC 8 .

Program language used : FORTRAN V .

High speed storage required : 50 000 words.

No of bits in a word : 36 .

Overlay structure : none .

No of magnetic tapes required : 1 (for output).

Other peripherals used : Card reader, line printer.

No of cards in combined program and test deck : 5148 .

Card punching code : IBM 026 .

Keywords : Atomic structure, angular momentum, spectroscopic notation, coupling, determinantal states, angular matrix element, reduced matrix element, W operators, creation operator, annihilation operator, coefficients of fractional parentage, quasispin, Slater integrals, hyperfine structure operators, multipole operators, n-particle operators.

Nature of the physical problem.

The program generates the decomposition of an atomic state into Slater determinants from its description in the usual spectroscopic notation. The output is directly usable by the program EXCGH [1]. The program can also compute matrix elements and reduced matrix elements of operators $\tilde{a}$, a^{+} , $a^{(1/2)}$, $\sum\limits_{i<j\ldots<k} w_i^{(1)} w_i^{(1')} \ldots w_j^{(2)} w_j^{(2')} \ldots w_k^{(n)}$ as well as products of such operators coupled in any way. The results are given in an exact $a\sqrt{b}/c\sqrt{d}$ form.

Method of solution.

Each shell is generated by the projection method. Couplings are computed from 3jm coefficients. Matrix elements are calculated from determinantal states.

Restrictions on the complexity of the problem.

Each shell is given in SL coupling. There are no restrictions for further coupling between shells and operators.

Typical running time. The test run containing 16 computations takes 19s . In general, computation of determinantal states is fast, but computation of matrix elements can be very long.

Unusual features of the program. FORTRAN V instructions INCLUDE and PARAMETER, intrinsic functions FLD , ENCODE and DECODE.

References

[1] J. J. Labarthe, C. P. C. (2nd submitted paper).

1. Introduction.

The program TERM described in this paper is the first link of a chain of 3 programs aiming at computing 2nd order values in non relativistic atomic physics. It constructs the development in Slater determinants of an atomic state given in the spectroscopic notation, i. e. each shell is SL coupled and the various shells can be coupled in an arbitrary way. As a by-product the program also computes matrix elements.

The second program of the chain, EXCGH, which is described in [1] constructs from angular considerations a compact set of excited terms for 2nd order calculations adapted to the physical problem under way and computes the angular energy matrix. The perturbed radial orbitals are determined by the third program EDD [2], which optimises an analytic description of the orbitals.

The programs TERM and EXCGH perform angular calculations using determinantal states and not Racah's algebra (except vector coupling coefficients). Thus computational times may be very long for complicated matrix elements. But in the usual uses of the programs these times are short.

In the program TERM the computations are done in an exact way by representing square roots of rational numbers as in Rotenberg et al. [3].

The matrix elements or reduced matrix elements (as defined in [4] page 42) that can be computed in TERM are those of annihilation and creation operators $\left(\tilde{a}(n\ell)\right.$, $a^{+}(n\ell)$ or $a^{(1/2)}(n\ell)$ (1/2 is the quasi spin) as defined by Judd [5]$\left.\right)$, operators :

$$\sum_{i<j\ldots<k} w_i^{(1)} w_i^{(1')} \ldots w_j^{(2)} w_j^{(2')} \ldots w_k^{(n)} \qquad (1)$$

where $i,j\ldots k$ are electron labels and where the $w^{(a)}$ are the $w^{\varkappa k}(n\ell,n'\ell')$ one-particle operators defined by Feneuille [6] ($a=1,1'\ldots2,2'\ldots n$ stands for $\varkappa,k,n\ell$ and $n'\ell'$), and products of such operators. Factors are included converting these operators to electrostatic, hyperfine structure, spin-orbit, multipole or fractional parentage operators.

2. Method of solution.

An example of input data is :

```
J = 7/2,9/2 $
(4F2:3H4 ; 6S:1/2 ; (4,1/2)J,J/
F(Q) W(0,3)(4F,6S) . W(0,3)(6S,4F)
/(4F2:3H4 ; 6S:1/2)J,J)*
```

which produces as result the coefficients of the Slater integral $G^3(4f,6s)$ in the energies of the two states

$|(4f^2\ {}^3H_4\ ,\ 6s\ {}^2S_{1/2})J,M_J\rangle$ (where $M_J=J$ take the values 7/2 and 9/2). The two ways in which the bra and ket are written above are both allowed to represent the same state.

The decoding of data produces a series of elementary operations :

(i) construct the state in shell $n\ell^p$ with given k , S , L , M_S and M_L values ($k=1,2\ldots$ if there are several terms of the same S_L values) (see section 2.1) ;

(ii) construct an elementary operator (a of w) ;

(iii) construct a Kronecker product (i. e. put 2 shells/operators one after the other) ;

(iv) construct a coupling $(j_1,j_2)j_3,m_3$ (i. e. form a sum weighted by Clebsch-Gordan coefficients) ;

(v) determine a matrix element ; this necessitates the construction of the sequence of operators (see section 2.2) ;

(vi) initiate loops on variables (in the above example $J=7/2,9/2$) .

2.1 Construction of determinantal states $n\ell^p$ S L M_S M_L .

The determinants $d_1,d_2\ldots d_N$ of shell $n\ell^p$ which are eigenfunctions of S_z and L_z with respective eigenvalues S and L , are ordered following the alphabetical order defined by the «alphabet» :

$\overset{+}{\ell},\overset{+}{\ell-1}\ldots\overset{+}{-\ell},\overset{-}{\ell},\overset{-}{\ell-1}\ldots,\overset{-}{-\ell}$.

We put $\hat{P} = \prod_{S_i=S+1}^{S_{MAX}} (\hat{S}^2 - S_i(S_i+1)) \prod_{L_j=L+1}^{L_{MAX}} (\hat{L}^2 - L_j(L_j+1))$

where S_{MAX} and L_{MAX} are the maximum values for shell $n\ell^p$

$\hat{P}$ transforms $d_1,d_2\ldots d_N$ in eigenvectors of $\hat{S}^2$ and $\hat{L}^2$ of eigenvalues $S(S+1)$ and $L(L+1)$ respectively.

The method consists in forming a basis of the span of vectors $\hat{P}d_1,\hat{P}d_2\ldots\hat{P}d_N$ following Schmidt process. Practically the process is stopped at the K-th basis vector (K given in data by $n\ell^p$:K:S,L or $K=1$ if not given ; see section 5.1.9).

Eventually state S L M_S M_L is obtained from the shift operators S_- and L_- .

2.2 Determination of the sequence of operators.

The operator is decomposed in a sum of products of one-particle operators of the type :

$$\sum_i w_i^{(1)} w_i^{(2)} \dots w_i^{(p)} \qquad (2)$$

or of the annihilation-creation type. The action of such operators on determinantal states is very easy to program.

For example $\sum_{i<j} w_i^{(1)} w_j^{(2)}$ is computed from

decomposition $\frac{1}{2}(\sum_i w_i^{(1)})(\sum_i w_i^{(2)}) - \frac{1}{2}\sum_i w_i^{(1)} w_i^{(2)}$. (3)

Since $w_i^{(1)}$ and $w_j^{(2)}$ (with $i \neq j$) commute decomposition (3) is not unique. One could also utilise :

$$\frac{1}{2}(\sum_i w_i^{(2)})(\sum_i w_i^{(1)}) - \frac{1}{2}\sum_i w_i^{(2)} w_i^{(1)} .$$

We now describe the algorithm used to decompose operator (1). The various indices $\varkappa$, k , q , Q , $n_1\ell_1$, $n_2\ell_2$, $\varkappa'$, k' ... characterising the one particle operator $w_{qQ}^{\varkappa k}(n_1\ell_1, n_2\ell_2)\, w_{q'Q'}^{\varkappa' k'}(n_2\ell_2, n_3\ell_3)\dots$ will be represented by a label $i \in \{1,2\dots,n\} = I$. So $w_j^{(i)}$ acts on electron j (where $j \in \{1,2\dots,\text{number of electrons}\} = J$) and stands for $w_j^{(1)} w_j^{(1')}\dots$ in eq. (1) with all projection numbers defined.

For each subset H of I formed of labels $(h_i)_{1\leqslant i\leqslant \nu}$ such that $h_1 < h_2 < \dots < h_\nu$ we put :

$$w_j^{(H)} = w_j^{(h_1)} w_j^{(h_2)} \dots w_j^{(h_\nu)} . \qquad (4)$$

Let $(H_i)_{1\leqslant i\leqslant k}$ be a partition of I . Putting the H_i in boxes we form a <u>flat</u> F :

$$F = \begin{array}{|c|c|c|c|}\hline H_1 & H_2 & \ldots & H_k \\ \hline \end{array} \tag{5}$$

We shall add flats and multiply them by rational numbers treating them as a basis of a vector space $\mathcal{F}$.

For flat F in eq. (5) we define :

$$F^A = \sum_{\substack{\alpha\in J\\ \beta\in J\\ \ldots\\ \nu\in J}} w_\alpha^{(H_1)} w_\beta^{(H_2)} \ldots w_\nu^{(H_k)} \tag{6}$$

and :

$$F^D = \sum_{\substack{\alpha\in J\\ \beta\in J\\ \ldots\\ \nu\in J\\ \text{all } \alpha,\beta\ldots\nu \text{ different}}} w_\alpha^{(H_1)} w_\beta^{(H_2)} \ldots w_\nu^{(H_k)} \quad . \tag{7}$$

It is seen that F^D is not dependent on the order of the H_i , whereas F^A is. By linearity X^A and X^D are defined for any $X\in\mathcal{F}$.

Put $$E_n = \begin{array}{|c|c|c|c|}\hline \{1\} & \{2\} & \{3\}\ldots & \{n\} \\ \hline \end{array} \quad . \tag{8}$$

The aim of the decomposition is to express E_n^D as a X^A with $X\in\mathcal{F}$.

We shall denote the set of partitions of I in k elements by $\mathcal{P}_k$, in any number of elements by $\mathcal{P} = \bigcup_{k=1}^{n} \mathcal{P}_k$. We order disjoint subsets of I in the following way :

$$H = \{h_1,\ldots,h_\nu\} < H' = \{h'_1,\ldots,h'_{\nu'}\}$$

if $\nu > \nu'$ where $\nu(\nu')$ is the number of elements of H (H') or if $\nu = \nu'$, $h_1 < h'_1$ where h_1 (h'_1) is the smallest element in H (H') .

We shall say that partition $(H'_i)_{1\leqslant i\leqslant v'} \in \mathcal{P}$ is coarser than partition $(H_i)_{1\leqslant i\leqslant v} \in \mathcal{P}$ if each H_i $(1\leqslant i\leqslant v)$ is included in one H'_j and if the two partitions are different.

We define for flat F in eq. (5) :

$$R_q(F) = \Sigma \begin{array}{|c|c|c|c|}\hline H'_1 & H'_2 & \cdots & H'_q \\ \hline \end{array} \qquad (9)$$

where $H'_1 < H'_2 < \ldots < H'_q$ and where the sum is over the partitions $(H'_i)_{1\leqslant i\leqslant q} \in \mathcal{P}_q$ coarser than partition $(H_i)_{1\leqslant i\leqslant k}$. We see that $R_q(F) = 0$ if $q \geqslant k$. By linearity the operator R_q is defined on the vector space $\mathcal{F}$.

Starting from E_n eq. (8) we define recurrently :

$$\begin{aligned} E_{n-1} &= E_n - R_{n-1}(E_n) \\ &\ldots\ldots \\ E_q &= E_{q+1} - R_q(E_{q+1}) \\ &\ldots\ldots \\ E_1 &= E_2 - R_1(E_2) \quad . \end{aligned} \qquad (10)$$

Then a solution of the decomposition problem is given by the equation :

$$E_n^D = E_1^A \quad . \qquad (11)$$

<u>Proof</u> : Writing eq. (6) for E_n^A and gathering the w having the same electron labels in each term of the sum we get :

$$E_n^A = \sum_{(H_i)\in\mathcal{P}} \begin{array}{|c|c|c|}\hline H_1 & \cdots & H_k \\ \hline \end{array}^{\,D} \quad . \qquad (12)$$

Extracting the term E_n^D in the r.h.s. of (12) and iterating :

$$
\begin{aligned}
E_n^D &= E_n^A - \sum_k R_k(E_n)^D \\
&= E_n^A - \sum_k R_k(E_n)^A + \sum_{k'<k} R_{k'} R_k (E_n)^D \\
&= E_n^A + \sum_{1\leqslant i} \; \sum_{k_1<k_2\ldots<k_i} (-)^i R_{k_1} R_{k_2} \ldots R_{k_i} (E_n)^A \quad . \qquad (13)
\end{aligned}
$$

Using eq. (10) to obtain E_1 in terms of E_n this last expression is seen to equal E_1^A. Other decompositions could be obtained by modifying the ordering of the subsets of I.

The program uses the algorithm described by eq. (10) : having constructed the sum of flats E_{q+1}, the sum E_q is obtained by adding to E_{q+1} the flats of q boxes obtained from E_{q+1} by the operator $-R_q$ (there may happen cancellations only among these new flats, not with those of E_{q+1}).

3. Description of the program.

The role of the various subroutines is described in table 1 . Subroutines whose name begins with DC serve to decode the input data, those beginning with ER serve in error detecting, with PRT in printing, with RG in doing arithmetics in Rotenberg form, with WK in constructing states or computing matrix elements.

4. Unusual features of the program.

The following FORTRAN V pecularities are used in the program.

4.1 PARAMETER and INCLUDE .

For example, instead of writing a statement :

```
COMMON/T/T(100)
```

in N subroutines, we write

```
INCLUDE T
```

after having defined a FORTRAN PROCEDURE T containing :

```
PARAMETER TP = 100
COMMON/T/T(TP)   .
```

In the program an extensive use is made of these statements, which permit to modify easily the dimensions : only the PARAMETER card has to be changed, and the whole of the program is to be recompiled.

As a guide for modifying dimensions, at the end of each run, the program prints the value of each PARAMETER , as well as the value which would have been sufficient for the run (utilised value).

4.2 FLD function.

The FLD FORTRAN function is an intrinsic function for bit manipulation which is described in detail in [7]. It is used in the following form :

$$\mathrm{FLD}(a,\ell,A) = \mathrm{FLD}(b,\ell,B)$$

which replaces bits $a,a+1,\dots,a+\ell-1$ in word A by bits $b,b+1,\dots,b+\ell-1$ of word B . The bits in a word are numbered from 0 to 35.

4.3 DECODE function [7].

It is used in the following form :

```
DECODE(f,A)list
```

which has the effect of reading word A (and following words) and filling the «list» according to FORMAT f .

4.4 ENCODE function.

It is used only in subroutine DCW :

```
    ENCODE(6,17,MEMOIR),(TRV(C3+I),I=0,5)
 17 FORMAT(6A1)
```

which has the effect of filling MEMOIR with the first alphanumerical characters in the 6 words TRV(C3) , TRV(C3+1) - - TRV(C3+5) .

5. Input data.

It consists of cards. The position of the data on cards is arbitrary, columns 73 - 80 being ignored. Blanks are ignored except in some keywords (sections 5.1.13 and 5.3.3) which must be written without blanks. The input data uses the symbols ':' (5-8) and ';' (6-8-11) where we indicate the perforation code, with the convention of enclosing in single quotes special characters or strings of characters .

Each run can consist of one or several computations, the input data for each computation ending with a '*' .

The program prints the values of the PARAMETER's and stops when reading the keyword 'END' of 'FIN' written without blanks, and followed only by blanks.

Each computation takes one of the forms :

a) Z1 $\underline{\$}$ Z2 $\underline{*}$

b.) Z2 $\underline{*}$

where we underline characters '$' and '*' to indicate that they must appear exactly as written. The specifications for Z1 and Z2 are given in sections 5.3 and 5.1.15 respectively. Z1 (absent in b) defines commands and loops. Z2 describes the atomic state or matrix element to be computed : it can depend on variables that must be defined in Z1 . The state or element is then computed for all values taken by the variables. In the example given at the beginning of section 2 , Z1 corresponds to 'J = 7/2,9/2' indicating that the calculation is to be made twice with the variable J taking the value 7/2 and then 9/2.

Z2 , as can be seen from the same example, is very similar to the ordinary spectroscopic notation. So the unit :

'4F2:3H4'

represents the coupled subshell $4f^2\,{}^3H_4$. In the input language this unit is called a CNQ . It is formed of two smaller units : '4F2' (which represents a subshell and is called an $n\ell^P$) and '3H4' (which represents quantum numbers and is called an NQ) linked by character ':' .

The input language is described below by defining units of increasing complexity. Once the units $n\ell^P$ and NQ have been defined, an option (corresponding to the above example) for a CNQ is defined as :

$n\ell^P \;\underline{:}\; NQ$

5.1 Description of zone Z2 .

5.1.1 Integer. It is an unsigned integer, blanks ignored so '1‸0' represents 10 ; '+1' and '-1' are not integers ; '0' is an integer.

5.1.2 Half integer. Two cases :

a) integer

b) integer/2 (error if integer is even)

Examples : 3 ; 3/2 representing 3 and 3/2 .

5.1.3 Unsigned variable. Two cases :

a) half integer

b) an arbitrary name beginning with a letter and not containing the following 9 characters { (,) , ; , comma , = , + , - , . , $ } .

At most the 1st 6 non-blank characters are kept.

Type of an unsigned variable : in case a) the unsigned variable is said to be of type N (numerical), in case b) if the name begins with an M (resp S , resp L , resp J) it is said to be of type M (resp S , resp L , resp J). Otherwise the type is undetermined.

Examples : 3 ; J ; MJ1 ; K (of respective types : N ; J ; M ; undetermined).

5.1.4 Variable. It is of the form : sg unsigned variable where sg is ∅ (blank zone), '+' or '-' .

Type of a variable : if sg is ∅ or '+' the type is that of the unsigned variable, if sg is '-' the type is M except for '-0' which is of type N .

Examples : -3/2 (of type M) ; +J1 (of type J).

Of course if J1 is an unsigned variable defined in zone Z1 and taking a certain value, -J1 is considered to be defined and taking the opposite value.

5.1.5 ^{2S+1}L and $^{2S+1}L_J$, representing the usual spectroscopic notations. ^{2S+1}L is of the form : integer letter and $^{2S+1}L_J$ of the form : ^{2S+1}L half integer where letter is one of the following characters :

$$\left\{ S , P , D , F , G , H , I , K , L , M , N , O \right\} .$$

Examples : 1S0 ; 2P3/2 representing $^1S_0$ and $^2P_{3/2}$.

5.1.6 $n\ell^p$, representing the $n\ell$ shell filled with p electrons. Two cases : a) integer letter,

b) integer letter integer,

where letter is as in 5.1.5 . Case a) corresponds to $p=1$. One must have $n > \ell$ and $0 < p \leqslant 2(2\ell+1)$.

Examples : 2S2 ; 2P2 ; 4F representing $2s^2$, $2p^2$ and $4f$.

5.1.7 cpl , representing a coupling .

Two cases : a) (J1,J2)J3,MJ

b) (J1,J2)J3 or (J1,J2)J3 .

where J1 , J2 and J3 are variables of types ≠M

MJ is a variable of arbitrary type, representing the projection of J3 . Note in type b) that J3 is free (its projection is not given) . This can be indicated by '.' following J3 .

Examples : (S,L)J. ; (1/2,1/2)K,-K .

5.1.8 NQ , representing quantum numbers S , L , J and their projections or part of these quantum numbers. The possible cases are described in table 2 , where columns NQS , NQL and NQJ (corresponding to names of decoding arrays) indicate how each description is interpreted. When S , L and J are given J represents the coupling of S and L .

Remarks : 1) When M , TM or VM designates a '.' the corresponding S , L or J is free.

2) A '.' after a variable is possible if and only if the variable represents a free momentum which is not coupled inside NQ (So in 'S , L , J.' S is coupled but not J).

3) As a guide for writing NQ it is advised to use as much as possible the $^{2S+1}L_J$ and ^{2S+1}L notations for representing numerical variables, the other cases being reserved to other descriptions. For example S=1 , L=1 , J=0 , M_J=0 can be written 3P0,0 (case 7), whereas the notations 1,1,0,0 (case 11) and 3P,0,0 (case 10) represent S=1 , L=1 , M_S=0 , M_L=0 .

Examples : see following section.

5.1.9 CNQ representing a shell + quantum numbers.

Three cases : a) $n\ell^p$

b) $n\ell^p$: NQ

c) $n\ell^p$: K : NQ

where K is a variable (taking values 1,2,...) whose meaning is explained in section 2.1 .

When S , L are not given (case a) ; cases b) and c) with NQ of cases 1 or 4) then p must equal 1 , $4\ell+1$ or $4\ell+2$. In case a) when p=1 or $4\ell+1$ the implicit S=1/2 , $L=\ell$ are free, when $p=4\ell+2$ the implicit S=0 , L=0 are associated with projection quantum numbers and so cannot be coupled.

Examples : 4S for 4s ^2S ;

2P6 for $2p^6\ ^1S$, M_S=0 , M_L=0 ;

2P6:1S for $2p^6\ ^1S$;

3D3:2D,1/2,2 for $3d^3\ ^2D$, $M_S=1/2$, $M_L=2$, case 10 for NQ ;

4F5:5/2,L. for $4f^5$, S=5/2 , L , case 5 for NQ ;

2P5:1/2,1. for $2p^5\ ^2P$ case 5 for NQ whereas

2P5:1/2,1 is read as $2p^5\ ^2P_{1/2}$, $M_J=1$ (resulting in an error because $M_J > J$) case 4 for NQ ;

3D4:2:3F4,-4 for the 2nd state $3d^4\ ^3F_4$, $M_J=-4$, case 7 for NQ ;

2P:3/2 for $2p\ ^2P_{3/2}$, case 1 for NQ ;

2P:2P,.,1 or 2P:1/2,1,.,1 or 2P:1/2,.,1,1 for $2p\ ^2P$, $M_L=1$ (S is free), cases 10, 11 and 12 for NQ .

5.1.10 NQW , representing quantum numbers $\varkappa$, k , K (coupling of $\varkappa$ and k) , q , etc. used in operators w or a . The possible forms are cases 8, 11, 12 and 13 of NQ to which is added the form J , J' (J and J' variables of types $\neq$M) which is interpreted as case 5 of NQ (whereas in NQ it would be interpreted as case 4). Of course the meaning of NQS (resp. NQL , NQJ) is now $\varkappa$ (resp. k , K).

Examples : see following section.

5.1.11 Wop representing operator $w^{\varkappa k}_{qQ}(n\ell,n'\ell')$.

It is of the form :

W seq qn (nℓ,n'ℓ')

nℓ and n'ℓ' are $n\ell^p$ of case a) (without p)

seq has 3 possible forms : a) ' (apostrophe)

b) M

c) ∅ (blank zone) .

The meaning of seq will be seen in section 5.2 .

qn has 3 possible forms :

a) (NQW) i. e. NQW limited by 2 parenthesis.

b) cpl

c) (K.K') where K and K' are variables of type ≠M (equal in principle).

So $w^{\varkappa k}$, $w^{\varkappa k}_{q}$, $w^{\varkappa k}_{Q}$ and $w^{\varkappa k}_{qQ}$ are represented by case a), $w^{(\varkappa k)K}$ and $w^{(\varkappa k)K}_{Q}$ by case a) or b) and $w^{(k\cdot k)}$ by case c).

Examples : W(0,2)(2P,2P) for $w^{02}(2p,2p)$, the NQW '0,2' being interpreted as case 5 of NQ ;

W(1.1)(2P,2P) for $w^{(1.1)}(2p,2p)$;

W(1,2)1,0(3P,3P) for $w^{(1,2)1}_{0}(3p,3p)$;

W'(0,K)K(3P,3P) or W'(0,K,K)(3P,3P) for $w^{(0,K)K}(3p,3p)$;

WM(1,2,-1,0)(3P,3P) or WM(1,-1,2,0)(3P,3P) for $w^{1\,2}_{-1\,0}(3p,3p)$, cases 11 and 12 for NQW ;

W(1,2,1,0)(3P,3P) for $w^{12}_{10}(3p,3p)$, case 11 for NQW .

5.1.12 Aop representing the operators $a^{+\,1/2\ \ell}_{\ \ m_s\ m_\ell}(n\ell)$, $\tilde{a}^{1/2\ \ell}_{m_s\ m_\ell}(n\ell)$, $a^{1/2\ 1/2\ \ell}_{q\ \ m_s\ m_\ell}(n\ell)$, $a^{+(1/2\ \ell)j}_{\qquad\ m_j}(n\ell)$, etc.

4 cases :

1) A(Q,NQW)(nℓ)

2) A(Q,J1,J2)K(nℓ)

3) A(Q,J1,J2)K,M(nℓ)

4) A qs (nℓm)

nℓ is $n\ell^{p}$ of case a) (without p)

Q is a variable of type ≠M representing the quasi-spin (its value must be 1/2 and its projection cannot be given). K is a variable (of type ≠M). M is a variable.

In case 1 NQW is interpreted as $1/2$, ℓ , j , etc.

In cases 2 and 3 the variables J1 and J2 (representing $1/2$ and ℓ) are coupled in K or K , M .

In case 4, qs can take the forms :

a) ∅
b) -
} to represent $\tilde{a}$

c) + to represent a^+

d) (Q) giving the quasi-spin

and nℓm can take the forms :

a) nℓ

b) nℓ , MS , ML where MS (resp ML) is a '.' or a variable representing the projection of $1/2$ (resp ℓ). Note that $1/2$ and ℓ are implicit.

Examples : A+(4F) for $a^{+\ 1/2\ 3}\ (4f)$;

A(1/2,1/2,-1/2,2,.)(3D) or A(1/2,1/2,2,-1/2,.)(3D) or A(1/2)(3D,-1/2,.) for $a^{1/2\ \ 1/2\ \ 2}_{\quad\ \ -1/2}\ (3d)$;

A(2P) or A-(2P) for $\tilde{a}^{1/2\ 1}\ (2p)$;

A(Q,1/2,1)3/2(2P) or A(Q,1/2,1,3/2)(2P) for $a^{Q\ (1/2,1)3/2}\ (2p)$.

5.1.13 Fact representing a numerical factor has the form :

F (option)

where option is one of the words :

{G , Q , S , L , SC2 , SO , SL , S.O. , S.L. , C , CPF , CFP} .

These words must be written without blanks.

Effect of Fact . The value of the factor depends on the Wop placed after it (on the 2 Wop placed after in case 4 , or on the A_{op}

as well as on the bra and ket in case 10) and convert it into a more convenient operator (like $\vec{S}$, $\vec{L}$, etc).

case 4 : The following operator gives the angular coefficient of the Slater integrals $R^k(n_1\ell_1\ n_2\ell_2\ n_3\ell_3\ n_4\ell_4)$, $G^k(n_1\ell_1\ n_3\ell_3)$ (if $n_2\ell_2 = n_3\ell_3$ and $n_1\ell_1 = n_4\ell_4$) and $F^k(n_1\ell_1\ n_2\ell_2)$ (if $n_1\ell_1 = n_3\ell_3$ and $n_2\ell_2 = n_4\ell_4$) :

$$F(Q)\ W(0,k)\ (n_1\ell_1,n_3\ell_3) \cdot W(0,k)\ (n_2\ell_2,n_4\ell_4)$$

(F(Q) can be replaced by F(G))

case 5 : F(S) W(1,0)1,m(nℓ,nℓ) equals S^1_m acting on a nℓ electron.

case 6 : F(L) W(0,1)1,m(nℓ,nℓ) equals L^1_m acting on a nℓ electron.

case 7 : F(SC2) W(1,2)1,m(nℓ,n'ℓ') equals $-\sqrt{10}(s\ C^2)^1_m$ when acting between nℓ and n'ℓ' electrons.

case 8 : F(SO) W(1.1) (nℓ,nℓ) equals s.ℓ acting on a nℓ electron. F(SO) can be replaced by F(S.O.) , F(SL) or F(S.L.) .

case 9 : F(C) W(0,k)k,m(nℓ,n'ℓ') equals C^k_m between nℓ and n'ℓ' electrons.

case 10 : (x //F(CFP) $\tilde{a}$(nℓ) //y) = (x|}y)

and (x //F(CFP) a^+(nℓ) //y) = (x{|y)

giving coefficients of fractional parentage. F(CFP) can be replaced by F(CPF) .

5.1.14 Conf . It can represent several things ranging from a CNQ to a matrix element. The possible forms and their interpretations are given on table 3.

A coupling of type 3 or 3' on momenta represented by variables J1 and J2 is made by cpl = '(J1,J2)J3' etc. It must be performed on free momenta and must be unambiguous.

So, the following examples are in error :

... S , L , MS , ML ; (S,L)J (S , L not free)

... S , L ... S , LP ; (S,LP)J (ambiguity on S)

but ... S , L ... S , LP ; (S,S)S1

and 2P2 : 3P ; (1,1)2,-2 are valid.

In type 4 conf 1 must contain no projection quantum number. It can have 4 free momenta : S_1 , L_1 , S_2 , L_2 which are then SL coupled (NQ not of case 1 or 4) or it can have 2 free momenta J_1 , J_2 which are then coupled by NQ (of case 1 or 4).

In type 8 the '.' must be followed by '(', 'W', 'A' or 'F'. Conf 1 and conf 2 must have the same number p of free momenta. A scalar product is then made between the i-th momenta of conf 1 and conf 2 for each i = 1,2...p . If conf terminates with a '.' (as for example : conf = 'W(0,1) (1S,1S);(0,1)1.'), conf conf' will be interpreted as a scalar product. This can be avoided by writing (conf)conf' or conf ; conf' or suppressing in conf the final point.

Examples :

1) 'conf A ; conf B ; cpℓ' represents a coupling (type 3) effectuated within conf 1 = 'conf A ; conf B' (Kronecker product). This could also be given as : '(conf A ; conf B)cpℓ' (coupling of type 3').

2) 'conf A ; conf B cpℓ' is interpreted as the Kornecker product of conf A and 'conf B cpℓ' where the coupling is effectuated within conf B only. This could also be given as 'conf A ; (conf B ; cpℓ)' . Note that example 2 cannot be interpreted as example 1 because conf 1 = 'conf A ; conf B' contains an unparenthesized ';' and that

example 1 cannot be interpreted like example 2 as the Kronecker product of conf A and conf 2 = 'conf B ; cpℓ' because conf 2 contains an unparenthesized ';' .

3) 2P5:3/2;3P;(3/2,1)K;(K,1/2)J or 2P5:3/2(3P)(3/2,1)K(K,1/2)J for $2p^5\ {}^2P_{3/2}\ 3p\ K,J$ (jk-coupling) .

4) 2P5:1/2(3P:S,1)(1/2,1)K(K,S)J for $2p^5\ {}^2P_{1/2}\ 3p\ K,J$ (jk-coupling) and where S is introduced to avoid an ambiguity (S has to be defined by S=1/2 in Z1).

5) (4F13:7/2(6S;6P)3P2)J for $4f^{13}\ {}^2F_{7/2}\ 6s6p\ {}^3P_2\ J$.

6) (2S;2P)S0,L0(4F)(L0,3)L(S0,L)K(K,1/2)J for $(2s2p)S_0L_0\ 4f\ L,K,J$ in the LS_0-coupling scheme .

5.1.15 Zone Z2 . Three cases :

a) conf K or /conf K)

b) (conf B/conf 0/conf K)

c) (conf B//conf 0//conf K)

representing respectively a ket , a matrix element and a reduced matrix element.

conf B and conf K are conf that do not contain Aop , Wop , Fact or scalar products (conf of type 8).

conf 0 is a conf that does not contain CNQ .

In cases a) and b) there must be no free momenta of value different from zero.

In case c), conf B , conf 0 and conf K must have the same number p of free momenta. The matrix element is then reduced with respect to the i-th momenta of conf B , conf 0 and conf K , for i=1...p .

Example : Let us return to the example at the beginning of section 2,

corresponding to the computation of a matrix element (case b) and indicate how the decoding is performed (these details are printed by the program if the SPRINT command (5.3.3) is used). The various conf's are numbered with integers from 1 to 15 showing the order of their decoding.

The bra = conf B appears as conf 2 of type 3 and composed of conf 3 = '4F2:3H4;6S:1/2' and of a cpℓ = '(4,1/2)J,J' which indicates that the free momenta 4 and 1/2 of conf 3 are coupled in J,J . Conf 3 itself represents the Kronecker product (type 2) of conf 4 = '4F2:3H4' and conf 5 = '6S:1/2' which are conf's of type 5 (i. e. CNQ).

The decoding of the operator = conf 0 = conf 7 is a follows :

conf 9 = 'F(Q)' is of type 7 (i. e. Fact)

conf 10 = 'W(0,3)(4F,6S)' and conf 11 = 'W(0,3)(6S,4F)' are of type 6 (i. e. Wop)

conf 8 = 'conf 9 conf 10' is of type 2 (Kronecker product)

and the full operator conf 7 appears as the scalar product of conf 8 and conf 11 .

The decoding of the ket = conf K = conf 12 is interpreted in the following way :

The Kronecker product of conf 14 = '4F2:3H4' and conf 15 = '6S:1/2' (which are of type 5) is called conf 13 . The ket is then obtained from conf 13 by a coupling performed according to type 4 with NQ = 'J,J' .

Let us note that the units '/conf 0/conf K)' and '(conf B/conf 0/conf K)' also appear respectively as conf 6 and conf 1 (and of types 10 and 11 ; similarly a reduced matrix element appears as a conf of type 12).

Once Z2 has been decoded as above, subroutine DCSET sets up the sequence of elementary operations. Operations 1-18 construct the following 'configurations' :

1) $w^{03}(4f,6s)$ which consists in a set of 7 'levels' representing the operators $w^{03}_{qQ}(4f,6s)$ $(q=0\ ,\ Q=-3\ldots3)$

2) $w^{03}(6s,4f)$

3) $w^{03}(4f,6s\ w^{03}(6s,4f)$ containing 49 'levels' obtained by the Kronecker product of configurations 1 and 2.

4) $w^{03}(4f,6s)\ w^{03}(6s,4f)^{(0,0)0}_{\quad\ 0}$ obtained from a coupling within configuration 3 (also containing 49 levels)

5) $w^{03}(4f,6s)\ w^{03}(6s,4f)^{(00)0\ (33)0}_{\quad\ 0\qquad 0}$ containing 1 'level' from a coupling within configuration 4

6) $4f^2\ {}^3H$ which consists of 33 levels ($M_S=-1,0,1,M_L=-5\ldots5$)

7) $4f^2\ {}^3H_4$ (9 levels) (coupling)

8) $6s\ {}^2S$

9) $6s\ {}^2S_{1/2}$

10) $4f^2\ {}^3H_4\ 6s\ {}^2S_{1/2}$ (9×2 levels) (Kronecker product)

11) $(4f^2\ {}^3H_4\ 6s\ {}^2S_{1/2})J,J$ (1 level) (coupling) which corresponds to the bra

12) $4f^2\ {}^3H$ that appears in the ket . In fact this configuration has already been constructed by operation 6, so operation 12 does not imply a new construction.

13-17) as configurations 7-11 to complete the construction of the ket
18) (conf B/conf O/conf K) (1 level) representing the matrix element.

The three last operations 19-21 are multiplications by factors (one corresponds to 'F(Q)' , the other two transform coupling operations 4 and 5 to scalar products.

The 33 levels of configuration 6 $(4f^2\ {}^3H)$ and the 2 levels of configuration 2 $(6s\ {}^2S)$ are constructed (as explained in section 2.1) and stored. Note that in $4f^2\ {}^3H$ $M_S=1$ (L free) only 11 levels $(M_L=-5,\ldots 5)$ would be stored. The example $4f^2\ {}^3H_6$ $M_J=6$ would also imply the construction and storage of the 33 levels of $4f^2\ {}^3H$; it is better to give it as $4f^2\ {}^3H$ $M_S=1$, $M_L=5$ which only implies the storage of one level.

The decomposition (3) of the operator is generated as explained in section 2.2 . The contribution to the matrix element from each term of decomposition (3) is then computed by giving the projection quantum numbers all possible values compatible with the couplings. For each new set of these values the series of elementary operations k-21 is run (k is the lowest configuration modified by the change of projection quantum numbers).

5.2 Sequence of operators.

To represent a product of operators $\tilde{a}$, a^+ or eq (1), like for example :

$$(\sum_i w_i^{(1)} w_i^{(2)})\ a^+ (\sum_{i<j} w_i^{(3)} w_j^{(4)})(\sum_i w_i^{(5)}) \qquad (14)$$

where i and j are electron labels, one writes the operators in the usual order determining seq in Wop (section 5.1.11) by the following rules :

(i) Put a prime on the first W operator after a Σ symbol (that is seq has the form a). If this W is the first operator (reading from left to right) or just after an Aop the prime can be omitted (that is seq may be of form c).

(ii) If a W operator wears the same electron label as the preceding W operator put an M after the W in Wop (i. e. seq is of form b).

The operator (14) will be represented by :

$$W \dots WM \dots A^{+} \dots W \dots W \dots W' \dots \qquad (15)$$

where the ... are omitted parts of the operators or couplings.

In (15) it is possible to put primes on the 1st and 3rd W operators.

5.3 Description of zone Z1, serving to define variables and commands.

It must not contain either '\$' or '*'

It has the form $S_1 \underline{;} S_2 \underline{;} S_3 \dots \underline{;} S_n$

or S_1

where S_i $(1 \leqslant i \leqslant n)$ is a sum, loop or command (see below).

The S_i are decoded with increasing i .

In sections 5.3.1 and 5.3.2 V designates an unsigned variable not of type N and not previously defined.

5.3.1 Sum , which defines V as a sum of other unsigned variables. The possibles forms are :

$V \underline{=} \pm A$ or $V \underline{=} A$

$V \underline{=} \pm A \pm B$ or $V \underline{=} A \pm B$

$V \underline{=} \pm A \pm B \pm C$ or $V \underline{=} A \pm B \pm C$

where '±' is one of the characters '+' or '-' and where A , B

and C are unsigned variables previously defined or unsigned variables of type N .

Examples : S=1 ; ML=-2 ; J=S-1 (S being previously defined).

