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Method for Calculating Matrix Elements between Configurations with Several Open l Shells*

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A simple procedure applicable to a digital computer is given for calculating matrix elements of F- and G-type operators between configurations that involve several partially filled l or j shells. The new procedure uses "partially coupled" basis functions, instead of traditional "uncoupled" (determinantal) or "coupled" basis functions, and may provide a simpler method for calculating configuration mixing in highly excited states of very complex atoms or for calculating nuclear shell-model energies.

I. INTRODUCTION

FOR a first approximation, one can obtain spectroscopic properties of complex atoms,[1] such as iron, from LS-genealogy scheme[2] wave functions (i.e., eigenfunctions labeled by $LSJM_J$ and genealogy or parentage). However, the observed energy structures of complex atoms do not follow such simple predictions exactly. Furthermore, many bright spectral lines originate in transitions which are forbidden in this approximation (two-electron jumps and intersystem lines). Thus a useful spectroscopic description of complex atoms must allow mixing of terms and mixing of configurations.

This mixing can be quite complicated. For example, in neutral iron one should consider (i) mixing terms with different parentage, such as $3d^64s(a^4D)4p$ and $3d^64s(a^6D)4p$; (ii) mixing nearly degenerate configurations such as $3d^64s^2$, $3d^74s$, and $3d^8$; (iii) mixing configurations within a complex,[3] such as $3s^23p^63d^64s^2$, $3s^23p^43d^84s^2$, $3s^23p^53d^74s4p$, etc.; (iv) mixing singlets and triplets, etc.

The mixing of terms and configurations can be determined once one knows the relevant off-diagonal matrix elements of Coulomb- and magnetic-interaction operators, or, more generally, F- and G-type operators,[2]

$$F\equiv\sum_i f_i,\quad G\equiv\sum_i\sum_{j<i} g_{ij}.$$

Such matrix elements can be expressed in the form $\sum r_kR^k$ in terms of radial integrals R^k and coefficients r_k that depend only on spin and angle variables. In treating very complex atoms, one desires matrix elements between wave functions that have several partially filled l shells. Although the calculation of such matrix elements presents no fundamental difficulty in principle, the actual computations using traditional methods may be so cumbersome that they are not feasible.

II. TRADITIONAL APPROACHES

Traditional calculations of F- and G-type matrix elements fall into two broad classes, according to the nature of the basis functions used. In the older approach, widely used for simple atoms, one expresses the LS-genealogy function (or any other approximate wave function) as a linear combination of *uncoupled* or *m-scheme* basis functions [so called because each such N-electron function is labeled by the quantum numbers $\{m_l(i)m_s(i)\}$ in addition to the configuration labels $\{n(i)l(i)\}$]. Frequently one uses antisymmetrized m-scheme functions, commonly called determinantal wave functions (dwf's). Various techniques are available for finding the expansion coefficients for LS-genealogy functions (or other angular-momentum functions) in terms of the dwf basis (Sec. III, below). Given these coefficients, one only needs to calculate matrix elements between dwf's, using well-known formulas.[2]

Determinantal basis functions are well suited to machine computation, since all calculations can be reduced to repetitions of simple operations. The dwf's are particularly suited to atoms possessing only closed l shells or a single valence orbital. The basic practical disadvantage of the dwf basis, apart from possible awkwardness in finding expansion coefficients, arises from the large catalog of basis functions required for describing atoms with many open l shells. For example,[4] the complex with nine $n=3$ orbitals (mixing $3s^23p^63d$, $3s3p^63d^2$, etc.) requires as many as 436 dwf's.

The conventional alternative to such uncoupled basis functions is a basis of *coupled* functions—eigenfunctions of various collective angular-momentum operators. The familiar j-j coupling functions and LS-genealogy functions fall into this class. The usefulness of coupled basis functions is largely a result of papers by Racah,[5] who showed how to express matrix elements of F- and G-type tensor operators between simple coupled functions in terms of Racah coefficients and coefficients of fractional parentage (cfp). Racah's approach has since been ex-

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[1] By complex atom, I mean an atom whose excited configurations involve several partially filled l shells.

[2] E. U. Condon and G. H. Shortley, *The Theory of Atomic Structure (TAS)* (Cambridge University Press, New York, 1935).

[3] Configurations with the same set of principal quantum numbers $\{n(i)\}$ and same parity make up a complex [D. Layzer, Ann. Phys. (N. Y.) **8**, 271 (1959)].

[4] E. A. Godfredson, thesis, Harvard University, 1963 (unpublished).

[5] G. Racah, (a) Phys. Rev. **62**, 438 (1942); (b) **63**, 367 (1943); (c) **76**, 1352 (1949).

tended by numerous authors[6] to include most of the commonly occurring matrix elements. In particular, Innes and Ufford[7] have shown how to calculate matrix elements of very general F- and G-type operators between configurations having an arbitrary number of open l shells. Their method involves sequential recouplings of groups of equivalent particles, to bring selected groups to the end of a chain.[8] Any Coulomb- or magnetic-interaction matrix element can be obtained, by use of their prescription, as a sum over products of Racah coefficients and (up to four) cfp.

Coupled basis functions are particularly suited to use in a semiempirical approach to atomic and nuclear structure, since a single such basis function often gives a reasonable approximation to the actual wave function of a complex atom. (That is, the quantum number labels used in the familiar compilations of energy levels are "approximately good" quantum numbers.) In some cases, it is possible to investigate analytically the effects of configuration mixing.[9] The algorithm described by Innes and Ufford[7] is somewhat awkward to program in full generality for a computer. The general form involves summation over various dummy angular momenta, a source of inaccuracy for numerical work. Using various identities,[7] one can often simplify specific matrix elements to expressions that involve no dummy indices. The major practical difficulty, apart from possible awkwardness in simplifying the prescription of Innes and Ufford,[7] then arises from the variety of expressions for matrix elements, involving different numbers of Racah coefficients and cfp, which can occur as one investigates a very complex atom.

It is possible to overcome partially these practical limitations of the traditional approaches by using a compromise "partially coupled" scheme of basis functions. In the next section, I shall review the notion of coupling schemes, to make clear the difference between the proposed scheme and traditional schemes. Later sections provide the necessary simple formulas for computing F- or G-type matrix elements.

III. "FORMAL" COUPLING SCHEMES

In conventional studies of complex N-electron atoms, the basic building blocks are N-electron product functions ϕ^N which are products of N single-electron orbitals u:

$$\phi^N(ab\cdots k|12\cdots N)=u(a|1)u(b|2)\cdots u(k|N). \quad (3.1)$$

The label a stands for four quantum numbers: $n(a)$, $l(a)$, $m(a)$, and $\mu(a)$, while the number 1 denotes position and spin coordinates of the first electron:

$$u(a|1)=r_1^{-1}P(a|r_1)Y_{lm}(\vartheta_1\varphi_1)\chi(\mu|s_1). \quad (3.2)$$

The product function in Eq. (3.1) is an uncoupled or m-scheme function; it contains electron coordinates in the definite ordering 1, 2, $\cdots$, N. A dwf is the linear combination of product functions that is antisymmetric with respect to interchange of any two-electron coordinates. Using the electron-permutation operator $\mathcal{P}_p$ or the antisymmetrizing operator $\mathcal{A}$, we can write a determinantal basis function

$$\begin{aligned}\tilde{\Phi}_{\mathrm{dwf}}{}^N(a\cdots k)&=(N!)^{-1/2}\textstyle\sum_p(-1)^p\mathcal{P}_p\phi^N(a\cdots k|1\cdots N)\\&\equiv\mathcal{A}\phi^N(a\cdots k|1\cdots N). \quad (3.3)\end{aligned}$$

(In the following, a tilde will denote a function that is antisymmetric in all coordinates; the symbol Φ will denote a basis function; when necessary, a subscript on Φ will distinguish various coupling schemes.)

The conventional "coupled" basis functions (possibly antisymmetrized) are eigenfunctions of various intermediate angular momenta, such as L and S or j_1 and j_2, as well as total angular momentum J; eigenvalues of these operators provide the labels that distinguish different basis functions. For example, an antisymmetric j-j coupling basis function for N nonequivalent orbitals might be

$$\begin{aligned}\tilde{\Phi}_{jj}{}^N(j_aj_b(J_{ab}),j_c(J_{abc}),\cdots,j_kJM)\\=\mathcal{A}\Phi_{jj}{}^N(\cdots JM|1\cdots N). \quad (3.4)\end{aligned}$$

These functions are linear combinations of product functions; the coefficients of the linear combination are independent of one's choice of radial functions P.

It will be convenient to speak of a *formal coupling scheme* as any prescription for selecting linear combinations of product functions that depends only on the properties of spherical harmonics and spin functions $\chi(\mu|s)$. In this sense, the familiar LS-genealogy and j-j coupling wave functions, as well as the dwf's, are formal coupling schemes. The so-called "intermediate-coupling" functions, as well as mixed-configuration functions, are *not* formal coupling schemes; although they are useful for theoretical analyses, they do not provide a practical set of basis functions, since in practice one must reduce such functions to some formal coupling scheme in order to evaluate matrix elements explicitly.

The angular-momentum coupling operation is defined by the Clebsch-Gordan (CG) coefficient:

$$\begin{aligned}\Phi^N(\cdots(J'),jJM|1\cdots N-1N)=\textstyle\sum(J'\bar{M}',j\bar{m}|JM)\\\times\Phi^{N-1}(\cdots J'\bar{M}'|1\cdots N-1)\Phi^1(j\bar{m}|N) \quad (3.5)\end{aligned}$$

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[6] Cf. A. Arima, H. Horie, and Y. Tanabe, Progr. Theoret. Phys. (Kyoto) **11**, 143 (1954) and texts by U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959); B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Company Inc., New York, 1963); and A. de Shalit and I. Talmi, *Nuclear Shell Theory* (Academic Press Inc., New York, 1963).

[7] F. R. Innes and C. W. Ufford, Phys. Rev. **111**, 194 (1958).

[8] An equivalent method was presented by S. F. Boys in a series of papers in Proc. Roy. Soc. (London) **A200**, 542 (1950); **A201**, 125 (1950); **A206**, 489 (1951); **A207**, 181 (1951); **A207**, 197 (1951); **A217**, 235 (1953).

[9] K. Rajnak and B. G. Wybourne, Phys. Rev. **132**, 280 (1963).

(sum on barred quantities). Here the Nth particle, in the single-particle function Φ^1, has been coupled to the remaining $N-1$ particles. Sequential applications of Eq. (3.5) to a function of N nonequivalent orbitals will eventually give Φ^N as a linear combination of simple product functions.[10,11] Such a function is readily antisymmetrized.

For wave functions that involve equivalent electrons, one conventionally uses functions for which successive groups of equivalent orbitals (l shells or subconfigurations) are coupled together. One can uncouple successive orbitals from an antisymmetrized function of equivalent orbitals by supplementing the CG coefficient of Eq. (3.5) with a coefficient of fractional parentage (cfp)[12]:

$$\tilde{\Phi}^N(j^N\alpha JM)=\sum(\bar{J}\bar{M},j\bar{m}|JM)(j^N\alpha J[\![j^{N-1}\bar{\alpha}\bar{J})\\ \times\Phi^{N-1}(j^{N-1}\bar{\alpha}\bar{J}\bar{M})\Phi^1(j\bar{m}|N) \quad (3.6)$$

(sum over barred quantities). Here the last (Nth) electron has been uncoupled, leaving a function that is antisymmetric in $N-1$ electrons. (The label α denotes additional quantum numbers, such as seniority, needed to specify the wave function completely.)