5.3.2 Loop , which defines V as a loop variable.

Three cases : a) (A,B,V)

where A and B are variables, not of type M , of type N or previously defined.

V will take the values $|A-B|$, $|A-B|+1$, ... that are less than or equal to $|A+B|$. Thus if $|A-B|$ is an integer, V runs on the values triangular with A and B .

b) V = A,B,C

c) V = A,B

where A , B and C are variables previously defined (or of type N).

In case b) V will vary from A to B at most, with increment C .

Case c) is the same as b) the increment being 1 (or -1 , only if A and B are ± integers and $B < A$).

Examples: M=1/2 , -1/2 $ 2P : 3/2 , M *

M will take the value 1/2 and then -1/2 .

(1,L,J) where L has been defined ; K=0,6,2 ; MS=-S,S .

5.3.3 Command. It can be one of the following words, written without blanks :

PUNCH	for writing a ket on file 15 .
PRINT	for printing the determinants obtained.
SPRINT	which has the effect of printing a large number of intermediate results.

ENABLE	the computation is not stopped in case of detection of an error, i. e. the loop variables jump to their next value.
C	followed by anything not containing character = serves as a title.

6. Data output.

All data input is printed and numbered.

Square roots of rational numbers (value of matrix element, weight of determinant) are given as f a b c d where f is the floating point value and $a\sqrt{b}/c\sqrt{d}$ is the exact value.

Orbitals in shell $n\ell$ are numbered from 1 to 2 $(2\ell+1)$ with m_ℓ and then m_s increasing.

Example : in 2p shell, orbitals $\overset{-}{-1}\quad \overset{-}{0}\quad \overset{-}{1}\quad \overset{+}{-1}\quad \overset{+}{0}\quad \overset{+}{1}$

are numbered 1 2 3 4 5 6 .

The command PUNCH makes the state to be written on file 15 in a FORMAT usable as input data for program EXCGH (see sections 3.1.1, 3.2.10, 3.2.11 and 3.2.3 of [1]).

7. Errors detected.

7.1 Overflow of dimensions.

For changing dimensions see section 4.1 .

The meaning of each PARAMETER is given in table 4, except for WOP (which must be equal to LGSUP), ROTP (which is the number of prime

numbers used in the Rotenberg description +2) and PRIMEP (which is the number of prime numbers tabulated). ROTP and PRIMEP can be modified as long as :

$$\mathrm{PRIMEP} > \mathrm{ROTP}-2 \geqslant 1 \quad .$$

7.2 Data errors.

When the data is not written exactly as described in sections 5.1 and 5.3 , the execution jumps to next computation after going through the decoding process once again in order to print all decoding steps (this is equivalent to having the SPRINT command (5.3.3) in case of decoding error).

Other errors are detected : repeated shells in a bra or ket, shells unfitted in bra, operator and ket (in particular not correct numbers of electrons), wrong factor in front of Aop or Wop , wrong values of SL in a shell, wrong projection (in J , M if $J+M$ is not $0,1,2,\dots,2J$) , wrong $\varkappa k$ in W or A operator, coupling not triangular and errors in arithmetical calculations like overflows of products or sums. When such an error occurs the execution jumps to next computation, unless the option ENABLE (5.3.3) is enforced.

Error messages are printed clearly.

Examples : 1) (1S;2S;3S)3S1,0*

```
*ERROR* IN CONFIGURATION DECODING : WRONG NUMBER OF MOMENTA IN (   )NQ
```

2) (1,1,M)$...* or (1,1,1)$...*

```
*ERROR* DATA BADLY WRITTEN : ILLEGAL J IN (A,B,J)
```

3) (4F6:7F)//W(1.1)(4F,4F)//4F6:7F)*

The 1st ')' should be deleted. The error occurs because the program cannot interpret '4F6:7F)' as a conf . The error message states that this conf is of type 0 .

8. Description of test run.

In the first execution $(2p3p)^1P,0,1$ and $(1s2p)^1P,0,1$ states and two $3d^4\ ^3F,1,3$ states are constructed. The output file 15 is listed.

In the 2nd execution, various examples of matrix elements are given :

cards 1-2 : This is the example of section 2 (see also 5.1.15 example).

cards 3-17 : Mean values for state $3s3p\ ^3P, M_S=M_L=1$ of the part of S_z acting on electron $3s$ (cards 3-5), the part of L_z (cards 6-8), $\vec{S}.\vec{L}$ (cards 9-11), C_0^2 (cards 12-14) or $-\sqrt{10}\ (sC^2)_0^1$ (cards 15-17) acting on electron $3p$.

cards 18-21 : Coefficients of the Slater integral $R^1(1s\ 3p\ 3p\ 3d)$ in the off-diagonal matrix element between the RS terms $1s^2 3s3p\ ^3P$ and $((1s3d)^{2S+1}D(3s3p)^3P)^3P$ for S=0 and 1 .

cards 22-25 : Mean value of operator L^2 for term $3d^3\ ^2D$.

cards 26-28 : Coefficients of fractional parentage

$(4f^6\ ^7F\{|4f^5\ ^6L)$ for L=1, 3 and 5 .

cards 29-33 : Matrix element of $(a^{qs\ell}\ a^{qs\ell})^{100}_{100}$ between the RS terms $3d^3\ ^2D$ and $3d\ ^2D$.

References.

[1] J. J. Labarthe, C. P. C. (2nd submitted paper).

[2] J. J. Labarthe, C. P. C. (3rd submitted paper).

[3] M. Rotenberg, R. Bivins, N. Metropolis, J. K. Wooten, The 3j and 6j symbols, Crosby Lockwood, London 1959.

[4] B. R. Judd, Operator Techniques in Atomic Spectroscopy, McGraw-Hill, N.Y., 1963.

[5] B. R. Judd, Second Quantization and Atomic Spectroscopy, The Johns Hopkins Press, Baltimore, 1967.

[6] S. Feneuille, J. Phys. Radium 28 (1967) 61.

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Captions of tables.

Table 1 : Role of subroutines.

Table 2 : Possible forms for NQ .

S , L and J represent variables of types $\neq$M (also in descriptions ^{2S+1}L and $^{2S+1}L_J$, internal variables of type N are defined to represent S , L and J).

M represents a '.' or a variable of arbitrary type.

TM represents a '.' or a variable of type M .

VM represents a '.' or a variable of type M or N .

TS and TJ represent variables respectively of types S and J .

Table 3 : Possible forms for conf .

The * indicates the place where the last ')' is opened.

conf 1 and conf 2 represent smaller conf's .

Table 4 : Parameters.

Table 1.

DATUM	BLOCK DATA
CPLSET	see DCSET
DCBCL	decoding of 1st zone (section 5.3)
DCBOK	decoding of (b/0/k) or /k) (section 5.1.15)
DCCFG	decoding of conf (5.1.14)
DCCMD	decoding of command (5.3.3) or option in Fact (5.1.13)
DCCNQ	decoding of CNQ (5.1.9)
DCCPL	decoding of cpl (5.1.7)
DCDENT	decoding of half integer (5.1.2)
DCENT	decoding of integer (5.1.1)
DCFACT	decoding of Fact (5.1.13)
DCHALF	FUNCTION for writing half integers
DCINIT	initialisations
DCJ	decoding of variable (5.1.4)
DCJS	decoding of unsigned variable (5.1.3)
DCNLP	decoding of $n\ell^{p}$ (5.1.6)
DCNQ	decoding of NQ (5.1.8)
DCSET	setting up of the series of elementary operations (section 2) to be performed. It uses subroutines CPLSET and UNION
DCSPEC	decoding of $^{2S+1}L_J$ (5.1.5)
DCW	decoding of operators A and W (5.1.11-12)
DCZON	search of given characters in any zone
ERAV	detection of overflows in dimensions
ERPOS	printint of walk-back through subroutines in case of error
ERPRT	printing of error messages

Table 1 (continued)

ERSET	initialisations for ERAV
HAUT	determining point of entry in the series of elementary operations after a change of loop variables.
PRTCFG	printing/writing on file 15
PRTDC	dump of decoding arrays
PRTPAR	printing of the PARAMETER's at end of run
PRTRG	printing of rational numbers
RGB	computation of 3j
RGCG	
RGENT	converting square root to Rotenberg form
RGFACT	computation of factors converting W operators to electrostatic operator etc..
RGINV	computation of inverses
RGPD	checking that there is no overflow in product
RGPRM	initialisations for RG-type subroutines
RGPROD	computation of product
RGPUIS	computation of $b^{(1)x} = b(b-1)\ldots(b-x+1)$
RGRAT	converting from Rotenberg to $a\sqrt{b}/c\sqrt{d}$ form
RGRTS	finding squared factors in integers
RGSD	checking that there is no overflow in sum
RGSPLY	simplification of aa'/bb'
RGSQRT	computation of square root
RGSUM	computation of sum
RGSUMQ	computation of norm
RGTRSL	moving Rotenberg numbers
RGUNPW	computation of $(-1)^{y}x$

Table 1 (continued)

RGVAL	FUNCTION converting from Rotenberg to floating point form.
UNION	see DCSET
WKAC	creation/annihilation of one electron
WKADD	adding one state
WKBCL	setting up of loops
WKBOK	computation of (b/0/k). WKOTS is used
WKCMD	working through the series of elementary operations
WKCPL	coupling
WKEXTR	see WKPTRN
WKKRON	Kronecker product
WKMULT	scalar multiplication of a level
WKMVAL	computation of projection numbers
WKNIV	computation of the address of a state
WKNVAV	advancing to next state
WKOK	no effect
WKOTS	see WKBOK
WKPTRN	determination of the operator represented by a flat (2.2). Uses WKEXTR
WKSHFT	applying shift operators
WKSL	construction of shell (2.1)
WKSUIT	finding the sequence of operators (2.2)
WKTBL	tabulation of operators S or L
WKTBOP	tabulation of the one-particle operator represented by a box in a flat (2.2)
WKTRSL	moving states
WKW	constructing Wop

Table 2

commas	case	description	NQS	NQL	NQJ
0	1	J			J
		J.			
	2	^{2S+1}L	S	L	
		$^{2S+1}L.$			
		$^{2S+1}L_J$			J
		$^{2S+1}L_{J.}$			
1	4	J , M with J not of type S			J,M
	5	TS , L	TS	L	
		S , L.	S		
		S. , L			
		S. , L.			
	6	^{2S+1}L , J	S	L	J
		^{2S+1}L , J.			
	7	$^{2S+1}L_J$, M	S	L	J,M
2	8	S , L , J	S	L	J
		S , L , J.			
	9	^{2S+1}L , TJ , M	S	L	TJ,M
	10	^{2S+1}L , VM , M	S,VM	L,M	
3	11	S , L , VM , M with L of type L or N	S,VM	L,M	
	12	S , TM , L , M	S,TM	L,M	
	13	S , L , TJ , M with L of type L or N	S	L	TJ,M

Table 3

interpretation	type	description
error	0 20 21 22	
coupling effectuated within conf 1	3	conf 1 $\underline{;}$ cpl
	3'	conf 1 $\overset{*}{\text{c}}$pl where conf 1 contains no unparenthesised ';'
	4	$\underline{(}$conf 1$\underline{)}$NQ
Kronecker product	2	conf 1 $\underline{;}$ conf 2 conf 1 $\overset{*}{\text{c}}$onf 2 where conf 2 contains no unparenthesised ';'
		conf 1 Fact conf 1 Wop conf 2 Aop in operator
CNQ	5	CNQ in bra or ket
Wop or Aop	6	Wop or Aop in operator
Fact	7	Fact in operator
scalar product	8	conf 1 $\underline{.}$ conf 2 in operator
transfer	9	$\overset{*}{\underline{(}}$conf 1$\underline{)}$ conf 1 included in bra operator or ket.

Table 4

PARAMETER	not to be exceeded by the number of :
BCDCP	loop + sum variables
CCHP	shells
CGP	elements in operator table
CHOP	operating shells
DECP	conf (in decoding)
DESCRP	orbitals inscribed in all determinants
JDCP	variables + implicit variables
LGSUP	Wop and Aop in an operator
MARGEP	products in a 3j coefficient
NCONFP	configurations (in computing)
NDETP	determinants in all states
NFAP	factors + internal factors
NJMP	momenta in all configurations
NNIVP	intermediate states
NOPERP	elementary operations
NQP	NQ + NQW
NSUIP	flats
TRVP	characters read, blanks included, for each computation.

```
 *****    1.PUNCH$(2P;3P)1P,U,1*                                                                  4933. ***
 *****    2.PUNCH$(1S;2P)1P,U,1*                                                                  4934. ***
 *****    3.PUNCH$1S*                                                                             4935. ***
 *ERROR*  OPTION NOT YET AUTHORIZED :  MORE THAN ONE LEVEL
          ABOVE ERROR OCCURED AT TEST NUMBER -1 OF WKCMD
                WKCMD  CALLED AT TEST NUMBER  1 OF WKBCL
 *****    4.PUNCH;K=1,2$3D4:K;3F,1,3*                                                             4936. ***
 K       = 1
 K       = 2
 *****    5.      END                                                                             4937. ***
 PARAMETER = MAXIMUM VALUE ( UTILIZED VALUE)
          BCDCP  =  100 (    2 )
          CCHP   =   30 (    2 )           JDCP    =  100 (   13 )         NFAP    =   15 (    0 )         NSUIP   =   40 (    0 )
          CGP    =  112 (   40 )           LGSUP   =    6 (    0 )         NJMP    =  150 (    9 )         PRIMEP  =  100 (  100 )
          CHUP   =   10 (    0 )           MARGEP  =  100 (    6 )         NNIVP   =  500 (   15 )         ROTP    =   13 (   13 )
          DECP   =   50 (    4 )           NCONFP  =   50 (    5 )         NOPERP  =   80 (    5 )         TRVP    =  836 (  209 )
          DESCRP = 3500 (  128 )           NDETP   = 1000 (   33 )         NQP     =   40 (    3 )         WOP     =    6 (    0 )
```

```
@ELT,S TPF$.A                                                                  4939
ELT017 RL1B70 12/13-20:20:44-(0,)
000001        000    I
000002        000    "     1  1  2  1
000003        000    GET 2P 6
000004        000    GET 3P 2
000005        000    "    -1  1  2  1
000006        000    GET 2P 5
000007        000    GET 3P 3
000008        000    "    -1  1  2  1
000009        000    GET 2P 3
000010        000    GET 3P 5
000011        000    "     1  1  2  1
000012        000    GET 2P 2
000013        000    GET 3P 6
000014        000    I
000015        000    "     1  1  1  2
000016        000    GET 1S 2
000017        000    GET 2P 3
000018        000    "    -1  1  1  2
000019        000    GET 1S 1
000020        000    GET 2P 6
000021        000    I
000022        000    FILE ERROR
000023        000    I
000024        000    "    -1  5  2  3
000025        000    GET 3D 3 6 910
000026        000    "     1  5  2  3
000027        000    GET 3D 4 7 910
000028        000    "    -1  1  1 15
000029        000    GET 3D 5 6 910
000030        000    "    -1  1  1 10
000031        000    GET 3D 5 7 810
000032        000    I
000033        000    "     1  3  1  5
000034        000    GET 3D 5 6 910
000035        000    "    -1  2  1  5
000036        000    GET 3D 5 7 810
```

```
*****   1.J=7/2,9/2$(4F2:3H4;6S:1/2;(4,1/2)J,J/F(Q)W(0,3)(4F,6S).W(0,3)(6S,4F)/(4F     4941. ***
*****   2.    2:3H4;6S                                                                 4942. ***
*****   3.:1/2)J,J)*                                                                   4943. ***
J       = 7/2
  NIV
   1 -.28571429+000     -2      1      7      1
J       = 9/2
  NIV
   1 -.28571429-001     -1      1     35      1
*****    4.((3S;3P)3P,1,1/                                                             4944. ***
*****    5.F(S)W(1,0)1,0(3S;3S)                                                        4945. ***
*****    6./(3S;3P)3P,1,1)*                                                            4946. ***
  NIV
   1  .50000000+000     -1      1      2      1
*****    7.((3S;3P)3P,1,1/                                                             4947. ***
*****    8.F(L)W(0,1)1,0(3P,3P)                                                        4948. ***
*****    9./(3S;3P)3P,1,1)*                                                            4949. ***
  NIV
   1  .10000000+001      1      1      1      1
*****   10.((3S;3P)3P,1,1/                                                             4950. ***
*****   11.F(SO)W(1,1)(3P,3P)                                                          4951. ***
*****   12./(3S;3P)3P,1,1)*                                                            4952. ***
  NIV
   1  .50000000+000      1      1      2      1
*****   13.((3S;3P)3P,1,1/                                                             4953. ***
*****   14.F(C)W(0,2)2,0(3P,3P)                                                        4954. ***
*****   15./(3S;3P)3P,1,1)*                                                            4955. ***
  NIV
   1 -.20000000+000     -1      1      5      1
*****   16.((3S;3P)3P,1,1/                                                             4956. ***
*****   17.F(SC2)W(1,2)1,0(3P,3P)                                                      4957. ***
*****   18./(3S;3P)3P,1,1)*                                                            4958. ***
  NIV
   1 -.20000000+000     -1      1      5      1
*****   19.S=0,1$                                                                      4959. ***
*****   20.(1S2(3S;3P)3P,1,1/                                                          4960. ***
*****   21.F(0)W(0,1)(1S,3P).W(0,1)(3P,3D)                                             4961. ***
*****   22./((1S;3D)S.,2(3S;3P)3P)3P,1,1)*                                             4962. ***
S       = 0
  NIV
   1 -.33333333+000     -1      1      3      1
S       = 1
  NIV
   1 -.47140452+000     -1      2      3      1
*****   23.(3D3:2D,1/2,2/                                                              4963. ***
*****   24. F(L)W(0,1)1(3D;3D).                                                        4964. ***
*****   25.F(L)W'(0,1)1(3D,3D)                                                         4965. ***
*****   26./3D3:2D,1/2,2)*                                                             4966. ***
  NIV
   1  .60000000+001      6      1      1      1
*****   27.CFP     ;                                                                   4967. ***
*****   28.L=1,5,2$                                                                    4968. ***
*****   29.(4F6:7F//F(CPF)A+(4F)//4F5:5/2;L.)*                                         4969. ***
L       = 1
  NIV
   1 -.37796447+000     -1      1      1      7
```

```
L      = 5
 NIV
  1  .57735027+000     1     1     1     3
L      = 5
 NIV
  1 -.72374686+000    -1    11     1    21
*****  30.C    A(1/2)    ,                                                4970. ***
*****  31.Q=1/2$                                                          4971. ***
*****  32.(3D3:2D,1/2,2/                                                  4972. ***
*****  33.A(Q)(3D)A(Q)(3D)(Q,Q)1,1(1/2,1/2)0,0(2,2)0,0                    4973. ***
*****  34./3D :2D,1/2,2)*                                                 4974. ***
Q      = 1/2
 NIV
  1 -.10583005+001    -2     7     5     1
*****  35.G SEVERAL MEANS OF COMPUTING THE SAME MATRIX ELEMENT      $      4975. ***
*****  36.(2P2:3P,1,1/                                                    4976. ***
*****  37. W (0,2)(2P,2P)                                                 4977. ***
*****  38..W'(0,2)(2P,2P)                                                 4978. ***
*****  39./2P2:3P,1,1)*                                                   4979. ***
 NIV
  1  .83333333+000     5     1     6     1
*****  40.(2P2:3P,1,1/                                                    4980. ***
*****  41. (A+(2P)A(2P))0.,2.                                             4981. ***
*****  42..W'(0,2)(2P,2P)                                                 4982. ***
*****  43./2P2:3P,1,1)*                                                   4983. ***
 NIV
  1 -.83333333+000    -5     1     6     1
*****  44.(2P2:3P,1,1/                                                    4984. ***
*****  45. W (0,2,(2P,2P)                                                 4985. ***
*****  46..(A+(2P)A(2P))0.,2.                                             4986. ***
*****  47./2P2:3P,1,1)*                                                   4987. ***
 NIV
  1 -.83333333+000    -5     1     6     1
*****  48.(2P2:3P,1,1/                                                    4988. ***
*****  49. (A+(2P)A(2P))0.,2.                                             4989. ***
*****  50..(A+(2P)A(2P))0.,2.                                             4990. ***
*****  51./2P2:3P,1,1)*                                                   4991. ***
 NIV
  1  .83333333+000     5     1     6     1
*****  52.   FIN                                                          5148. ***
PARAMETER = MAXIMUM VALUE ( UTILIZED VALUE)
          BCDCP  =  100 (    5 )
          CCHP   =   30 (    9 )      JDCP   =  100 (   33 )      NFAP   =   15 (    5 )      NSUIP  =   40 (    3 )
          CGP    =  112 (   56 )      LGSUP  =    6 (    4 )      NJMP   =  150 (   59 )      PRIMEP =  100 (  100 )
          CHOP   =   10 (    4 )      MARGEP =  100 (   12 )      NNIVP  =  500 (   86 )      ROTP   =   13 (   13 )
          DECP   =   50 (   25 )      NCONFP =   50 (   26 )      NOPERP =   80 (   29 )      TRVP   =  836 (  529 )
          DESCRP = 3500 (  366 )      NDETP  = 1000 (  209 )      NQP    =   40 (   13 )      WOP    =    6 (    4 )

@DATA,N EXCABS.,T.
DATA 17 RL70-5 12/13-20:22:12
END DATA.  IMAGE COUNT: 34

@XQT TCHAK.EXCGH
UNIVAC 1110 TIA/ORSAY-RE-ENT-LIBRARY
```

ANNEXE C

Generator of atomic excited terms from angular considerations.

J. J. LABARTHE

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Classification : Atomic Physics. Structure.

Program Summary.

Title of program : EXCGH .

Computer : UNIVAC 1110 ; Installation : Université d'Orsay, France.

Operating system : UNIVAC 1110 EXEC 8 .

Program language used : FORTRAN V .

High speed storage required : 46 000 words.

No. of bits in a word : 36 .

Overlay structure : none .

No. of magnetic tapes required : 2 (for output).

Other peripherals used : Card reader, line printer.

No. of cards in combined program and test deck : 3221 .

Card punching code : IBM 026 .

Keywords : Atomic structure, excitations, angular, Configuration Interaction, Multiconfigurational Hartree-Fock, MCHF, Energy matrix, Slater integrals, specific isotope shift, hyperfine structure, spin-orbit, dipole, second order, Slater determinants, Russell-Saunders.

Nature of the physical problem.

The program generates the excited terms adapted to the computation of 2nd order values of the operators H (energy), Σ (specific isotope shift), hyperfine structure (sC^2 , C^2 , ℓ , s), spin-orbit and dipole C^1 . It computes the angular part of the energy matrix and various operators and edits the results in a form suitable for Froese's multi-configurational Hartree-Fock program [1].

Method of solution.

Determinantal states of given M_S and M_L values are used. Angular matrix element are computed from the $c^k(\ell m,\ell' m')$ coefficients [2]. In each excited configuration the basis formed of Slater determinants is reduced to a minimum number of states contributing to the 2nd order.

Restrictions on the complexity of the problem.

$n\ell$ shell with $\ell \leqslant 5$.

Typical running time.

For case 1 of test run 0.9 s , including the computation of the c^k coefficients. For case 2 of test run 0.1 s .

Unusual features of the program : FORTRAN V instructions INCLUDE and PARAMETER , intrinsic functions FLD and DECODE .

References.

[1] C. Froese-Fischer, C. P. C. 1 (1969) 151, 14, 145 (1978).

[2] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press 1963) p. 175.

1. Introduction and theory.

In a multiconfigurational Hartree-Fock (MCHF) calculation, one aims to determine a wavefunction of the form

$$|\Phi\rangle = \alpha|f\rangle + \beta_1|e_1\rangle + \beta_2|e_2\rangle + \dots \quad . \tag{1}$$

We consider the atomic non-relativistic case where $|f\rangle$, $|e_1\rangle$, $|e_2\rangle$ ... are Russell-Saunders (RS) terms of the same LS values, and where the hamiltonian is

$$H = H_0 + Q \qquad \text{with} \quad H_0 = \sum_i (p_i^2/2m + V_i(r)) \tag{2}$$

$V(r)$ central field potential, Q electrostatic interaction of the electrons.

Usually one chooses wavefunction (1) according to the physical problem studied. Suppose we are interested in computing the mean value of operator A . The first order parts $|e_j\rangle$ $(j=1,2\dots)$ of eq. (1) contributing to the 2nd order value of A are those for which :

$$(f/H/e_j)(e_j/A/f) \neq 0 \quad . \tag{3}$$

In paper [1] we described a method for choosing the terms in eq. (1), only by angular considerations, in order that in each excited configuration the minimum number of RS terms satisfying eq. (3) is retained.

The program EXCGH following this method constructs the $|e_i\rangle$ states and computes the angular part of the energy matrix and various operators for the multiconfigurational wavefunction (1).

As input we give p states $|f_i\rangle$ $(1 \leqslant i \leqslant p)$, that we call <u>initial states</u>, which are described as sums of Slater determinants with the same

M_L , M_S values (the same for all initial states) :

$$|f_i\rangle = w_i\ \{n\ell\ m_\ell m_s,\dots\} + w_i'\ \{\ \dots\ \} + \dots \qquad (4)$$

As input we also give the excited configurations : each one is obtained by a biexcitation $ab \rightarrow cd$ or monoexcitation $a \rightarrow b$ ($a \equiv n\ell$, etc are names of shells) from one of the initial states $|f_i\rangle$.

Within each excited configuration the program constructs a basis as small as possible of <u>excited states</u> $|e_j\rangle$ such that

$$\left.\begin{array}{l}(f_i/H/e_j) \neq 0 \\ (f_i/A/e_j) \neq 0\end{array}\right\} \qquad \begin{array}{l}\text{for at least one } i \ (1 \leqslant i \leqslant p) \\ \text{and for each } j \ .\end{array} \qquad (5)$$

Condition (5) is more general than condition (3), several initial states being allowed instead of just one. This is useful (i) when in wavefunction (1) several terms have large weights so that it might be necessary to perturb them at the same time and (ii) when one wants to calculate 2nd order values of non diagonal matrix elements like $(f_1/C^1/f_2)$ for oscillator strengths.

The operator A can be H itself, Σ (the specific isotope shift operator), any of the hyperfine structure (hfs) operators of types sC^2, C^2 , ℓ , s or the set of them all, the spin-orbit operator $\sum_i \vec{s}_i \cdot \vec{\ell}_i$ or the dipole operator C^1 .

As options, for monoexcitations of the type $n\ell \rightarrow n'\ell$ it is possible to suppress Brillouin's term [2] and for biexcitations of the type $ab \rightarrow n\ell, n'\ell$ it is possible to keep only «forbidden» terms ([3], see also appendix A in [1]).

2. Description of the program.

The role of subroutines is described in table 1 .

The following steps are gone through :

Computation of the $c^k(\ell m,\ell' m')$ coefficients in floating point form $c^k = a\sqrt{b}/c\sqrt{d}$ from the integers a b c d which are given in the BLOCK DATA DATUM . For ℓ,ℓ' lesser or equal to 5 there are 4795 non zero coefficients.

Reading and checking of data

Computation of $(f_i/H/f_j)$ $(1 \leqslant i \leqslant j \leqslant p)$.

Loops on excitations : determination of the excited determinants using subroutine EXC , reduction of the states (steps 1 and 2 of [1]) by calling subroutine CORE .

Computation of $(e_i/H/e_j)$ $(i \leqslant j)$

Printing and writing on file 9 using subroutines SORTIE and PRT .

Unusual features of the program.

This program like the program TERM [4] makes use of the FORTRAN V instructions INCLUDE and PARAMETER which permit to modify the dimensions in an easy way, and of the intrinsic functions FLD and DECODE . All section 4. of [4] remains valid for this program.

3. Data input.

The input consists of cards read. The role of each card, which is described in detail in section 3.2, is determined by the character in column 1 . For instance a card beginning with W (such a card will be called a W card or of type W) serves to define a weight.

3.1 Order of cards.

3.1.1 Description of an initial state.

The state $f_i = w \{\underbrace{k_1, k_2}_{a}, \underbrace{k_3 \dots}_{b}\} + w' \{\underbrace{k'_1, k'_2}_{a}, \underbrace{k'_3 \dots}_{b}\} + \dots$

is defined with the following cards (we just indicate the type of the cards and what their role is) :

T	card indicating the beginning of the description of an initial state
W	weight of the 1st determinant
D	orbitals of shell a : k_1 , k_2
D	orbitals of shell b : k_3 ...
...	
W	weight of the 2nd determinant
D	orbitals of shell a : k'_1 , k'_2
...	

The output file 15 of program TERM [4] which contains exactly the above sequence of cards is directly usable as input for the program EXCGH .

3.1.2 Description of a case.

The structure giving the initial states f_i $(1 \leqslant i \leqslant p)$ is :

$$\left.\begin{array}{l} T \\ \dots \end{array}\right\} f_1$$

$$\left.\begin{array}{l} T \\ \dots \end{array}\right\} f_2 \qquad \text{each } f_i \text{ is as in preceding section}$$

$$\left.\begin{array}{l} T \\ \dots \end{array}\right\} f_p$$

* indicates the end of the case.

Shells filled in all initial states $|f_i\rangle$ $(1 \leqslant i \leqslant p)$ can be given by N or C cards. These cards, as well as cards of types M , R , S , X , Y or Z , can be placed anywhere before the * card.

Excitations made from initial state f_i are given by E cards placed anywhere within the description of state $|f_i\rangle$, i. e. after the initial T card of the state and before the T card of the following state (or before the * card for state $|f_p\rangle$).

3.1.3 Repetition structure.

Several cases can be treated in the same run :

$$\left.\begin{array}{l} \dots \\ * \end{array}\right\} \quad \text{case 1}$$

$$\left.\begin{array}{l} \dots \\ * \end{array}\right\} \quad \text{case 2} \qquad \text{each case as in the preceding section.}$$

...

*

F indicates the end of the run.

If in cases k and k+1 the initial states are respectively $|f_i>$ ($1 \leqslant i \leqslant p$) and $|f'_i>$ ($1 \leqslant i \leqslant p$) where each $|f'_i>$ can be obtained from $|f_i>$ by changing the weights, it is then possible to use the repetition structure, i. e. omit <u>all</u> C , N and D cards in case k+1 . In order to make use of this structure, it is allowed to enter determinants with null weights (W card, blank but for the W). Moreover if all weights are unchanged for state i , i. e. if $|f'_i> = |f_i>$ it is then possible to omit <u>all</u> W cards in the description of $|f'_i>$.

3.1.4 Simplifications of data within a case.

a) The 1st T card can be suppressed if there is a card of type D , W or E in state $|f_1>$.

b) The W card can be suppressed in state $|f_i>$ if there is only one weight (=1) .

c) If there are only filled shells (and so only one initial state) there is no need for W and D cards.

3.2 Role of cards.

The type of a card is its first character.

The name of a shell is always given in A3 FORMAT . The ℓ value of the shell is determined by the 1st S , P , D , F , G or H appearing in the name from left to right. The n value plays no role in the program. Examples : 6S ($n=6$, $\ell=0$) SP ($n=0$, $\ell=0$) .

For cards of types R , S , X , Z and title cards (see section 3.2.15.a) only the last card of a given type is significant.

For cards of types C , D , N and Y , all cards are significant. So :

```
D‸‸‸2p‸1
D‸‸‸2p‸2
N‸‸‸1s
N‸‸‸2s
Y‸‸‸1
Y‸‸‸2
```

is equivalent to

```
D‸‸‸2p‸1‸2
N‸‸‸1s‸2s
Y‸‸‸1‸2
```

3.1.1 Type * . End of case.

3.2.2 Type C . $a_1, a_2 \ldots a_{24}$ FORMAT(3X,24A3)

Each non blank a_i $(1 \leqslant i \leqslant 24)$ is a spectator filled shell, i. e. it is not inscribed in the determinants. If a_i occurs in an excitation it is transformed in an inscribed filled shell (cf. type N).

3.2.3 Type D . opt , a , k_1 , $k_2 \ldots k_{14}$ FORMAT(2X,A1,A3,14I2) .

It gives a part of a determinant containing orbitals from shell a . Within a $n\ell$ shell the orbitals are numbered by k from 1 to $2(2\ell+1)$ with m_ℓ and then m_s increasing. Example : for $\ell=1$: $\overset{-}{-1}$, $\overset{-}{0}$, $\overset{-}{1}$, $\overset{+}{-1}$, $\overset{+}{0}$, $\overset{+}{1}$ correspond respectively to k = 1 , 2 , 3 , 4 , 5 , 6 .

a) if opt $\neq$ '-' , the part of the determinant is $\{k_\alpha, k_\beta \ldots\}$ where k_α $(k_\beta \ldots)$ is the first (2nd...) non zero k_i $(1 \leqslant i \leqslant 14)$.

b) if opt = '-' the part of the determinant is $\{1,2 \ldots \hat{k}_\mu \ldots \hat{k}_\nu \ldots, 2(2\ell+1)\}$ where $\hat{k}$ means that k is omitted, and where k_μ , k_ν ... are the k_i $(1 \leqslant i \leqslant 14)$ different from zero.

Note that in case b) the order of the k_i has no meaning.

3.2.4 Type E . a , b , c , d , opt FORMAT(3X,4A3,I3) .

Describes the excitation ab → cd .

For the monoexcitation $\alpha \rightarrow \beta$ put :

$a = \alpha$ and b = '^^^' (blank zone), or a = '^^^' and $b = \alpha$ as well as c = '^^^' and $d = \beta$, or $c = \beta$ and d = '^^^' .

The excitation $\alpha x \rightarrow \beta x$ is treated like the monoexcitation $\alpha \rightarrow \beta$.

opt determines the operator A in $(f/A/e_i) \neq 0$, according to table 2. If opt $\leqslant 0$ Brillouin's term is suppressed.

3.2.5 Type F . End of run. Provokes the impression of the PARAMETER's (see section 5.1) and their effectively utilised value.

3.2.6 Type M . Message : columns 2-80 are written on columns 1-79 on file 9 .

3.2.7 Type N . $a_1, a_2 \ldots a_{24}$ FORMAT(3X,24A3) .

Each non blank a_i $(1 \leqslant i \leqslant 24)$ is a filled shell which is inscribed in every determinant of every initial state.

3.2.8 Type R . The description of all states is printed.

3.2.9 Type S . The computation of all matrix elements not containing at least an initial state is suppressed. For example, if there is one initial state, only matrix elements $\langle 1|H|i\rangle, \langle 1|A|i\rangle$ $(i=1,2\ldots)$ are computed.

3.2.10 Type T . Marks the beginning of an initial state.

3.2.11 Type W . Describes weight w .

a) if 'R' is punched in 2nd column

w FORMAT(3X,F12.8)

b) otherwise : a , b , c , d FORMAT(3X,4I3)

then the weight is $\begin{cases} =0 & \text{if } b \text{ or } c \text{ or } d=0 \\ =a\sqrt{b}/c\sqrt{d} & \text{if } bcd \neq 0 \end{cases}$.

3.2.12 Type X . RHO,H,NO FØRMAT(3X,2F6.0,I6) .

If this card does not appear RHO = -3 , H = 1/16 , NO = 160 . Used only for writing 1st Froese HF card on file 9 .

3.2.13 Type Y . $s_1, s_2, \ldots, s_{15}$ FORMAT(3X,15I2) .

The excited states $s_i \neq 0$ $(1 \leqslant i \leqslant 15)$ that would appear in a run without Y cards are deleted.

3.2.14 Type Z . IZ FORMAT(3X) .

Defines the value of the nuclear charge. If there is no Z cards IZ = number of orbitals (spectator shells included), corresponding to a neutral atom. Serves only for writing 1st Froese HF card on file 9 .

3.2.15 Other types .

a) If columns 1-3 are left blank

IATOM,ITERM FØRMAT(3X,2A6)

which serves as a title, and for writing 1st Froese HF card on file 9 .

b) Otherwise the card is ignored.

4. Data output.

The output in files 9 and 10 is in the form of card images.

4.1 Results printed.

a) All input cards (they are numbered).

b) Description of initial and excited states as sums of determinants (if there is a R card in the case).

c) Matrix elements between all pairs of states $i \leqslant j$ (or only states with $1 \leqslant i \leqslant p$ = number of initial states if a S card (3.2.9) is read) for the following operators (the example is for the state $3s3p, M_S=M_L=1$) .

\+ V + Q : Given in terms of Slater F , G , R and central-field I integrals.

For diagonal elements, the average energy E_{av} of the configuration is subtracted.

Example : -.16666666 G 1(3S 3P) corresponding to $-\frac{1}{6} G^1(3s,3p)$.

\+ s_z : (contact term of hfs). The matrix element of $\sum_{i=1}^{N} s_{iz}\, \delta(\vec{r}_i)$ (N = number of electrons) is printed.

Example : .50000000 PSI(3S)*PSI(3S) corresponding to $\frac{1}{2}|\Psi_{3s}(0)|^2$

+ ℓ_z, : (orbital term of hfs).

+ $-\sqrt{10}(sC^2)^1_0$ (spin dipole term of hfs).

+ C^2_0 (quadrupole term of hfs).

The matrix elements of $\sum_{i=1}^{N} \ell_{zi}\, r_i^{-3}$, $\sum_{i=1}^{N} -\sqrt{10}(sC^2)^1_{0\,i}\, r_i^{-3}$ and $\sum_{i=1}^{N} C^2_{0\,i}\, r_i^{-3}$ are printed.

Example : 1.00000000 HFS/L A(3P 3P)

-.20000000 HFS/SC2 A(3P 3P)

-.20000000 HFS/C2 B(3P 3P)

corresponding to $\langle r^{-3}\rangle_{3p}$ (ℓ part) , $-\frac{1}{5}\langle r^{-3}\rangle_{3p}$ (sC^2 part) and $-\frac{1}{5}\langle r^{-3}\rangle_{3p}$ (C^2 part).

+ spin-orbit : $\sum_{i=1}^{N} \xi(r_i)\vec{s}_i\cdot\vec{\ell}_i$ (the radial part $\xi(r_i)$ is of no importance here).

Example : .50000000 ZETA (3P 3P) corresponding to $\frac{1}{2}\zeta_{3p}$

$\frac{1}{2}\zeta_{3p} = \frac{1}{2}(R_{3p}|\xi|R_{3p})$.