Wave functions that are coupled according to the prescription (3.5)–(3.6) may be recoupled[5a] in a different ordering, by use of a Racah coefficient:

$$\tilde{\Phi}(\cdots(J'),j_aj_bJ_{ab}(J''),\cdots)\\ =\sum(2J_{ab}+1)^{1/2}(2\bar{J}+1)^{1/2}W(J_{ab}j_aj_b\bar{J},J''J')\\ \times\tilde{\Phi}(\cdots(J'),j_a(\bar{J}),j_b(J''),\cdots). \quad (3.7)$$

IV. PARTIALLY COUPLED FUNCTIONS

The preceding formulas make it a simple matter to transform from one angular-momentum formal coupling scheme to another. Using tables of cfp[12] and routines for CG coefficients and Racah coefficients, one can easily program a computer to perform such transformations.[11]

This suggested a formal coupling scheme in which the basis functions are characterized by the quantum numbers of groups (l shells) of q equivalent orbitals: the labels

$$\{[n(i)j(i)]^{q(i)}\alpha(i)J(i)M(i)\}$$

in "partial j-j coupling" or the labels

$$\{[n(i)l(i)]^{q(i)}\alpha(i)L(i)M_L(i)S(i)M_S(i)\}$$

in "partial LS coupling." I shall refer to such formal coupling schemes as Group-M (GM) schemes, to emphasize the use of labels M_J or M_L and M_S for each group of equivalent orbitals. In common with dwf's, partially coupled basis functions generally have no direct connection with actual wave functions of complex atoms. Their only purpose is to act as intermediaries for calculating matrix elements.

The antisymmetric GM scheme function for K groups of equivalent orbitals is simply the antisymmetrical product of K functions:

$$\tilde{\Phi}_{GM}{}^{p+q+\cdots}(AB\cdots)\\ =\mathcal{A}\Phi^p(A|1\cdots p)\Phi^q(B|p+1\cdots p+q)\cdots, \quad (4.1)$$

where

$$A\equiv[n(A)l(A)]^p\alpha(A)S(A)M_S(A)L(A)M_L(A),\\ B\equiv[n(B)l(B)]^q\alpha(B)S(B)M_S(B)L(B)M_L(B)\ \cdots,$$

stand for the quantum numbers of the various groups or subconfigurations.

It is a simple matter to express antisymmetric coupled functions, such as LSJ functions, in terms of GM-scheme functions; the expansion coefficients for a function with K groups of orbitals are simply the products of $2K-1$ CG coefficients:

$$\tilde{\Phi}_{LS}{}^N(\cdots(L'S'),L(i)S(i)(L''S''),\cdots,LSJM)\\ =\sum\cdots(L'\bar{M}_L{}',L(i)\bar{M}_L(i)|L''\bar{M}_L{}'')\\ \times(S'\bar{M}_S{}',S(i)\bar{M}_S(i)|S''M_S{}'')\cdots(L\bar{M}_L,S\bar{M}_S|JM)\\ \times\tilde{\Phi}_{GM}{}^N(\cdots L(i)\bar{M}_L(i)S(i)\bar{M}_S(i)\cdots). \quad (4.2)$$

When all groups are either closed l shells or single orbitals, the GM-scheme functions are just dwf's; when only a single group contains more than one orbital (except for closed l shells), the GM-scheme is identical to the familiar LM_LSM_S scheme.

The action of the antisymmetrizer $\mathcal{A}$ in Eq. (4.1) is easily found if we note that this is a combination of antisymmetrization *within* a group and antisymmetrization *between* groups.[13] The number of ways of selecting q electrons, in *any ordering*, out of a population of N electrons is the binomial coefficient

$$\binom{N}{q}\equiv\frac{N!}{q!(N-q)!}. \quad (4.3)$$

After selecting q_1 electrons, one can select q_2 from the remaining $N-q_1$, then select q_3 from the remaining $N-q_1-q_2$, and so on. The total number $\mathfrak{N}$ of such partitions of N electrons into K groups is

$$\mathfrak{N}=\binom{N}{q_1}\binom{N-q_1}{q_2}\cdots\binom{N-q_1-q_2\cdots q_{K-1}}{q_K}\\ =\frac{N!}{(q_1)!(q_2)!\cdots(q_K)!}. \quad (4.4)$$

Let the *standard selection* of q electrons out of N be defined as the selection of the first q electrons, $1\cdots q$.

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[10] The coefficients of this linear combination can be written as CG coefficients by inspection.

[11] These coefficients can also be obtained quite generally using projection operators; cf. P. O. Löwdin, Rev. Mod. Phys. 36, 966 (1964).

[12] cfp's for LS coupling have been given by G. Racah [Refs. 5(b), 5(c)]; N. Rosenzweig, Phys. Rev. 88, 580 (1952); F. Rohrlich, Astrophys. J. 129, 441 (1959); and B. Judd (Ref. 6). For j-j coupling they are given in de Shalit and Talmi, Ref. 6 and B. F. Bayman and A. Lande, Ann. Phys. (to be published).

[13] Chapter 37 of de Shalit and Talmi, Ref. 6.

Any other selection can be obtained from this standard selection by interchanging electrons between the selected group and the remaining $N-q$ electrons. If the number of such interchanges is *even* (*odd*) the selection will be called *even* (*odd*). We can now write Eq. (4.1) as

$$\tilde{\Phi}_{\mathrm{G}M}{}^{p+q+\cdots r}(AB\cdots K)$$
$$=\mathfrak{N}^{-1/2}\sum Q_r\cdots Q_qQ_p\tilde{\Phi}^p(A)\tilde{\Phi}^q(B)\cdots\tilde{\Phi}^r(K)\,, \quad (4.5)$$

where the operator Q_t selects t electrons out of $N-p-q-\cdots r$ unselected electrons and introduces the sign $+1$ or -1 as the selection is even or odd. The summation runs over all possible selections, including the standard selection shown in Eq. (4.1). The factor $\mathfrak{N}^{-1/2}$ preserves normalization if the single-particle orbitals are normalized.