+ C^1_0 (dipole) : $\sum_{i=1}^{N} r_{iz} = \sum_{i=1}^{N} r_i\, C^1_{0\,i}$

Example : between the states $2p3p\ ^1P\ M_L=1$ and $1s2p\ ^1P\ M_L=1$:

.40824829 DIPOLE (1S/R/3P)

corresponding to $\frac{1}{\sqrt{6}}\langle r\rangle_{1s-3p}$.

Remark : The printing order of the shells is : shells read on C cards, then on N cards, D cards and finally on E cards .

4.2 File 9 .

This file contains images of cards directly usable as input by Froese's MCHF program [5] and by the program EDD [6]. Namely :

a) 1st Froese HF card ;

b) orbitals and occupation numbers ;

c) expression of energy : this is the set of matrix elements of $V+Q$, the non diagonal elements being doubled and E_{av} being subtracted. For a description of the FORMAT see section 3.2 of [6].

4.3 File 10 .

It contains the description of initial and excited states as sums of determinants.

5. Errors detected.

5.1 Overflow of dimension.

It gives a diagnostic stating that PARAMETER so and so is too small. The meaning of each PARAMETER is given in table 3. For correction see section 4.1 of [4]. In table 4 we give the PARAMETER's , which are of structural nature and must not be modified.

5.2 Data errors.

Input data is thoroughly checked and detection of an error usually cancels the case.

5.2.1 Shells. A name for a shell is bad if it does not contain S , P , D , F , G or H . A shell must not appear twice on C and N cards. It must not appear at the same time on C (or N) cards and D cards.

5.2.2 Determinants. On D cards (cf. section 3.2.3) one must have $0 \leqslant k_i \leqslant 2(2\ell+1)$ $(1 \leqslant i \leqslant 14)$. The orbitals of a determinant must be different.

5.2.3 Initial states. In state $f = w^{(1)}\{\ \} + w^{(2)}\{\ \} + \ldots$ one must have $|w^{(1)}|^2 + |w^{(2)}|^2 + \ldots = 1$. Each determinant must have the same shell structure (same number of orbitals, same shells, same occupation numbers) and the same M_S and M_L values. All determinants must be different.

The various initial states must have the same number of orbitals and the same M_S and M_L values.

5.2.4 Excitations. E cards must have exactly the structure described in section 3.2.4 (the value of opt is checked).

In excitations $ab \rightarrow cd$ and $\alpha \rightarrow \beta$ a , b and α must appear on C , N or D cards. An error on an E card cancels the excitation, but not the case.

5.3 Execution errors .

The following errors, in a given excitation produce a diagnostic, but do not cancel the execution : no excited determinant ; no matrix element between initial states and excited determinants ; suppression of Brillouin's

term asked for when it does not exist ; the reduction of the excitation cannot be done (system of rank zero) ; combinations $R^k \pm R^{k'}$ that cannot be formed when opt $\geqslant 51$ (opt read on E card) ; all states in the excitation have been deleted (for example by Y cards).

6. Description of test run.

6.1 1st case.

There is one initial state : $|(3s3p)\ ^3P,1,1\rangle$ of Mg on which we effect the excitation 1s → 3d , having in view the computation of the specific isotope shift.

We also list the content of file 9 .

6.2 2nd case.

There are 2 initial states of He : $|(1s2p)\ ^1P,0,1\rangle$ and $|(2p3p)\ ^1P,0,1\rangle$ of opposite parities. We perform the excitation 1s2p → 3pd which gives a contribution to the dipole moment.

This case could be treated using the output file 15 of the program TERM [4] as input in a calculation consisting of the following two steps.

1. Execute program TERM with input :

```
PUNCH$ (2P ; 3P)1P,0,1*
PUNCH$ (1S ; 2P)1P,0,1*
END
```

2. Execute program EXCGH with input from file 15 followed by :

```
EXC‸1S‸2P‸3P‸D‸‸‸8
*
F
```

7. Acknowledgment.

The author thanks J. Bauche for suggesting the problem and the method.

References.

[1] J. J. Labarthe, J. Phys. B, 6 (1973) 1761.

[2] J. Bauche and M. Klapisch, J. Phys. B, 5 (1972) 29.

[3] J. C. Keller, Thèse, Université de Paris 1972.

[4] J. J. Labarthe, C. P. C. (submitted as 1st paper).

[5] C. Froese-Fischer, C. P. C. 1 (1969) 151, 14, 145 (1978).

[6] J. J. Labarthe, C. P. C. (submitted as 3rd paper).

Captions of tables.

Table 1 : Role of subroutines.

Table 2 : Operator for which the reduction is made.

Table 3 : List of PARAMETER's which may be modified.

Table 4 : List of PARAMETER's not to be modified.

Table 1

Name	Role
ADD	computes matrix element between two states.
CALCUL	computes matrix element between two determinants.
CONTR	eliminates angular coefficients equal to zero.
CORE	reduces the set of states (steps 1 and 2 of [1]).
DATUM	BLOCK DATA.
EAV	computes the mean value of the energy in a configuration.
ERSET 1 ERSET 2 ERSET 3	check dimensions.
EXC	generates excited determinants.
EXCIT	main program.
INSRK	inscribes angular coefficient of integral.
PRT SORTIE	print and write on file 9.
VERIF	checks dimensions.
W	decodes name of shell.

Table 2.

$\lvert \mathrm{opt} \rvert$	A
0 or 1	$Q + V$
2	$\Sigma + V$
3	hfs (ℓ_z , $(sC^2)^1_0$, C^2_0 and s_z)
4	ℓ_z
5	$(sC^2)^1_0$
6	C^2_0
7	s_z [$\lvert\Psi\rvert^2$]
8	C^1_0 [dipole]
51	$Q + V$ } only the "forbidden" states
52	Σ } are kept

Table 3.

PARAMETER	not to be exceeded by the number of
IDFOP	inscribed orbitals in all initial states (= number of inscribed electrons * number of initial determinants).
IRKP	integrals between initial states and a given excited configuration.
ITEP	initial states.
NBDEXP	excited determinants.
NBDFOP	determinants in initial states.
NBELP	inscribed electrons.
NBETAP	states.
NBEXCP	excitations.
NBRKP	integrals.
NBWFP	shells.
NCPLEP	pairs of states between which matrix elements are computed.
NELPOP	$\sum_{n\ell} 2(2\ell+1)$, where the sum is over the shells, spectator shells excluded.
NFINP	matrix elements to be printed.
RELCP	D cards.
RES	shells read on C or N cards.

Table 4.

PARAMETER	value	signification
CKP	4795	number of $c_k(\ell m \ell' m')$ coefficients.
INTSUP	6	number of monoelectronic operators (V excepted).
LLLP	6	maximum $\ell+1$.
LLLP1	5	LLLP - 1 .
LLLP2	21	LLLP (LLLP+1) / 2 .
LLLP3	441	$(\text{LLLP2})^2$
LMLP	36	$(\text{LLLP})^2$
MOY1P	21	dimension of data for computing E_{av} .
MOY2P	56	
NPP	21	number of printed PARAMETER's .

```
************************************************************************************************************
*****    1.    MG 3P                                                                3035 *****EXCIT2
*****    2. N    1S 2S 2P                                                           3036 *****EXCIT2
*****    3. DT+ 3S 2                                                                3037 *****EXCIT2
*****    4. DT+ 3P 6                                                                3038 *****EXCIT2
*****    5. EXC 1S     3D     2                                                     3039 *****EXCIT2
*****    6. *                                                                       3040 *****EXCIT2
     EXCITATION  1 REDUCTION FOR SIGM+V
THE SYSTEM OF     1 VECTORS IS OF RANK     1
ORBITALS FROM  1 10  6
NUMBER OF ELECTRONS 12
NUMBER OF DETERMINANTS IN INITIAL STATE(S)  1
NUMBER OF INTEGRALS       1 * F       5 * G       2 * R       0 * I

1ST FROESE HF CARD
 ATOM  TERM  WF CF NF NG NR     Z   RHO     H      NO   INITIAL STATES
MG 3P         6  2  1  5  2    12-3.000.06250    160        T  T  1

          EXCITATION  1 NUMBER OF DETERMINANTS   6

 CONFIG       2

FROESE HF ORBITAL CARDS
                                                   CONFIGURATIONS
          EL   N   L   SCREEN               ACC IND  1  2

          1S   1   0                        0.6 -1   2  1
          2S   2   0                        0.6 -1   2  2
          2P   2   1                        0.6 -1   6  6
          3S   3   0                        0.6 -1   1  1
          3P   3   1                        0.6 -1   1  1
          3D   3   2                        0.6 -1   0  1

( 1 / H / 1 ) =
   .50000000 PSI( 3S)* PSI( 3S)   -.16666666 G 1( 3S 3P)        1.00000000 HFS/L     A( 3P 3P)    .50000000ZETA( 3P 3P)
  -.20000000 HFS/C2    B( 3P 3P)   -.20000000 HFS/SC2  A( 3P 3P)

( 1 / H / 2 ) =
   .66666665 R 1( 1S 3P, 3P 3D)     .10000000 HFS/SC2  A( 3D 1S)     -.20000000 R 2( 1S 3P, 3D 3P)     .10000000 HFS/C2    B( 3D 1S)

( 2 / H / 2 ) =
  -.49999999 HFS/L     A( 3P 3P)   -.02000000 HFS/C2    B( 3P 3P)    .20000000 F 2( 3P 3D)           .50000000 PSI( 3S)* PSI( 3S)
  -.09999999 G 2( 3S 3D)           -.09999999 HFS/C2    B( 3D 3D)   -.09999999 HFS/SC2  A( 3D 3D)    .49999999 G 1( 1S 3P)
  1.49999999 HFS/L     A( 3D 3D)    .74999999ZETA( 3D 3D)            .03333333 G 1( 3P 3D)          -.08571428 G 3( 3P 3D)


************************************************************************************************************
*****    7. T  (2P;3P)1P,0,1                                                        3041 *****EXCIT2
```

```
*****    8. W     1   1   2   1                                        3042 *****EXCIT2
*****    9. DET 2P 6                                                   3043 *****EXCIT2
*****   10. DET 3P 2                                                   3044 *****EXCIT2
*****   11. W    -1   1   2   1                                        3045 *****EXCIT2
*****   12. DET 2P 5                                                   3046 *****EXCIT2
*****   13. DET 3P 3                                                   3047 *****EXCIT2
*****   14. W    -1   1   2   1                                        3048 *****EXCIT2
*****   15. DET 2P 3                                                   3049 *****EXCIT2
*****   16. DET 3P 5                                                   3050 *****EXCIT2
*****   17. W     1   1   2   1                                        3051 *****EXCIT2
*****   18. DET 2P 2                                                   3052 *****EXCIT2
*****   19. DET 3P 6                                                   3053 *****EXCIT2
*****   20. T    (1S,2P)1P,0,1                                         3054 *****EXCIT2
*****   21. W     1   1   1   2                                        3055 *****EXCIT2
*****   22. DET 1S 2                                                   3056 *****EXCIT2
*****   23. DET 2P 3                                                   3057 *****EXCIT2
*****   24. W    -1   1   1   2                                        3058 *****EXCIT2
*****   25. DET 1S 1                                                   3059 *****EXCIT2
*****   26. DET 2P 6                                                   3060 *****EXCIT2
*****   27. EXC 1S 2P 3P D   8                                         3061 *****EXCIT2
*****   28. *                                                          3062 *****EXCIT2
     EXCITATION  1 REDUCTION FOR C1
THE SYSTEM OF     2 VECTORS IS OF RANK    1
THE SYSTEM OF     1 VECTORS IS OF RANK    1
ORBITALS FROM  1 TO  4
NUMBER OF ELECTRONS  2
NUMBER OF DETERMINANTS IN INITIAL STATE(S)  6
NUMBER OF INTEGRALS       2 * F       5 * G       2 * R       0 * I

1ST FROESE HF CARD
 ATOM  TERM  WF CF NF NG NR     2  RHO     H     NO  INITIAL STATES
MG 3P          4  3  2  5  2      2-3.000.06250   160         T  T  2

           EXCITATION  1 NUMBER OF DETERMINANTS   6

 CONFIG        3

FROESE HF ORBITAL CARDS
                                                        CONFIGURATIONS
               EL  N  L  SCREEN                   ACC IND  1  2  3

               2P  2  1                           0.6 -1   1  1  0
               3P  3  1                           0.6 -1   1  0  1
               1S  1  0                           0.6 -1   0  1  0
               D   0  2                           0.6 -1   0  0  1

( 1 / H / 1 ) =
    .50000000 HFS/L    A( 2P 2P)    .10000000 HFS/C2   B( 2P 2P)   -.20000000 F 2( 2P 3P)        .10000000 HFS/C2   B( 3P 3P)
    .26666666 G 2( 2P 3P)          -.83333334 G 0( 2P 3P)           .50000000 HFS/L    A( 3P 3P)

( 1 / H / 2 ) =
    .40624829 DIPOLE( 1S/ R/ 3P)

( 2 / H / 2 ) =
   1.00000000 HFS/L    A( 2P 2P)   -.20000000 HFS/C2   B( 2P 2P)    .49999999 G 1( 2P 1S)

( 1 / H / 3 ) =
```

```
     .28867513 DIPOLE( D / R/ 2P)

 ( 2 / H / 3 ) =
     .28284270 R 2( 2P 1S, 3P D )     .47140450 R 1( 2P 3P, D 1S)

 ( 3 / H / 3 ) =
   -.49999999 HFS/L     A( 3P 3P)   -.02000000 HFS/C2   B( 3P 3P)    .20000000 F 2( 3P D )          -.09999999 HFS/C2   B( D  D )
    .13333333 G 1( 3P D )           .29999999 G 3( 3P D )            1.49999999 HFS/L    A( D  D )


*******************************************************************************************************************************
***** 29. F                                                                                 3063 *****EXCIT2
PARAMETER = MAXIMUM VALUE (UTILISED VALUE)
           CKP    = 4795 ( 4795 )               IDFOP  =  500 (   12 )         INTSUP =    6 (    6 )          IRKP   =  20 (   4 )
           ITEP   =    6 (    2 )               LLLP   =    6 (    6 )         LLLP2  =   21 (   21 )          MOY1P  =  15 (  15 )
           MOY2P  =   56 (   56 )               NBDEXP =  700 (   10 )         NBDFOP =   50 (    6 )          NBELP  =  70 (  12 )
           NBETAP =   40 (    3 )               NBEXCP =   22 (    1 )         NBRKP  =  400 (   43 )          NBWFP  =  26 (   6 )
           NCPLEP =   45 (    6 )               NELPOP =  150 (   28 )         NFINP  =  150 (   22 )          RELCP  = 500 (  12 )
           RES    =  100 (    3 )
```

```
@ELT,S TPF$.A                                                                     3066
ELT017 RLIB70 12/13-20:22:31-(0,)
000001        000    MG 3P          6  2  1  5  2     12-3.000.06250   160          T  T  1
000002        000     1S  1  0                          0.6 -1  2  1
000003        000     2S  2  0                          0.6 -1  2  2
000004        000     2P  2  1                          0.6 -1  6  6
000005        000     3S  3  0                          0.6 -1  1  1
000006        000     3P  3  1                          0.6 -1  1  1
000007        000     3D  3  2                          0.6 -1  0 -1
000008        000         .20000000F2( 5 2, 6 2)
000009        000        -.16666666G1( 4 1, 5 1)
000010        000        -.09999999G2( 4 2, 6 2)
000011        000         .49999999G1( 1 2, 5 2)
000012        000         .03333333G1( 5 2, 6 2)
000013        000        -.08571428G3( 5 2, 6 2)
000014        000        1.33333330R1( 1 5 1, 5 6 2)
000015        000        -.39999999R2( 1 5 1, 6 5 2)
000016        000    MG 3P          4  3  2  5  2      2-3.000.06250   160          T  T  2
000017        000     2P  2  1                          0.6 -1  1  1  0
000018        000     3P  3  1                          0.6 -1  1  0  1
000019        000     1S  1  0                          0.6 -1  0  1  0
000020        000     D   0  2                          0.6 -1  0  0  1
000021        000        -.20000000F2( 1 1, 2 1)
000022        000         .20000000F2( 2 3, 4 3)
000023        000         .26666666G2( 1 1, 2 1)
000024        000        -.83333334G0( 1 1, 2 1)
000025        000         .49999999G1( 1 2, 3 2)
000026        000         .13333333G1( 2 3, 4 3)
000027        000         .29999999G3( 2 3, 4 3)
000028        000         .56568541R2( 1 3 2, 2 4 3)
000029        000         .94280900R1( 1 2 2, 4 3 3)
```

ANNEXE D

Analytic approximations of radial orbitals for multiconfigurational Hartree - Fock computations.

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Classification : Atomic Physics. Structure.

Program Summary.

Title of program : EDD .

Computer : UNIVAC 1110 ; Installation : Université d'Orsay, France.

Operating system : UNIVAC 1110 EXEC 8 .

Program language used : FORTRAN V .

High speed storage required : 52 000 words.

No of bits in a word : 36 .

Overlay structure : none.

No of magnetic tapes required : 3 (for output).

Other peripherals used : Card reader, line printer, card puncher (option).

No of cards in combined program and test deck : 5209 .

Card punching code : IBM 026 .

Keywords : Atomic structure, non relativistic, excitations, virtual orbital, analytic, configuration interaction, multiconfigurational Hartree-Fock, MCHF, Slater functions, non-orthogonality, central field integral, energy, specific isotope shift, second order, crossed second order, simplex method.

Nature of the physical problem.

An analytic non-relativistic atomic multiconfigurational variational program.

Central field integrals and non orthogonality between orbitals are accepted. The program makes it possible easily to determine approximate excited orbitals in order to have initial values for the numerical multiconfigurational (MCHF) program [1]. All necessary input for [1] is written in file 9.

Method of solution.

The various orbitals can be described numerically, analytically or developed on basis orbitals (numerical orbitals or Slater functions). The various parameters are determined to minimize the energy or the 2nd order energy by a 2-loop simplex method (inner loop for development coefficients, outer loop for exponents).

Restrictions on the complexity of the problem.

$n\ell$ shells with $\ell \leqslant 5$; excited configurations must be obtained from configuration 1 by bi- or monoexcitations ; non-orthogonality between orbitals must be such that in the expression of energy the most complicated overlaps are of the type $(n\ell/n'\ell)(n_1\ell'/n_2\ell')$ with $\ell \neq \ell'$.

Typical running time. For determining one orbital to a good precision, the necessary time is 1 - 2 minutes.

Unusual features of the program : FORTRAN V instructions INCLUDE , PARAMETER , intrinsic functions FLD and DECODE . A required diagonalisation subroutine is not included in the deck.

Reference : [1] C. Froese-Fischer, C. P. C. 1 (1969) 151, 14, 145 (1978).

1. Introduction and theory.

EDD is an atomic non-relativistic multiconfigurational variational program. The radial orbitals can be of 3 types : (i) numerical, (ii) analytical or (iii) developed on basis orbitals which can themselves be of types (i) and (ii). The energy calculated by diagonalisation or in the 2nd order approximation is minimised by the simplex method [1] (see also [2]). In fact there are two nested simplex loops : the inner one for the development coefficients and the outer one for the parameters describing the analytic orbitals.

The program was originally developed to generate initial approximations to orbitals for use in Froese's multiconfigurational Hartree-Fock (MCHF) program [3]. Indeed when the orbitals have small occupation numbers there are convergence difficulties. The program EDD is extremely easy to use for that purpose since it utilises part of Froese's data input, and punches the remaining necessary input.

Other possible uses of the program EDD are :

(i) configurations may differ by a $n\ell$-$n\ell'$ excitation, resulting in the introduction of off-diagonal central-field integrals $I_{n\ell\ n'\ell} = \int_0^\infty R_{n\ell}(r)\left[-\frac{d^2}{dr^2} - \frac{2Z}{r} + \frac{\ell(\ell+1)}{r^2}\right]R_{n'\ell}(r)$, where the radial orbital $R_{n\ell}(r)$ is normalized by $\int_0^\infty [R_{n\ell}(r)]^2 dr = 1$.

(ii) non orthogonality between orbitals is allowed as long as in the expression of the energy the most complicated overlaps are of the type $(n\ell/n'\ell)(n_1\ell'/n_2\ell')$ with $\ell \neq \ell'$.

(iii) determination of virtual orbitals, as defined by Sternheimer [4].

This determination is done by replacing off-diagonal energy integrals by integrals $(a|r|b)$ for dipole, $(a|r^{-3}|b)$ and $\Psi_a(0)\ \Psi_b(0)$ for hfs or $J(a,c)\ J(b,d)$ [7] for specific isotope shift.

The program also computes the specific isotope shift by the formulae of Stone [5] and of Vinti [6]. For more details see also [7].

Before computing the energy each orbital is represented numerically. What is computed is in fact $R_{n\ell}(r)\sqrt{r}$ which differs also from the representation used in Froese's program ($R_{n\ell}(r)/\sqrt{r}$). The orbitals are computed at points

$$r_i = \frac{1}{Z} \exp(-RHO + H * (i-1)) \qquad (1)$$

$i = 1, 2, \ldots$ exactly as in Froese's program.

2. Description of the program.

The role of subroutines is given in table 1.

2.1 Arrangement of memory.

Some arrays (for example AM) have dimensions that can be modified during the execution of the program (see section 3.1). All these arrays are disposed on a large array T ; for example T(UAM) is the first word of array AM where UAM is an address computed in the main program EDDA . To make the program easier to read, array AM is used with its own name by defining

```
EQUIVALENCE (T,AM) .
```

The first word of array AM is thus referenced as AM(UAM) and not as AM(1) .

2.2 Diagonalisation program.

The program uses subroutine MXEIG for the diagonalisation of symmetric real matrices, which being from the mathematical library of the computing center at Orsay is not included in the deck. This subroutine is called only once in subroutine OPTIM where its input/output is thoroughly described on comment cards.

2.3 Unusual features of the program.

The description of the FORTRAN V instructions INCLUDE , PARAMETER and of the intrinsic functions FLD and DECODE for bit manipulations can be found in section 4 of [8].

3. Data input.

It consists of cards, (i) for modifying the program parameters (section 3.1), (ii) for giving the angular data (section 3.2) and (iii) for giving the radial data (section 3.3). These cards are read respectively in (i) EDDA (ii) EDD1 and (iii) ANALYT .

The program can be used without knowing the possibilities described in sections 3.1 and 3.2.6 .

3.1 Modification of the program parameters.

There are two types of program parameters :

a) modifiable parameters that can be modified during execution. They are described on table 2.

b) internal parameters, described on table 3, which can be modified only by modifying the program as explained in section 4.1 of [8].

The modifiable parameters can be redefined by reading PARAMETER cards bearing the names of the modifiable parameters, that have the same structure as the FORTRAN V PARAMETER instruction with the following differences :

a) columns 1-80 are used ;

b) the word PARAMETER must be written without blanks and on one card ; arithmetics are not allowed ;

c) the continuation cards must be indicated with a + character in column 6, columns 1-5 are then ignored.

<u>Example</u> :
```
PARAMETER    BLOP=2 , LOCP =
^^^^^+ 6
  PARAMETER      NCRKP=8
```

As a guide for modifying parameters, their values and the values that would have been sufficient for the run (utilised value) are printed at the end of the run.

3.2 <u>Reading the angular data.</u>

The formats of Froese's program [3] are used. These cards are also the output (file 9) of the program EXCGH [9].

<u>3.2.1</u> Read the following card (1st Froese MCHF card)

FORMAT(2A6,5I3,3F6·0,I6,12X,I3) :

IATOM,ITERM, names

NB,	number of orbitals
LETA,	number of configurations
NBF,NFG,NBR	number of Slater integrals F , G and R
Z,	charge of nucleus
RHO,H,	initial point and step size (see eq. (1))
NO,	ignored
ITE	number of initial configurations (taken to be 1 if ITE=0).

3.2.2 For each $I = 1$,NB read the card(s) (MCHF orbital card) FORMAT(A3,2I3,30X,13F3.0) :

WWF(I),	name of the orbital, from which the program extracts the $n\ell$ values
NN(I),LLL(I),	$n\ell$ values which are not used in the program (but compared with those taken from WWF(I))
(APR(I,K),K=1,LETA)	occupation numbers of the orbital in configurations 1 to LETA .

If LETA > 13 read the remaining occupation numbers in the FORMAT(26F3.0) .

3.2.3 The role of the cards in the remaining angular and radial data is determined by the structure (usually the character in column 1) of the cards, not by their order.

3.2.4 Orthogonality/Non-orthogonality cards (O/N cards) .

A card with respectively an O or N in 1st column

FØRMAT(3X,24A3) $a_1,a_2 \ldots a_{24}$

effect : the orbitals $a_1,a_2 \ldots a_{24}$ are pairwise identical or (non-) orthogonal.

Remarks 1) The orbitals read in 3.2.2 are supposed orthogonal. If they are not use N cards before giving the integrals (section 3.2.5).

2) The E cards imply orthogonalities (3.2.6).

Example :

N‸‸‸1S‸2S‸3S‸4S

0‸‸‸1S‸2S

means that $ns \not\perp n's$ if $n<n'$ and $(n,n')\neq(1,2)$

and $1s \perp 2s$.

3.2.5 Energy matrix.

The expression of the energy is of the form :

$$E = E_{av} + \sum_{\substack{i\leqslant j\\ k}} w_i\, w_j\, c_k\, \mathcal{J}^k\,(abcd)\ Ov \quad . \qquad (2)$$

The sum is on the pairs of configurations $i\leqslant j$ and on radial integrals $\mathcal{J}^k$ depending on orbitals a,b,c,d (a is the number, not the name of the orbital). c_k is a numerical coefficient

w_i is the weight of configuration i

Ov is an overlap (or 1)

$E_{av} = \sum_i w_i^2\, E_{av,i}$ where $E_{av,i}$ is the average energy of the configuration of configuration i .

For each term $w_i\, w_j\, c_k\, \mathcal{J}^k$ (abcd) Ov in eq. (2) a card is needed with a character '(' or '['(punching code : 5-8-12) in column 15 and the type of the integral {F, G, R, T, I} in column 13 .

There are two formats :

For type R if $\mathfrak{J}^k$ (abcd) is the Slater integral $R^K(a,b,c,d)$

FORMAT(F12.8,1X,I1,2(1X,3I2)) c_k , K , a , b , i , c , d , j

i and j can be permuted. The integral R^9 is interpreted as :

$R^9(a,b,c,d) = J(a,c)\ J(b,d)$ (isotope shift integrals).

For types F , G , I or T

FORMAT(F12.8,A1,I1,2(1X,2I2)) c_k , type , K , a , i , b , j

when $\mathfrak{J}^k$ is the Slater integral $F^K(a,b)$ or $G^K(a,b)$ (if type is 'F' or 'G'), the central-field integral $I(a,b)$ (if type is 'I') or the integral $T_K(a,b)$ (if type if 'T').

The T integrals are :

$T_5(ab) = T_6(ab) = T_7(ab) = (a|r^{-3}|b)$

$T_8(ab) = \Psi_a(0)\ \Psi_b(0)$

$T_9(ab) = (a|r|b)$.

F^9 and G^9 are interpreted as isotope shift integrals like R^9 .

The overlap which must be of the form 1, (a'/b') or (a'/b')(a"/b") is automatically constructed, and need not be included in the input.

3.2.6 Construction of excitations.

The program can be used without knowing what is described in this section.

The orbitals appearing in configurations 1 - ITE are named core orbitals, the other virtual orbitals. Each configuration $i \geqslant 2$ is obtainable from configuration 1 by a mono- or biexcitation. Two excitations

are said to be of the same type if they involve the same core orbitals and if the virtual orbitals have the same orbital momenta ℓ (but they may have different names). If there are n excitations of a same type, these excitations are labeled from 1 to n . So each excitation is characterized by a type/label. The program lists these LETA-1 type/label.

Example 2s , 2p and 3s are the core orbitals

```
EXCITATION  2S  2P  3S  P1  1
EXCITATION  2S  2P  S   P1  1
EXCITATION  2S  2P  P2  SA  2
EXCITATION  2S  2P  3S  P1  2
```

excitations 1 and 4 (or 2 and 3) are of the same type.

The program permits the construction of a multiconfigurational wave function (angular part) containing configuration 1 and configurations obtained by excitations of the listed types. The virtual orbitals are initially supposed non orthogonal and can have new names. A given type/label excitation can be repeated several times. Orbitals initially non orthogonal may be made orthogonal.

The cards to be read are :

(i) E cards indicating the excitations to be constructed. These cards are recognized by an E in 1st column.

FØRMAT(3X,2A3,7(2A3,I3)) $a , b , c_1 , d_1 , \alpha_1 , c_2 , d_2 , \alpha_2 \ldots c_7 , d_7 , \alpha_7$

which produces the excitations $ab \rightarrow c_1 d_1$

$ab \rightarrow c_2 d_2$

$\ldots$

$ab \rightarrow c_7 d_7$ such that $c_i d_i \neq$ blanks

if $\alpha_i > 0$ only the excitation of label α_i of type $ab \rightarrow c_i d_i$ is constructed
if $\alpha_i = 0$ all excitations of type $ab \rightarrow c_i d_i$ are constructed.

The orbitals $c_1 d_1 \ c_2 d_2 \ldots c_7 d_7$ are pairwise identical or orthogonal.

<u>Remarks</u> 1) if there are no E cards the constructed wave function is identical to the one read on cards 3.2.1, 3.2.2 and 3.2.5 ;

2) to keep only configuration 1 use a Z card (i. e. with Z in 1st column).

(ii) if needed, O/N cards (3.2.4) modifying orthogonalities.

(iii) command cards. The various command cards are described in table 4. The last command must be a X , H or $*$ card.

<u>Example</u> : To treat the multiconfigurational wave function :

$$w_1 | 1s^2 \ 2s^2) + w_2 | (p1)^2 \ 2s^2) + w_3 | 1s^2 \ (p2)^2) + w_4 | 1s^2 \ (p3)^2)$$

where $p1 \not\perp p2$, $p1 \not\perp p3$ and $p2 \perp p3$, enter the angular data corresponding to $w_1 | 1s^2 \ 2s^2) + w_2 | p^2 \ 2s^2) + w_3 | 1s^2 \ p^2)$

with only one p orbital. The necessary E cards are :

```
E^^^1S^1S^P1^P1^^1
E^^^2S^2S^P2^P2^^1^P3^P3^^1    .
```

There is no need of N or O cards.

To generalise the example, the input angular data will be a multiconfigurational wave function with only one virtual orbital of each ℓ . There is an exception for excitations like $2p3p \rightarrow dd'$ where a second virtual orbital is used. In this case the expression of the energy (NBR in 3.2.1, R-integral cards in 3.2.2) has generally to be augmented

by antisymmetrization. This happens, between the excited configurations 2p3p→dd' containing both d and d' and 2p3p→ad not containing d' (a is different from orbital d'). Corresponding to the integral c $R^k(bd',ba)$ ($b \neq d$ is a core orbital) it is necessary to add the antisymmetrised integral : $-c\, R^k(bd,ba)$.

Indeed, the initial wave function is computed by supposing $d \perp d'$, in configuration 2p3p→ad d becomes d1 , in configuration 2p3p→dd' , dd' becomes d2 d2' and $d1 \not\perp d2'$. The off-diagonal energy matrix element contains $c\, R^k(b\ d2'\ b\ a)(d1/d2)$ and $-c\, R^k(b\ d2\ b\ a)(d1/d2')$ which is generated from the antisymmetrised integral that does not appear in the initial computation with $d \perp d'$.

3.2.7 This section is for those skipping section 3.2.6 . Read an H card (with H in 1st column). The reading of input continues in ANALYT (section 3.3) .

3.3 Reading the radial data.

The aim is

(i) to give the radial orbitals, which can be of 3 types : numerical, analytic, developed. The numerical orbitals can also be unchanged (that is kept as they were in the previous case) or S.O. (see last remark of 3.3.1). The parametrised orbitals are recomputed every time their parameters are changed in the simplex method by the Schmidt orthogonalisation process. The order of orthogonalisation is the order of appearance of the orbitals in this section.;

(ii) to give the method of optimisation. Several optimisations can be made. Before each optimisation it is possible to augment the number of basis

orbitals, to increase the analytic description of an analytic orbital, to fix or free parameters and also to modify the values of the parameters and their increments. If the values of the parameters are not modified, the pay off of the preceding optimisation is not lost.

3.3.1 Numerical orbital.

A numerical orbital is given by the same deck of cards as in Froese's program [3] viz.

a) a card with 'ATOM' written on columns 2-5 (the card is recognized by this word) :

FORMAT(32X,A3,I6,12X,D19.8) a , n_0 , A_0

a is the name of the orbital,

n_0 the number of points and A_0 is such that

$$R_a(r) \sim A_0 r^{\ell+1} \quad \text{when} \quad r \to 0 \ .$$

b) enough cards to read

FØRMAT(7F11.7) (YM(i), i= 1,n_0)

YM(i) is the value $R_a(r_i)/\sqrt{r_i}$ at point r_i of eq. (1).

Remarks : 1) if $n_0 >$ NPOINP then $n_0 =$ NPOINP .

2) Another value of A_0 is computed from the first points of YM . It replaces the preceding value if they are too different.

3) The cards in b) are listed only if a R card has been read (see 3.3.9).

4) It is possible to read an orbital not defined in the angular data. The following orbitals will be made orthogonal to it. The orbital will appear with the type S.O. .

3.3.2 Analytic orbital.

The A cards (with an A written in column 1) permit the definition of a sum of Slater functions :

$$S_a(r) = \sum_{i=1}^{n} A_i \, r^{\ell+1+k_i} \, e^{-\alpha_i r} \qquad (3)$$

with $A_1 = 1$ and where the A_i $(i \neq 1)$ and α_i are parameters.

The orbital a has then a radial part $R_a(r)$ which is obtained by orthonormalising $S_a(r)$ to the previous orbitals a must be orthogonal to. The Slater function $r^{\ell+1+k} e^{-\alpha r}$ reaches its maximum near a point r_i of the numerical mesh eq. (1). We shall call that i $(1 \leqslant i \leqslant \text{NPOINP})$ the center of the Slater function.

The format of an A card is :

FORMAT(1X,I2,A3,11(I2,A1,I3)) incr , a ,

(k_i , opt_i , center_i , i=1,11) .

This card states that orbital a is an analytic orbital and adds a term to eq. (3) for each $\text{center}_i \neq 0$. It defines the parameters NPAR+1,NPAR+2... (where NPAR was the number of previously defined outer-loop parameters) representing α_1 , A_2 , α_2 ... . The initial value of A_i $(i \neq 1)$ is zero, its increment is 1. The initial value of α_i is such that the center of the corresponding Slater function is center_i ; its increment is what is necessary to displace the center to center_i+incr (10 is a convenient value for incr). All these parameters are free except if opt_i is '*' which fixes α_i .

Remark : the values, increments and types of the parameters can be defined more precisely with C , T , V or L cards (3.3.7).

3.3.3 Developed orbital.

It is possible to use the following representation

$$\begin{aligned} R_{a1}(r) &= A_{11}\ B_{b1}^{(\ell)}(r) + A_{12}\ B_{b2}^{(\ell)}(r) + \dots \\ R_{a2}(r) &= A_{21}\ B_{b1}^{(\ell)}(r) + A_{22}\ B_{b2}^{(\ell)}(r) + \dots \end{aligned} \tag{4}$$

where the A_{ij} depend on inner loop parameters and the $B_{bj}^{(\ell)}(r)$ are orthonormal basis orbitals.

For that define :

a) The basis orbitals with a B card (B in column 1)

FORMAT(3X,24A3) b1,b2,...,b24

bj is a new name containing S , P , D , F , G or H (which determines the basis). For each basis orbital define the type which can be numerical (3.3.1) or analytic (3.3.2). In normal use each basis orbital is made to depend on one exponent only (n=1 in eq. (3)).

b) The orbitals to be developed with a D card (D in column 1)

FORMAT(3X,24A3) a1,a2,...,a24 .

Attribution of the parameters A_{12}, A_{13} ... in eq. (4) are considered as parameters and numbered NPAR2-1, NPAR2-2, ... (notice the inverse order starting from NPARP , where NPAR2 was the last inner loop parameter defined). A_{11} is determined from the normalisation condition $\sum_i A_{1i}^2 = 1$.

If a2 is orthogonal to a1 the following parameters are A_{23}, A_{24}, ... (indeed A_{21} and A_{22} are determined by orthonormalisation conditions).

If a2 is not orthogonal to a1 the following parameters are A_{22}, A_{23}, ...

The initial values of these parameters are zero.

Remarks 1) The number of orthogonal developed orbitals must be less than or equal to the number of basis orbitals at any time while reading the input data.

2) The number of basis orbitals can be increased at any time.

3.3.4 Unchanged orbitals.

They are defined by a K card (K on 1st column)

FORMAT(3X,24A3) a1,a2,...,a24 .

The orbitals a1,...,a24 are numerical orbitals taking the same values as in the previous case.

Remark : If orbitals a1,a2,... do not appear in ATOM , A , D or K cards and if they appeared in the previous case with the same order as the order of the cards 3.2.2, everything happens as if there was a card

```
K^^ a1 a2 ...
```

placed after the H card.

3.3.5 Redefining the orthogonalities.

O/N cards (3.2.4) can be read before the 1st G card (3.3.8).

3.3.6 An example to be avoided.

In the following example

```
B^^^SA^SB  \
A^^^SA...   |
            }  1s  is developed on basis  SA , SB
A^^^SB...   |
D^^^1S     /
A^^^2S...  }   2s  is analytic.
```

If 1s ⊥ 2s , in fact 2s will be computed from the Schmidt process applied to SA , SB , 2s which is rather abnormal. So it is advised not to make analytic orbitals follow developed orbitals.

3.3.7 Actions on the parameters.

Several actions are possible, depending on the character in 1st column :

C or T FORMAT(1X,I2,7E11.5) $n,x_n,x_{n+1},\dots,x_{n+6}$

In case C (resp. T) it has the effect of giving the value x_k to parameter (resp. increment) k for $n \leqslant k \leqslant \min(n+6,\mathrm{NPARP})$.