The formula for the matrix element of an F- or G-type operator U between GM functions is

$$\langle{}^pA\cdots{}^rK|U|{}^{p'}A'\cdots{}^{r'}K'\rangle$$
$$\equiv\langle\tilde{\Phi}_{\mathrm{G}M}{}^{p+\cdots r}(A\cdots K)|U|\tilde{\Phi}_{\mathrm{G}M}{}^{p'+\cdots r'}(A'\cdots K')\rangle$$
$$=(\mathfrak{N}\mathfrak{N}')^{-1/2}\langle\tilde{\Phi}^p(A)\cdots\tilde{\Phi}^r(K)|\sum Q_p{}^\dagger\cdots Q_r{}^\dagger$$
$$\times U\sum Q_{p'}\cdots Q_{r'}|\tilde{\Phi}^{p'}(A')\cdots\tilde{\Phi}^{r'}(K')\rangle\,, \quad (4.6)$$

where $Q^\dagger$ acts to the left (sinistrally) and Q acts to the right (dextrally). Because of the equivalence of electrons and the summation over electrons in the operator F or G, one need only examine one particular sinistral partition, say the standard partition, and multiply this result by the number of sinistral partitions $\mathfrak{N}$. Noting the value of $(\mathfrak{N}/\mathfrak{N}')^{1/2}$ from Eq. (4.4) we obtain[14]

$$\langle{}^pA\,{}^qB\cdots{}^rK|U|{}^{p'}A'\,{}^{q'}B'\cdots{}^{r'}K'\rangle$$
$$=\left(\frac{(p')!\cdots(r')!}{(p)!\cdots(r)!}\right)^{1/2}\langle\tilde{\Phi}^p(A)\cdots\tilde{\Phi}^r(K)|$$
$$\times U\sum Q_{r'}\cdots Q_{p'}|\tilde{\Phi}^{p'}(A')\cdots\tilde{\Phi}^{r'}(K')\rangle. \quad (4.7)$$

Here $\tilde{\Phi}^p(A)$ contains electrons $1\cdots p$ (antisymmetrized), $\tilde{\Phi}^q(B)$ contains electrons $p+1$ through $p+q$ (antisymmetrized), etc. Equation (4.7) can now be specialized to F and G operators.

V. F-TYPE OPERATORS

Let

$$f(a,b)\equiv\langle u(a|i)|f_i|u(b|i)\rangle \quad (5.1)$$

be the matrix element of a single-particle operator taken between two single-particle orbitals. For simplicity, assume that the radial wave functions P are orthonormal, as are the angle and spin functions Y_{lm} and $\chi(\mu|s)$. (The generalization to nonorthogonal functions will be indicated.) Then, since Eq. (4.7) is just a linear combination of integrals over all electron coordinates, one need consider only two types of matrix elements $\langle\Gamma|F|\Gamma'\rangle$: those in which the configuration of Γ is the same as the configuration Γ', and those in which the configurations differ in the occupation numbers q_i of two groups.[3]

A. No Odd Groups

If the configurations are the same, then only for the standard dextral partition will identical orbitals pair off during integration. The factor $(\mathfrak{N}/\mathfrak{N}')^{1/2}$ is unity, the summation over Q_i drops out, and Eq. (4.7) becomes

$$\langle{}^pA\cdots{}^rK|F|{}^pA'\cdots{}^rK'\rangle$$
$$=\bar{\delta}(A)\langle\tilde{\Phi}^p(A)|\sum_{i=1}^{p}f_i|\tilde{\Phi}^p(A')\rangle+\cdots$$
$$+\delta(K)\langle\tilde{\Phi}^r(K)|\sum_{i=N-r}^{N}f_i|\tilde{\Phi}^r(K')\rangle\,, \quad (5.2)$$

where the symbol $\bar{\delta}(A)$ is *unity* if *all* quantum numbers for all groups *except* A are equal in Γ and Γ', and is *zero* otherwise. ($\bar{\delta}$ is proportional to the products of radial orthogonality integrals $\int P_aP_bdr$ so it will be zero only if the radial functions are orthogonal.)

The summation over p electrons in Eq. (5.2) merely gives p equal contributions. We can use Eq. (3.6) to find the contribution of the last electron of the group. For convenience, let the symbol $\langle A\{\bar{A},\bar{a}\rangle$ denote the combination of a cfp and two CG coefficients, so that Eq. (3.6) reads:

$$\tilde{\Phi}^N(A)=N^{-1/2}\sum\langle A\{\bar{A},\bar{a}\rangle\tilde{\Phi}^{N-1}(\bar{A})u(\bar{a}/N)\,. \quad (5.3)$$

In the partial LS scheme, this coefficient is

$$\langle A\{\bar{A},\bar{a}\rangle\equiv\langle l^N\alpha LM_LSM_S\{l^{N-1}\bar{\alpha}\bar{L}\bar{M}_L\bar{S}\bar{M}_S,l\bar{m}\tfrac{1}{2}\bar{\mu}\rangle$$
$$=N^{1/2}(l^N\alpha LS[\![l^{N-1}\bar{\alpha}\bar{L}\bar{S})(\bar{L}\bar{M}_L,l\bar{m}|LM_L)$$
$$\times(\bar{S}\bar{M}_S,\tfrac{1}{2}\bar{\mu}|SM_S)\,. \quad (5.4)$$

For two electrons, the cfp is unity (if $L+S=$ *even*), so

$$\langle l^2LM_LSM_S\{lm\tfrac{1}{2}\mu,lm'\tfrac{1}{2}\mu'\rangle$$
$$=\sqrt{2}(lm,lm'|LM_L)\times(\tfrac{1}{2}\mu,\tfrac{1}{2}\mu'|SM_S)\,.$$

The cfp is also unity for closed shells, so

$$\langle l^{4l+2}0000\{l^{4l+1}lm\tfrac{1}{2}\mu,\,l-m\tfrac{1}{2}-\mu\rangle=(-1)^{l-m+\frac{1}{2}-\mu}\,.$$

For consistency, it proves convenient to define the $\langle A\{\bar{A},a\rangle$ symbol for a single electron as unity:

$$\langle l^1lm\tfrac{1}{2}\mu\{0,lm\tfrac{1}{2}\mu\rangle\equiv1\,.$$

The factor $N^{1/2}$ is included in the definition of $\langle A\{\bar{A},a\rangle$ for subsequent convenience, since it always occurs with the cfp. Using this uncoupling procedure on the last orbital of a group, we find that the contribution of the last electron to the matrix element of Eq. (6.2) is

$$\langle\tilde{\Phi}^p(A)|f_p|\tilde{\Phi}^p(A')\rangle$$
$$=p^{-1}\sum\langle A\{\bar{A},\bar{a}\rangle\langle A'\{\bar{A},\bar{a}'\rangle f(\bar{a},\bar{a}') \quad (5.5)$$