V FORMAT(1X,5A1,24A3) i_1,j_1,j_2,j_3,j_4,a1,a2,...,a24

where i_1 is V (variable) or F (fixed)

j_k is an S , P , D , F , G , H or blank $(1 \leqslant k \leqslant 4)$

aN is the name of an orbital or blanks $(1 \leqslant N \leqslant 24)$. The outer loop parameters involving the orbitals aN or orbitals with ℓ given by j_k are freed (if i_1 is V) or fixed (if i_1 is F).

Remark : it is not allowed to give an orbital twice on the same V card.

L FORMAT(1X,79I1) $i_1 \dots i_{79}$.

The parameter k $(1 \leqslant k \leqslant 79)$ is fixed if i_k is odd, freed if i_k is even.

The parameter k + 79 $(1 \leqslant k \leqslant 79)$ is fixed if $i_k > 1$, freed if $i_k \leqslant 1$.

X FORMAT(1X,I2,1X,I2,1X,F10.8) p,q,f

where $p > q$. It defines a relation. The value x_p of the outer loop parameter p will be computed from parameter q (x_q) with the formula : $x_p = f\,x_q$. If $f=0$, f is redefined to be

$f = \frac{x_p}{x_q}$ at the time of the reading.

Remarks 1) The parameter p will appear as fixed. Do not free if (with V or L cards after the X card), since the effect of the X card cannot be suppressed.

2) If x_p and x_q are the exponents of two Slater functions with the same k , ℓ the center of these Slater functions will remain at a fixed distance.

3.3.8 Optimisation.

An optimisation is made whenever a G card (G in 1st column) is met.

FORMAT(1X,I5,L3,E10•5,I3,E10•5)

NBCALC,	maximum number of steps in the outer simplex loop.
DIAG,	the energy is computed by diagonalisation if DIAG = •TRUE• , by the 2nd order if DIAG = •FALSE• .
CONVER,	the simplex loops end when the relative variations of the energy are less than CONVER .
INDIC,	an option in the simplex method , it is advised to use INDIC = -2 .
EPP	accuracy to which the computation are made.

Remark : if NBCALC = 0 => NBCALC = 100

DIAG is blank => DIAG = •FALSE•

CONVER = 0 => CONVER = $5\ 10^{-6}$

INDIC = 0 => INDIC = -2

$EPP < 10^{-7}$ => $EPP = \max(10^{-7}, \frac{CONVER}{10})$.

3.3.9 Various instructions.

Cards beginning with

F	printing the program parameters (3.1) and STOP .
*	end of case. If there was no G card in the case, everything is as if there was a G card with the values in the remark (3.3.8) and placed before the * card. After this card the reading continues with the angular data of a new case (section 3.2).
S	The numerical orbitals are renormalised (scaled) when this card is read.
R	Printing more results.
P	Punching, for each optimisation the weights and the MCHF orbital cards, and the orbitals on PUNCH cards.
PRINT or PUNCH (written on columns 1-5)	FORMAT(5X,A1,24A3) i,a1,a2,...,a24 Printing (case PRINT) or writing on file 9 (case PUNCH) a) if a1 is blank, all the orbitals (if i is +) or only the parametrised orbitals (if i is not +). The basis orbitals are excluded. Only to be used after a G card. b) if a1 is not blank, the orbitals a1,a2,...,a24 . Remarks : The printing/writing occurs at the time of reading the card. In case a P card was read before, the orbitals on PUNCH cards are punched.
I	FORMAT(1X,I2,4A3) k , a , b , c , d adding the integral $R^k(a,b,c,d)$ to the list of integrals and computing its value. Only to be placed after the last G card,

to avoid unnecessary calculations. The following conventions are used :

$I(a,b) \; = R^0(a,\wedge\wedge\wedge,b,\wedge\wedge\wedge) = R^0(\wedge\wedge\wedge,a,\wedge\wedge\wedge,b)$

$J(a,c)\; J(b,d) = R^9(a,b,c,d)$

$(a|r^{-3}|b) = R^k(a,\wedge\wedge\wedge,b,\wedge\wedge\wedge)$ with $k = 15$, 16 or 17

$\Psi_a(0)\; \Psi_b(0) = R^{18}(a,\wedge\wedge\wedge,b,\wedge\wedge\wedge)$

$(a|r|b) = R^{19}(a,\wedge\wedge\wedge,b,\wedge\wedge\wedge)$.

4. Data output.

4.1 Results printed.

Listing of input cards except numerical orbitals (3.3.1).

Printing of angular matrix if a R or P card is read in EDD (3.2.6).

For each optimisation : Orbital and type of each parameter.

Description of the basis.

Allowed range for the center of the Slater functions (it depends on EPP , ℓ and k).

The Schmidt orthogonalisation process which is given on the table N ORDER ORTHOGONALITIES : it is made on the orbitals N with ORDER(N) > 0 with increasing values of ORDER and by imposing the described ORTHOGONALITIES .

Types of the orbitals

Integrals of orthonormality of numerical orbitals.

Expression of the energy (only if a R card has been read). Eq. (2) is printed, where the fixed integrals are summed numerically and where the variable integrals appear in the form $C_k * \alpha * \beta$ α is the number of integral $\mathfrak{J}^k$ and $\beta = (i-1)\mathrm{NRECP}+j$ if the overlap is $\mathrm{Ov}(i)\ \mathrm{Ov}(j)$ $(\mathrm{Ov}(1)=1)$.

Steps of the outer simplex loop. For each step the type of the STEP in the simplex method, the number of steps taken by the inner simplex loop, the value of the function minimised (which is the part of the energy depending on the parameters) and the weights of the states are printed. Moreover whenever a lower energy value YMIN is attained, the values XMIN of the parameters are printed : if the lower value is attained in the inner simplex loop the parameters NPAR2 - NPARP are printed ; if it is attained in the outer simplex loop the parameters 1-NPAR and NPAR2 - NPARP are printed.

At the end of each optimisation the program prints :

The energy matrix, the weights and (if DIAG = .TRUE.) the diagonalised matrix and eigenvectors.

The analytic orbitals (values of A_i , k_i , $(\mathrm{center})_i$ and α_i of eq. (3)).

For each orbital $n\ell$ values of $\varepsilon_{n\ell}$, A_0 , occupation number and σ , mean value of r , r^2 , r^{-3} and r^4 (same data as in Froese's program [3]).

Matrix elements of r^{-3} , r^{-2} , r^{-1} and r .

The developed orbitals which are given in terms of their development on the basis and in terms of the A_i in an equivalent analytic description like eq. (3) where the Slater functions are those generating the basis.

The isotope shifts, computed by the formula of Stone (1st column for the specific part) or of Vinti (2nd column, for the specific + normal parts). The first line gives the values for the full MCHF wave-function, the following three lines the contributions of orders 1, 2 and higher. From the Vinti formula and the energy calculated the specific isotope shift is extracted (spec Vinti) and split in contributions or orders 1, 2 and higher. Details are printed if a R card has been read.

Isotope shift J integrals.

At the end of the case values of the integrals and overlaps are printed. Orbitals on a PRINT card are printed numerically just after the PRINT card (section 3.3.9).

4.2 Data written on files or punched.

In file 9 is written as card images the following data for use in the MCHF program [3].

1) 1st MCHF card (as 3.2.1)

2) If a P card in read in EDD (3.2.6) :

   α) MCHF orbital cards (as 3.2.2)

   β) the angular energy matrix (as 3.2.5)

3) For each optimisation :

   α) the weights w_i

   β) the MCHF orbital cards with values of σ , $\varepsilon_{n\ell}$ and A_0 .

4) In the FORMAT of 3.3.1, the orbitals given on PUNCH cards (3.3.9).

   Items 3) and 4) are also punched if a P card is read in ANALYT (3.3.9).

Whenever a lower energy value is attained in the simplex method, the parameters which are printed are also written in file 10 in the form of C cards (3.3.7). After each optimisation file 10 is rewound and the final values of the parameters and increments are written, always in file 10 as C at T card images. This file thus permits to restart an interrupted execution with the best reached values of the parameters : The same deck of cards is used, suppressing the G cards corresponding to completed optimisations and adding file 10 before the G card corresponding to the interrupted optimisation.

Subroutine CALCJ writes on file 11 the values of the specific isotope shifts.

5. Error detection.

In case of error the execution jumps to next case (starting after next * card) unless the option ENABLE (section 3.2.6) makes the calculation to be attempted.

5.1 Overflow of dimensions.

For correction see section 3.1 . An error in the PARAMETER cards (3.1) stops the execution.

5.2 Errors in angular data.

In the first card (3.2.1) one must have $0<Z<137$, $-20\leqslant RHO\leqslant 20$, $0.0001\leqslant H\leqslant 10$.

The names of the orbitals must contain a S , P , D , F , G or H .

Occupation numbers must be between 0 and $2(2\ell+1)$.

All orbitals must be used.

Configurations 2 to LETA must be bi- or monoexcitations of configuration 1 .

The numbers of integrals F , G and R are checked.

It is checked that each integral can effectively occur between the indicated configurations (shells fitted, triangular couplings) and that the overlap is 1 , (a'/b') or (a'/b')(a"/b") .

The excitations read (E cards 3.2.6) must be in the list.

5.3 Errors in radial data.

Each orbital must be of one and only one type (numerical, analytic or developed).

Basis orbitals must have new names, and cannot be developed.

D cards are only for orbitals already defined in the angular data.

A cards are only for defined orbitals in the angular data or in B cards.

The number of cards after an ATOM card is checked, but an error does not cancel the execution.

Relations (X cards) must be between parameters 1-NBPAR .

The basis must be large enough.

There is an error in the orthogonalisation order if a numerical orbital is orthogonalised to a parametrised orbital or if the Schmidt process is not feasible (orthogonalisation to 2 non orthogonal orbitals).

The numerical orbitals must be orthonormalised.

5.4 Non convergence.

The execution jumps to next case if the outer simplex loop is not converging (number of steps is too small).

6. Description of the test run.

It is a multiconfigurational calculation on B III :

$$1s^2\ 2s + 2s(p1)^2\ {}^2S \quad .$$

The orbitals 1s and 2s from Be II are given numerically and scaled. The virtual orbital p1 is developed on the basis PA , PB consisting of Slater functions. The outer simplex loop (on the two exponents) converges in 58 steps.

In file 9 is written the necessary input data for a computation by Froese's program [3].

The output file 9 of program EXCGH [9] can be used to enter the angular data of EDD (section 3.2). For example, the test run could be treated in the following way :

1. Execute program EXCGH with input :

```
‸‸‸BIII‸2S
D‸‸‸2S‸2
N‸‸‸1S
E‸‸‸1S‸1S‸P1‸P1
S
*
F
```

2. Execute program EXCGH with file 9 replacing the angular data and followed by :

```
H
   ATOM BEII...       } remaining radial data of test run.
   ....
```

7. Acknowledgment.

I am grateful to J. Bauche for suggesting the problem.

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Captions of tables.

Table 1 : Role of subroutines

Table 2 : Modifiable parameters.

Table 3 : Internal parameters. To increase LLLP it is necessary to complement the arrays (parametrised by MOY1P and MOY2P) giving E_{av} . Parameter BSP (number of basis) must be equal to LLLP .

Table 4 : Commands in EDD .

Table 1.

EDDA	main program. reading PARAMETER cards (3.1). computation of addresses. the execution then continues in EDD1 .
ANALYT	reading the radial part of the data (3.3). initialisations. calling CHECK and OPTIM . at the end of a case the execution goes back to EDD1 .
CALCJ	computation of specific isotope shifts.
CHECK	checking of data and initialisations.
COCO	determining from which pair of configutations is coming a given integral.
COMP	computation of an orbital.
DEKINT	decoding of an integral.
ECRIRE	editting Slater integrals.
EDD1	reading the angular part of the data (3.2). construction of the energy matrix. the execution then continues in ANALYT .
FSJ	computation of isotope shift integrals.
GIE	computation of Slater integrals.
IMPR1	writing results at the end of an optimisation.
IMPR2	writing results at the end of a case.
MODWF	determining which are the orbitals modified after a change of the values of the parameters.
ONDE	calculating the numerical value of the orbitals modified by a change of the values of the parameters.

Table 1 (continued).

OPTIM	running the simplex loops and computing the energy.
PRD1	printing developed orbitals.
PRT	writing the angular data.
RECC	finding if an overlap multiplies an integral.
RELTN	computing outer loop parameters from relations.
RNMEAN	computing $(a\|r^k\|b)$
ROK	construction of the expression of the energy (computing fixed integrals).
SCAL	scalar product between two numerical orbitals.
SCAM	scalar product between two orbitals.
SETBD	inscribing developed or basis orbitals.
SETCOF	finding the coefficients of the developed orbitals.
SETRK	computation of integrals containing developed orbitals in terms of integrals containing basis orbitals.
SIM	determination of the next values of the parameters by the simplex method.
VERIF	checking dimensions.
W	reading orbital names.

Table 2.

PARAMETER	not to be exceeded by the number of
BLOP	basis orbitals for a given ℓ .
LOCP	analytic orbitals.
LODP	Slater functions *3-1 in analytic orbitals.
NBETAP	configurations.
NBPARP	parameters.
NBRKP	different integrals.
NBWFP	orbitals.
NCPLEP	pairs of configurations connected by matrix elements.
NCRKP	Slater integrals involving basis orbitals.
NERGP	parametrised integrals in the expression of the energy (identical integrals are counted as often as they occur).
NETP	configurations constructed in EDD1 (3.2.6).
NFINP	Slater integrals constructed in EDD1 (3.2.6).
NPOINP	points at which orbitals are numerically calculated.
NP593	Slater integrals read in EDD1 (3.2.5).
NP6621	words needed in the simplex method.

Table 3.

PARAMETER	not to be exceeded by
TBWFP	the modifiable parameter NBWFP .
TBETAP	" NBETAP .
TLOP	" BLOP .
TOCP	" LOCP .
FCSP	the number of developed orbitals.
ISP	the number of isotope shift integrals.
LLLP	$\ell+1$ (for shell $n\ell$).
NRECP	the number of overlap integrals.
NRLTP	" of relations between parameters (X cards).
PARAME	the total length of the arrays depending on modifiable parameters.
RKMAXP	the maximal value of k in r^k (that occurs in Slater integrals).

Table 4.

1st character	effect
P	printing and writing on file 9 as card images the constructed angular data : the written cards are those described in sections 3.2.1, 3.2.2 and 3.2.5 .
R	printing the angular data constructed.
S	suppressing (i/H/j) if $i \neq 1$ and $j \neq 1$.
ENABLE (columns 1-6)	execution continues after the detection of an error. This command remains valid in ANALYT (3.3) .
H	constructing angular data. After this card the reading of input data continues in ANALYT (3.3) .
*	constructing angular data. After this card the reading of input data starts on a new case in EDD (3.2.1).
F	printing the program parameters and STOP .
Z	see remark 2 of (i) section 3.2.6 .
X	constructing angular data. After this card the reading of input data continues at point (i) of section 3.2.6 , with the same initial multiconfigurational wavefunction.

```
*******************************************************************************************************************
*****   1.  BIII 2S       3  2  1  1  0      5-3.000,06250   160            T   T                     4513 *****EDD
UTILISED SPACE
FIXED AND C1 (EDD)       1 TO 14239          C2 (EDD) 19249 TO 22528
FIXED AND C1(ANYT)       1 TO 18512          C2(ANYT) 19309 TO 22528
*****    2.   1S  1   0                                   2  0                                     4514 *****EDD1
*****    3.   2S  2                                       1  1                                     4515 *****EDD1
*****    4.   P1      1                                   0  2                                     4516 *****EDD1

*******************************************************************************************************************
EXCITED STATES . CASE NO 1
EXCITATION     1S  1S   P1  P1  1
*****    5.     .47999999F2( 3 2, 3 2)                                                             4517 *****EDD1
*****    6.    1.15470050G1( 1 1  3 2                                                              4518 *****EDD1
*****    7.  H                                                                                     4519 *****EDD1
 BIII 2S       3  2  1  1  0       5-3.000.06250   160             T  T
ORBITALS
                                                      CONFIGURATIONS
          EL  N  L  SCREEN                    ACC IND  1  2

          1S  1  0                            0.6 -1   2  0
          2S  2  0                            0.6 -1   1  1
          P1  0  1                            0.6 -1   0  2

ORTHOGONALITIES

   1S  1
   2S  0  1

   P1  1



*****    8.  ATOM  BEII  TERM 2S     ELECTRON 1S   112  4.00 AZERO     0.146732043D-02      4520 *****ANALYT
*****   25.  ATOM  BEII  TERM 2S     ELECTRON 2S   118  4.00 AZERO     0.318707001D-01      4537 *****ANALYT
*****   43.  S                                                                               4555 *****ANALYT
 1S RENORMALISED BY MULTIPLYING BY   .12500+01
 2S RENORMALISED BY MULTIPLYING BY   .12500+01
*****   44.  B    PA                                                                              *****ANALYT
*****   45.  A10  PA    55                                                                   4557 *****ANALYT
*****   46.  D    P1                                                                              *****ANALYT
*****   47.  B    PB                                                                              *****ANALYT
*****   48.  A10  PB  1   30                                                                 4560 *****ANALYT
*****   49.  G                                                                               4561 *****ANALYT


METHOD OF OPTIMISATION :   NBCALC =   100   CONVER =   .00005000   INDIC = -2
COMPUTATION OF ENERGY WITHOUT DIAGONALISATION

PARAMETERS      1. (VAR.)  PA  2. (VAR.)  PB
PARAMETERS     90. (VAR.)  P1
BASIS S
```

```
PARAMETERS   2 +   1

   NO     STEP              D(ENERGY)                WEIGHTS
                                       YMIN = -.21917250-01   XMIN
                                                             .000000
                                       YMIN = -.21918865-01   XMIN
                                                            -.781250-02
    1     ENTER    20    -.21918865-01            1.000000   -.024040
    2     INIT     20    -.97266339-02            1.000000   -.022030
    3     INIT     14    -.21917250-01            1.000000   -.024069
                                       YMIN = -.21918865-01   XMIN
                                                             .687289+01  .216095+01 -.781250-02
    4     SYM      26    -.15032145-01            1.000000   -.013635
    5     SYM      16    -.97262331-02            1.000000   -.022044
    6     MIDDLE   19    -.19295013-01            1.000000   -.018502
   58     END       1    -.22025140-01            1.000000   -.024507

   ENERGY MATRIX

       -.23339788+02
        .89872687+00         .13337397+02

   WEIGHTS

        .10000000+01         -.24507045-01
```

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PARAMETRISED ORBITALS
  NF          COEF        K   N        ALPHA                   COEF        K   N        ALPHA                   COEF     K   N        ALPHA

   PA.           1.00000000 (2, 57,     5.75670022)
   PB.           1.00000000 (3, 64,     5.64763570)

 ATOM    BIII        TERM  25            CHARGE =      5        TOTAL ENERGY   =     -23.356813
                                                                               MEAN VALUES OF
      EL          E(NL)            AZ(NL)        OCC       SIGMA          R               R**2            1/R**3            R**4        LONG
      1S       17.794416        18.341556      2.000        .482        .331996          .149141          .000000          .058407      112
      2S        2.742649         3.983860      1.001       1.711       1.824055         3.896767          .000000        26.167375      118
      P1       54.352672       128.628437       .001       7.731        .366166          .158463        98.257329          .043929       98
      PA         .000000        91.812826       .000       7.303        .434277          .226315        63.591566          .095608       96
      PB         .000000      -194.057022       .000       6.593        .627652          .525523       128.873016          .522692       98
```

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DEVELOPED ORBITALS
 P1(BASIS P )        .97995945        -.19919708
       =        .99999999 E( PA)        -.33245941 E( PB)


SPECIFIC ISOTOPE SHIFT


                              (MM/M)SPEC , (MM/M)(SPEC+NORM) =       .55617144+00       .44875966+02
                                                                     .00000000          .49814646+02
                                                                     .55647297+00      -.49620692+01
                                                                    -.30153245-03       .23388863-01
(MM/M)SPEC VINTI (S1+S2+S3) =       .21519153+02 (    .26479858+02 -.50061194+01    .45414002-01 )


INTEGRALS OF ISOTOPE SHIFT

       J( P1 1S) = -.44358032+01            J( P1 2S) = -.12276327+01
*****  50. PUNCH                                                                        *****ANALYT
ATOM  BIII  TERM 2S    ELECTRON P1    98  5.00 AZERO        .12862844+003
*****  51. *                                                                       4563 *****ANALYT


    VALUE OF INTEGRALS I F G R AND T

  1* I( 1S 1S)       -12.40210211           5* I( 2S 2S)         -2.59880840           9  I( P1 P1)          5.86906427

  2*F0( 1S 1S)         2.84156391           3*F0( 1S 2S)          .68556716           7 F0( 2S P1)          .67604733
 10 F0( P1 P1)         2.47073168          11 F2( P1 P1)         1.21190532

  4*G0( 1S 2S)         .04447385            6 G1( 1S P1)         1.55664065           8 G1( 2S P1)          .02853472
```

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@ELT,S TPF$.A                                                         4568
ELT017 RL1870 12/13-20:25:54-(0,)
000001        000    BIII 2S      3  2  1  1  0      5=3.000,06250   160          T  T
000002        000    CONF 1        1.00000000
000003        000    CONF 2       -.02450704
000004        000    1S  1  0   .48  17.7944  18.34160.6 -1  2  0
000005        000    2S  2  0  1.71   2.7426   3.98390.6 -1  1  1
000006        000    P1  0  1  7.73  54.3527 128.62840.6 -1  0  2
000007        000    ATOM  BIII  TERM 2S    ELECTRON P1    98  5.00 AZERO        .12862844+003
000008        000       .1199012   .1311442   .1434033   .1567640   .1713178   .1871627   .2044031
000009        000       .2231505   .2435230   .2656458   .2896510   .3156780   .3438723   .3743864
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000011        000       .7217813   .7806472   .8434755   .9103964   .9815198  1.0569299  1.1366794
000012        000      1.2207824  1.3092072  1.4018683  1.4986179  1.5992365  1.7034236  1.8107880
000013        000      1.9208381  2.0329726  2.1464721  2.2604918  2.3740553  2.4860524  2.5952378
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000016        000      2.8340000  2.7008330  2.5491398  2.3810783  2.1993499  2.0071411  1.8080357
000017        000      1.6058969  1.4047200  1.2084683  1.0208952   .8453694   .6847132   .5410693
000018        000       .4158090   .3094905   .2218739   .1519923   .0982739   .0587014   .0309939
000019        000       .0127910   .0018210  -.0039634  -.0062924  -.0065339  -.0056916  -.0044406
000020        000      -.0031845  -.0021245  -.0013263  -.0007766  -.0004269  -.0002201  -.0001062
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ANNEXE E

Z. Physik 270, 311–318 (1974)

Ab-Initio Interpretation of $\langle r^{-3}\rangle$ Electronic Quantities in the hfs of Mg I $3s\,3p\ {}^3P$ and ${}^1P$

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Abstract. It has been known for a long time that, in a two-electron arc spectrum, the properties of the ${}^3P$ and ${}^1P$ terms of the lowest $s\,p$ configuration cannot be interpreted correctly in a pure-configuration model. Following the experimental determination of the hyperfine constant $A(3s\,3p\ {}^1P_1)$ in Mg I by Kluge and Otten, this paper presents the ab-initio interpretation of the $\langle r^{-3}\rangle_{3p}$ hyperfine electronic quantities in $3s\,3p$ through the use of the multiconfigurational Hartree-Fock method. It appears that taking into account the effects of the monoelectronic excitations $3s \rightarrow n\,d$, $2p \rightarrow n\,p$ and $3p \rightarrow n\,p$ leads to ab-initio evaluations in very good agreement with experiment. The case of the $3p \rightarrow n\,p$ excitation, to which Brillouin's theorem should apply in principle, is discussed. Using the same method, a refined evaluation is proposed for the nuclear electric-quadrupole moment of Mg^{25} ($Q=0.200\pm0.01$ barn).

I. Introduction

The alkaline-earth-like spectra, though apparently simple, are known to exhibit puzzling peculiarities. One of these is the large difference between the electronic quantities $\langle r^{-3}\rangle$ relevant to the hyperfine structures (hfs) in the ${}^3P$ and ${}^1P$ terms of the lowest *sp* configuration.

Such differences appeared first in the analysis of the hfs of mercury [1], cadmium [2] and baryum [3]. In 1966, Lurio [4] gave a semi-empirical interpretation for them, through a modification of the Breit-Wills theory [5]. Recently, Kluge and Otten [6] achieved accurate measurements for the lowest $sp\ {}^1P_1$ levels of magnesium, calcium, and strontium, which lead to still larger differences than for the atoms quoted above. In the preceding paper, Kluge and Sauter [7] give an extensive review of the different phenomena and methods which provide some information on the comparative electronic properties of the $sp\ {}^3P$ and ${}^1P$ terms. Moreover they notice that, for the very light atoms Be and Mg, Lurio's interpretation is not suitable, because it overlooks the influence of the magnetic interactions other than spin-orbit.

In the present work, we have obtained ab-initio evaluations of $\langle r^{-3}\rangle$ quantities in the $3s\,3p\ {}^3P$ and ${}^1P$ terms of Mg I. The complexity of that case is moderate enough for a first attempt on that type of problem and hopefully sufficient to allow generalization to heavier atoms.

We first deduce from the measured values what we call experimental values of the two $\langle r^{-3}\rangle_{3p}$ magnetic parameters in Russell-Saunders (RS) coupling. From the theoretical point of view, these parameters would evidently be equal if they were simply the mean value of r^{-3} for the $3p$ radial function. Actually they are not equal, due to contributions coming from the admixture of $3s\,3p$ with higher configurations. They are called *effective* parameters because allowing them to have unequal values avoids, in pure RS coupling, any explicit introduction of these perturbing configurations in the interpretation of the hfs.

To obtain ab-initio evaluations of these effective parameters, we apply the multiconfigurational Hartree-Fock (MCHF) method. We also treat the case of the second-order corrections which could not be evaluated through the used MCHF computer code. Eventually we obtain, through the same methods, an evaluation of the $\langle r^{-3}\rangle_{3p}$ quantity relative to the electric-quadrupole hyperfine interaction, yielding a refined value of the nuclear electric-quadrupole moment Q.

II. Experimental Values of the $\langle r^{-3}\rangle$ Quantities

In 1962, Lurio [8] measured accurately the magnetic hyperfine constants A of the $^3P_1$ and $^3P_2$ levels of the $3s\,3p$ configuration in the arc spectrum of Mg^{25}:

$$A(^3P_1) = -144.945 \pm 0.005\ \mathrm{MHz}$$

$$A(^3P_2) = -128.440 \pm 0.005\ \mathrm{MHz}$$

(values corrected for the mixing between close sublevels with the same F-value).
Recently, Kluge and Otten [6] obtained the constant A for the $^1P_1$ level of the same configuration:

$$A(^1P_1) = -7.7 \pm 0.5\ \mathrm{MHz}.$$

a) Russell-Saunders Approximation

To exploit these three A values, we first assume that the considered levels strictly obey Russell-Saunders (RS) coupling, but that they may result from the mixing between $3s\,3p$ and other configurations. *For each term* we are allowed to introduce four hyperfine electronic constants, i.e. a_{3s}, a_{3p}, b_{3p} and c_{3p} in the notation of Bordarier, Judd and Klapisch [9]. The a, b and c constants correspond respectively to the $s^{(1)}$, $l^{(1)}$ and $\{s^{(1)}C^{(2)}\}^{(1)}$ parts (called respectively the s, l and $s\,C$ parts) of the magnetic-hfs operators:

$$\mathscr{H}_m = \mathscr{H}_l + \mathscr{H}_{sC} + \mathscr{H}_s \equiv (2\beta\,\beta_N\,\mu_N/I)$$
$$\cdot \sum_i \left[\left(l_i^{(1)} - \sqrt{10}\,\{s_i^{(1)}\,C_i^{(2)}\}^{(1)} \right) / r_i^3 + (8\pi/3)\,\delta(\vec{r}_i)\,s_i^{(1)} \right] \cdot I^{(1)}$$

[10, p. 85]. In the non-relativistic limit for a pure $s\,p$ configuration, $a_p = 0$ and $b_p = c_p$.
For the $s\,p\,{}^3P$ term, we obtain, by the standard tensor-operator method:

$$A(^3P_1) = a_s/4 + a_p/4 + b_p/2 + c_p/2$$

$$A(^3P_2) = a_s/4 + a_p/4 + b_p/2 - c_p/10.$$

Evidently, three of the four parameters can be eliminated by considering the difference $A(^3P_1) - A(^3P_2)$, which yields

$$c_{3p}^{\mathrm{RS}}(^3P) = -27.51 \pm 0.01\ \mathrm{MHz} \qquad \text{(for the term } ^3P).$$

For the ^1P term, all three spin-dependent parameters are useless, because $S=0$; we obtain $A(^1P_1) = b_p$, whence

$$b_{3p}^{\mathrm{RS}}(^1P) = -7.7 \pm 0.5\ \mathrm{MHz} \qquad \text{(for the term } ^1P).$$

b) Deviations from Russell-Saunders Coupling

We now take into consideration the (small) influence of the magnetic interactions on the coupling in $3s\,3p$. We write, for the intermediate-coupling expansions of the $J=1$ levels:

$$\psi([^3P_1]) = (1-\varepsilon^2)^{\frac{1}{2}}\,\psi(^3P_1) + \varepsilon\,\psi(^1P_1)$$

$$\psi([^1P_1]) = (1-\varepsilon^2)^{\frac{1}{2}}\,\psi(^1P_1) - \varepsilon\,\psi(^3P_1).$$

To evaluate ε, we assume, following King and Van Vleck [11] and Lurio [4], that the spin-orbit constant ζ_p in the off-diagonal element between $^3P_1$ and $^1P_1$ is λ_p times what it is in the diagonal elements for the ^3P levels. But we do not rely on the (very small) deviation from the Landé interval rule in ^3P to get the value of λ_p. Indeed Kluge and Sauter [7] indicate that the value so found is $\lambda_p = 1.8$ and that this unphysical result ($\lambda_p > 1$ contradicts the physical idea that the $3p$ electron is more loosely bound in the ^1P term) reflects the importance of magnetic interactions other than spin-orbit.
Consequently we turn to previous determinations of λ_p from the $s\,p$ fine structures of heavier alkaline-earth-like atoms [11]. From calcium to mercury, we observe that $0.76 < \lambda_p < 0.84$, with the same value $\lambda_p = 0.81$ in the two true alkaline-earth atoms immediately heavier than Mg. The values obtained from the lifetime values of the $J=1$ $ns\,np$ levels [7, Table 6] are also close to 0.8. We finally choose $\lambda_p = 0.80 \pm 0.04$ for our problem.
This leads to the approximate value

$$\varepsilon = -\lambda_p\,\zeta_{3p}\sqrt{2}/2\,[E(^1P) - E(^3P)] \simeq -0.0017,$$

in fair agreement with the value -0.0020 obtained by Swagel and Lurio [25] and quoted by Kluge and Sauter [7, Table 3].
Because ε is almost zero, its effects on the hfs of the levels can be approximated by the quantity $\Delta A = \mp\varepsilon(-a_s + a_p - c_p)/\sqrt{2}$ (the upper sign corresponds to ^1P, the lower to ^3P), which is the product of $\mp 2\varepsilon$ by the off-diagonal hyperfine constant between $^3P_1$ and $^1P_1$. In this expression, the a_s, a_p and c_p parameters are those corresponding neither to ^3P nor to ^1P, but to the off-diagonal element between ^3P and ^1P. The largest is a_s, which is λ_s times $a_s(^3P)$, with, according to Kluge and Sauter [7], λ_s close to 1.15 (the MCHF results which will be presented in Table 4 lead to $\lambda_s = 1.10$). To obtain $a_s(^3P)$, we use the value of $A(^3P_2)$, in which

– we neglect $a_p(^3P)$, which is due to core polarization by the loosely bound $3p$ electron and to relativistic corrections;

– we assume $b_p(^3P) \simeq c_p(^3P)$; an ab-initio evidence for this approximate relation is given in § VI. Then $a_s(^3P) = -470$ MHz. Coming back to ΔA, we take into account the λ_s factor, we neglect again a_p and we take, for the off-diagonal parameter c_p, the approximate value

$$-[b_p(^3P)\cdot b_p(^1P)]^{\frac{1}{2}} \simeq -15\ \mathrm{MHz}.$$

We finally obtain $\Delta A = \pm 0.67$ MHz, a value which should not be wrong by more than 25%.

These corrections must be subtracted from the experimental A constants for the $J=1$ levels. We derive

$$c_{3p}^{\mathrm{corr}}(^3P) = -26.4 \pm 0.3\ \mathrm{MHz}$$

$$b_{3p}^{\mathrm{corr}}(^1P) = -8.4 \pm 0.7\ \mathrm{MHz}$$

which are values corrected for intermediate-coupling effects. Knowing $I(\mathrm{Mg}^{25}) = 5/2$ and $\mu(\mathrm{Mg}^{25}) = -0.8551$ [12], we deduce the values

$$\langle r_{sC}^{-3}\rangle_{3p}(^3P) = 0.809 \pm 0.009 \text{ atomic unit (a.u.)}$$

$$\langle r_l^{-3}\rangle_{3p}(^1P) = 0.257 \pm 0.021 \text{ a.u.}$$

and

$$\rho = \langle r_{sC}^{-3}\rangle_{3p}(^3P)/\langle r_l^{-3}\rangle_{3p}(^1P) = 3.15 \pm 0.3,$$

which we must now try to interpret.

III. Application of the HF and MCHF Methods

a) Use of the HF Method

The best known ab-initio method for atoms is certainly the Hartree-Fock (HF) method. In 1966, Klapisch [13] obtained with Froese's computer code [14] the HF functions of the ^3P and ^1P terms of the lowest $s\,p$ configurations in the alkaline-earth atoms. For magnesium, he obtained, in this monoconfigurational scheme,

$$\langle r^{-3}\rangle_{3p}(^3P) = 0.6073 \text{ a.u.}$$

$$\langle r^{-3}\rangle_{3p}(^1P) = 0.1239 \text{ a.u.}$$

From these values, we deduce

$$\rho = \langle r^{-3}\rangle_{3p}(^3P)/\langle r^{-3}\rangle_{3p}(^1P) = 4.9.$$

The agreement with experiment is very poor. However, the HF value already indicates that the smaller $\langle r^{-3}\rangle$ value corresponds to the ^1P term. This qualitative fact is easily understood by considering that the electrostatic repulsion between the electrons $3s$ and $3p$ is (in the central-field scheme) larger in the ^1P than in the ^3P term. The more loosely bound $3p$ electron is thus pushed outwards when one goes from ^3P to ^1P, and its $\langle r^{-3}\rangle$ value decreases consequently.

b) MCHF Method: Principles and their Application

Since 1966, a new computer code has been built by Froese-Fischer [15], which allows to compute multiconfigurational Hartree-Fock (MCHF) functions, as first obtained by Hartree *et al.* [16]. The principle of the MCHF method is the following. Once a given set of Russell-Saunders terms from various configurations is assumed to contribute appreciably to the wavefunction of a level, the MCHF method yields the radial orbital functions and the weights of the terms which minimize the total energy E of the level. All the terms must correspond to the same ^{2S+1}L symbol, because the used hamiltonian $\mathscr{H}$ is, as in the HF method, purely kinetic and electrostatic.

To refine the HF values, we first aim to obtain the second-order corrections to the hfs. We define these corrections as in the perturbation scheme, namely, as deriving from the mixing, with the HF monoconfigurational wavefunction $\psi_0 \equiv |1s^2\,2s^2\,2p^6\,3s\,3p\cdot SLJIFM_F)$, of states ψ_{exc} from singly-excited configurations such that

$$(\psi_0|\,\mathscr{H}\,|\psi_{\mathrm{exc}})(\psi_{\mathrm{exc}}|\,\mathscr{H}_{\mathrm{hfs}}\,|\psi_0) \neq 0$$

where $\mathscr{H}_{\mathrm{hfs}}$ is the hfs operator.

In the following, we call an "excitation" the symbol $n\,l \rightarrow n'\,l'$, for n, l, l' – but generally not n' – fixed; it represents the process of mixing ψ_0 with states of all excited configurations where one electron $n\,l$ in ψ_0 is replaced by one electron $n'\,l'$. For Mg I $1s^2\,2s^2\,2p^6\,3s\,3p\ ^{1,3}P$, the relevant excitations are:

for the l part of the hfs: $2p \rightarrow 3p, n\,p$

for the $s\,C$ part: $1s, 2s, 3s \rightarrow n\,d$ and $2p \rightarrow 3p, n\,p, n\,f$.

In addition to these, one may think of the $3p \rightarrow n\,p$ excitation. But, at first sight, it appears that this excitation should not be considered if one is interested only in second-order corrections. This is a consequence of Brillouin's theorem [17]: if the radial functions of the electrons $1s$, $2s$, $2p$, $3s$ and $3p$ have been obtained through the HF method, the off-diagonal matrix element

$$(1s^2\,2s^2\,2p^6\,3s\,3p\,SLM_S M_L|\,\mathscr{H}\,|1s^2\,2s^2\,2p^6\,3s\,n\,p\cdot SLM_S M_L)$$

is zero for any $n\,p$ radial function orthogonal to the $2p$ and $3p$ ones. In spite of this theorem, we shall see in § V, from the first numerical results, why the $3p \rightarrow n\,p$ excitation was finally introduced.

We consider now one of the retained excitations, denoted $n\,l \rightarrow n'\,l'$, and one of the two relevant parts of the magnetic hfs. If $n'l' \neq 3p$, we are faced with an infinite series of excited $n'l'$ radial functions (infinity in the radial space) and generally, for each such $n'l'$ function, with a number of different ${}^1P$ and ${}^3P$ terms (plurality in the angular space). For example, there appear nine different ${}^3P$ terms in $1s^2\,2s^2\,2p^5\,np\,3s\,3p$. Fortunately, in an MCHF computation aiming to second-order corrections only, this whole lot of excited terms can be reduced to one for every excitation [18]. We consider, for example, the case of the $2p \to np$ excitation. The angular reduction is particularly simple in our problem. From angular-momentum selection rules, we see immediately that

$$(1s^2\,2s^2\,2p^6\,3s\,3p\;{}^3PJIFM_F|\,\mathscr{H}_{sC}\,|1s^2\,2s^2$$
$$\cdot[(2p^5\,np)\,SL,(3s\,3p)\,S'L']\;{}^3PJIFM_F)$$

is different from zero only if $(SL)=(12)$ and $(S'L')=(11)$, and that

$$(1s^2\,2s^2\,2p^6\,3s\,3p\;{}^1PJIFM_F|\,\mathscr{H}_l\,|1s^2\,2s^2$$
$$\cdot[(2p^5\,np)\,SL,(3s\,3p)\,S'L']\;{}^1PJIFM_F)$$

is different from zero only if $(SL)=(01)$ and $(S'L')=(01)$. As concerns the radial space, the total contribution of the infinite number of excited configurations with different n values can be reproduced, to second order, through one excited configuration, which we denote $1s^2\,2s^2\,2p^5\,p_{II}\,3s\,3p$.

Due to the fact that the p_{II} and $3p$ radial functions are necessarily orthogonal in the MCHF procedure, the effects of the $2p \to 3p$ excitation must be computed in another way (see § IV.b).

c) Chosen Excited States

Considering the list of relevant excitations, the MCHF computation for $\langle r_{sC}^{-3}\rangle_{3p}({}^3P)$ should contain six configurations and that for $\langle r_l^{-3}\rangle_{3p}({}^1P)$ two configurations. For two different reasons we worked in a different manner.

First the $3s \to nd$ excitation has a particular rôle. Indeed the $3d\,3p$ configuration lies, in the Mg I spectrum, not very high above $3s\,3p$. So we expect that the $3s \to nd$ excitation, although giving no second-order effect on $\langle r_l^{-3}\rangle_{3p}({}^1P)$, can give appreciable higher-order effects. We therefore introduce that excitation in both computations.

Secondly, the MCHF computer code works safely only if the weights of the excited configurations are not too small. This is due to unavoidable inaccuracies in the numerical integration process. Unfortunately, this problem appeared in the computation of three excitations for the sC part, namely $1s$ and $2s \to nd$ and $2p \to nf$. We chose to deal with those excitations by an analytical method (§ IV).

Table 1. Off-diagonal elements of $\mathscr{H}$

Calculation	Configurations	Off-diagonal element
$({}^3P)$	C_1–C_2	$\sqrt{2}R^1(3s\,3p,3p\,d_{III})/3$ $-\sqrt{2}R^2(3s\,3p,d_{III}\,3p)/5$
	C_1–C_3	$\sqrt{15}R^0(2p\,3p,3p\,p_{II})/3$ $+\sqrt{15}R^2(2p\,3p,3p\,p_{II})/75$
	C_2–C_3	$-\sqrt{30}R^1(2p\,p_{II},3s\,d_{III})/15$
$({}^1P)$	C_1–C_2	$\sqrt{2}R^1(3s\,3p,3p\,d_{III})/3$ $+\sqrt{2}R^2(3s\,3p,d_{III}\,3p)/5$
	C_1–C_3	$\sqrt{2}R^0(2p\,3p,3p\,p_{II})/2$ $-\sqrt{2}R^2(2p\,3p,3p\,p_{II})/10$
	C_2–C_3	0

Table 2. Matrices of the hfs contributions to $\langle r^{-3}\rangle_{3p}$

	C_1	C_2	C_3
Calculation $({}^3P)$			
C_1	$\langle r^{-3}\rangle_{3p}$	$-\sqrt{2}\langle r^{-3}\rangle_{3s-d_{III}}/2$	$-\sqrt{15}\langle r^{-3}\rangle_{2p-p_{II}}/5$
C_2		$\langle r^{-3}\rangle_{3p}/10+\langle r^{-3}\rangle_{d_{III}}/2$	0
C_3			$7\langle r^{-3}\rangle_{2p}/40+\langle r^{-3}\rangle_{3p}/20$ $+7\langle r^{-3}\rangle_{p_{II}}/40$
Calculation $({}^1P)$			
C_1	$\langle r^{-3}\rangle_{3p}$	0	$-\sqrt{2}\langle r^{-3}\rangle_{2p-p_{II}}$
C_2		$-\langle r^{-3}\rangle_{3p}/2+3\langle r^{-3}\rangle_{d_{III}}/2$	0
C_3			$\langle r^{-3}\rangle_{2p}/4+\langle r^{-3}\rangle_{3p}/2$ $+\langle r^{-3}\rangle_{p_{II}}/4$

d) MCHF Numerical Results

We are now left with two 3-configuration MCHF calculations, denoted $({}^3P)$ and $({}^1P)$: for both $\langle r_{sC}^{-3}\rangle_{3p}({}^3P)$ and $\langle r_l^{-3}\rangle_{3p}({}^1P)$, we study the mixing between the relevant LS terms of $1s^2\,2s^2\,2p^6\,3s\,3p$ (denoted C_1), $1s^2\,2s^2\,2p^6\,d_{III}\,3p\,(C_2)$ and $1s^2\,2s^2\,2p^5\,p_{II}\,3s\,3p\,(C_3)$; following a recent paper [19], we denote d_{III} and p_{II} the virtual orbitals describing the relevant correlation effects in the M- and L-shells respectively, with the p_{II} radial function being orthogonal to $2p$ and $3p$.

We first built the matrices for the electrostatic hamiltonian $\mathscr{H}$ and the relevant parts of $\mathscr{H}_{\text{hfs}}$. To eliminate any relative-phase ambiguity as concerns the states, we present in Table 1 the off-diagonal matrix elements of $\mathscr{H}$ between configurations. For $\mathscr{H}_{\text{hfs}}$, we list in Table 2 the diagonal and off-diagonal quantities which contribute directly to the $\langle r^{-3}\rangle$ effective parameters to be computed: for example the excitation $3s \to d_{III}$ contributes to $\langle r_{sC}^{-3}\rangle_{3p}({}^3P)$, to second order, through the additive expression $-\sqrt{2}\,w_1 w_2 \langle r^{-3}\rangle_{3s-d_{III}}$, where w_1 and w_2 are the weights of the configurations C_1 and C_2 in the MCHF state.

We obtained the two 3-configuration wavefunctions, using the computer code of Froese-Fischer [15] and

Table 3. Weights w_i of the MCHF configurations C_i and total electronic energies

Calculation	w_1	w_2	w_3	Energies	
				HF [13]	MCHF
(^3P)	0.99307	−0.11750	−0.00336	−199.5455	−199.5514
(^1P)	0.97574	−0.21893	−0.00095	−199.4701	−199.4821

Table 4. Orbital properties of the MCHF results (in a.u.)

Orbitals	Calculation (^3P)			Calculation (^1P)		
	ε	A_0	$\langle r\rangle$	ε	A_0	$\langle r\rangle$
$1s$	98.1674	80.2813	0.1306	98.2755	80.2819	0.1306
$2s$	7.6335	20.2675	0.6909	7.7365	20.2726	0.6908
$2p$	4.6718	52.0121	0.6838	4.7728	52.0209	0.6838
$3s$	0.6858	4.0884	3.1143	0.6236	4.4905	2.9274
$3p$	0.3781	8.3563	4.0056	0.2531	5.4724	5.2389
d_{III}	0.6859	0.4675	4.2231	0.6236	0.6854	4.2119
p_{II}	4.7057	58.4207	1.3884	4.7940	48.4596	1.9350

Table 5. Values of the $\langle r^{-3}\rangle_{nl-n'l'}$ quantities (in a.u.)

$n\,l-n'\,l'$	Calculation (^3P)	Calculation (^1P)
$2p-2p$	24.9614	24.9687
$3p-3p$	0.6298	0.2751
$d_{\mathrm{III}}-d_{\mathrm{III}}$	0.0355	0.0372
$p_{\mathrm{II}}-p_{\mathrm{II}}$	25.3095	17.4658
$3s-d_{\mathrm{III}}$	0.0345	0.0348
$2p-p_{\mathrm{II}}$	24.0396	20.0562

the matrices of $\mathscr{H}$ (Table 1). For both calculations

– Table 3 gives the weights w_i of the configurations C_i and the total electronic HF and MCHF energies (in a.u.),

– Table 4 gives the main features of the radial functions $R_{nl}(r)$ obtained, i.e., for each $n\,l$ orbital, ε_{nl} (the orbital energy), $A_0(n\,l)=[R_{nl}(r)/r^{l+1}]_{r=0}$ and $\langle r\rangle_{nl}$ (the mean value of r),

– Table 5 gives the values of the quantities

$$\langle r^{-3}\rangle_{nl-n'l'}=\int_0^\infty R_{nl}(r)\,R_{n'l'}(r)\,\frac{1}{r^3}\,dr$$

relevant to the final evaluation of the $\langle r^{-3}\rangle_{3p}$ effective values which are the aim of this work.

From those results and the matrices of $\mathscr{H}_{\mathrm{hfs}}$ (Table 2) it is straightforward to obtain, in this approximation, the effective values

$$\langle r_{sC}^{-3}\rangle_{3p}(^3P)=0.752\text{ a.u.}$$

$$\langle r_l^{-3}\rangle_{3p}(^1P)=0.311\text{ a.u.}$$

and their ratio $\rho=2.4$.

IV. Results for the Excitations $1s, 2s\rightarrow n\,d$ and $2p\rightarrow nf, 3p$

a) $1s, 2s\rightarrow n\,d$ *and* $2p\rightarrow nf$

For $\langle r_{sC}^{-3}\rangle_{3p}(^3P)$, we now consider the cases of the $1s$, $2s\rightarrow n\,d$ and $2p\rightarrow nf$ excitations. We have said above that, because the weights of these excited wavefunctions are too small, numerical inaccuracies in the MCHF procedure are prohibitive for the determination of the relevant virtual orbitals.

Consequently, we built an independant computer code to obtain analytical approximations for the orbitals denoted d_{I}, d_{II} and f_{II}. We suppose first that any of these radial functions can be expanded in terms of Slater-type basis functions:

$$R_{nl}(r)=\sum_i a_i\,r^{n_i}\,e^{-\zeta_i r}.$$

Starting from some values of the a_i, n_i and ζ_i quantities, the code optimizes the a_i and ζ_i parameters in order to minimize the second-order energy contribution $\dfrac{-(ND)^2}{\Delta E}$, where (ND) is the off-diagonal matrix element of $\mathscr{H}$ and ΔE the (positive) energy difference between ψ_0 and the considered excited state. Due to the fact that the radial functions in ψ_0 are fixed to be the numerical HF functions quoted above, all necessary integrals are computed numerically. The optimizing procedure is effected through the SIMPLEX method [20]. Of course, throughout this procedure, the excited orbital $R_{nl}(r)$ is maintained normalized.

For angular selection rules as above (§ III.b), the only excited terms useful to second order are those con-

Table 6. Weights and second-order energy contributions (in a.u.)

Excitation	Weight	Energy contribution
$1s \rightarrow d_I$	-0.000052	$-0.19 \cdot 10^{-6}$
$2s \rightarrow d_{II}$	0.00091	$-0.42 \cdot 10^{-5}$
$2p \rightarrow f_{II}$	-0.0014	$-0.60 \cdot 10^{-5}$

Table 7. Virtual orbitals for the excitations $1s, 2s \rightarrow d$ and $2p \rightarrow f$ (unnormalized)

$$R_{d_I}(r) = r^3 e^{-9.2593r} + 0.33781 r^3 e^{-14.107r} + 1.6552 r^4 e^{-11.359r}$$
$$R_{d_{II}}(r) = r^3 e^{-1.3752r} + 1.0477 r^3 e^{-4.2695r} - 0.89429 r^4 e^{-4.3563r}$$
$$R_{f_{II}}(r) = r^4 e^{-1.7877r} + 0.25184 r^4 e^{-5.8700r} - 0.29685 r^5 e^{-5.4008r}$$

d_I: $A_0 = 858.5$, $\langle r \rangle = 0.374$

d_{II}: $A_0 = 72.2$, $\langle r \rangle = 2.33$

f_{II}: $A_0 = 87.7$, $\langle r \rangle = 2.61$

taining respectively the groups $(1s\, d_I)^3D$, $(2s\, d_{II})^3D$ and $(2p^5 f_{II})^3D$. For the three calculations:

- Table 6 gives the weights of the excited RS terms and their second-order contributions to the energy,
- Table 7 gives the analytical expressions for the radial functions $R_{nl}(r)$ obtained (in unnormalized form) and their main features.

Eventually the off-diagonal $\langle r^{-3} \rangle_{nl-n'l'}$ integrals useful for the contributions to $\langle r_{sC}^{-3} \rangle (^3P)$ are

$$\langle r^{-3} \rangle_{1s-d_I} = 172$$
$$\langle r^{-3} \rangle_{2s-d_{II}} = -0.48$$
$$\langle r^{-3} \rangle_{2p-f_{II}} = 1.36.$$

The total second-order contribution of these excitations to $\langle r_{sC}^{-3} \rangle_{3p} (^3P)$ is

$$-\sqrt{2}(\langle r^{-3} \rangle_{1s-d_I} w_4 + \langle r^{-3} \rangle_{2s-d_{II}} w_5)$$
$$-6 \langle r^{-3} \rangle_{2p-f_{II}} w_6 / \sqrt{10},$$

where w_4, w_5 and w_6 are the respective weights of the excited states. We find for its numerical value $+0.0169$.

b) $2p \rightarrow 3p$

The evaluation of the second-order effects of the $2p \rightarrow 3p$ excitation is just a matter of numerical computation of the off-diagonal elements of $\mathscr{H}$ and $\mathscr{H}_{\mathrm{hfs}}$, because all the necessary radial functions are known from the HF results. The resulting contributions to the $\langle r^{-3} \rangle_{3p}$ effective parameters are respectively $+0.0095$ for the sC part in ^3P and -0.0099 for the l part in ^1P.

Adding all contributions, the total $\langle r^{-3} \rangle_{3p}$ values are now respectively 0.779 and 0.301 a.u., with the ratio $\rho = 2.6$. This value of ρ is quite different from the experimental one (3.15 ± 0.3; see § II.b), although we have taken into account the whole list of second-order effects which should contribute in principle (see § III.b). This appears to be due to an inadequate application of Brillouin's theorem, which we discuss in the next paragraph.

V. Excitation $3p \rightarrow np$

a) Discussion on the Application of Brillouin's Theorem

We consider again the case of the $3p \rightarrow np$ excitation (see § III.b). Indeed the off-diagonal matrix element

$$(1s^2\, 2s^2\, 2p^6\, 3s\, 3p\, SLM_SM_L | \mathscr{H} | 1s^2\, 2s^2\, 2p^6\, 3s\, np \cdot SLM_SM_L)$$

is zero for any np radial function orthogonal to $2p$ and $3p$ *if* the radial functions $1s$, $2s$, $2p$, $3s$ and $3p$ are the HF radial functions. But, at this stage of our work, the best radial functions which we have found are those from the MCHF computations. Those functions are different from the HF functions: the best example for this is the $3p$ radial function for the ^1P term, whose $\langle r^{-3} \rangle$ value is 0.1239 in the HF computation [13] and 0.2751 in the MCHF computation (Table 5).

We conclude that we cannot any more take advantage of Brillouin's theorem to exclude the $3p \rightarrow np$ excitation from the list of second-order effects.

b) Analytical Treatment of the $3p \rightarrow np$ Excitation

The copy of Froese's computer code which we had at hand did not allow the introduction, in the MCHF procedure, of two terms whose off-diagonal element for the hamiltonian $\mathscr{H}$ contains monoelectronic integrals, due to the kinetic energy and electron-nucleus interaction. Unfortunately, $|3s\, 3p\, SL)$ and $|3s\, np\, SL)$ are two such terms. We were therefore obliged to evaluate the effects of the $3p \rightarrow np$ excitation analytically.

For the sake of simplicity, we limited ourselves to the introduction of only one other excitation than $3p \rightarrow np$, namely $3s \rightarrow nd$, whose introduction leads to the essential differences between the HF and MCHF radial functions. We could choose between two equivalent ways of computing the combined effects of these two excitations: first, the mixing of $3s\, 3p$, $3s\, p_{III}$ and $d_{III}\, 3p$, with the $3p$ and p_{III} functions being orthogonal; secondly, the mixing of $3s\, 3p$ with $d_{III}\, 3p'$, with no orthogonality constraint on the $3p$ and $3p'$ functions [17]. For computing reasons, we adopted the second scheme.

Noting that the radial functions $1s$, $2s$, $2p$ and $3s$ would probably not be appreciably changed through the introduction of the $3p \rightarrow np$ excitation, we fixed

Table 8. Analytical results for the mixing $(3s\,3p+d_{\mathrm{III}}\,3p')$ (in a.u.)

	(^3P)		(^1P)	
	$\langle r\rangle$	$\langle r^{-3}\rangle$	$\langle r\rangle$	$\langle r^{-3}\rangle$
$3p$	4.04	0.627	5.52	0.244
$3p'$	3.23	1.155	3.45	0.930
d_{III}	4.18	0.035	4.40	0.034
$w(3s\,3p)$	0.993		0.968	
$w(d_{\mathrm{III}}\,3p')$	−0.122		−0.249	
Total energy	−199.5520		−199.4897	

them to their numerical description which results from the MCHF computations in § III.d. As for the $3p, d_{\mathrm{III}}$ and $3p'$ radial functions, we expanded each of them on a Slater-type basis, and we optimized them with the same computer code as above (see § IV).

Table 8 gives properties of the analytical functions, the weights $w(3s\,3p)$ and $w(d_{\mathrm{III}}\,3p')$ and the total energies obtained. Comparing with the MCHF energies in Table 3, we see that, as could be anticipated, the decrease in energy is much larger for ^1P than for ^3P. Eventually the only useful off-diagonal quantities are, in the ^3P calculation, $\langle r^{-3}\rangle_{3s-d_{\mathrm{III}}}=0.036$ and the overlapping integral between $3p$ and $3p'$, equal to 0.962.

VI. Discussion. Quadrupole Electric Moment of Mg^{25}

In the preceding paragraphs, the results are presented in an a priori order. For the final table (Table 9), we prefer to use an a posteriori order. In the first three columns of this table, we present the values of the effective parameters $\langle r_{sC}^{-3}\rangle_{3p}(^3P)$ and $\langle r_l^{-3}\rangle_{3p}(^1P)$ and their ratio ρ in the following series of approximations:

- the HF result for the average of the $3s\,3p$ configuration, i.e. a kind of "central-field" result,
- the HF results (§ II.a) [13],
- the MCHF results for the mixing of $3s\,3p$ and $d_{\mathrm{III}}\,3p$; these results were not presented above, but are, for what concerns these two configurations, very close to the results of § III.d. We present them to stress the fact that, for the ^1P term, the change in $\langle r^{-3}\rangle_{3p}$ between the HF and MCHF results of § III.d is due to the introduction of the $3s\to n\,d$ excitation,
- analytical results for the mixing of $3s\,3p$ and $d_{\mathrm{III}}\,3p'$, which allows for the $3p\to n\,p$ excitation (§ V),
- same results as before, with addition of the second-order effects due to the $2p\to n\,p$ excitation (§§ III.d and V.b); the figures relevant to the evaluation of these effects are taken from Tables 2, 3 and 5,
- same results as before, with addition of the second-order effects due to the excitations of $1s$, $2s\to n\,d$ and $2p\to 3p, nf$ (§ IV),
- same results as before with addition of the relativistic correction. Here we use the approximation obtained by Judd [21] on the basis of Casimir's theory: we multiply the non-relativistic result by $(1+83\,Z^2\,\alpha^2/80)$ for $\langle r_l^{-3}\rangle_p$ and by $(1+5441\,Z^2\,\alpha^2/2160)$ for $\langle r_{sC}^{-3}\rangle_p$, with $\alpha=1/137$ and $Z=12$ for Mg,
- the experimental values (§ II).

The comparison between the last two lines of this table is rather satisfactory: the $\langle r^{-3}\rangle_{3p}$ effective parameter for the ^1P term and the ratio ρ agree with the experimental values, and the other $\langle r^{-3}\rangle$ value is close (2%) to experiment. The first five lines show that three types of excitations have by far the largest influence on this result:

- $3s\to n\,d$, which strongly modifies the $3p$ function in the ^1P term; it acts on $\langle r^{-3}\rangle_{3p}$ through higher-order (rather than second-order) effects;
- $3p\to n\,p$ which, as a consequence of the preceding excitation, has a larger influence in the term ^1P, because of Brillouin's theorem;
- $2p\to n\,p$, which brings about the same relative increment (+20%) for both terms, and, consequently, does not affect ρ much.

The remaining excitations which are efficient to second order of perturbation, namely $1s, 2s\to n\,d$ and $2p\to nf$, $3p$, bring much smaller contributions to $\langle r^{-3}\rangle_{3p}$.

The agreement we obtain between theory and experiment tends to confirm the fact, already apparent in previous results [24, 19], that the higher-than-second orders of perturbation contribute quite generally to the orbit-dependent hfs parts for less than 5%

Table 9. Evaluations for $\langle r^{-3}\rangle_{3p}$ effective parameters (in atomic units) in ^3P and ^1P and the ratio $\rho=\langle r_{sC}^{-3}\rangle(^3P)/\langle r_l^{-3}\rangle(^1P)$

	$\langle r_{sC}^{-3}\rangle_{3p}(^3P)$	$\langle r_l^{-3}\rangle_{3p}(^1P)$	ρ	$\langle r_Q^{-3}\rangle_{3p}(^3P)$
HF: average of $3s\,3p$	0.501	0.501	1	0.501
HF [13]	0.607	0.124	4.90	0.607
MCHF: $3s\,3p+d_{\mathrm{III}}\,3p$	0.625	0.252	2.48	0.625
$3s\,3p+d_{\mathrm{III}}\,3p'$	0.626	0.203	3.08	0.626
id. + $(2p\to n\,p)$	0.750	0.255	2.94	0.844
ibid. + $(1s, 2s\to n\,d)$ and $(2p\to 3p, nf)$	0.777	0.246	3.16	0.840
With relativity included	0.792	0.248	3.20	0.847
Experiment	0.809 ± 0.009	0.257 ± 0.021	3.15 ± 0.30	

altogether (the exception being, here, the case of the $3s \rightarrow nd$ excitation).

We could evaluate the quantity $b_p(^3P)$, using the same method as for $c_p(^3P)$ and $b_p(^1P)$, in order to justify the assumption $b_p(^3P) = c_p(^3P)$, used in § II.b. As concerns the results for the mixing $3s\,3p + d_{\mathrm{III}}\,3p'$, the values of $b_p(^3P)$ and $c_p(^3P)$ are clearly identical; the final result is $\langle r_l^{-3} \rangle_{3p}(^3P) = 0.765$ a.u., a value close to that of $\langle r_{sC}^{-3} \rangle_{3p}(^3P)$ in Table 9.

Considering the satisfactory results obtained on the magnetic hfs parameters, we computed, exactly in the same way, the radial parameter for the electric-quadrupole hyperfine interaction in the ^3P term, denoted $\langle r_Q^{-3} \rangle_{3p}(^3P)$. The corresponding results appear in the last column of Table 9. For the excitations of $1s$, $2s$ and $2p$, it is clear that the relevant excited states are built from $(3s\,3p)^3P$ and $(1s\,d_{\mathrm{I}})$, $(2s\,d_{\mathrm{II}})$, $(2p^5\,p_{\mathrm{II}})$ or $(2p^5\,f_{\mathrm{II}})$ coupled to ^1D. For the approximate relativity correction, the non-relativistic result is to be multiplied by the factor $(1 + \frac{49}{45} Z^2 \alpha^2)$ [22]. The figures for the $s\,C$ and Q parts of the ^3P hfs (first and fourth columns) are identical in the first four lines: this is due to the fact that the matrix elements for $\{s^{(1)} C^{(2)}\}_0^{(1)}$ and $C_0^{(2)}$ are proportional for states containing only $m_s = +\frac{1}{2}$ electrons in the open shells.

The final result, $\langle r_Q^{-3} \rangle_{3p}(^3P) = 0.847$, can be attributed an uncertainty of 5%, in view of the good agreement between theory and experiment observed for the magnetic $\langle r^{-3} \rangle$ effective parameters. The formula for the experimental hfs constant

$$B(^3P_2) = \tfrac{2}{5} e^2 Q \langle r^{-3} \rangle_{3p} \quad [8]$$

leads to the value $Q(\mathrm{Mg}^{25}) = 0.200 \pm 0.01$ barn.

As the treatment in this paper accounts for all crossed-second-order corrections to the hfs, this value of Q can be considered as including the Sternheimer correction.

VII. Conclusion

Concerning the computing procedure, we conclude that the MCHF method yields, without too much labor, fairly accurate results for the evaluation of orbit-dependent hyperfine electronic parameters, provided

– the MCHF computer code can treat the $nl \rightarrow n'l$ excitations without constraining the excited orbital to be orthogonal to all the occupied orbitals with the same symmetry; a recent version of Froese's computer code [23] fulfills this condition;

– the excited states which enter the MCHF wave-function with too small a weight can be treated safely. In the present work these states bring only small contributions, which could be computed approximately by an analytical program. But this is not the case, for example, with the $1s \rightarrow nd$ excitation in the ground terms of the $2p$-series atoms [19], in spite of its weight smaller than 0.001 in absolute value.

Kelly applied the many-body perturbation theory (MBPT), with much success, to the hyperfine $\langle r^{-3} \rangle$ parameters in the ground term of oxygen [24]. It would be interesting to see in which way (especially, to which order of perturbation) the MBPT method describes the very large difference between the $\langle r^{-3} \rangle_{3p}$ factors in Mg I $3s\,3p\,^3P$ and ^1P.

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ANNEXE F

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COMPARISON BETWEEN MAGNETIC-HYPERFINE-STRUCTURE PARAMETERS IN ScI AND TiI

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Résumé. — Les effets de second ordre dus à l'interaction de configuration sur les paramètres concernant les parties de structure hyperfine magnétique dépendant de l'orbite ont été évalués *a priori* dans les termes fondamentaux du Scandium et du Titane. Les importances relatives des différentes excitations sont discutées. Les valeurs du rapport $\alpha = a_l/a_{sC}$ obtenues dans Sc et Ti sont respectivement 1,07 et 1,05.

Abstract. — *Ab initio* calculations of the second-order effects of the configuration interaction on the orbit-dependent magnetic-hyperfine-structure parameters in the $3d^N\,4s^2$ configuration have been performed. The importance of the contributions of the different excitations is discussed and a comparison is made between Sc and Ti. The ratio $\alpha = a_l/a_{sC}$ is found to be 1.07 and 1.05 in Sc and Ti respectively.

To take into account the effects of the configuration interaction on the hyperfine structure, three radial parameters are needed, for a given pure Russell-Saunders term. They correspond to the three parts of the magnetic effective hamiltonian : the orbital part, the spin dipole part and the core polarization part. This means that the $\langle r^{-3} \rangle$ quantities are different for the orbital part and for the spin dipole part. It is convenient, in the case of a pure Russell-Saunders term αSL of an l^N configuration, to define correction factors Δ_x such as

$$\langle r_x^{-3} \rangle = (1 + \Delta_x) \langle r^{-3} \rangle \quad (x \equiv l \quad \text{or} \quad sC)$$

where Δ_x depends on αSL.

Using the second order perturbation theory, the Δ factors can be written as linear combinations of radial integrals arising from the different excitations which occur. Bauche-Arnoult [1] gives the formal expression of the Δ factors for the Hund terms of d^N and f^N configurations. These expressions exhibit some striking features : the formal expression of $\Delta_l - \Delta_{sC}$ is the same for d and d^2, d^3 and d^4, d^6 and d^7, d^8 and d^9, except for the part arising from the excitation d → g. The ratio of hfs parameters

$$\alpha = \frac{a_l}{a_{sC}} = \frac{1 + \Delta_l}{1 + \Delta_{sC}},$$

which can be written $1 + (\Delta_l - \Delta_{sC})$ since the Δ correction factors are small compared to unity, should therefore have the same value for the Hund terms of two neighbouring elements (if we assume that the similar radial integrals change very little from one element to the next one in the series and if we neglect the contribution of the d → g excitation).

In the $3d^N\,4s^2$ series, the pairs are (Sc, Ti), (V, Cr), (Fe, Co) and (Ni, Cu). Childs and Greenebaum [2] have gathered the experimental data avialable in this series. For Fe and Co the data agree well with the prediction since $\alpha_{Fe} = 0.94 \pm 0.03$ and $\alpha_{Co} = 0.924$. Unfortunately the ground configurations of Cr and Cu are not of the $3d^N\,4s^2$ type and therefore these hyperfine structures have not been measured by atomic beam resonance. Furthermore, in Cu, the distance between $^2D_{3/2}$ and $^2D_{5/2}$ is 2 042 cm^{-1}. This would not allow the off-diagonal hyperfine-structure studies which are necessary if we consider the three independent parts of the hamiltonian.

For these reasons our attention has been drawn to the pair (Sc, Ti). Several experiments have been performed. Fricke *et al.* [3] have measured the hfs of the ^2D levels of Sc. Childs [4] has been able to determine the off-diagonal hyperfine-structure, because the distance between $^2D_{3/2}$ and $^2D_{5/2}$, here, is only 168 cm^{-1}. The values of the three magnetic hfs parameters lead to the ratio $\alpha = 1.13^{+0.27}_{-0.10}$. As concerns Ti, Childs [2] has deduced, from the experimental result on the three levels ^3P of Channappa and Pendlebury [5], $\alpha = 1.03$. We concluded, at that time, that the prediction was valid. However, more recently, Gebauer *et al.* [6] have obtained in Sc a value of α with a much better accuracy : $\alpha = 1.123 \pm 0.010$.

TABLE I

	Contribution	Analytical Sc	Analytical Ti	MCHF Sc	MCHF Ti
1s → d′	$-\Delta_{sC^2}$	− 0.000 687	− 0.000 712		
2s → d′	$-\Delta_{sC^2}$	− 0.010 284	− 0.010 925	− 0.010 550	− 0.009 765
3s → d′	$-\Delta_{sC^2}$	− 0.004 625	− 0.002 862		
4s → d′	$-\Delta_{sC^2}$	− 0.000 705	− 0.000 427		
2p → p′	$\Delta_l - \Delta_{sC^2}$	+ 0.085 089	+ 0.079 477	+ 0.084 273	+ 0.079 383
3p → p′	$\Delta_l - \Delta_{sC^2}$	+ 0.052 878	+ 0.018 662	+ 0.053 309	+ 0.017 725
2p → f′	$-\Delta_{sC^2}$	− 0.016 008	− 0.015 251	− 0.016 014	− 0.015 509
3p → f′	$-\Delta_{sC^2}$	− 0.020 286	− 0.017 684	− 0.020 610	− 0.017 557
1s → 3d	$-\Delta_{sC^2}$	− 0.000 020	− 0.000 024		
2s → 3d	$-\Delta_{sC^2}$	− 0.003 364	− 0.003 632		
3s → 3d	$-\Delta_{sC^2}$	− 0.009 363	− 0.007 931		
4s → 3d	$-\Delta_{sC^2}$	+ 0.000 316	+ 0.000 122		
3d → s′	$-\Delta_{sC^2}$	0	0		
3d → d′	$\Delta_l - \Delta_{sC^2}$	0	0		
3d → g′	$-\Delta_{sC^2}$	0	+ 0.008 635		
	Total	+ 0.072 941	+ 0.047 448		

Therefore, in order to understand the discrepancy between α_{Ti} and α_{Sc}, we performed *ab initio* evaluations of the α quantities.

For each configuration of the type : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^N\ 4s^2$, seven kinds of excitations can occur :

i) excitations from a closed shell to an empty shell :

1s, 2s, 3s, 4s → d′

2p, 3p → p′

2p, 3p → f′

ii) excitations from a closed shell to the open shell :

1s, 2s, 3s, 4s → 3d

iii) excitations from the open shell to an empty shell:

3d → s′, d′, g′

(we note that the excitations of a closed shell 1s, 2s, 3s, 4s to an empty shell s′ give a contribution only to the Fermi contact term, that we do not consider here).

From Bauche-Arnoult [1] the formal expression of $\Delta_l - \Delta_{sC}$ is the same for Sc and Ti for the excitations i) and ii). In the third case, $\Delta_l - \Delta_{sC}$ is zero for 3d → s′ and d′ for both elements. 3d → g′ gives 0 for Sc and a non zero value for $3d^2\ 4s^2\ {}^3F$ of Ti.

The separate effects of each excitation can be described in terms of one virtual orbital since the excitations involve only one electron. Each virtual orbital was determined as an analytical function by optimization [7]. For each of the largest contributions to Δ_l and Δ_{sC} (> 0.01), it appeared feasible to check our result by making another calculation, using a Multiconfigurational Hartree-Fock program (MCHF) [8]. The MCHF procedure has been used here for obtaining the virtual orbital relevant to the true second order effect, that is, with vanishing weights for all excited configurations. In the five cases that we considered, the results obtained by the two methods are very close (Table I).

If we examine each excitation separately, we see that 2p, 3p → p′ give contributions much larger than the other ones, due to the large spatial overlapping of the radial functions. The following ones in order of importance are 2p, 3p → f′, the excitations of the *n*s closed shells being ten times weaker.

Comparing Sc and Ti we see that, except for 3p → p′, the large contributions do not differ by more than 20 %. For the inner shells 1s, 2s and 2p, the differences are very small : less than 10 %. For 3s and 4s they are somewhat larger.

The sum of the contributions of the different excitations to $\Delta_l - \Delta_{sC}$ is given at the bottom of the table. Omitting the last figures, we have summarized the results in table II. The effects of relativity are expected to be about 1 % for both Sc and Ti, reducing the calculated value of α [9].

In conclusion, as it was expected [1], when we consider the second order effects, the *ab initio* evaluations of α for Sc and Ti lead to values which are close (in spite of the excitation d → g in Ti, which turns

TABLE II

	Sc	Ti
$\alpha_{\text{calculated}}$	1.07	1.05
$\alpha_{\text{calc. with relativity}}$	1.06	1.04
$\alpha_{\text{experimental}}$	1.12 ± 0.01	1.03

out to be 1 % of the α_{Ti} value). The problem of the bad agreement with the experimental α_{Sc} value remains. However : on the one hand, the configuration-mixing wave functions are not yet known for the even low levels of ScI ; on the other hand, calculations including higher-order effects, in particular near-degeneracy effects, would be of great interest. In order to check the agreement with other experimental results, similar second-order calculations for the other elements of the series would be instructive.

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ANNEXE G

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Fine and Hyperfine Structures and Isotope Shifts in the Arc Spectrum of Mercury

Part II. *Empirical interpretation*

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Abstract

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An empirical study of the mercury atom is reported. For the odd *6snp* ($n = 6$–8), *6p′* and *6s5f* configurations, the levels are studied by the parametrical method with configuration interaction. Hyperfine structure and isotope shift parameters are determined for these configurations, taking into account second order hyperfine interaction effects. For the even *6snd* ($n = 6$–8) configurations and the 199 and 201 isotopes an empirical study is made by diagonalizing the total (fine + hyperfine) hamiltonian, neglecting configuration interaction. The *6sns* ($n = 7$–10) configurations are also considered. We discuss the electronic a_{6s} factor and propose the value: $a_{6s} = 1.351$ cm^{-1} for ^{199}Hg.

1. Introduction

In the preceding paper (part I) we have reported precise determinations in the mercury atom of the levels, hyperfine structures (for 199 and 201 isotopes) and isotope shifts (for the seven stable isotopes) in the *6snl* ($n \leqslant 10$, $l = 0$–3) and $d^9s^2p(6p')$ configurations.

We now present, in this part II, an empirical study based on these results yielding energy, hyperfine structure and isotope shift parameters. The odd *6snp* ($n = 6$–8), *6p′* and *6s5f* configurations are considered (§ 2), taking into account configuration interaction and second order hyperfine interaction effects. The even *6snd* ($n = 6$–8) configurations are studied in § 3 for the 199 and 201 isotopes by diagonalizing the total (fine + hyperfine) hamiltonian, but neglecting configuration interaction. The *6sns* ($n = 7$–10) configurations are considered in § 4. In § 5 we discuss the electronic a_{6s} factor, comparing it with previous works.

2. Odd configurations

An empirical interpretation has been made, following the method described by Racah [1]. The calculations were made on the Orsay University's Univac 1110 by use of computer codes [2] developed in our laboratory. The configurations and interactions included in the calculations are shown in Table I. Our calculation extends the work of Martin et al. [3] by adding the *6s8p* configuration. In Table I the obtained values of the parameters and of the standard errors are given, along with the results from ref. [3] (which are displayed under the heading MST). In the *6s6p* configuration, we assume, following King and Van Vleck [4], Lurio [5] and Martin et al. [3], that the spin-orbit constant ζ_p in the off-diagonal element between $^3P_1$ and $^1P_1$ is λ times what it is in the diagonal elements for the ^3P levels. Parameters without standard errors in Table I were fixed, except for the $\zeta_{np,n'p}$ ($6 \leqslant n < n' \leqslant 8$) configuration interaction spin-orbit paramete which were determined by: $\zeta_{npn'p} = (\zeta_{np}\zeta_{n'p})^{\frac{1}{2}}$. Several values of these fixed parameters were tried around values suggested by the work of Martin et al.