(sum over barred quantities). If we sum over equivalent

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[14] Equation (4.7), the generalization of formulas in Ref. 14, has been given by D. Layzer, Z. Horak, M. N. Lewis, and D. P. Thompson, Ann. Phys. (N. Y.) **29**, 101 (1964).

electrons Eq. (5.2) becomes

$$\begin{aligned}\langle {}^pA\cdots{}^rK|F|{}^pA'\cdots{}^rK'\rangle\\ =\bar{\delta}(A)\sum\langle A\{\bar{A},\bar{a}\rangle\langle A'\{\bar{A},\bar{a}'\rangle f(\bar{a},\bar{a}')+\cdots\\ +\bar{\delta}(K)\sum\langle K\{\bar{K},\bar{k}\rangle\langle K'\{\bar{K},\bar{k}'\rangle f(\bar{k},\bar{k}')\,.\end{aligned}\tag{5.6}$$

B. Two Odd Groups

The second type of (nonzero) F-type matrix element occurs when the configurations Γ and Γ' have the form

$$\begin{aligned}\langle\Gamma|F|\Gamma'\rangle=\langle\cdots{}^pA\cdots{}^{q-1}B\cdots|\\ \times F|\cdots{}^{p-1}A'\cdots{}^qB'\cdots\rangle.\end{aligned}\tag{5.7}$$

One "odd" electron occurs in the group ${}^pA$ on the left, and in the group ${}^qB$ on the right; all other groups possess identical quantum numbers on left and right. The factor $(\mathcal{N}/\mathcal{N}')^{1/2}$ becomes $(q!/p!)^{1/2}$. To apply Eq. (4.7) we note that the "odd" electron in Γ can be any of p in the group ${}^pA$. Each contributes an equal matrix element; one can consider the matrix element of the last electron of the group and multiply by p. Whichever electron one chooses to consider, the dextral ordering of Eq. (4.7) must place this electron into the group ${}^qB$. The resulting matrix element is

$$\begin{aligned}\langle\cdots{}^pA\cdots{}^{q-1}B\cdots|F|\cdots{}^{p-1}A'\cdots{}^qB'\cdots\rangle\\ =\bar{\delta}(A+B)(-1)^{\sigma_{AB}}\langle A\{A',a\rangle\langle B'\{B,b'\rangle f(a,b')\,,\end{aligned}\tag{5.8}$$

where $(-1)^{\sigma_{AB}}$ represents a phase factor. This phase depends on the number of interchanges that are required to pair off the standard ordering in Γ with the standard ordering in Γ'. This number is the total number of electrons in all the groups between ${}^pA$ and ${}^{q-1}B$ (as given in the label Γ), plus the number of groups between ${}^pA$ and ${}^{q-1}B$. If the occupation numbers are denoted by q_i, the phase is

$$\sigma_{ij}=(q_{i+1}+q_{i+2}+\cdots+q_j)+(j-i)\tag{5.9}$$

for a matrix element involving groups i and j.

Equations (5.6) and (5.8) for GM-scheme wave functions correspond to Eqs. (6^68) and (6^69) of Ref. 2 for dwf's.

VI. G-TYPE OPERATORS

Let

$$g(ab,cd)\equiv\langle u(a|i)u(b|j)|g_{ij}|u(c|i)u(d|j)\rangle\tag{6.1}$$

denote the matrix element of a two-particle operator g_{ij} between two single-particle orbitals. For the familiar Coulomb expansion,

$$g_{ij}=\frac{1}{r_{ij}}=\sum_k\frac{r_<{}^k}{r_>{}^{k+1}}\mathbf{C}^{(k)}(i)\cdot\mathbf{C}^{(k)}(j)\,,\tag{6.2}$$

this has the form

$$\begin{aligned}g(ab,cd)=\delta(m_s(a),m_s(c))\delta(m_s(b),m_s(d))\\ \times(-1)^{m_l(c)-m_l(a)}\textstyle\sum_k c^k(l(a)m_l(a),l(c)m_l(c))\\ \times c^k(l(b)m_l(b),l(d)m_l(d))R^k(ab,cd)\,,\end{aligned}\tag{6.3}$$

where

$$\begin{aligned}R^k(ab,cd)=\int dr_1\int dr_2\,P(a|r_1)P(c|r_1)\\ \times\frac{r_<{}^k}{r_>{}^{k+1}}P(b|r_2)P(d|r_2)\end{aligned}\tag{6.4}$$

$$\begin{aligned}c^k(lm,l'm')=(lm|C_q{}^{(k)}|l'm')\quad(q\equiv m-m')\\ =(-1)^k(l'm',kq|lm)(l0,k0|l0)\,.\end{aligned}\tag{6.5}$$

In the GM-scheme, G-type matrix elements $\langle\Gamma|G|\Gamma'\rangle$ fall into five classes, depending on the number of unpaired or "odd" electrons in the groups of Γ and Γ'. The possible arrangements are:

$$\langle\cdots{}^pA\cdots{}^qB\cdots|G|\cdots{}^pA'\cdots{}^qB'\cdots\rangle,\tag{6.6}$$

$$\langle\cdots{}^pA\cdots{}^{q-1}B\cdots|G|\cdots{}^{p-1}A'\cdots{}^qB'\cdots\rangle,\tag{6.7}$$

$$\langle\cdots{}^pA\cdots{}^{q-1}B\cdots|G|\cdots{}^{p-2}A'\cdots{}^qB'\cdots\rangle,\tag{6.8}$$

$$\begin{aligned}\langle\cdots{}^pA\cdots{}^{q-1}B\cdots{}^{r-1}C\cdots|\\ \times G|\cdots{}^{p-2}A'\cdots{}^qB'\cdots{}^rC'\cdots\rangle,\end{aligned}\tag{6.9}$$

$$\begin{aligned}\langle\cdots{}^pA\cdots{}^qB\cdots{}^{r-1}C\cdots{}^{s-1}D\cdots|\\ \times G|\cdots{}^{p-1}A'\cdots{}^{q-1}B'\cdots{}^rC'\cdots{}^sD'\cdots\rangle.\end{aligned}\tag{6.10}$$

The following results for these matrix elements generalize Eq. (7^69) of Ref. 2.