Table I. *Parameter values for odd configurations* (*in cm^{-1}*)

		Fitted	
Configuration	Parameter	MST	This work
$5d^{10}6s6p$	A		$48\,574 \pm 50$
	$G^1(sp)$	$19\,143 \pm 243$	$19\,151 \pm 198$
	ζ_p	$4\,288 \pm 75$	$4\,243 \pm 61$
	$\lambda\zeta_p$	$3\,528 \pm 410$	$3\,417 \pm 337$
$5d^{10}6s7p$	A		$70\,918 \pm 42$
	$G^1(sp)$	$2\,310$	$2\,125 \pm 179$
	ζ_p	677 ± 73	789 ± 77
$5d^{10}6s8p$	A		$76\,818 \pm 42$
	$G^1(sp)$		400 ± 170
	ζ_p		259 ± 50
$5d^96s^26p$	A		$87\,754 \pm 452$
	$F^2(dp)$	$14\,525 \pm 525$	$13\,435 \pm 647$
	$G^1(dp)$	$4\,830 \pm 180$	$4\,865 \pm 159$
	$G^3(dp)$	$4\,606$	$7\,429 \pm 1\,028$
	ζ_d	$6\,094 \pm 41$	$6\,132 \pm 37$
	ζ_p	$4\,894 \pm 76$	$5\,093 \pm 93$
$5d^{10}6s5f$	A		$77\,240 \pm 33$
	$G^3(sf)$	7	7
	ζ_f	0	0
CI $6p$–$6p'$	$R^2(dpsp)$	$-9\,000$	$-9\,000$
	$R^1(dpps)$	$-9\,000$	$-9\,000$
$7p$–$6p'$	$R^2(dpsp)$	$-4\,084$	$-3\,680$
	$R^1(dpps)$	$-4\,084$	$-3\,680$
$8p$–$6p'$	$R^2(dpsp)$		$2\,000$
	$R^1(dpps)$		$2\,000$
$6p$–$7p$	$\zeta_{6p,7p}$	$1\,700$	$1\,823$
$6p$–$8p$	$\zeta_{6p,8p}$		$1\,046$
$7p$–$8p$	$\zeta_{7p,8p}$		449
$6p'$–$5f$	$R^2(dfsp)$	550	550
	$R^3(dfps)$	382	382

The calculated energies, g factors and compositions (in percents) are given in Table II.

By making use of the obtained empirical wave functions the (200–202) isotope shifts were interpreted. If the composition of one level, as read in the last column of Table II, is $\sum_k \alpha_k^2 C_k$, then we assumed (sharing rule) that the isotope shift of this level was $\sum_k \alpha_k^2(\text{I.S.})_k$ where $(\text{I.S.})_k$ is "the isotope shift of the C_k pure configuration". These $(\text{I.S.})_k$ parameters were obtained (Table III) by a least squares fit from the experimental values. The isotope shifts calculated from these $(\text{I.S.})_k$ are given in Table IV and compared with the observed values.

Table II. *Calculated levels, g values and composition for odd configurations*

Value in parentheses not included in the fit

J	Designation	Observed level (cm^{-1})	Calculated level (cm^{-1})	O–C (cm^{-1})	Observed g_J	Calculated g_J	Composition (%)		
0	$6p\ ^3P$	37 685	37 686	−1			99		
	$7p\ ^3P$	69 516	69 469	47			99		
	$8p\ ^3P$	76 447	76 444	3			99		
	$6p'\ ^3P$		90 579				99		
1	$6p\ ^3P$	39 412	39 411	1	1.486	1.485	97	3 $6p\ ^1P$	
	^1P	54 069	54 068	0	1.016	1.017	93	4 $6p'\ ^1P$	3 $6p\ ^3P$
	$7p\ ^3P$	69 662	69 717	−56		1.468	93	6 $7p\ ^1P$	1 $6p\ ^1P$
	^1P	71 295	71 291	3		1.031	90	5 $7p\ ^3P$	3 $6p'\ ^1P$
	$8p\ ^3P$	76 467	76 470	−3		1.403	80	19 $8p\ ^1P$	
	^1P	76 863	76 862	1		1.099	76	18 $8p\ ^3P$	2 $6p'\ ^1P$
	$6p'\ ^3P$	78 813	79 701	(−888)	1.210	1.226	56	20 $6p'\ ^1P$	13 $6p'\ ^3D$
	^1P	88 760	88 760	0		0.904	61	27 $6p'\ ^3D$	8 $6p'\ ^3P$
	^3D	93 737	93 738	−1		0.865	59	32 $6p'\ ^3P$	9 $6p'\ ^1P$
2	$6p\ ^3P$	44 043	44 043	−0	1.500	1.500	99	1 $6p'\ ^3P$	
	$6p'\ ^3P$	68 886	68 975	−88		1.430	55	27 $7p\ ^3P$	14 $6p'\ ^3D$
	$7p\ ^3P$	71 207	71 169	38		1.458	73	16 $6p'\ ^3P$	7 $6p'\ ^3D$
	$8p\ ^3P$	76 823	76 825	−1		1.491	98	1 $6p'\ ^1D$	1 $6p'\ ^3D$
	$5f\ ^3F$	77 237	77 237	−0		0.667	100		
	$6p'\ ^1D$	78 676	78 619	57	1.117	1.116	45	22 $6p'\ ^3P$	19 $6p'\ ^3D$
	^3F		85 451			0.749	76	24 $6p'\ ^1D$	
	^3D		94 916			1.090	58	26 $6p'\ ^1D$	11 $6p'\ ^3F$
3	$6p'\ ^3F$	70 932	70 887	45	1.087	1.097	52	32 $6p'\ ^1F$	16 $6p'\ ^3D$
	$5f\ ^3F$	77 239	77 240	−1		1.083	100		
	^1F	77 241	77 241	−0		1.000	100		
	$6p'\ ^3D$	80 128	80 192	−64		1.254	76	23 $6p'\ ^1F$	1 $6p'\ ^3F$
	^3F		93 716			1.066	47	45 $6p'\ ^1F$	8 $6p'\ ^3D$
4	$6p'\ ^3F$	76 945	76 924	21		1.250	86	14 $5f\ ^3F$	
	$5f\ ^3F$	77 287	77 289	−2		1.250	86	14 $6p'\ ^3F$	

Table III. *200–202 isotope shifts for pure configurations (10^{-3} cm^{-1})*

Configuration	Isotope shift
$6s7p$	1±3
$6s7p$	18±4
$6s8p$	23±3
d^9s^2p	251±4
$6s5f$	16±3

Table IV. *200–202 isotope shifts for odd configurations: observed and calculated values*

Levels		(200–202) isotope shift (10^{-3} cm^{-1})		
		Observed	Calculated	O–C
$6s6p$	$^3P^0_0$	2.1	1.9	0.2
	$^3P^0_1$	1.0	2.2	− 1.2
	$^3P^0_2$	0.	3.4	− 3.4
	$^1P^0_1$	15.6	11.2	4.4
$(d^9s^2p)6p'$	$^3P^0_2$	175.9	187.5	−11.6
$6s7p$	$^3P^0_0$	16.9	18.0	− 1.1
	$^3P^0_1$	17.7	18.8	− 1.1
	$^3P^0_2$	95.2	80.1	15.1
	$^1P^0_1$	22.2	28.4	− 6.2
$6s8p$	$^3P^0_0$	17.7	23.1	− 5.4
	$^3P^0_1$	22.2	23.9	− 1.7
	$^3P^0_2$	25.0	27.0	− 2.0
	$^1P^0_1$	42.3	32.8	9.5
$(d^9s^2p)6p'$	$^3F^0_4$	227.3	219.6	7.7
$6s5f$	$^3F^0_2$	15.3	16.5	− 1.2
	$^3F^0_3$	15.3	16.4	− 1.1
	$^1F^0_3$	15.3	16.3	− 1.0
	$^3F^0_4$	50.7	48.1	2.6
$(d^9s^2p)6p'$	$^1D^0_2$	243.3	246.2	− 2.9
$6p'$	$^1P^0_1$		241.9	

Table V. *^{199,201}Hg hyperfine structure parameters (10^{-3} cm^{-1})*

Configuration	Parameter	^{199}Hg	^{201}Hg
$6s6p$	a_{6s}	1 276±57	−472±20
	a_{6p}	20±18	−7±6
	b_{6p}		−62±142
$6s7p$	a_{6s}	1 346±55	−496±20
	a_{7p}	1±18	−0±6
	b_{7p}		−12±169
$6s8p$	a_{6s}	1 324±81	−494±28
	a_{8p}	0 fixed	0 fixed
	b_{8p}		2±168
$d^9s^2p(6p')$	a_{5d}	44±29	−22±7
	a_{6p}	20 fixed	−7 fixed
	b_{5d}		−104±146
	b_{6p}		−78±177
$6s5f$	a_{6s}	1 291±100	−505±36

The hyperfine structures were interpreted in terms of the hyperfine parameters [6]:

$$a_{6s} = \frac{16\pi}{3}\mu_B\mu_N(\mu_I/I)\,|\Psi_{6s}(0)|^2$$

$$a_{nl} = 2\mu_B\mu_N(\mu_I/I)\langle r^{-3}\rangle_{nl} \qquad (l \neq 0)$$

$$b_{nl} = e^2Q\langle r^{-3}\rangle_{nl} \qquad (l \neq 0)$$

where μ_I/I is the nuclear g factor and Q the nuclear electric-quadrupole moment. These parameters were taken to be different in various configurations and the obtained values are given in Table V. The experimental hyperfine structure values were corrected for 2nd order effects, the so-called interaction between hyperfine splittings of neighbouring levels, using the classical

Table VI. ^{199,201}*Hg A and B factors: observed values, values corrected for 2nd order effects, and calculated values* (10^{-3} cm^{-1})

Values in parentheses not included in the fit

Levels		^{199}Hg: A factor				^{201}Hg: A factor				^{201}Hg: B factor			
		Obs.	Corrected for 2nd order	Calc.	Corr.–calc.	Obs.	Corrected for 2nd order	Calc.	Corr.–calc.	Obs.	Corrected for 2nd order	Calc.	Corr.–calc.
$6s6p$	$^3P_1^0$	492.1	492.2	479.0	13.2	−181.9	−181.9	−177.0	−4.9	−9.3	−9.3	−5.6	−3.6
	$^3P_2^0$	302.4	302.4	324.4	−22.0	−111.8	−111.8	−120.0	8.2	13.3	13.3	12.2	1.1
	$^1P_1^0$	−119.6	−119.6	−112.5	−7.1	44.2	44.2	41.6	2.6	7.9	7.9	11.0	−3.1
$(d^9s^2p)6p'$	$^3P_2^0$	119.4	119.4	110.2	9.1	−44.2	−44.2	−43.8	−0.4	−9.6	−9.6	−12.6	3.0
$6s7p$	$^3P_1^0$	541.3	542.6	534.0	8.6	−200.8	−200.6	−196.7	−3.9	−1.7	−0.9	−0.9	−0.0
	$^3P_2^0$	229.9	228.8	254.0	−25.2	−84.4	−84.5	−94.7	10.1	−3.9	−5.2	−4.0	−1.2
	$^1P_1^0$	−185.3	−187.2	−182.8	−4.4	69.5	69.2	67.2	2.0	1.6	1.8	1.8	0.0
$6s8p$	$^3P_1^0$	462.3	473.1	632.8	(−159.7)	−175.6	−174.2	−236.1	(61.9)	−5.4	0.6	0.1	0.5
	$^3P_2^0$	328.8	325.0	325.1	−0.1	−120.7	−121.3	−121.4	0.1	2.6	−1.5	−1.0	−0.4
	$^1P_1^0$	−80.0	−86.3	−288.9	(202.6)	31.9	31.1	107.5	(−76.4)	−0.3	0.4	−0.5	0.8
$(d^9s^2p)6p'$	$^3F_4^0$	43.0	42.9	41.6	1.2	−15.8	−15.8	−17.8	2.0	−13.4	−13.4	−12.3	−1.2
$6s5f$	$^3F_2^0$	−265.0	−210.7	−214.8	4.1	76.7	84.9	84.0	0.9	14.8	−13.4	−0.0	−13.4
	$^3F_3^0$	−154.6	−133.3	51.1	(−184.4)	55.5	58.8	−20.0	(78.8)	−16.2	102.1	−0.0	102.1
	$^1F_3^0$	178.9	198.5	2.7	(195.8)	−79.5	−76.6	−1.1	(−75.5)	−36.1	−86.0	0.0	−86.0
	$^3F_4^0$	147.1	148.8	142.7	6.1	−55.3	−55.0	−56.1	1.0	−6.6	−2.5	−1.9	−0.6
$(d^9s^2p)6p'$	$^1D_2^0$			45.8		−21.7	−21.7	−16.9	−4.7	−24.2	−24.2	−23.5	−0.7
$6p'$	$^1P_1^0$			103.4									

method of Woodgate (ref. [7], equation (B5), p. 144; the perturbing levels being those in Table II). The parameters were obtained by a least squares fit from the A and B factors so corrected for 2nd order effects. In Table VI we give, for each level, the observed value, the value corrected for 2nd order effects, and the calculated value of the A and B factors for ^{199}Hg and ^{201}Hg.

3. $6snd$ ($n = 6$–8) configurations

Since the work of Schüler and Jones [8] it has been recognized that the fine and hyperfine structures in the $6snd$ configurations are of the same order of magnitude. We carried out an empirical study by diagonalizing the total (fine + hyperfine) hamiltonian. No configuration interaction was included. The obtained parameters are given in Table VII. As in the odd configurations, a spin-orbit λ parameter was introduced (λ turns out to be about 0.64 for the three $6snd$ configurations). We also introduced a hyperfine parameter, $a'_{6s} = a_{6s} + \delta a_{6s}$ in the off-diagonal matrix element between $^1D_2$ and $^3D_2$, differing from the diagonal ^3D hyperfine a_{6s} parameter. Following the notation of Kluge and Sauter [9] we have $a'_s = \lambda_s a_s$ with $\lambda_s < 1$ ($\lambda_s = 0.9921$ for the $6s6d$ configurations in agreement with the work of Huet [10, 11]). In the simple Hartree-Fock method, λ_s is interpreted as $\lambda_s^{HF} = \Psi_{6s}(0)/\Psi_{6s'}(0)$ where Ψ_{6s} and $\Psi_{6s'}$ are the $6s$ radial orbitals in the ^1D and ^3D terms respectively. This Hartree-Fock value is $\lambda_s^{HF} = 1.011$ for the $6s6d$ configuration [12], so that our empirical value is not explained in this *ab initio* scheme. The standard errors solely indicate the precision with which the equations are solved and do not take into account the experimental errors.

The value obtained for a_{6s} in the $6s6d$ configuration (^{199}Hg) is in good agreement with the values previously obtained by Landais [13] $a_{6s} = (1\,334.7 \pm 2.0)$ 10^{-3} cm^{-1} and by Chantepie and Barrat [14] $a_{6s} = (1\,334.9 \pm 1.4)$ 10^{-3} cm^{-1}.

4. $6sns$ configurations ($n = 7$–10)

Values for the hyperfine parameters $a_{6s} + a_{ns}$ ($n = 7$–10) were extracted by neglecting configuration interaction (but by taking into account off-diagonal matrix elements of the hyperfine hamiltonian). The results are given in Table VIII.

5. Discussion of results

We discuss the various a_{6s} values obtained for ^{199}Hg in the preceding empirical study. This will tell us how far we can trust the obtained wavefunctions. We then propose a value for a_{6s}.

Table VII. *Parameter values and standard errors for 6snd configurations* (10^{-3} cm^{-1})

Parameters	Configurations				
	^{199}Hg			^{201}Hg	
	$6s6d$	$6s7d$	$6s8d$	$6s6d$	$6s7d$
$W = -(2/5)G^2(sd)$	38 055.5 ± 0.5	42 165.0 ± 0.2	30 266.2 ± 0.3	38 056.7 ± 0.7	42 169.7 ± 0.6
ζ_d	38 062.0 ± 0.2	17 969.7 ± 0.1	9 553.5 ± 0.1	38 061.7 ± 0.2	17 969.9 ± 0.2
$\lambda\zeta_d$	24 532.6 ± 0.2	11 691.7 ± 0.1	6 104.2 ± 0.3	24 532.0 ± 0.2	11 689.4 ± 0.4
a_{6s}	1 334.8 ± 0.8	1 344.6 ± 0.2	1 347.1 ± 0.4	−493.6 ± 0.4	−497.9 ± 0.4
δa_{6s}	−12.2 ± 1.0	−9.0 ± 0.3	−3.6 ± 0.8	3.9 ± 0.6	2.3 ± 0.6
a_{nd}	0.65 ± 0.10	0.14 ± 0.02	0 fixed	−0.14 ± 0.06	0.005 ± 0.061
b_{nd}				1.2 ± 0.8	1.1 ± 0.7

Table VIII. *Values of* $(a_{6s}+a_{ns})$ *(*10^{-3} *cm*$^{-1}$*) and of* $(10^3/n_a^3)\,dn_a/dn$ *for 6sns configurations*

Configurations	^{199}Hg	^{201}Hg	$(10^3/n_a^3)\mathrm{d}n_a/\mathrm{d}n$
6s7s	1 434.00	− 530.25 ± 0.07	84.2
6s8s	1 378.20	− 509.61 ± 0.04	27.9
6s9s	1 364.19	− 502.5 ± 3.0	12.6
6s10s	1 355.93		6.7

Table IX. *Recapitulation of* a_{6s} *values (*10^{-3} *cm*$^{-1}$*) for* ^{199}*Hg*

Odd configurations	a_{6s}	Even configurations	a_{6s}
6s6p	1 276 ± 57	6s6d	1 334.8 ± 0.8
7p	1 346 ± 55	7d	1 344.6 ± 0.2
8p	1 324 ± 81	8d	1 343.1 ± 0.4
5f	1 291 ± 100	$4d^{10}6s$ (Hg II)	1 351.177245 ...

As seen from Table IX the a_{6s} values from the odd configurations (*6snp* and *6s5f*) have relative errors (5–8 %) which are large compared to the errors of the hyperfine measurements (see Table V in the preceding paper (Part I)). We can put the blame on our wavefunctions. However the treatment of the odd configurations presented in our study, which takes into account the configuration interactions and the second-order hyperfine correction from the near configurations, is nevertheless an improvement on earlier treatments. For example, the result obtained by Smith [15] $a_{6s} = 1\,166.4 \pm 12$ mK from the hyperfine levels of the *6s6p* is in reality 20 % too small. On the contrary the a_{6s} values from the *6snd* ($n = 6$–8) configurations (Table IX) vary slowly with n, and the error (of the order of 0.1 %) is now about equal to the measurements of the hyperfine structures. The authors of the studies [10, 11, 13] and [14] were also interested in the determination of a_{6s} from the *6s6d* configuration. Our values are very near to theirs.

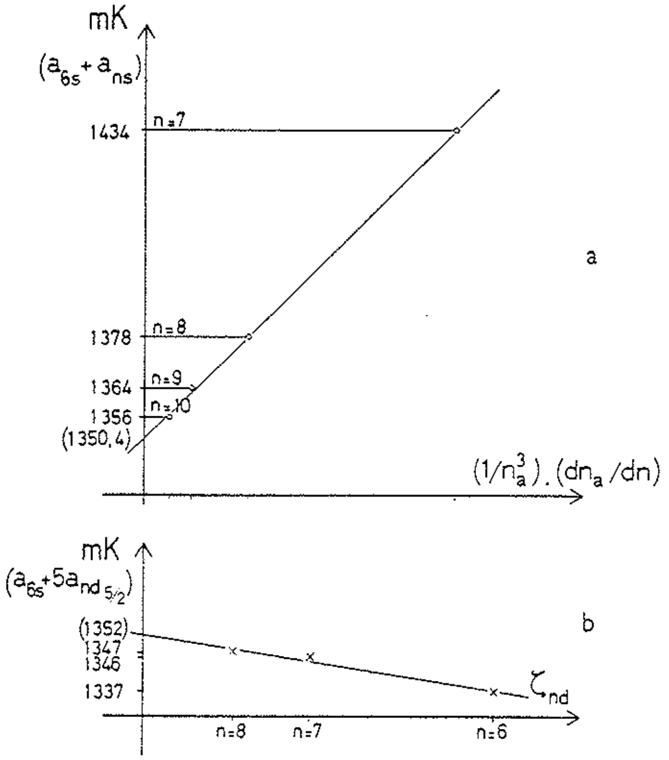

Fig. 1. (*a*) Determination of a_{6s} for ^{199}Hg by extrapolation of the *6sns* series. (*b*) Determination of a_{6s} for ^{199}Hg by extrapolation of the *6snd* series.

The a_{6s} values of Table IX from the *6snd* configuration do not agree with the extremely accurate value $a_{6s} = 1\,351.1772$ mK [16] obtained from the ground state of Hg II ($d^9s\,^2S_1$). However, by extrapolating the *6sns* and *6snd* series to $n \to \infty$ it is possible to obtain limiting values for the a_{6s} electronic factor. The graphs of the $A(^3S_1) = (a_{6s} + a_{ns})$ factor versus $Z_iZ_a^2/n_a^3(\mathrm{d}n_a/\mathrm{d}n)$ (which is proportional to $|\Psi_{ns}(0)|^2$ according to the Goudsmit–Fermi–Segré formula [17]) and of $6A(^3D_3) = a_{6s} + 5a_{nd5/2}$ (where $a_{nd5/2} = 24a_{nd}/35$) versus the ζ_d spin-orbit parameter are plotted in Fig. 1 from Tables VII and VIII. The limit $n \to \infty$ gives the a_{6s} values 1 350.4 and 1 352 mK respectively, in agreement with the value from Hg II. We thus adopt the value $a_{6s} = 1\,351$ mK. This value is rather different from the ones obtained in the *6snd* ($n = 6$–8) configurations, so the a_{nl} ($l \neq 0$) parameters which have values of some mK, cannot be expected to be realistic.

6. Conclusion

The interpretation of the measured hyperfine structures of the levels in the odd configurations (*6snp* ($n = 6$–8) and *6s5f*) though not entirely satisfactory, improves former studies. The situation is much better for the even configurations (*6sns* ($n = 7$–10) and *6snd* ($n = 6$–8)) where it was possible to determine a correct value for the a_{6s} electronic parameter, which agrees with the value from the $^2S_1$ ground state of the mercury ion. However, in the case of the even *6snd* configurations some anomalies remain unexplained, such as the anomalous value of λ_s (less than 1) and the inverted fine structure, which perhaps might be explained by a relativistic calculation using the central field approximation as in the interpretation of the inverted fine structure of the *nD* levels of sodium by Luc-Koenig [18].

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ANNEXE H

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LETTER TO THE EDITOR

Calculation of hyperfine-structure second-order effects on the isotope shifts in Sm I

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Abstract. Contributions of the isotope shifts due to the second order of the hyperfine-structure interaction in the subconfigurations f^6 ^7F sp and f^5 (^6H–^6F) ds^2 of Sm I have been calculated. These shifts for ^{147,149}Sm are smaller than $0{\cdot}1 \times 10^{-3}$ cm^{-1}.

The fact that the dipole part

$$\mathrm{M1} = \frac{\mu}{I} T \,.\, I \tag{1}$$

(I is the spin of nucleus, μ/I is the nuclear g factor and T is the electronic operator) of the hyperfine-structure (HFS) operator can produce isotope shifts in odd isotopes has been recognised since the work of Schüler and Jones (1932) on Hg I (see also Gerstenkorn *et al* 1977). The isotope shift of a level $|\alpha J\rangle$ for an odd isotope is measured by a weighted average on the $|\alpha JF\rangle$ sublevels ($F = I + J$). The second-order correction to the energy $E_{\alpha JIFM}$ of the state $|\alpha JIFM\rangle$ due to the HFS operator (1) is given by

$$\sum_{\alpha' J' F'}{}' \frac{|\langle \alpha JIFM|\mathrm{M1}|\alpha' J' IF' M\rangle|^2}{E_{\alpha JIFM} - E_{\alpha' J' IF' M}}. \tag{2}$$

Neglecting the dependence of $E_{\alpha JIFM}$ on F and M in the denominators of equation (2), the average on FM of (2), which is given by the formulae of Woodgate (1966), has the form of the product of $[(I+1)/I]\mu^2$ by a purely electronic quantity.

If such second-order effects were strong enough, the points involving odd isotopes in a King plot would not lie on the straight line determined by the even isotopes. The King plots published by Hansen *et al* (1967) concern five optical transitions of Sm I (even isotopes: 144–154; odd isotopes: 147 and 149) and of Nd I (even isotopes: 142–150; odd isotopes: 143 and 145). Some of the points for odd isotopes seem to lie slightly off the straight lines, corresponding to contributions to the line shifts smaller than 10^{-3} cm^{-1}. Since this value is also of the order of magnitude of the experimental errors for odd isotopes, it seemed worthwhile to calculate the second-order effects of the HFS operator on the isotope shifts.

This calculation has been made for ^{147}Sm ($I = \frac{7}{2}$) and for ^{149}Sm ($I = \frac{7}{2}$), for the 127 levels in the subconfigurations f^6 ^7F sp, f^5 ^6H ds^2 and f^5 ^6F ds^2, using the intermediate-coupling wavefunctions of the empirical interpretation of Carlier *et al* (1968). The perturbing levels in equation (2) were taken to be the levels in

Table 1. Parameters of the HFS operator

Parameters	Values (au)
$\langle r^{-3}\rangle_{(10)6s}$	77·0[a]
$\langle r^{-3}\rangle_{(10)4f}$	−0·216[b]
$\langle r^{-3}\rangle_{(01)4f}$	6·38[b]
$\langle r^{-3}\rangle_{(12)4f}$	6·50[b]
$\langle r^{-3}\rangle_{(10)6p}$	−0·14[c]
$\langle r^{-3}\rangle_{(01)6p}$	4·14[c]
$\langle r^{-3}\rangle_{(12)6p}$	5·65[c]
$\langle r^{-3}\rangle_{(10)4f'}$	0
$\langle r^{-3}\rangle_{(01)4f'}$	7·44[d]
$\langle r^{-3}\rangle_{(12)4f'}$	7·44[d]
$\langle r^{-3}\rangle_{(10)5d}$	0
$\langle r^{-3}\rangle_{(01)5d}$	2·82[d]
$\langle r^{-3}\rangle_{(12)5d}$	2·82[d]

[a] From the interpolation of the a_{6s} values in $_{61}$Pm II (Reader 1966) and $_{63}$Eu II (Krebs and Winkler 1960) multiplied by $(\Psi_{6s}(0)\ \mathrm{Sm\ I}/\Psi_{6s}(0)\ \mathrm{Sm\ II})^2$ with the Hartree–Fock values for $\Psi_{6s}(0)$: 7·97 au for Sm II and 7·19 au for Sm I $f^6\ ^7F\ (sp)_{av}$.

[b] Childs and Goodman (1972).

[c] From the spin–orbit coupling constant $\zeta_{6p} = 1219\ \mathrm{cm}^{-1}$ (Carlier *et al* 1968) using the method described in Bordarier *et al* (1965 p 87).

[d] Hartree–Fock values for $f^5\ (^6F\text{–}^6H)_{av}\ s^2d$.

these subconfigurations. The energy-difference denominators (as in equation (2)) were given the experimental values, whenever they were known and otherwise the theoretical values. The operator T in equation (1) was expressed in terms of the parameters listed in table 1

$$T = 2\beta\beta_N \sum_j \left(\langle r^{-3}\rangle_{(10)6s} s_j + \langle r^{-3}\rangle_{(10)4f} s'_j + \langle r^{-3}\rangle_{(01)4f} l_j + \langle r^{-3}\rangle_{(12)4f} V_j + \ldots\right)$$

where β and β_N are the Bohr and nuclear magnetons, $V^{(1)}_m = -\sqrt{10}\{sC^2\}^{(1)}_m$, the sum on j is over the electrons, s acts only between 6s orbitals, s', l and V between 4f orbitals.

In table 2, we give the results obtained for the levels having an absolute value of the shift divided by μ^2 larger than 10^{-5} cm^{-1}.

These shifts are very small (less than $0{\cdot}1 \times 10^{-3}$ cm^{-1}) and presently beyond experimental reach. In each shift the main contribution is due to the 6s electrons, as can be seen by comparing columns 1 and 2 (column 1 is for a calculation in which all parameters are zero, except $\langle r^{-3}\rangle_{(10)6s}$). The differences between columns 1 and 2 are due to the 4f electrons. The 6p electrons and the 4f′ and 5d electrons (in $f^5\ s^2d$) have a negligible influence.

The second-order effect due to the quadrupole interaction, calculated in the same way, was found to be negligible. The lines of Sm I studied by Hansen *et al* (1967) are between some of the levels studied here and levels in the term $f^6\ ^7F\ s^2$. Since the contact part of the HFS operator for the 6s electron does not contribute within the $f^6\ s^2$ configuration, the deviations of the isotope line shifts can be attributed to the second-order shifts of the higher levels. These levels, having very small second-order shifts, do not appear in table 2 except for the $^5F_3$ level. In view of our results, even with increased experimental accuracy, deviations from straight lines in the King plots would be difficult to observe for these lines.

Table 2. Isotope shifts due to the second order of the HFS interaction in ^{147}Sm and ^{149}Sm. Column 1 is with the parameter $\langle r^{-3}\rangle_{(1016)}$ only and column 2 is with all parameters. To obtain the shifts in 10^{-5} cm^{-1} the values are to be multiplied by μ^2, with μ expressed in nuclear magnetons: $\mu_{147} = -0{\cdot}80$ and $\mu_{149} = -0{\cdot}67$ (Woodgate 1966).

J	E_{exp}	Name	Shift/μ^2 (10^{-5} cm^{-1})	
			1	2
0	13796·36	^{9}G	−4	−1
	17810·85	^{7}F^a	9	2
	18309·02	(^{6}H)^{7}F	0	−2
1	14863·85	^{9}F	−1	−1
	16112·33	^{5}D	−2	−2
	16690·76	^{7}D^a	12	5
	17769·71	^{7}F^a	−3	−1
	18985·70	^{5}F	0	−1
2	16116·42	^{7}G^b	1	1
	16681·74	^{5}D	−7	−3
	17190·19	^{7}F^a	−2	−1
	18075·67	(^{6}H)^{7}H	−1	−1
	19009·52	(^{6}H)^{7}G	1	1
3	15507·35	^{9}D	−1	−1
	17243·55	^{5}D	1	0
	18209·04	^{5}G	2	2
	19210·09	(^{6}H)^{7}H	3	3
	20459·30	^{5}F	2	1
4	16131·54	^{9}D	−1	−1
	19191·64	^{7}F^a	−2	−2
	20163·00	(^{6}H)^{7}F	4	4
5	16859·31	^{9}D	−1	−1
	19264·63	^{7}D^a	3	3
	20153·47	^{7}F^a	−4	−4
6	19254·29	^{7}G^a	−3	−3
7	19005·65	^{9}F	−2	−2

The second-order effects studied here were limited to perturbations by near levels (and also within two configurations) and so the larger shifts are obtained for levels close to one another, for example 16690·76 ($J = 1$) and 16681·74 ($J = 2$). Perturbations due to far-lying levels, which are somewhat tricky to calculate because of the $\delta(r)$ singularity in the contact HFS operator (a singularity which is removed by considering a nucleus with finite size), might alter the conclusions of this letter.

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ANNEXE I

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Generating functions for the coupling–recoupling coefficients of SU(2)

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Abstract. A general formula for the generating function of an arbitrary coupling–recoupling coefficient of SU(2) is derived via the Bargmann formalism and graphical calculations. The result is expressed in terms of sums over two finite sets only of subgraphs of the Jucys graph of the coefficient. A new explicit expression for the coefficient is obtained.

Index of notations

We give the main notations and the paragraphs in which they are defined.

§ 1: CRC: coupling–recoupling coefficient
§ 2: G: Jucys graph
k_i, κ_i, λ_i: l indices; τ_i, ξ_i, η_i: corresponding variables
$L = (l_1, \ldots, l_{n_G})$: array of the n_G l indices of a CRC
E_G: set of all L
$G_L = G_{jm\ldots}$: value of the CRC
N_L: normalization constant equation (1)
Φ_G: generating function
§ 4: (ab): branch
$[a \ldots z],]a \ldots z]$ etc: paths
$(a \ldots z)$: circuit
$\mathscr{B}(D)$: set of the elements of diagram D
K_G, Ω_G: sets of closed and open diagrams of G
$\mathscr{D}, \mathscr{D}_V, \bar{\mathscr{D}}_V, \mathscr{R}_V, F_G, F'_G, H_G, H'_G, Q_G$: sets of diagrams
§ 5: $M(D), \epsilon(D), L(D), l_i(D)$: functions of diagram D
§ 7: $\alpha, \beta, \bar{\beta}$: sets of branches
a, b, c, d, f: matrices
v, w: vectors $|d|$: number
§ 8.1: $\pi(C)$: function of circuit C
§ 8.2: $S_{t,k}, S'_{t,k}, R_{t,k}, F''_G, U_{t,k}$: sets of diagrams
ω_t, ω'_t: sets of subscripts.

1. Introduction

A coupling–recoupling coefficient (CRC) of SU(2) is most easily described by its Jucys graph (Jucys and Bandzaitis 1965, El Baz 1969, Bordarier 1970). Generating functions for the $3j$, $6j$ and $9j$ coefficients were obtained by Schwinger (1952, see also Biedenharn and Van Dam 1965 pp 229–79) in a creation and annihilation operator approach. In a treatment of the SU(2) group based on entire function spaces Bargmann (1962, see also Biedenharn and Van Dam 1965, pp 300–16) obtained generating functions for the $3j$ and $6j$ coefficients. Generating functions for some other CRC were derived in the Bargmann scheme: by Wu (1972) for the $9j$ and by Huang and Wu (1974) for the $12j$ and $15j$ coefficients.

In this paper a general formula for the generating function of an arbitrary CRC is derived. For a Jucys graph G we define the generating function of the CRC it represents (§ 2). The significance of graph G is made clear in § 3. We introduce certain graphs drawn on G that we call diagrams of G (§ 4). A monomial $M(D)$ is defined (§ 5) for every diagram D of graph G. The final formula for the generating function is expressed in terms of the sums of $M(D)$ over two finite sets of diagrams of G.

At first, we use the method Bargmann (1962, see also Biedenharn and Van Dam 1965, pp 300–16) used to obtain the generating function of the $6j$ coefficient. A general CRC is obtained essentially from $3j$ coefficients by summations on projection quantum numbers. Its generating function is expressed in terms of integrals of a product of generating functions of $3j$ coefficients. An algebraic expression for the generating function is then obtained (§ 7) by carrying out the integrations. At this point there is a slight difference from Bargmann's method: here all the integrations are carried out at one stroke whereas in Bargmann (1962, see also Biedenharn and Van Dam 1965, pp 300–16), Wu (1972) and Huang and Wu (1974) the integrations are carried out in several steps.

In § 8 the algebraic expression is transcribed in terms of sums over generally infinite sets of diagrams and these sums are reduced. The final formula only contains finite sums.

The usefulness of the generating functions is illustrated in § 9 where an explicit formula for an arbitrary CRC is extracted and in § 10 where an example of recursion relations is given. Also in § 9 we prove that the symmetries of the $3j$, $6j$ and $9j$ coefficients induced by invertible linear transformations on the j of the coefficients, are the known symmetries of the coefficients.

2. Definition of the generating function Φ_G

In this section we define a number of notations, most of which are adopted from Bargmann (1962, see also Biedenharn and Van Dam 1965, pp 300–16), and the generating function Φ_G of a Jucys graph G.

We utilize Jucys graphs with only two types of free branches (co- and contravariant) and one kind of vertex. The diode symbols represent $2jm$ coefficients. For the sake of simplicity we shall assume most of the time that the graphs do not contain diode symbols.

A Jucys graph G is made up of a vertices, b free branches and c bound branches. Here G is considered as a structure, not assigning peculiar values to the j and m. For every vertex v, where three branches j_1, j_2 and j_3 meet, we define:

$$J_v = j_1+j_2+j_3, \qquad k_i = J_v-2j_i \qquad (1 \leqslant i \leqslant 3).$$

We call k_1, k_2, k_3 the l indices of vertex v. The triangle condition (j_1, j_2, j_3) is equivalent to the condition: $k_i \in N$ $(1 \leqslant i \leqslant 3)$ (N is the set of non-negative integers). For every free branch (j, m) we define $\kappa = j+m$, $\lambda = j-m$ that we call the l indices of the free branch. The condition m projection of j is equivalent to $\kappa \in N$, $\lambda \in N$. We arrange the l indices of the vertices and free branches as an ordered set $L = (l_1, l_2, \ldots, l_{n_G})$ with

$n_G = 3a+2b$. When the j and m take all possible values compatible with triangle and projection conditions, L runs on a subset E_G of N^{n_G} (the l indices are not independent: to every bound branch j_1 corresponds the relation $k_2+k_3 = k_2'+k_3'$ $(=2j_1)$, to every free branch (j_1, m_1) the relation $\kappa_1+\lambda_1 = k_2+k_3$ $(=2j_1)$). For every $L \in E_G$, corresponding to particular values of j and m, we denote the value of the CRC by G_L or by $G_{j_1 m_1 \ldots}$ and we define a normalization constant

$$N_L = \left(\frac{\Pi(J_v+1)!}{[L!]}\right)^{1/2}, \tag{1}$$

where the product runs over the vertices of G and $[L!] = l_1! l_2! \ldots l_{n_G}!$.

We now define the generating function Φ_G of graph G as an entire function of $\tau = (\tau_1, \tau_2, \ldots, \tau_{n_G}) \in C^{n_G}$ by

$$\Phi_G = \sum_{L \in E_G} N_L G_L \tau^{[L]}, \tag{2}$$

where $\tau^{[L]} = \tau_1^{l_1} \tau_2^{l_2} \ldots \tau_{n_G}^{l_n}$. We say that τ_i is the variable corresponding to the l index l_i. Instead of τ_i, we shall often use the notation ξ_i or η_i corresponding respectively to l indices of the type κ or λ.

3. Elementary operations on graphs and generating functions

The graphs of the $3j$ coefficient $\left(\begin{smallmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{smallmatrix}\right)$ and of the $2jm$ coefficient $\delta_{jj'}\,\delta_{mm'}$ are represented on the left of figures 1 and 2. Their generating functions are known and will be given in § 6. The most general CRC is obtained from $3j$ and $2jm$ coefficients by carrying out a sequence of elementary operations: product, change of type of an index (co- and contravariant), permutation of j and summation on m. In terms of graphs these operations are: union of graphs, changes of the type of a free branch and sign of a vertex, connecting of two free branches. When these elementary operations (to which we add the change of direction of a free branch) are made on Jucys graphs, the generating functions transform in a definite way that we now describe in detail.

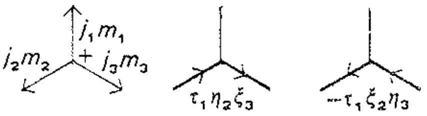

Figure 1. The graph, two open diagrams and their associated monomials for the $3j$ coefficient.