A. No Odd Groups

When the configurations of Γ and Γ' are identical, the matrix element is the sum of *intergroup* interactions, proportional to $g(aa,aa)$, and *intragroup* interactions, proportional to the *direct* part $g(ab,ab)$ and the exchange part $g(ab,ba)$.

The intergroup interaction is the sum of matrix elements of the type

$$\langle\cdots\tilde{\Phi}^p(A)\cdots|\textstyle\sum_{i<j\epsilon p}g_{ij}|\cdots\tilde{\Phi}^p(A')\cdots\rangle\tag{6.11}$$

for each group, since only the standard dextral ordering of Eq. (4.7) gives a nonzero result. Equation (6.11) is the sum of $\binom{p}{2}=p(p-1)/2$ identical matrix elements; we use Eq. (5.3) to uncouple the last and the next-to-the-last electron and obtain the result

$$\begin{aligned}\bar{\delta}(A)\sum\langle A\{\bar{A},\bar{a}\rangle\langle\bar{A}\{\bar{A}'',\bar{a}''\rangle\langle A'\{\bar{A}',\bar{a}'\rangle\\ \times\langle\bar{A}'\{\bar{A}'',\bar{a}'''\rangle\tfrac{1}{2}g(\bar{a}\bar{a}'',\bar{a}'\bar{a}''')\end{aligned}\tag{6.12a}$$

(note that the numbers p and $p-1$ are included in the $\langle\cdots\{\cdots\rangle$ factors).

The intragroup contributions arise from qp possible *even* dextral orderings giving the direct interaction and an equal number of *odd* dextral orderings giving exchange interactions. These give the matrix element

$$\begin{aligned}\bar{\delta}(A+B)\sum\langle A\{\bar{A},\bar{a}\rangle\langle A'\{\bar{A},\bar{a}'\rangle\langle B\{\bar{B},\bar{b}\rangle\langle B'\{\bar{B},\bar{b}'\rangle\\ \times[g(\bar{a}\bar{b},\bar{a}'\bar{b}')-g(\bar{a}\bar{b},\bar{b}'\bar{a}')].\end{aligned}\tag{6.12b}$$

Here $\bar{\delta}(A+B)$ is zero unless all groups except A and B

are identical in Γ and Γ'. The total matrix element of type (6.6) is the sum over all groups of Eqs. (6.12a) and (6.12b).

B. Two Odd Groups

When the configurations Γ and Γ' differ by the placement of a single electron, as in Eq. (6.7), the factor $(\mathcal{N}/\mathcal{N}')^{1/2}$ becomes $(q/p)^{1/2}$. The matrix element sums over all possible locations of a second electron. This electron may either be located in groups A or B, or it may be in any third group C:

$$\langle \cdots {}^{p}A \cdots {}^{q-1}B \cdots {}^{r}C \cdots | \times G | \cdots {}^{p-1}A' \cdots {}^{q}B' \cdots {}^{r}C' \cdots \rangle . \quad (6.13)$$

Taking the second electron from group A, we obtain $\binom{p}{2}$ equal contributions proportional to $g(aa,ab)$. Equation (5.9) gives the phase σ_{AB} of these elements, with the result

$$\bar{\delta}(A+B)(-1)^{\sigma_{AB}} \sum \langle A\{\bar{A},\bar{a}\rangle \langle \bar{A}\{\bar{A}'',\bar{a}''\rangle \langle A'\{\bar{A}'',\bar{a}'\rangle \times \langle B'\{B,b'\rangle \tfrac{1}{2} g(\bar{a}\bar{a}'',\bar{a}'b') . \quad (6.14a)$$

(The numerical factor $(p-1)^{1/2}(q)^{1/2}$ goes into the $\langle \cdots \{ \cdots \rangle$ coefficients.) A similar equation holds when group B contains the second electron:

$$\bar{\delta}(A+B)(-1)^{\sigma_{AB}} \sum \langle A\{A',a\rangle \langle B\{\bar{B},\bar{b}\rangle \langle B'\{\bar{B},\bar{b}'\rangle \times \langle \bar{B}\{\bar{B}'',\bar{b}''\rangle \tfrac{1}{2} g(a\bar{b},\bar{b}'\bar{b}'') . \quad (6.14b)$$

Finally, when the second electron comes from one of the other groups, say C, we obtain pr equal direct interactions and pr equal exchange interactions

$$\bar{\delta}(A+B+C)(-1)^{\sigma_{AB}} \sum \langle A\{A',a\rangle \langle B'\{B,b'\rangle \langle C\{\bar{C},\bar{c}\rangle \times \langle C'\{\bar{C},\bar{c}'\rangle [g(a\bar{c},b'\bar{c}')-g(ac,\bar{c}'b')] . \quad (6.14c)$$

The matrix element (6.13) is the sum of Eq. (6.14a), (6.14b), and all possible groups C with Eq. (6.14c).

When the configurations Γ and Γ' contain two "odd" electrons as in Eq. (6.8), the factor $(\mathcal{N}/\mathcal{N}')^{1/2}$ is $(q(q-1)p(p-1))^{1/2}$ and the number of identical matrix elements is $\binom{p}{2}$. All these matrix elements have positive phase; the result is

$$\langle \cdots {}^{p}A \cdots {}^{q-2}B \cdots | G | \cdots {}^{p-2}A' \cdots {}^{q}B' \cdots \rangle = \bar{\delta}(A+B) \sum \langle A\{\bar{A},\bar{a}\rangle \langle \bar{A}\{A',a'\rangle \langle B'\{\bar{B},\bar{b}'\rangle \times \langle \bar{B}\{B,b\rangle \tfrac{1}{2} g(\bar{a}a',\bar{b}b') . \quad (6.15)$$

C. Three Odd Groups

When Γ and Γ' have the form of Eq. (6.9), the number of equal contributions $\binom{p}{2}$ again balances the denominator of $(\mathcal{N}/\mathcal{N}')^{1/2}$, and the phase depends on the number of electrons and groups between groups B and C. The result is

$$\langle \cdots {}^{p}A \cdots {}^{q-1}B \cdots {}^{r-1}C \cdots | G | \cdots {}^{p-2}A' \cdots {}^{q}B' \cdots {}^{r}C' \cdots \rangle = \bar{\delta}(A+B+C)(-1)^{\sigma_{BC}} \sum \langle A\{\bar{A},\bar{a}\rangle \langle \bar{A}\{A',a\rangle \times \langle B'\{B,b'\rangle \langle C'\{C,c'\rangle \tfrac{1}{2} g(\bar{a}a,b'c') . \quad (6.16)$$

D. Four Odd Groups

At most, Γ and Γ' can differ in four pairs of occupation numbers. For this case, preceding arguments give the result

$$\langle \cdots {}^{p}A \cdots {}^{q}B \cdots {}^{r-1}C \cdots {}^{s-1}D \cdots | \times G | \cdots {}^{p-1}A' \cdots {}^{q-1}B' \cdots {}^{r}C' \cdots {}^{s}D' \cdots \rangle = \bar{\delta}(A+B+C+D)(-1)^{\sigma_{AC}+\sigma_{BD}} \times \langle A\{A',a\rangle \langle B\{B',b\rangle \langle C'\{C,c'\rangle \langle D'\{D,d'\rangle \times [g(ab,c'd')-g(ab,d'c')] . \quad (6.17)$$

VII. SUMMARY

The formulas of the last two sections permit one to compute matrix elements between any two configurations. In a typical calculation, one may start with a collection of LS-genealogy functions and expand these in terms of GM-scheme functions, using either the explicit formulas (3.5) and (3.6) or else projection operators to obtain the expansion coefficients. Then one applies the GM-scheme formulas of the form

$$\langle \Gamma | F | \Gamma' \rangle = \sum \langle A\{A'',a\rangle \langle B'\{B'',b'\rangle f(a,b') , \quad (7.1)$$

$$\langle \Gamma | G | \Gamma' \rangle = \sum \langle A\{A'',a\rangle \langle B'\{B'',b'\rangle \langle C\{C'',c\rangle \times \langle D'\{D'',d'\rangle g(ab',cd') , \quad (7.2)$$

given in the preceding sections.[15] A digital computer can easily carry out the entire process, using only a table of cfp's and a subroutine for CG coefficients.

A specific example may clarify the preceding abstract discussion. Consider the lowest lying odd-parity term of neutral titanium,[16] nominally the $z\,{}^5G^0$ term of the configuration

$$[1s^2\, 2s^2\, 2p^6\, 3s^2]3p^6\, 3d^2\, 4s\, 4p .$$

The wave function for an $M_L=0$, $M_S=0$ state of this term is partly the LSM-scheme wave function $\tilde{\Phi}_{LSM}{}^{22}(\gamma_1)$, labeled by the quantum numbers

$$\gamma_1 \equiv [{}^1S](3p^6\, {}^1S),\ (3d^2\, {}^3F)^3F,\ (4s\, {}^2S)^4F,\ (4p\, {}^2P)^5G_{00}$$

and is partly a mixture of wave functions belonging to other configurations, such as

$$\gamma_2 \equiv [{}^1S](3p^5\, {}^2P),\ (3d^3\, {}^2{}_1D)^3F,\ (4p^2\, {}^3P)^5G_{00} .$$

The interelectron Coulomb interaction mixes these two wave functions through the matrix element

$$\langle \gamma_1 | \sum 1/r_{ij} | \gamma_2 \rangle = r_1(\gamma_1\gamma_2) R^1(3p4s,3d4p) - r_2(\gamma_1\gamma_2) R^2(3p4s,4p3d) , \quad (7.3)$$

where R^1 and R^2 are generalized "direct" and "exchange" integrals. To calculate the coefficients r_1 and r_2, one has basically three options, depending on which of three schemes of basis functions one uses.

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[15] The present paper emphasizes the *similar* form of all matrix elements. In particular instances, these simplify considerably; sums over dummy magnetic quantum numbers can be written in terms of Racah coefficients.

[16] C. E. Moore, Natl. Bur. Std. (U. S.), Circ. 467, Vol. 2.

Using coupled LSM-scheme functions and the algorithms of Racah,[5,6] one can write the "direct interaction" coefficient as

$$r_1(\gamma_1\gamma_2) = -(d^3\,{}^2{}_1D[\![d^2\,{}^3F)$$

$$\times(2\times3\times5\times7)^{\frac{1}{2}}\begin{Bmatrix}1 & 2 & 1\\ 3 & 3 & 2\end{Bmatrix}\begin{Bmatrix}3 & 1 & 3\\ 1 & 4 & 1\end{Bmatrix}\begin{Bmatrix}1 & \frac{1}{2} & \frac{3}{2}\\ \frac{1}{2} & 2 & 1\end{Bmatrix} \quad (7.4)$$

$$= -1/(60)^{1/2} = -0.1290994.$$

The "exchange interaction" coefficient r_2 between these two configurations can be written as a similar product of three 6-j symbols and a cfp, but the specific coefficient $r_2(\gamma_1\gamma_2)$ is zero because of an intermediate-spin selection rule [only quartet terms of d^3 will mix with $\tilde{\Phi}_{LSM}{}^{22}(\gamma_1)$].