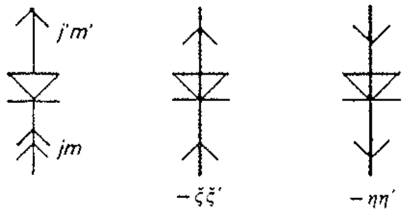

Figure 2. The graph, two open diagrams and their associated monomials for the $2jm$ coefficient.

3.1. *Product*

To the product of two CRC of graphs G' and G'' corresponds the union of the graphs $G = G' \cup G''$ and the product of the generating functions $\Phi_G = \Phi_{G'} \Phi_{G''}$.

3.2. *Types of a free branch*

CRC with co- and contravariant indices are described by graphs with two types of free branches (figure 3, where, as in the following, we represent part of the graph as a box). The generating function of G is denoted by $\Phi_G(\xi, \eta, \tau_B)$, where, as in the following, the variables τ_B correspond to the l indices L_B of part B of the graph and the first variables correspond to the l indices of part $G-B$ (here the variables ξ, η correspond to the l indices of the free branch κ, λ). Graphs G and G' of figure 3 are related by $G'_{jm\ldots} = (-1)^{j-m} G_{j-m\ldots}$ or in terms of l indices $G'_{\kappa\lambda L_B} = (-1)_{\lambda\kappa L_B}$. We then have:

$$\Phi_{G'}(\xi', \eta', \tau'_B) = \Phi_G(-\eta', \xi', \tau'_B).$$

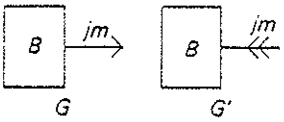

Figure 3. Change of the type of a free branch.

3.3. *Sign of a vertex*

At each vertex the branches are ordered but for a cyclic permutation. This order is indicated by a + or − sign. For the graphs in figure 4 we have

$$G'_{j_1 j_2 j_3\ldots} = (-1)^{j_1+j_2+j_3} G_{j_1 j_2 j_3\ldots}$$

or

$$G'_{k_1 k_2 k_3 L_B} = (-1)^{k_1+k_2+k_3} G_{k_1 k_2 k_3 L_B}$$

and

$$\Phi_{G'}(\tau'_1, \tau'_2, \tau'_3, \tau'_B) = \Phi_G(-\tau'_1, -\tau'_2, -\tau'_3, \tau'_B),$$

where the variables $\tau'_1, \tau'_2, \tau'_3$ correspond to the l indices k_1, k_2, k_3 of the vertex.

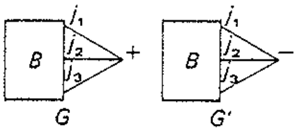

Figure 4. Change of the sign of a vertex.

3.4. *Contraction*

For the CRC $G'_{j'm'\,j''m''\ldots}$ (figure 5) the contraction on the co- and contravariant indices m' and m'' is made when $j' = j''$ by summing over $m' = m''$. Graph G corresponds to the definition:

$$G_{L_B} = \sum_{m'} G'_{j'm'\,j'm'\ldots} = \sum \delta_{\kappa'\kappa''}\,\delta_{\lambda'\lambda''}\,G'_{\kappa'\lambda'\kappa''\lambda''L_B},$$

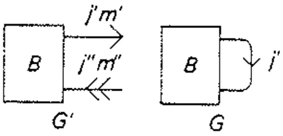

Figure 5. Contraction.

where the second sum is over $L' = (\kappa', \lambda', \kappa'', \lambda'', L_B) \in E_{G'}$ with given L_B. The corresponding graph G is also given in figure 5. Since $N_{L'} = (\kappa'!\, \lambda'!\, \kappa''!\, \lambda''!)^{-1/2} N_{L_B}$, the generating function of G is obtained from the series expansion of $\Phi_{G'}(\xi', \eta', \xi'', \eta'', \tau_B)$ by replacing $\xi'^{\kappa'}\, \eta'^{\lambda'}\, \xi''^{\kappa''}\, \eta''^{\lambda''}$ by $\kappa'!\, \lambda'!\, \delta_{\kappa'\kappa''}\, \delta_{\lambda'\lambda''}$. Remarking that

$$\kappa'!\, \lambda'!\, \delta_{\kappa'\kappa''}\, \delta_{\lambda'\lambda''} = \int \bar{\xi}^{\kappa'}\, \bar{\eta}^{\lambda'}\, \xi^{\kappa''}\, \eta^{\lambda''}\, \mathrm{d}\mu_1(\xi)\, \mathrm{d}\mu_1(\eta)$$

(where for $z = x + \mathrm{i}y$, $\bar{z} = x - \mathrm{i}y$ $\mathrm{d}\mu_1(z) = \pi^{-1}\, \mathrm{e}^{-z\bar{z}}\, \mathrm{d}x\, \mathrm{d}y$ is integrated over R^2) the generating function Φ_G can be expressed as:

$$\Phi_G(\tau_B) = \int \Phi_{G'}(\bar{\xi}, \bar{\eta}, \xi, \eta, \tau_B)\, \mathrm{d}\mu_1(\xi)\, \mathrm{d}\mu_1(\eta).$$

3.5. Direction of a bound branch

From the definition of contraction, for two CRC represented by graphs G and G' (figure 6) differing by the direction of branch j_1 we have

$$G'_{j_1 j_2 j_3 \ldots} = (-1)^{2j_1} G_{j_1 j_2 j_3 \ldots}$$

or

$$G'_{k_1 k_2 k_3 L_B} = (-1)^{k_2 + k_3} G_{k_1 k_2 k_3 L_B}$$

and

$$\Phi_{G'}(\tau'_1, \tau'_2, \tau'_3, \tau'_B) = \Phi_G(\tau'_1, -\tau'_2, -\tau'_3, \tau'_B).$$

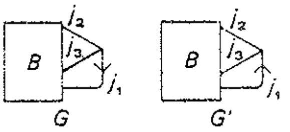

Figure 6. Change of the direction of a bound branch.

Likewise, changing the direction of the diode symbol in the $2jm$ coefficient (figure 2) gives a factor $(-1)^{2j}$ and a similar relation between generating functions.

4. Diagrams

This paragraph is devoted to the definition of certain graphs drawn on the Jucys graph. For a Jucys graph G we denote by $a, b \ldots$ the vertices, by $(ab)_s$ or $(ba)_s$ with $s = 1, \ldots n$ the n branches ($n \leqslant 3$) connecting a and b. A *passage at vertex b* is defined as the ordered set of two different branches $\phi = (ab)_s$ and $\phi' = (bc)_{s'}$ which are linked at vertex b. We represent it by $]\phi\ \phi'[$ or $]a\ b\ c[$, where to simplify notations subscripts s and s' are not expressed. Similarly, from now on, branch $(ab)_s$ will be denoted by (ab), omitting subscript s. Branch ϕ (or ϕ') and passage $]\phi\ \phi'[$ are said to be *connected*. A *path* is an ordered sequence of alternating branches and passages connected one to the following.

Example: $\phi = (ab)$, $]\phi\ \phi'[$, $\phi' = (bc)$, $]\phi'\phi''[$, $\phi'' = (cd)$.

This path is represented by $[a\,b\,c\,d]$ or $[\phi\,b\,c\,\phi'']$. The *direction* of the path on branch ϕ' is the one from b to c. The *extremities* of $[\phi\,b\,c\,\phi'']$ are branches ϕ and ϕ''. We use the notations $]a\,b\,c\,d]$ or $]\phi\,b\,c\,\phi'']$ to represent the path obtained from the preceding one by striking out branch ϕ, and similarly $[\phi\,b\,c\,\phi''[$, $]\phi\,b\,c\,\phi''[$ etc. Paths $[\phi\,b \ldots z\,\phi']$ and $[\phi'\,z \ldots b\,\phi]$ are said to be *reversed*. A *free path* is a path whose extremities are free branches. A *directed circuit* is an ordered cycle of alternating branches and passages connected one to the following.

Example: $\phi = (ab),\,]\phi\,\phi'[,\, \phi' = (bc),\,]\phi'\phi''[,\, \phi'' = (ca),\,]\phi'', \phi[$.

This circuit is represented by $(a\,b\,c)$ or $(b\,c\,a)$ or $(c\,a\,b)$ (this notation causes no confusion with that for branches). A *π circuit* is a circuit that can be separated into n identical circuits $(n > 1)$ (example: $(a\,b\,a\,b)$). A circuit which is not a π circuit is called *non-π*. Circuits $(a\,b\,c)$ and $(c\,b\,a)$ are said to be *reversed*; they both represent the same *non-directed* circuit. A set D of paths $P_1, P_2 \ldots$ and circuits $C_1, C_2 \ldots$ (or: paths and non-directed circuits) is called a *directed* (or: *non-directed*) *diagram* and it will be represented graphically on graph G by thick lines with directions indicated if necessary by arrows. We say that diagram D is *composed* of paths $P_1, P_2 \ldots$ and circuits $C_1, C_2 \ldots$. The passages and branches of a diagram D, each passage or branch being counted as many times as it appears in D are called the *elements of* D. Their set will be denoted by $\mathscr{B}(D)$. A diagram the elements of which are not repeated is said to be *simple*. A *closed diagram* is a simple diagram composed of n non-directed circuits $(n \geqslant 1)$. An *open diagram* is a simple diagram composed of one free path and of n non-directed circuits $(n \geqslant 0)$.

We define the following sets of diagrams of G, V being a set of branches of G:

$\mathscr{D} = \{\text{diagrams of } G\}$;
$\mathscr{D}_V = \{D \in \mathscr{D}: \text{some branches of } V \text{ appear in } \mathscr{B}(D)\}$; $\bar{\mathscr{D}}_V = \mathscr{D} - \mathscr{D}_V$;
$\mathscr{R}_V = \{D \in \mathscr{D}: \text{every branch of } V \text{ appears exactly once in } \mathscr{B}(D)\}$;
$K_G = \{\text{closed diagrams}\}$;
$\Omega_G = \{\text{open diagrams}\}$;
$H_G = \{\text{non-directed circuits}\}$;
$H'_G = \{\text{non-directed, non-}\pi\text{ circuits}\}$;
$F_G = \{\text{free paths}\}$;
$F'_G = \{\text{free paths with different extremities}\}$;
$Q_G = \{\text{simple free paths}\}$.

The sets K_G, Ω_G and Q_G are finite. The other sets are generally infinite.

5. The function $D \to M(D)$

In the following paragraphs, various algebraic expressions will be interpreted in terms of diagrams by means of a monomial $M(D)$ defined for every diagram D. If D is a directed diagram we construct the monomial $M(D)$ by multiplying the following factors which are associated with various parts of D:

(*a*) For every free branch jm belonging to $\mathscr{B}(D)$, of l indices κ, λ and corresponding variables ξ, η, we associate a factor given in figure 7 and depending on the type of the branch and on the direction of the diagram on the branch.

(*b*) For every passage $]j_1\,j_2[$ belonging to $\mathscr{B}(D)$ (vertex v is connected to branches j_1, j_2, j_3; the l indices of v are k_1, k_2, k_3 and the corresponding variables τ_1, τ_2, τ_3)

(see figure 8) we associate the factor τ_3 (or $-\tau_3$) if the order of the branches at the vertex is j_1, j_2, j_3 (or j_2, j_1, j_3).

(*c*) For every bound branch belonging to $\mathscr{B}(D)$ (figure 9) we associate a factor -1 (or $+1$) if the directions of the branch in D and G are identical (or opposite).

(*d*) Every time diagram D passes backwards through a diode symbol (figure 10) we associate a factor -1.

(*e*) For every circuit in D we associate a factor -1.

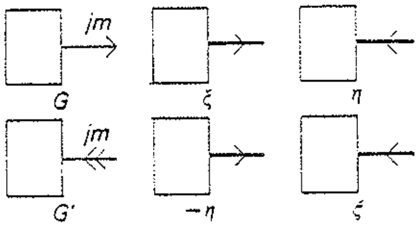

Figure 7. Computation of $M(D)$.

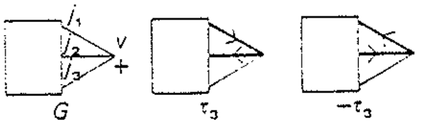

Figure 8. Computation of $M(D)$.

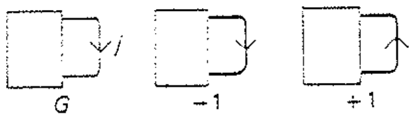

Figure 9. Computation of $M(D)$.

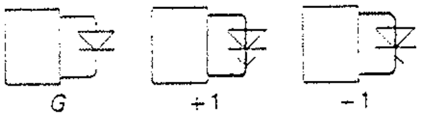

Figure 10. Computation of $M(D)$.

Remarks

(i) $M(D) = M(D')$ if D' is the diagram obtained by reversing the direction of some circuits in D. Thus $M(D)$ is also defined for non-directed diagrams.

(ii) $M(D'') = -M(D)$ if D'' is obtained by reversing the direction of a path of D whose extremities are bound branches.

(iii) The monomial $M(D)$ is transformed in the same way as the generating functions in the elementary operations in §§ 3.2, 3.3 and 3.5 (diagram D remaining unchanged).

(iv) If diagram D is composed of diagrams D_1 and D_2, then $M(D) = M(D_1)M(D_2)$. If diagrams D and D' are composed of n and n' circuits only and have the same set of elements, then $M(D) = (-1)^{n-n'}M(D')$.

(v) In the following paragraphs, there occur infinite sums $\Sigma\, M(D)$ and products $\Pi(1+M(D))$ over sets of diagrams like H_G, H'_G and F_G. Since the number of diagrams of these sets that have p elements is an $O(\mu^p)$ for $p \to \infty$, the sums and products are absolutely convergent for sufficiently small τ.

We also define the functions $D \to \epsilon(D)$ into $\{-1, +1\}$, $D \to l_i(D)$ into N $(1 \leqslant i \leqslant n_G)$ and $D \to L(D) = (l_1(D), l_2(D), \ldots, l_{n_G}(D))$ into N^{n_G} by setting $M(D) = \epsilon(D)\tau^{[L(D)]}$. We call $L(D)$ the l indices of diagram D. In § 9 it will be shown that the l indices of a diagram composed of circuits and free paths can be interpreted as the l indices of a CRC.

6. The generating functions for the 3*j* and 2*jm* coefficients

For the 3*j* (figure 1) we denote the l indices by k_1, k_2, k_3 (vertex), κ_i, λ_i (branch $j_i m_i$ $1 \leqslant i \leqslant 3$) and the corresponding variables by $\tau_1, \tau_2, \tau_3, \xi_i, \eta_i$ $(1 \leqslant i \leqslant 3)$. There are six open diagrams on the $3j$, two of which are drawn on figure 1. We have

$$\sum_{T\in\Omega_{3j}} M(T) = -\begin{vmatrix} \tau_1 & \tau_2 & \tau_3 \\ \xi_1 & \xi_2 & \xi_3 \\ \eta_1 & \eta_2 & \eta_3 \end{vmatrix},$$

so that equation (3.21) in Bargmann (1962, see also Biedenharn and Van Dam 1965, p 310) for the generating function of the $3j$ coefficient can be transcribed in terms of diagrams as:

$$\Phi_{3j} = \exp\left(- \sum_{T\in\Omega_{3j}} M(T) \right). \tag{3a}$$

The two open diagrams of the $2jm$ are given in figure 2, from which:

$$\Phi_{2jm} = \exp(\xi\xi' + \eta\eta') = \exp\left(- \sum_{T\in\Omega_{2jm}} M(T) \right). \tag{3b}$$

7. Algebraic expression of the generating function Φ_G

In this section we obtain an algebraic expression for the generating function Φ_G by starting from the generating functions for the $3j$ and $2jm$ coefficients and carrying out a sequence of elementary operations (§ 3). We represent (figure 11) graph G with its n bound branches i ($1 \leqslant i \leqslant n$) and p free branches i' ($1 \leqslant i \leqslant p$) of arbitrary types (not represented), so that the box B contains only the vertices and diode symbols of the graph.

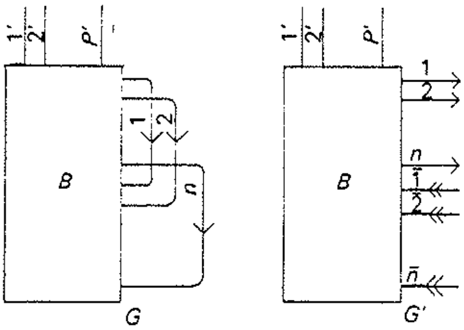

Figure 11. Obtainment of graph G by contractions on G'.

G is obtained from G' (figure 11) by n contractions, ie by connecting the free branches i and i ($1 \leqslant i \leqslant n$) of graph G' (elementary operation of § 3.4). Since G' is obtained from $3j$ and $2jm$ coefficients by the elementary operations of §§ 3.1, 3.2 and 3.3, we get using equations (3a, b) and remark (iii) of § 5:

$$\Phi_{G'} = \exp\left(- \sum_{T\in\Omega_{G'}} M(T) \right). \tag{4}$$

There is either zero or one open path (denoted by $[i\,k]$) starting from a given branch i and ending at another given branch k in graph G'. We recall that the paths obtained by removing branch i and/or k from $[i\,k]$ are denoted by $]i\,k[$, $[i\,k[$ and $]i\,k]$. If path $[i\,k]$ does not exist we put $M([i\,k]) = 0$. The branches i and k are taken from the sets $\beta = \{1, 2, 3 \dots n\}$, $\bar{\beta} = \{\bar{1}, \bar{2}, \bar{3} \dots \bar{n}\}$ and $\alpha = \{1', 2' \dots p'\}$. We put for $i \in \beta \cup \bar{\beta}$, $j \in \beta \cup \bar{\beta}$, $k \in \alpha$, $l \in \alpha$

$$a_{ij} = M(]i\,j[), \qquad b_{il} = M(]i\,l]), \qquad v_i = \sum_{l \in \alpha} b_{il}, \qquad c_{kj} = M([k\,j[),$$

$$w_j = \sum_{k \in \alpha} c_{kj}, \qquad d_{kl} = M([k\,l]) \qquad \text{and} \qquad |d| = \sum_{\substack{k \in \alpha \\ l \in \alpha}} d_{kl}.$$

Let

$$t = (\xi_1, \xi_2 \dots \xi_n, -\eta_{\bar{1}}, -\eta_{\bar{2}} \dots -\eta_{\bar{n}}), \qquad t' = (\xi_{\bar{1}}, \xi_{\bar{2}} \dots \xi_{\bar{n}}, -\eta_1, -\eta_2 \dots -\eta_n)$$

and

$$z = (\eta_1, \eta_2 \dots \eta_n, \xi_{\bar{1}}, \xi_{\bar{2}} \dots \xi_{\bar{n}})$$

be vectors of the space C^{2n}, where ξ_i, η_i are the variables corresponding to the l indices of the free branch $i \in \beta \cup \bar{\beta}$; $u\,.\,u' = \Sigma_{i=1}^{2n} u_i u_i'$ is the scalar product of $u = (u_1 \dots u_{2n}) \in C^{2n}$ and $u' = (u_1' \dots u_{2n}') \in C^{2n}$; at is the vector with component i given by $(at)_i = \Sigma_{j=1}^{2n} a_{ij} t_j$. We have $z = \tilde{f} t'$ with

$$f = \left(\begin{array}{c|c} 0 & 1_n \\ \hline -1_n & 0 \end{array} \right)$$

and

$$\sum_{T \in \Omega_G'} M(T) = z.at + z.v + w.t + |d| = t'.fat + t'.fv + w.t + |d|.$$

According to § 3.4 the generating function Φ_G is obtained from equation (4) by:

$$\Phi_G = \int \exp(-\bar{t}.fat - \bar{t}.fv - w.t - |d|)\, \mathrm{d}\mu_{2n}(t) \tag{5}$$

where $\mathrm{d}\mu_{2n}(t) = \Pi_{i=1}^{2n} \mathrm{d}\mu_1(t_i)$. The integral can be computed, for fa sufficiently small, by the method of the appendix of Bargmann (1962, see also Biedenharn and Van Dam 1965, pp 315–6):

$$\Phi_G = [\det(1 + fa)]^{-1} \exp[w\,.\,(1 + fa)^{-1} fv - |d|]. \tag{6}$$

8. Evaluation of the generating function in terms of closed and open diagrams

Most of the quantities in equation (6) were interpreted (§ 7) in terms of diagrams of G'. In this section interpretations in terms of diagrams of G are obtained. We first transform the determinant (§ 8.1) in equation (6), expressing it as a generally infinite product over the non-directed non-π circuits of G. With the aid of a formula in the appendix it is reduced to an expression containing only a finite sum over the closed diagrams of G. Similarly (§ 8.2) the exponent in equation (6) is shown to be minus the sum of $M(T)$ over the free paths T of G. It is then expressed in terms of finite sums only over the closed and open diagrams of G. Some examples are considered in § 8.3.

8.1. Transformation of determinant in equation (6)

Letting $x = -fa$ we have

$$\ln\det(1-x) = \mathrm{Tr}[\ln(1-x)] = -\left(\sum_{i} x_{ii} + \tfrac{1}{2}\sum_{ij} x_{ij}x_{ji} + \tfrac{1}{3}\sum_{ijk} x_{ij}x_{jk}x_{ki} + \ldots\right) \tag{7}$$

where the sums are made on $i \in \beta \cup \bar{\beta}, j \in \beta \cup \bar{\beta}, k \in \beta \cup \bar{\beta} \ldots$. We now interpret equation (7) in terms of diagrams of G. For $i \in \beta$, $j \in \beta \cup \bar{\beta}$, we have $x_{ij} = -a_{ij}$, $x_{ij} = a_{ij}$, hence $x_{ij} = M(P_{ij})$, $x_{ij} = M(P_{ij})$, where P_{ij} is the path of G composed of branch i and path $]ij[$ (as defined in § 7) and P_{ij} is the path of G composed of branch i and path $]ij[$. Here the paths $]ij[$ and $]ij[$ of G' which are contained in box B (figure 11) are interpreted as paths of G.

Every term of equation (7) is then of the form:

$$-x_{ij}x_{jk} \ldots x_{mi} = -M(P_{ij})M(P_{jk}) \ldots M(P_{mi}) = M(C)$$

where C is the circuit $P_{ij}, P_{jk} \ldots P_{mi}$. Conversely, let C be a non-directed circuit of q branches: if C can be separated into n identical non-π circuits S ($n \geqslant 1$), we set $\pi(C) = n$. Then $M(C) = -[-M(S)]^{\pi(C)}$. $M(C)$ appears $2q/\pi(C)$ times in equation (7). So equation (7) is transcribed as a sum on the non-directed circuits, and then on the non-directed non-π circuits:

$$\begin{aligned}\ln\det(1-x) &= 2\sum_{C \in H_G} M(C)/\pi(C) = 2\sum_{S \in H'_G} [M(S) - \tfrac{1}{2}(M(S))^2 + \tfrac{1}{3}(M(S))^3 - \ldots] \\ &= 2\sum_{S \in H'_G} \ln(1+M(S)).\end{aligned}$$

Hence

$$\det(1-x) = \left(\prod_{S \in H'_G} (1+M(S))\right)^2. \tag{8}$$

From equation (A.5) (with $V = \varnothing$ (null set)) in the appendix the product in equation (8) is expressed as a finite sum over the closed diagrams:

$$\det(1+fa) = \left(1 + \sum_{D \in K_G} M(D)\right)^2. \tag{9}$$

8.2. Transformation of the exponent in equation (6)

Expanding $(1-x)^{-1}$ in powers of x we get:

$$w\,.\,(1-x)^{-1}fv = \sum_{kil} c_{ki}(fb)_{il} + \sum_{kijl} c_{ki}x_{ij}(fb)_{jl} + \sum_{kijml} c_{ki}x_{ij}x_{jm}(fb)_{ml} + \ldots \tag{10}$$

where the sums are on $k \in \alpha, l \in \alpha, i \in \beta \cup \bar{\beta}, j \in \beta \cup \bar{\beta}, m \in \beta \cup \bar{\beta}, \ldots$. For $i \in \beta, l \in \alpha$ we have $(fb)_{il} = b_{il}$, $(fb)_{il} = -b_{il}$ and then $(fb)_{il} = -M(Q_{il})$, $(fb)_{il} = -M(Q_{il})$, where Q_{il} is the path of G composed of branch i and path $]il]$ of G' (now interpreted as of G) and Q_{il} is the path of G composed of branch i and path $]il]$.

Every term of equation (10) is then of the form:

$$c_{ki}x_{ij} \ldots x_{mn}(fb)_{nl} = -M([ki[)M(P_{ij}) \ldots M(P_{mn})M(Q_{nl}) = -M(T)$$

where T is the free path of G: $[ki[, P_{ij} \ldots P_{mn}, Q_{nl}$. Conversely to every free path T of

G there corresponds one term in equation (10), if T passes over a bound branch of G, or one term in $-|d|$ if T does not pass over a bound branch. The exponent in equation (6) is thus expressed as a sum over the free paths:

$$w \,.\, (1+fa)^{-1} fv - |d| = -\sum_{T \in F_G} M(T). \tag{11}$$

If T and T' are reversed free paths that start and end on the same free branch, then by § 5, remark (ii) $M(T) = -M(T')$ so that the sum in equation (11) can be limited to $T \in F'_G$.

We now define a procedure that decomposes every free path into a simple free path and circuits. It will then be possible to simplify equation (11). We need some notations.

Let $t = (\phi_1 u_1 u_2 \dots u_p \phi_{p+1}] \in Q_G$ be a simple free path of p vertices. We introduce the following two sets of labels occurring in t: $\omega_t = \{1, 2, \dots, p-1\}$, $\omega'_t = \omega_t \cup \{p\}$ and we put $\phi_i = (u_{i-1} u_i) \in \mathscr{B}(t)$ for $2 \leqslant i \leqslant p$. For $k \in \omega'_t$ let $S_{t,k}$ be the set of paths of the form $[u_k \dots z u_k \phi_{k+1}[$ that do not contain branches ϕ_i $(1 \leqslant i \leqslant k)$ and $S'_{t,k}$ the set of paths of $S_{t,k}$ that begin with branch ϕ_{k+1} (so $S'_{t,p} = \varnothing$). For $k \in \omega_t$ let $R_{t,k}$ be the set of non-directed circuits that pass over branch ϕ_{k+1} exactly once and that do not contain branches ϕ_i $(1 \leqslant i \leqslant k)$.

The procedure (P) is defined as follows. Let $T = [\Psi_1 a_1 a_2 \dots a_n \Psi_{n+1}] \in F'_G$ be a free path of n vertices and whose extremities Ψ_1 and Ψ_{n+1} are different free branches. We put $\Psi_k = (a_{k-1} a_k) \in \mathscr{B}(T)$ $(2 \leqslant k \leqslant n)$. If T is not simple let v be the first vertex in the sequence $a_1 a_2 \dots a_n$ that appears at least twice, k and k' the smallest and greatest numbers such that $a_k = a_{k'} = v$. Put $T' = [\Psi_1 a_1 \dots a_k a_{k'+1} \dots \Psi_{n+1}] \in F'_G$ and

$$T'' = [a_k a_{k+1} \dots a_{k'} \Psi_{k'+1}[.$$

Then T can be reconstructed by inserting path T'' into path T' at vertex a_k. Notice that T'' does not pass on branches Ψ_i $(1 \leqslant i \leqslant k)$ and that $\mathscr{B}(T) \neq \mathscr{B}(T') \cup \mathscr{B}(T'')$ in general. Repeating on T' the same process as on T, and iterating we obtain uniquely determined $t \in Q_G$, $\omega' \subset \omega'_t$ and for $k \in \omega'$ paths $T_k \in S_{t,k}$.

Conversely let $t \in Q_G$, $\omega' \subset \omega'_t$ and for $k \in \omega'$ paths $T_k \in S_{t,k}$, then by inserting, for every k in ω', path T_k at vertex u_k of t we obtain a free path $T \in F'_G$, which when decomposed by P gives back the same t, ω' and T_k. So the correspondence:

$$T \in F'_G \rightleftarrows \begin{cases} t \in Q_G \\ \omega' \subset \omega'_t \\ T_k \in S_{t,k}\ (k \in \omega') \end{cases} \tag{P}$$

is one-to-one.

Let F''_G be the set of paths $T \in F'_G$ such that in P every $T_k \in S'_{t,k}$.

If in P, for a given k, $T_k \in S_{t,k} - S'_{t,k}$ then it is of the form $T_k = [u_k Z y_1 y_2 \dots y_q Z u_k \phi_{k+1}[$, with identical first and last branches $(u_k Z)$ and $T'_k = [u_k Z y_q \dots y_2 y_1 Z u_k \phi_{k+1}[$ is a path of $S_{t,k} - S'_{t,k}$ that is different from T_k. By replacing T_k by T'_k in P we obtain T' instead of T, and from § 5, remark (ii) $M(T') = -M(T)$. Thus $\Sigma_{T \in F_G - F''_G} M(T) = 0$.

If $T \in F''_G$ we pursue the decomposition further. For a given k, let $r(k)$ be the number of times branch ϕ_{k+1} appears in $T_k \in S'_{t,k}$ $(r(k) \geqslant 1)$. T_k can be decomposed in an ordered sequence $C^k_1, C^k_2, \dots, C^k_{r(k)}$ of circuits of $R_{t,k}$. Conversely let $C^k_1, C^k_2, \dots, C^k_{r(k)}$ be an ordered sequence of arbitrary length $r(k) \geqslant 1$ of circuits of $R_{t,k}$. If $C^k_i = (u_k u_{k+1} \dots Z)$ we define path $P_i = [u_k u_{k+1} \dots Z u_k \phi_{k+1}[$. Then by joining paths $P_1 P_2 \dots P_{r(k)}$ we obtain a path T_k of $S'_{t,k}$.

In summary, the correspondence

$$T \in F''_G \rightleftarrows \begin{cases} t \in Q_G \\ \omega' \subset \omega_t \\ C_i^k \in R_{t,k} \qquad 1 \leqslant i \leqslant r(k), \qquad k \in \omega' \end{cases}$$

is one-to-one, and:

$$M(T) = M(t) \prod_{k \in \omega'} \prod_{i=1}^{r(k)} (-M(C_i^k)).$$

Putting $X_{t,k} = \Sigma_{C \in R_{t,k}} M(C)$, we have then:

$$\sum_{T \in F''_G} M(T) = \sum_{t \in Q_G} M(t) \prod_{k \in \omega_t} (1 - X_{t,k} + X_{t,k}^2 - X_{t,k}^3 + \ldots)$$

from which:

$$\sum_{T \in F_G} M(T) = \sum_{t \in Q_G} M(t) \prod_{k \in \omega_t} (1 + X_{t,k})^{-1}. \tag{12}$$

From equation (A.3) in the appendix, since $R_{t,k} = H'_G \cap \mathscr{R}_W \cap \overline{\mathscr{D}}_V$, with

$$V = \{\phi_2, \ldots \phi_k\} \quad (V = \varnothing \text{ if } k = 1) \qquad \text{and} \quad W = \{\phi_{k+1}\}$$

and putting $U_{t,k} = H'_G \cap \mathscr{D}_W \cap \overline{\mathscr{D}}_V$:

$$1 + X_{t,k} = \prod_{C \in U_{t,k}} (1 + M(C)).$$

The sets $(U_{t,k})_{k \in \omega_t}$ form a partition of $H'_G \cap \mathscr{D}_{W_t}$ where W_t is the set of the bound branches of t. Equation (12) becomes:

$$\begin{aligned} \sum_{T \in F_G} M(T) &= \sum_{t \in Q_G} M(t) \prod_{C \in H'_G \cap \mathscr{D}_{W_t}} (1 + M(C))^{-1} \\ &= \left(\prod_{C \in H'_G} (1 + M(C)) \right)^{-1} \sum_{t \in Q_G} M(t) \prod_{C \in H'_G \cap \overline{\mathscr{D}}_{W_t}} (1 + M(C)). \end{aligned}$$

And by equation (A.5) (used with $V = \varnothing$ and $V = W_t$) in the appendix:

$$\begin{aligned} \sum_{T \in F_G} M(T) &= \left(1 + \sum_{D \in K_G} M(D) \right)^{-1} \sum_{t \in Q_G} M(t) \left(1 + \sum_{D \in K_G \cap \overline{\mathscr{D}}_{W_t}} M(D) \right) \\ &= \left(1 + \sum_{D \in K_G} M(D) \right)^{-1} \sum_{T \in \Omega_G} M(T). \end{aligned} \tag{13}$$

From equations (6), (9), (11) and (13) we obtain the final expression for the generating function:

$$\begin{aligned} \Phi_G &= A^2 \exp\left(-A \sum_{T \in \Omega_G} M(T) \right) \\ A &= \left(1 + \sum_{D \in K_G} M(D) \right)^{-1}. \end{aligned} \tag{14}$$

The generating function Φ_G is thus expressed in terms of the finite sums of $M(D)$ over the closed and open diagrams of G. In order to write Φ_G explicitly one has to determine the closed and open diagrams of graph G and compute the corresponding monomials $M(D)$ by the rules in § 5.

8.3. Examples

For a $3nj$ coefficient, equation (14) simplifies to

$$\Phi_{3nj} = \left(1 + \sum_{D \in K_{3nj}} M(D)\right)^{-2}.$$

The $6j$ coefficient $\left\{\begin{smallmatrix} j_{01} & j_{02} & j_{03} \\ j_{23} & j_{13} & j_{12} \end{smallmatrix}\right\}$ is represented by a tetrahedron (figure 12) with vertices V_i $(0 \leqslant i \leqslant 3)$; branch j_{ik} $(i < k)$ connects V_i and V_k; we label the l indices of vertex V_i by k_{ij} $(0 \leqslant j \leqslant 3, j \neq i)$ and the corresponding twelve variables by τ_{ij}. There are seven closed diagrams (which are simple circuits): four circuits with three branches and three circuits with four branches; one of each kind is drawn in figure 12, and the corresponding $M(C)$ is given. From equation (14):

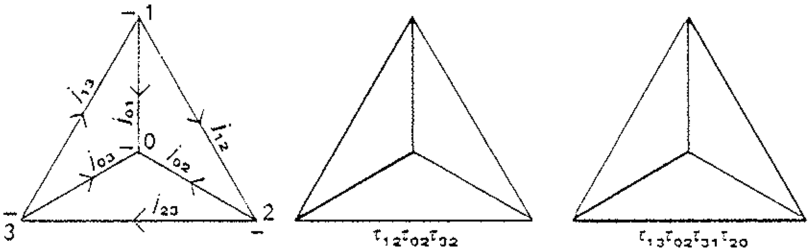

Figure 12. The graph, two closed diagrams and their associated monomials for the $6j$ coefficient.

$$\Phi_{6j} = (1 + \tau_{10}\tau_{20}\tau_{30} + \tau_{01}\tau_{31}\tau_{21} + \tau_{32}\tau_{02}\tau_{12} + \tau_{23}\tau_{13}\tau_{03} + \tau_{01}\tau_{10}\tau_{23}\tau_{32} + \tau_{02}\tau_{20}\tau_{13}\tau_{31} + \tau_{03}\tau_{30}\tau_{12}\tau_{21})^{-2}$$

which is equation (4.15) of Bargmann (1962, see also Biedenharn and Van Dam 1965, p 313).

The $9j$ coefficient

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \\ j_7 & j_8 & j_9 \end{Bmatrix}$$

is represented by a cartwheel diagram (figure 13) with vertices $V_1, V_2, V_3, V_{1'}, V_{2'}, V_{3'}$. The l indices of vertex V_i (or: $V_{i'}$) are labelled k_{ij} (or: k'_{ij}) $(1 \leqslant j \leqslant 3)$, the corresponding variables by τ_{ij} (or: τ'_{ij}). There are fifteen closed diagrams (which are simple circuits): nine circuits D_a $(1 \leqslant a \leqslant 9)$ with four branches and six circuits $D_{a'}$ $(1 \leqslant a \leqslant 6)$ with

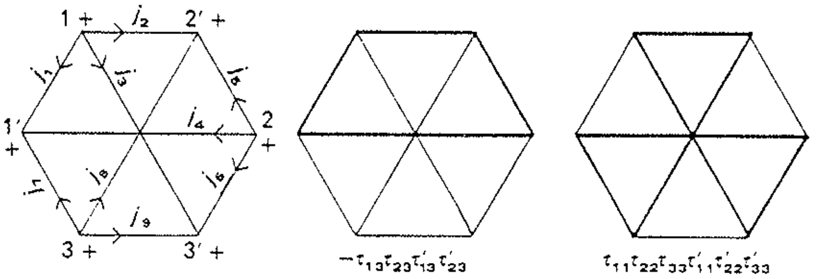

Figure 13. The graph, two closed diagrams and their associated monomials for the $9j$ coefficient.

six branches. We describe these closed diagrams (table 1) by their l indices $L(D_a)$ and the value of $\epsilon(D_a)$ (cf § 5). We also give the corresponding values of j_i. As will be clear from § 9 $-\epsilon(D_a)/2 = \frac{1}{2}$ $(1 \leqslant a \leqslant 9)$ or $-\epsilon(D_{a'})/4$ $(1 \leqslant a' \leqslant 6)$ is the value of the $9j$ coefficient with the indicated values of j_i. In figure 13 are drawn diagrams D_1 and $D_{1'}$. The generating function can be written down at once from table 1, thus reproducing the result of Wu (1972), but this will be omitted.

Table 1. Closed diagrams D_a $(a = 1, 2, \ldots, 9, 1', 2', \ldots, 6')$ of the $9j$ coefficient (figure 13): j indices, l indices (corresponding to vertices V_i), $\epsilon(D_a)$. Null values are omitted.

	$2j_i$									k_{ij}									k'_{ij}									
a	1	2	3	4	5	6	7	8	9	V_1			V_2			V_3			$V_{1'}$			$V_{2'}$			$V_{3'}$			ϵ
1	1	1		1	1							1			1						1			1				−1
2	1	1					1	1				1						1		1			1					
3				1	1		1	1							1			1	1			1						
4	1		1	1		1					1			1							1						1	
5	1		1				1		1		1						1			1						1		
6				1		1	1		1					1			1		1						1			
7		1	1		1	1				1			1											1			1	
8		1	1					1	1	1						1							1			1		
9					1	1		1	1				1			1						1			1			
1′		1	1	1		1	1	1		1				1				1	1				1				1	1
2′	1		1		1	1	1	1			1		1					1		1		1					1	−1
3′		1	1	1	1		1		1	1					1		1		1					1		1		−1
4′	1		1	1	1			1	1		1				1	1					1	1				1		1
5′	1	1			1	1	1		1			1	1				1			1				1	1			1
6′	1	1		1		1		1	1			1		1		1					1		1		1			−1

Huang and Wu (1974) have computed the generating function of the $12j$ coefficient represented in figure 14. Their result can be obtained from equation (14) in which there are 31 closed diagrams: 29 simple circuits and two diagrams composed of two circuits (one composite diagram D is represented (figure 14), and $M(D)$ is given in the notation of Huang and Wu 1974).

The graph G' for an njm coefficient is a tree in which there are no circuits. The generating function is then expressed by the same formula as for the $3j$ coefficient (equation (4)).

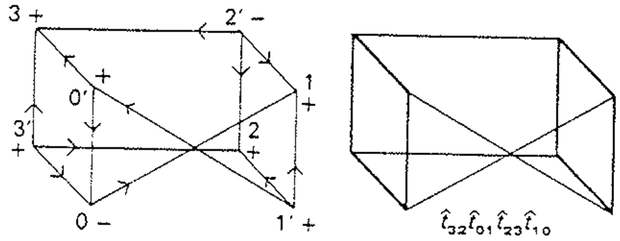

Figure 14. The graph, a closed diagram and its associated monomial for the $12j$ coefficient.

9. Explicit expression for the CRC

From the generating function, equation (14), we now obtain a general expression for any CRC. Symmetries are then briefly considered.

For a Jucys graph G let us denote respectively by T_i $(1 \leqslant i \leqslant p)$ and C_j $(1 \leqslant j \leqslant q)$ the open and closed diagrams. Expanding equation (14) we get

$$\Phi_G = \sum_{\alpha,\beta} \frac{(|\alpha|+|\beta|+1)!}{(|\alpha|+1)![\alpha!][\beta!]} \left(\prod_{i=1}^{p} (-M(T_i))^{\alpha_i} \prod_{j=1}^{q} (-M(C_j))^{\beta_j} \right), \tag{15}$$

where the sum is over $\alpha = (\alpha_1, \alpha_2, \ldots, \alpha_p) \in N^p$ and $\beta = (\beta_1, \beta_2, \ldots, \beta_q) \in N^q$; we have put $|\alpha| = \Sigma_{i=1}^{p} \alpha_i$, $|\beta| = \Sigma_{j=1}^{q} \beta_j$. By comparing equation (15) and equation (2) we obtain the expression:

$$G_L = N_L^{-1} \sum_{\alpha,\beta} \frac{(|\alpha|+|\beta|+1)!}{(|\alpha|+1)![\alpha!][\beta!]} \left(\prod_{i=1}^{p} (-\epsilon(T_i))^{\alpha_i} \prod_{j=1}^{q} (-\epsilon(C_j))^{\beta_j} \right), \tag{16}$$

where the summation is over the $\alpha \in N^p$, $\beta \in N^q$ such that

$$L = \sum_{i=1}^{p} \alpha_i L(T_i) + \sum_{j=1}^{q} \beta_j L(C_j) \tag{17}$$

and N_L as defined in equation (1).

The sum in equation (16) can be interpreted as being over all the possible ways of constructing diagrams from open and closed diagrams that have the same l indices as the calculated CRC.

For the $3j$ and $6j$ coefficients equation (16) can be written in terms of a summation on one integer and yields Racah's formulae.

To each closed or open diagram D $(= T_i$ or $C_j)$ with s vertices, t circuits $(t \geqslant 0)$ and r path $(r = 0$ or $1)$ there corresponds a CRC whose l indices are $L(D)$. The value of this CRC can be computed from equation (16) and is $(-1)^r 2^{-s/2}(-2)^t \epsilon(D)$. The $\epsilon(T_i)$ and $\epsilon(C_j)$ are thus interpreted in terms of the CRC whose l indices are the l indices of D.

9.1. *Symmetry*

Let E'_G be the set of $L \in E_G$ that satisfy polygonal conditions; we denote by E_i $(1 \leqslant i \leqslant r)$ the simple non-directed circuits and the simple free paths of G; we put $e_i = L(E_i) \in E'_G$. The set E'_G has the following properties:

(i) if $L_i \in E'_G$, $n_i \in N$ $(1 \leqslant i \leqslant h)$ then $\Sigma_{i=1}^{h} n_i L_i \in E'_G$;

(ii) if $L \in E'_G$ there exist $a_i \in N$ $(1 \leqslant i \leqslant r)$ such that $L = \Sigma_{i=1}^{r} a_i e_i$; moreover if $L = e_j$ the a_i are unique and $a_i = \delta_{ij}$.

Property (i) expresses the fact that E'_G is closed by addition. If $G_L \neq 0$ property (ii) stems from the above interpretation of equation (16), since the l indices L (which belongs to E'_G) can be written as in equation (17). In fact it is possible to prove property (ii) not assuming $G_L \neq 0$, but this will be omitted. The last part of property (ii) expresses that the e_j are extremal elements in E'_G.

We define a symmetry to be a function $\phi\colon E'_G \to E'_G$ such that $G_{\phi(L)} = X_L G_L$ where X_L is a simple algebraic expression. Let us look for symmetries such that ϕ is an invertible linear function. Then ϕ is a permutation of $(e_i)_{1 \leqslant i \leqslant r}$. Indeed putting

$$\phi(e_i) = \sum_{j=1}^{r} a_{ij} e_j \qquad \text{and} \qquad \phi^{-1}(e_i) = \sum_{j=1}^{r} b_{ij} e_j$$

(the a_{ij} and b_{ij} not necessarily uniquely determined) we have

$$e_i = \sum_{jk} b_{ij} a_{jk} e_k$$

and from property (ii) of E'_G we obtain if $b_{ij} \neq 0$, $a_{jk} = \delta_{ki}/b_{ij}$ for $1 \leqslant k \leqslant r$. Since $a_{ji} \in N$ and $b_{ij} \in N$, $a_{ji} = 1/b_{ij}$ implies $a_{ji} = 1$, and $\phi(e_j) = e_i$.

We examine the case of the $9j$ coefficient. The E_i are the fifteen closed diagrams D_a described on table 1. We put $d_a = L(D_a)$, where a runs over $A = \{1, 2 \ldots 9\}$ and $B = \{1', 2' \ldots 6'\}$. $s = \frac{1}{4} \Sigma_{a \in A \cup B} d_a \in E'_G$ is an invariant by ϕ. The only sums of three elements d_a that add up to s are:

$$d_{1'} + d_{4'} + d_{5'} = d_{2'} + d_{3'} + d_{6'} = s. \tag{18}$$

So ϕ is a permutation of $(d_i)_{i \in B}$. We have $d_{1'} = s - d_1 - d_5 - d_9$, $d_{2'} = s - d_1 - d_6 - d_8$ so $d_{1'} + d_{2'} = 2s - 2d_1 - d_5 - d_6 - d_8 - d_9$ and in general for $a \in B$, $b \in B$, $a \neq b$: $d_a + d_b = 2s - 2d_c - d_d - d_e - d_f - d_g$ where c, d, e, f, g are different indices of A, this expression being unique. From this it follows that ϕ is determined by the $\phi(d_i)_{i \in B}$: for example if $\phi(d_{1'}) = d_a, \phi(d_{2'}) = d_b$ then $\phi(d_1) = d_c$. Moreover, equation (18) is invariant by ϕ. This leaves for ϕ $6 \times 6 \times 2 = 72$ choices which are the known symmetries of the $9j$ coefficient.

For the $3j$ coefficient the six extremal elements of E'_G are linked only by a relation like equation (18). The same method yields the $6 \times 6 \times 2 = 72$ Regge (1958) symmetries (see also Biedenharn and Van Dam 1965, pp 296–7).

For the $6j$ the seven extremal elements of E'_G are linked only by relation:

$$e_1 + e_2 + e_3 = e_4 + e_5 + e_6 + e_7$$

and the same method gives the $6 \times 24 = 144$ Regge (1959) symmetries (see also Biedenharn and Van Dam 1965, pp 298–9).

We have thus proved that the only invertible linear symmetries of the $3j$, $6j$ and $9j$ coefficients are the known symmetries.

10. Recursion relations

By differentiating Φ_G, many relations between G_L can be obtained. We give an example when G is a $3nj$ coefficient. Since

$$\tau_i \frac{\partial}{\partial \tau_i}\left(\sum_{C \in K_G} M(C)\right) = \sum_{C \in K_i} M(C),$$

where K_i is the set of closed diagrams D whose l index $l_i(D)$ is different from zero (and then equal to 1), we get:

$$\left[\left(\sum_{C \in K_i} M(C)\right) \tau_k \frac{\partial}{\partial \tau_k} - \left(\sum_{C \in K_k} M(C)\right) \tau_i \frac{\partial}{\partial \tau_i}\right] \Phi_{3nj} = 0.$$

Put $G_L = 0$ if $L \notin E_G$. For $L \in E_G$ we obtain the recursion relations:

$$\sum_{L' \in L(K_i)} \epsilon(L')(l_k(L) - l_k(L')) N_{L-L'} G_{L-L'} = \sum_{L'' \in L(K_k)} \epsilon(L'')(l_i(L) - l_i(L'')) N_{L-L''} G_{L-L''}.$$

11. Concluding remarks

Some other known results come out quite easily from the present point of view: symmetries of the coefficients (compared with the symmetries of the graph); simplification of graphs with a branch $j = 0$ or containing a diode symbol linked to a bound branch; formula (25.15) in Jucys and Bandzaitis (1965) expressing a doubly stretched $9j$ coefficient in terms of a $3j$ coefficient.

The explicit formula, equation (16), expresses the CRC as a summation of products without factorization of terms. The usual method for the numerical computation of a CRC, say a $3nj$ coefficient, is to express it as a sum of products of $6j$ coefficients, each $6j$ coefficient being obtained by a summation of products and quotients of factorials. Equation (16) is thus less efficient for numerical calculations.

Appendix. Proof of some relations between sums and products over sets of diagrams

Two relations are of use in § 8. The first one equation (A.3) relates a sum and a product over sets of circuits that pass over a given branch w. It is obtained by calculating a determinant in two different ways. The second relation equation (A.5), which simplifies an infinite product to a finite sum is a consequence of the first one.

Let w be a branch joining vertices u and u' in a Jucys graph G and put $W = \{w\}$. Let μ be a subset of $H'_G \cup \mathscr{R}_W$ and ζ (or correspondingly: ζ') be a set of different paths of the form $[w\,u \ldots u\,w]$ (or: $]w\,u' \ldots u'\,w[$) and such that branch w appears only at the extremities. We designate by $\bar{\zeta}$ and $\overline{\zeta'}$ the sets composed of the reversed paths of ζ and ζ'. We put $v = \mu \cup \zeta \cup \zeta' \cup \bar{\zeta} \cup \overline{\zeta'}$ and we suppose that $\zeta \cup \zeta'$ and $\bar{\zeta} \cup \overline{\zeta'}$ are disjoint. The reversed path of $i \in v - \mu$ is designated by $\bar{i}$. For $i \in \mu$ we define $P(i)$ as a path obtained by opening circuit i at branch w. $P(i)$ will be interpreted as path $]w\,u' \ldots u\,w]$ or $[w\,u \ldots u'\,w[$ which give the same monomial $M(P(i))$. For $i \in v - \mu$ we put $P(i) = i$.

We now define a square matrix x composed of identical columns by putting $x_{ij} = M(P(i))$ for $i \in v, j \in v$.

Matrix x is of rank 1, so:

$$\det(1-x) = 1 - \sum_{i \in v} x_{ii} = 1 - \sum_{i \in \mu} M(P(i)) = 1 + \sum_{i \in \mu} M(i), \tag{A.1}$$

since for $i \in \zeta \cup \zeta'$, $M(\bar{i}) = -M(i)$ (§5, remark (ii)). We also compute: $\ln\det(1-x)$ by equation (7) of § 8.1:

$$\ln\det(1-x) = -\left(\sum_{i_1} N(i_1) + \tfrac{1}{2}\sum_{i_1 i_2} N(i_1, i_2) + \tfrac{1}{3}\sum_{i_1 i_2 i_3} N(i_1, i_2, i_3) + \ldots\right), \tag{A.2}$$

where we put $N(a, b, c \ldots z) = x_{ab}x_{bc} \ldots x_{za}$ and where the sums are over $i_k \in v$. As in § 8 we interpret the monomials $N(a \ldots z)$ in terms of circuits. But here some monomials, like $N(a)$ or $N(a, b, a', c)$ with $a \in \zeta$, $a' \in \zeta$, $b \in \mu$, $c \in \zeta'$ cannot be associated with a circuit. We now show that these monomials cancel. Let $S = (i_1, \ldots, i_m) \in v^m$ and put $i_{m+j} = i_j$ for $j = 1, 2 \ldots m$. If there exist integers k and k' $(1 \leqslant k < k' \leqslant 2m)$ such that both i_k and $i_{k'}$ belong to one of the sets $\zeta \cup \bar{\zeta}$ and $\zeta' \cup \overline{\zeta'}$ and such that $i_j \in \mu$ for $k < j < k'$ we call S non-c. Let s_m be the set of non-c $S \in v^m$ and put $s'_m = v^m - s_m - \mu^m$. Let Δ' (or: Δ) be the set of non-directed circuits that can be separated into circuits from μ (or: and paths from $v - \mu$) (each circuit and path may occur several times). If $S = (i_1 \ldots i_m) \in \mu^m \cup s'_m$

then $N(S) = -M(C)$, where C is the circuit of Δ formed from $P(i_1), P(i_2) \ldots P(i_m)$; if $S \in s_m$ there is no interpretation of $N(S)$ in terms of a circuit.

If $S = (i_1, \ldots, i_m) \in s_m \cup s'_m = \nu^m - \mu^m$, k being the first integer such that $i_k \notin \mu$, we define $f(S)$ as being the sequence of $\nu^m - \mu^m$ obtained from S by changing i_k into i_k. From the relations $N(S) + N(f(S)) = 0$, $f(s_m) = s_m$ and $f(s'_m) = s'_m$, we get

$$\sum_{S \in s_m} N(S) = \sum_{S \in s'_m} N(S) = 0.$$

If $C \in \Delta'$ and $C' \in \Delta - \Delta'$ are composed of m paths from $P(\nu)$, then $-M(C)$ appears $m/\pi(C)$ times in $\Sigma_{S \in \mu^m} N(S)$ and $-M(C')$ appears $2m/\pi(C')$ times in $\Sigma_{S \in s'_m} N(S)$; to get rid of this factor 2 we rewrite equation (A.2) as:

$$\ln \det(1-x) = -\sum_{m=1}^{\infty} \frac{1}{m}\left(\sum_{S \in \mu^m} N(S) + \tfrac{1}{2} \sum_{S \in s'_m} N(S)\right) = \sum_{C \in \Delta} \frac{M(C)}{\pi(C)}$$

and by the same method that gives equation (8), we get:

$$\det(1-x) = \prod_{C \in H'_G \cap \Delta} (1 + M(C)).$$

Comparing with equation (A.1) we get:

$$\prod_{C \in H'_G \cap \Delta} (1 + M(C)) = 1 + \sum_{i \in \mu} M(i).$$

In particular for a set V of branches of G by putting $\mu = H'_G \cap \mathscr{R}_W \cap \bar{\mathscr{D}}_V$ and by taking $\zeta \cup \zeta' \cup \bar{\zeta} \cup \overline{\zeta'}$ to be the maximal subset of $\bar{\mathscr{D}}_V$ compatible with the definition of ζ and ζ', we have $\Delta = H_G \cap \mathscr{D}_W \cap \bar{\mathscr{D}}_V$ and:

$$\prod_{C \in H'_G \cap \mathscr{D}_W \cap \bar{\mathscr{D}}_V} (1 + M(C)) = 1 + \sum_{C \in H'_G \cap \mathscr{R}_W \cap \bar{\mathscr{D}}_V} M(C). \tag{A.3}$$

Let A (or correspondingly: A') be the set of diagrams D composed only of different circuits from $H'_G \cap \mathscr{D}_W \cap \bar{\mathscr{D}}_V$ (or: $H'_G \cap \bar{\mathscr{D}}_V$). For a diagram D and a set of diagrams S we define $S \times D$ to be the set of composite diagrams made up of D and of a diagram D' from S. Let us write, for diagrams D and D', $D \sim D'$ if and only if $\mathscr{B}(D) = \mathscr{B}(D')$. It is clear that this is an equivalence relation in A (or: in A') defining a family $\mathscr{F}$ (or: $\mathscr{F}'$) of equivalence classes. If $\mathscr{A} \in \mathscr{F}$ (or $\mathscr{A} \in \mathscr{F}'$), $D \in \mathscr{A}$ and if D is not simple we say that $\mathscr{A}$ is not simple. Let $\mathscr{A}' \in \mathscr{F}'$ be an equivalence class of A' and $D' \in \mathscr{A}'$ such that D' is not simple, branch w appearing more than once in $\mathscr{B}(D')$. $\mathscr{A}'$ can be partitioned into sets of the form $\mathscr{A} \times D''$ with $D'' \in A' \cap \bar{\mathscr{D}}_W$ and $\mathscr{A} \in \mathscr{F}$ (and a set $\mathscr{A} \in \mathscr{F}$ if $D' \in A$) these $\mathscr{A}$ containing diagrams passing several times on branch w. Expanding the product, we rewrite equation (A.3) as:

$$1 + \sum_{\mathscr{A} \in \mathscr{F}} \sum_{D \in \mathscr{A}} M(D) = 1 + \sum_{C \in H'_G \cap \mathscr{R}_W \cap \bar{\mathscr{D}}_V} M(C). \tag{A.4}$$

By comparing diagrams whose set of elements is identical on both sides of equation (A.4) we see that $\Sigma_{D \in \mathscr{A}} M(D) = 0$ if $\mathscr{A} \cap \mathscr{R}_W = \varnothing$ and $\mathscr{A} \in \mathscr{F}$. Since

$$\sum_{D' \in \mathscr{A} \times D''} M(D') = \left(\sum_{D \in \mathscr{A}} M(D)\right) M(D'')$$

we obtain

$$\sum_{D' \in \mathscr{A}'} M(D') = 0$$

if $\mathscr{A}' \in \mathscr{F}'$ is not simple.

From that it follows:

$$\prod_{C \in H'_G \cap \mathscr{D}_V} (1 + M(C)) = 1 + \sum_{\mathscr{A}' \in \mathscr{F}'} \sum_{D' \in \mathscr{A}'} M(D') = 1 + \sum_{D \in K_G \cap \mathscr{D}_V} M(D). \qquad \text{(A.5)}$$

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ANNEXE J

Graphical method for computing the determinant and inverse of a matrix. Generating functions for harmonic oscillator integrals.

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Abstract

A graph G with n vertices is associated to the $n \times n$ matrix x. Det x and x^{-1}_{ij} are expressed in terms of sums over sets of subgraphs of G. The method is used to compute generating functions for products of overlaps involving harmonic oscillator wavefunctions.

1. Introduction.

The method of calculating determinants and inverses of matrices that we present in §. 2 is a graphical transcription of well known formulae. The method turns out to be very convenient for matrices with many zero elements. We illustrate the method in §. 3 by computing generating functions for products of integrals over harmonic oscillator wavefunctions. We expose two ways of calculating these generating functions, one which is essentially the method of Birtwistle (1977) and the other which uses ideas from Bargmann (1962, reprinted in Biedenharn and Van Dam, 1965, pp. 300-16) and is better in the case when the harmonic oscillators have the same frequency. These generating functions are expressed in terms of determinants and of inverse matrices with many zeros, so that our method is useful.

2. Graphical method for computing det x and x^{-1} .

We consider a $n \times n$ complex matrix $x = \Lambda - P$, where Λ is diagonal ($\Lambda_{ij} = 0$ if $i \neq j$) and where P has zeros on the diagonal : $P_{ii} = 0$ $(1 \leqslant i \leqslant n)$. To P we associate a graph G consisting of n vertices, noted by V_i $(1 \leqslant i \leqslant n)$, and where an arrow, noted by (ij) , goes from V_i to V_j for each $P_{ij} \neq 0$. Two examples of graphs corresponding to calculations in §. 3 are drawn on fig. 1 and 2. We define <u>path</u> [abc...de] as the ordered sequences of arrows (ab) , (bc) , ... , (de) and of the k $(k \geqslant 1)$ vertices V_a , V_b ... V_e . Thus [a] is a path with no arrow. Circuit (abc...de) consists of the ordered cycles of the k $(k \geqslant 2)$

arrows (ab), (bc) ... (de), (ea), and of vertices V_a, V_b ... V_e. Circuits (abc), (bca) and (cab) are identical. A set of m $(m \geqslant 0)$ circuits $C_1 \dots C_m$, such that each vertex of $C_1 \dots C_m$ appears only once in the set $\{C_1 \dots C_m\}$ is called a closed diagram. We denote the closed diagram composed of zero circuit by J. A set of one path T, and m $(m \geqslant 0)$ circuits $C_1 \dots C_m$ such that each vertex of T, $C_1 \dots C_m$ appears only once in the set $\{T, C_1 \dots C_m\}$ is called an open diagram. We denote the set of the closed (open) diagrams of G by K (Ω), and by Ω_{ij} the set of the open diagrams with a path of the form $[i \dots j]$.

For the graph of figure 2 (with $n=4$), the 9 closed diagrams of K are drawn on fig. 3 and Ω_{11}, Ω_{12}, Ω_{13} are represented on figures (4-6).

For each diagram D we denote by $\mathcal{A}(D)$ $(\mathcal{V}(D))$ the set of arrows (vertices) composing the path and/or circuits of D.

If D is a closed or open diagram with m circuits we define

$$M(D) = (-1)^m \left(\prod_{(ij) \in \mathcal{A}(D)} P_{ij} \right) \left(\prod_{k \notin \mathcal{V}(D)} \Lambda_{kk} \right) .$$

In particular : $M(J) = \prod_{i=1}^{n} \Lambda_{ii}$. Other examples of $M(D)$ are given in figures (3-6).

Now we have the following results :

$$\det(\Lambda - P) = \sum_{D \in K} M(D) \tag{1}$$

and

$$(\Lambda - P)^{-1}_{ij} = \frac{\sum_{T \in \Omega_{ij}} M(T)}{\sum_{D \in K} M(D)} . \tag{2}$$

Indeed, (1) is the graphical transcription of

$$\det x = \sum_{\sigma \in S_n} \varepsilon(\sigma)\, x_{1\sigma(1)}\, x_{2\sigma(2)} \cdots x_{n\sigma(n)} \quad .$$

As an example, for the permutation of $1 \ldots n$ $\sigma = (123)(45)(6)\ldots(n)$, written as a product of cyclic permutations, we have

$$\varepsilon(\sigma)\, x_{1\sigma(1)}\, x_{2\sigma(2)} \cdots x_{n\sigma(n)}$$

$$= [-(-x_{12})(-x_{23})(-x_{31})][-(-x_{45})(-x_{54})][x_{66}]\ldots[x_{nn}] = M(D)$$

where D is the closed diagram composed of circuits (123) and (45) .

Equation (2) is the graphical transcription of

$$(x^{-1})_{ij} = \frac{X_{ij}}{\det x}$$

where X_{ij} is the co-factor of x_{ji} in $\det x$.

If one has to calculate $v.(\Lambda - P)^{-1}\, w = \sum_{i=1}^{n} \sum_{j=1}^{n} v_i (\Lambda - P)^{-1}_{ij}\, w_j$ where $v = (v_1 \ldots v_n)$ and $w = (w_1 \ldots w_n)$ are two vectors of C^n , it is convenient to put $M'(T) = v_i\, M(T)\, w_j$ if $T \in \Omega_{ij}$. Then :

$$v\,.\,(\Lambda - P)^{-1}\, w = \frac{\sum_{T \in \Omega} M'(T)}{\sum_{D \in K} M(D)} \quad . \tag{3}$$

Let us emphasise that the interest of equations (1-3) is greater when the matrix P is sparse. The diagrams are then easily enumerated and the method described makes the calculations much easier, especially when formal (rather than numerical) expressions are required.

3. Generating functions for products of harmonic oscillator overlaps.

3.1 Generating function for the harmonic oscillator wavefunctions.

We denote the normalized one-dimensional harmonic oscillator functions by

$$|m\rangle = \frac{a^{\dagger m}}{\sqrt{m!}}\,|0\rangle \tag{4}$$

with $$a^{\dagger} = \sqrt{\frac{\omega}{2}}\, r - \frac{i}{\sqrt{2\omega}}\, P \tag{5}$$

(see Messiah (1959), book I, chapter XII).

The coherent state (Glauber, 1963)

$$|Z,\omega\rangle = e^{a^{\dagger}\bar{Z}}\,|0\rangle = \sum_{m=0}^{\infty} \frac{\bar{Z}^m}{\sqrt{m!}}\,|m\rangle \tag{6}$$

where $Z = x + iy \in C$, $\bar{Z} = x - iy$ serves as a generating function for the states of eq. (4). In the r-representation, state (6) is :

$$\langle r|Z,\omega\rangle = (\omega/\pi)^{1/4} \exp\{-(\omega\, r^2 + \bar{Z}^2)/2 + \sqrt{2\omega}\, r\, \bar{Z}\} \quad . \tag{7}$$

The functions of the harmonic oscillator centered at $-d$ are given by $$|m,\omega,d\rangle = e^{ipd}\,|m\rangle \quad . \tag{8}$$

3.2 Generating functions $S_n(t)$ for products of overlaps.

Birtwistle (1977) has given a general method for calculating generating functions of the type :

$$S_n(t) = \sum_{m_1,m_2..m_n \geqslant 0} \prod_{i=1}^{n} \langle m_i,\omega_i,d_i|m_{i+1},\omega_{i+1},d_{i+1}\rangle\, t_i^{m_i} \tag{9}$$

$(n \geqslant 2)$, $t = (t_1 \ldots t_n) \in C^n$ (when t is sufficiently small, all integrals in the following converge) and where as in the following

we identify labels 1 and $n+1$. These generating functions provide a means for evaluating chain integrals like $\langle a|b\rangle\langle b|c\rangle\langle c|a\rangle$, and sums of such integrals (Mnatsakanyan, 1971).

Introducing the operator :

$$Q(t,\omega) = \sum_{m=0}^{\infty} |m\rangle\langle m| \; t^{m} \quad . \tag{10}$$

We have :

$$Q(t,\omega) = \int d\mu_1(Z) \; |Z,\omega\rangle\langle Z\bar{t},\omega| \tag{11}$$

$d\mu_1(Z) = \pi^{-1} e^{-Z\bar{Z}}\, dxdy$ is integrated over R^2 , following the notation from Bargmann (1962, reprinted in Biedenharn and Van Dam, 1965, pp. 300-16). Equation (9) then reads :

$$S_n(t) = \operatorname{Tr} Q_1 \, Q_2 \, \dots \, Q_n \tag{12}$$

$$Q_k = e^{ipd_k} \, Q(t_k,\omega_k) \, e^{-ipd_k} \qquad (1 \leqslant k \leqslant n) \quad .$$

3.2.1 Calculation of $S_n(t)$: method A.

We sketch here the method of Birtwistle for computing $S_n(t)$. The trace in eq. (12) is computed in the r-representation :

$$S_n(t) = \int \langle r_n|Q_1|r_1\rangle\langle r_1|Q_2|r_2\rangle \dots \langle r_{n-1}|Q_n|r_n\rangle \; d^n r \tag{13}$$

$r = (r_1 \, \dots \, r_n)$ is integrated over R^n and

$$\langle r_{k-1}|Q_k|r_k\rangle = \langle r_{k-1}+d_k|Q(t_k,\omega_k)|r_k+d_k\rangle \quad .$$

The matrix element $\langle x|Q(t,\omega)|y\rangle$ can be easily computed from equations (11) and (7), by carrying out integrations similar to the

ones studied in the remaining of this section :

$$\langle x|Q(t,\omega)|y\rangle = (\omega/\pi)^{\frac{1}{2}}\,(1-t^2)^{-\frac{1}{2}}\exp\{\omega[2xyt-(1+t^2)(x^2+y^2)/2]/(1-t^2)\}\ . \tag{14}$$

Using eq. (10) and the expression of the harmonic oscillator function in terms of Hermite polynomials eq. (14) is seen to be nothing else than the Mehler formula (Bateman and Endélyi, 1955).

Equation (13) is of the form :

$$S_n(t) = \int A\exp\left(-r.(\Lambda-P)r + b.r + c\right)\,d^n r/\pi^{n/2} \tag{15}$$

$$A = \prod_{i=1}^{n}\left(\omega_i/(1-t_i^2)\right)^{\frac{1}{2}}$$

Λ is the $n\times n$ diagonal matrix :

$$\Lambda_{kk} = \frac{1}{2}\left(\frac{\omega_k\,(1+t_k^2)}{1-t_k^2} + \frac{\omega_{k+1}\,(1+t_{k+1}^2)}{1-t_{k+1}^2}\right) \qquad (1\leqslant k\leqslant n)\quad .$$

P is the symmetric $n\times n$ matrix, with all elements equal to zero but :

$$P_{k,k+1} = P_{k+1,k} = \frac{\omega_{k+1}\,t_{k+1}}{1-t_{k+1}^2} \qquad (1\leqslant k\leqslant n)\ ,\ \text{if}\quad n>2$$

$$P_{12} = P_{21} = \frac{\omega_1\,t_1}{1-t_1^2} + \frac{\omega_2\,t_2}{1-t_2^2} \qquad \text{if}\quad n=2$$

b is the n-vector :

$$b_k = -\frac{\omega_k\,d_k\,(1-t_k)}{1+t_k} - \frac{\omega_{k+1}\,d_{k+1}\,(1-t_{k+1})}{1+t_{k+1}} \qquad (1\leqslant k\leqslant n)$$

$$c = \sum_{k=1}^{n} -\,\omega_k\,\frac{1-t_k}{1+t_k}\,d_k^2$$

and where the cyclic condition $n+1\equiv 1$ is used.

The integral in eq. (15) is calculated in eq. (10) of Birtwistle (1977) :

$$S_n(t) = A\,(\det(\Lambda-P))^{-\frac{1}{2}} \exp\left(\frac{1}{4}\, b.(\Lambda-P)^{-1}\, b + c\right) \quad . \qquad (16)$$

The expressions in eq. (16) can be easily computed by the method of §. 2 with the graph of fig. 2 and diagrams like those in figures (3-6). But instead of giving explicit results for eq. (16), we turn to another method for computing $S_n(t)$ (eq. (12)).

3.2.2 Calculation of $S_n(t)$: method B .

Using eq. (11) we get for the trace in eq. (12) :

$$S_n(t) = \int d\mu_n(\zeta) \prod_{k=1}^{n} \langle Z_k t_k, \omega_k | e^{ip(d_{k+1}-d_k)} | Z_{k+1}, \omega_{k+1} \rangle \qquad (17)$$

where $\zeta = (Z_1, \ldots Z_n) \in C^n$, $d\mu_n(\zeta) = \prod_{k=1}^{n} d\mu_1(Z_k)$ and $n+1 \equiv 1$.

The matrix elements in eq. (17) are :

$$\langle Z,\omega | e^{ipd} | Z',\omega' \rangle$$

$$= (\cos\theta)^{\frac{1}{2}} \exp\Big\{\sin\theta\,(Z^2-\bar{Z}'^2)/2 + \cos\theta\, Z\bar{Z}' + \cos\theta(\sqrt{\omega}\; d\, \bar{Z}' - \sqrt{\omega'}\; d\, Z)/\sqrt{2}$$

$$- \cos\theta \sqrt{\omega\omega'}\; d^2/4\Big\} \qquad (18)$$

where $\sin\theta = \frac{\omega-\omega'}{\omega+\omega'}$, $\cos\theta = \frac{2\sqrt{\omega\omega'}}{\omega+\omega'}$.

The integral in eq. (17) is thus seen to be similar to that in eq. (15), but now the integration is over R^{2n} , so that in general the computation of $S_n(t)$ is simpler from eq. (15). However when the oscillators have the same frequency $\omega_k = \omega$ $(1 \leqslant k \leqslant n)$ in eq. (18) we have $\sin\theta = 0$, so that eq. (17) is of the form :

$$S_n(t) = \int d\mu_n(\zeta) \exp\{\bar{\zeta}.P\zeta + v.\zeta + \bar{\zeta}.w + c\} \qquad (19)$$

where P is the $n \times n$ complex matrix with all elements zero except $P_{k+1,k} = t_k \quad (1 \leqslant k \leqslant n)$;

$$v_k = -t_k\,(d_{k+1}-d_k)\sqrt{\omega/2} \quad ; \quad w_{k+1} = (d_{k+1}-d_k)\sqrt{\omega/2} \quad (1 \leqslant k \leqslant n) \quad ;$$

$$c = \sum_{k=1}^{n} -\,\omega(d_{k+1}-d_k)^2/4 \quad ; \quad n+1 \equiv 1 \quad .$$

The integral in eq. (19) can be computed by the method of the appendix of Bargmann (1962, reprinted in Biedenharn and Van Dam, 1965, pp. 315-6) :

$$S_n(t) = [\det(1-P)]^{-1} \exp\{v.(1-P)^{-1}w + c\} \quad . \qquad (20)$$

Here again, the expressions in eq. (20) can be computed by the method of §. 2, from equations (1) and (3). The graph of P is drawn in figure 1. There are only two closed diagrams, so that from eq. (1) :

$$\det\,(1-P) = 1 - t_1 t_2 \ldots t_n \quad .$$

Each of the sets Ω_{ij} contains only one open diagram, so that :

$$v.(1-P)^{-1}w = [\det(1-P)]^{-1} \sum_{i,j=1}^{n} -\frac{\omega}{2}\,(d_{j+1}-d_j)(d_i-d_{i-1}) \prod_{k=i}^{j} t_k$$

with the conventions that $\prod_{k=i}^{j} t_k = (\prod_{k=i}^{n} t_k)(\prod_{k=1}^{j} t_k)$ if $i > j$ and $d_0 = d_n$, $d_{n+1} = d_1$.

4. Conclusion.

Other fields of application of the graphical method can be found. For example, the generating function for coupling-recoupling coefficients of SU(2), such as the 3nj and njm coefficients, has been expressed by an equation like eq. (20) (Labarthe, 1975), where P is a $2n\times 2n$ matrix of the form

$$\begin{bmatrix} A & B \\ C & \tilde{A} \end{bmatrix}$$

A, B and C being $n\times n$ matrices such that : $\tilde{B} = -B$, $\tilde{C} = -C$, the tilde denoting the transposed matrix.

In this case, introducing the graph of the coupling-recoupling coefficient (El Baz, 1969), which has branches instead of arrows, so that paths go over the branches in two directions, it was shown that :

$$\det(1-P) = \Big(\sum_{D\in K} M(D)\Big)^2$$

where K is the set of the closed diagrams. For the exponent also there is a formula like eq. (3).

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Captions to figures.

Fig. 1 : G_1 graph of matrix P eq. (19).

Fig. 2 : G_2 graph of matrix P eq. (15).

Fig. 3 : K : the nine closed diagrams of G_2 $(n=4)$ and values of $M(D)$.

Fig. 4 : Ω_{11} for G_2 $(n=4)$.

Fig. 5 : Ω_{12} for G_2 $(n=4)$.

Fig. 6 : Ω_{13} for G_2 $(n=4)$.

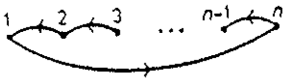

Fig. 1

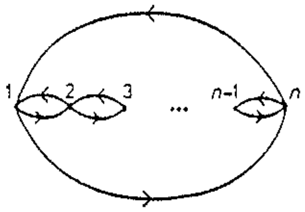

Fig. 2

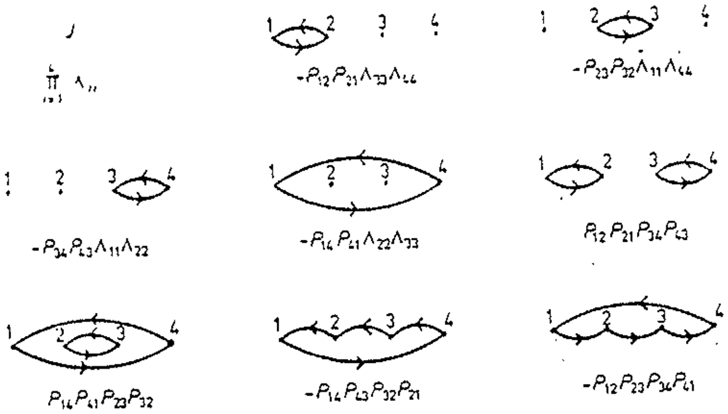

Fig. 3

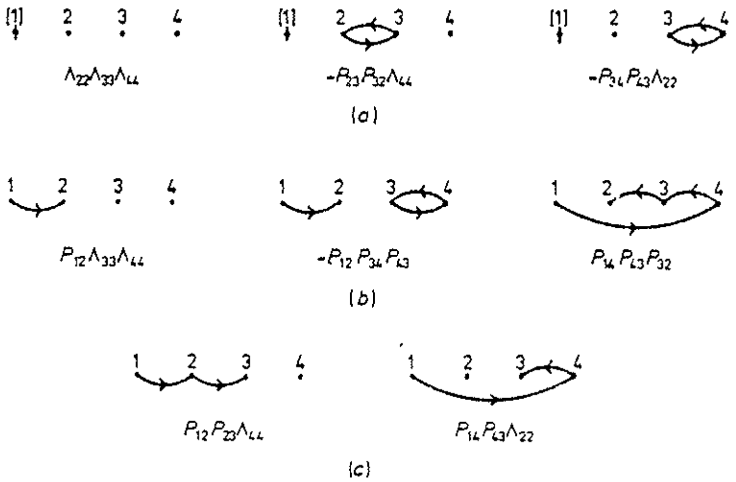

Fig. 4 (a), 5 (b) et 6 (c)