Alternatively, one could express the functions $\tilde{\Phi}_{LSM}{}^{22}(\gamma_1)$ and $\tilde{\Phi}_{LSM}{}^{22}(\gamma_2)$ in terms of dwf's, such as the functions labeled by

$$\Gamma_1' = [{}^1S](3p_{-1}{}^-\,3p_{-1}{}^+\,3p_0{}^-\,3p_0{}^+\,3p_1{}^-\,3p_1{}^+ \\ 3d_{-1}{}^-\,3d_0{}^-\,4s_0{}^+\,4p_1{}^+)$$

and

$$\Gamma_2' = [{}^1S](3p_{-1}{}^-\,3p_{-1}{}^+\,3p_0{}^-\,3p_0{}^+\,3p_1{}^- \\ 3d_{-1}{}^-\,3d_0{}^-\,3d_1{}^+\,4p_0{}^+\,4p_0{}^+).$$

The Coulomb matrix element between these particular two functions is

$$\begin{aligned}\langle\Gamma_1'|\textstyle\sum 1/r_{ij}|\Gamma_2'\rangle &= c^1(11,21)c^1(00,10)R^1(3p4s,3d4p) \qquad (7.5)\\ &\quad + c^2(11,10)c^2(00,21)R^2(3p4s,3p3d)\\ &= [1/(15)^{1/2}]R^1 - [\sqrt{3}/(125)^{1/2}]R^2\end{aligned}$$

and the desired matrix element is the sum of such elements, each multiplied by the appropriate expansion coefficients.

The third approach, outlined in the present paper, would use partially coupled basis functions, such as those labeled by

$$\Gamma_1 \equiv [{}^1S](3p^6\,{}^1S_{00}),\ (3d^2\,{}^3F_{-1-1}),\ (4s\,{}^2S_{0\frac{1}{2}}),\ (4p\,{}^2P_{1\frac{1}{2}})$$

and

$$\Gamma_2 \equiv [{}^1S](3p^5\,{}^2P_{-1-\frac{1}{2}}),\ (3d^3\,{}^2{}_1D_{0-\frac{1}{2}}),\ (4p^2\,{}^3P_{11}).$$

The expansion coefficients into this GM scheme are simply the products of CG coefficients. For example

$$\begin{aligned}(\gamma_1|\Gamma_1) &= (3\,-1,\,00|3\,-1)\times(3\,-1,\,11|40)\\ &\quad\times(1\,-1,\,\tfrac{1}{2}\tfrac{1}{2}|\tfrac{3}{2}\,-\tfrac{1}{2})\times(\tfrac{3}{2}\,-\tfrac{1}{2},\,\tfrac{1}{2}\tfrac{1}{2}|20)\\ &= 1/(28)^{1/2}\end{aligned}$$

$$\begin{aligned}(\gamma_2|\Gamma_2) &= (1\,-1,\,20|3\,-1)\times(3\,-1,\,11|40)\\ &\quad\times(\tfrac{1}{2}\,-\tfrac{1}{2},\,\tfrac{1}{2}\,-\tfrac{1}{2}|1\,-1)\times(1\,-1,\,11|20)\\ &= 1/(70)^{1/2}.\end{aligned}$$

The matrix element between these particular basis states has the form of Eq. (7.2) [specifically, it is Eq. (6.17)]:

$$\begin{aligned}\langle\Gamma_1|\textstyle\sum 1/r_{ij}|\Gamma_2\rangle &= \langle p^6\,{}^1S_{00}\{p^5\,{}^2P_{-1-\frac{1}{2}},\,p\,{}^2P_{1\frac{1}{2}}\rangle\times\langle s\,{}^2S_{0\frac{1}{2}}\{0,\,s\,{}^2S_{0\frac{1}{2}}\rangle\\ &\quad\times\langle d^3\,{}^2{}_1D_{0-\frac{1}{2}}\{d^2\,{}^3F_{-1-1},\,d\,{}^2D_{1\frac{1}{2}}\rangle\\ &\quad\times\langle p^2\,{}^3P_{11}\{p\,{}^2P_{1\frac{1}{2}},\,p\,{}^2P_{0\frac{1}{2}}\rangle\\ &\quad\times[c^1(11,21)c^1(00,10)R^1(3p4s,3d4p)\\ &\qquad + c^2(11,10)c^2(00,10)R^2(3p4s,4p3d)], \qquad (7.6)\end{aligned}$$

where for example,

$$\begin{aligned}\langle d^3\,{}^2{}_1D_{0-\frac{1}{2}}\{d^2\,{}^3F_{-1-1},\,d\,{}^2D_{1\frac{1}{2}}\rangle &\equiv \sqrt{3}(d^3\,{}^2{}_1D[\![d^2\,{}^3F)\times(3\,-1,\,21|20)\times(1\,-1,\,\tfrac{1}{2}\tfrac{1}{2}|\tfrac{1}{2}\,-\tfrac{1}{2})\\ &= \sqrt{6}\end{aligned}$$

$$\langle s\,{}^2S_{0\frac{1}{2}}\{0,\,s\,{}^2S_{0\frac{1}{2}}\rangle \equiv 1.$$

Thus

$$\langle\Gamma_1|\textstyle\sum 1/r_{ij}|\Gamma_2\rangle = \sqrt{6}[(1/(15)^{1/2})R^1 - (\sqrt{3}/(125)^{1/2})R^2]. \qquad (7.7)$$

Again, as with the dwf basis, the desired matrix element $\langle\gamma_1|\sum 1/r_{ij}|\gamma_2\rangle$ is the sum of such GM-scheme elements.

As this example shows, coupled functions (in this case LSM functions) provide the most convenient basis functions for hand calculations once one has obtained a formula such as Eq. (7.4). The GM-scheme functions (and *a fortiori* the m-scheme functions) require time-consuming summations over basis states. However, this summation is not a serious handicap if one relies on a digital computer for the numerical results.

For simple configurations, or for analytical investigations, the GM scheme is clearly at a disadvantage compared with the conventional m scheme or LS scheme. But as interest develops in more complicated configurations with five or six open l shells, and as machine computation becomes necessary, the GM scheme offers a potentially useful approach. The GM scheme is not suggested as a "physical" coupling scheme, but merely as a device to simplify computations; it offers some of the simplicity of the m scheme without requiring as many basis functions, yet retains some of the selection rules of coupled schemes.

Although I have used the terminology of LS coupling, the algorithms can obviously be applied to nuclear wave functions characterized by j and isospin t.

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