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ABSTRACT

The method of using annihilation and creation operators in the theory of atomic spectroscopy is examined in detail. Several examples of the effect of configuration interaction on a configuration $(n\ell)^N$ of equivalent electrons are discussed. Illustrations are provided by drawing out the Feynman graphs and interpreting them through the topologically equivalent angular-momentum graphs of Jucys. The tensorial character of the annihilation and creation operators is studied, and the connection between their reduced matrix elements and fractional parentage coefficients is illustrated by several examples. The introduction of quasi-spin, together with operators of conjugation and complementarity, permits matrix elements of different configurations to be related. A formal simplification takes place when triple tensors are used in the manipulations. The annihilation and creation operators for a given $n\ell$, taken with all their commutators, are interpreted as the infinitesimal operators of the rotation group in $8\ell + 5$ dimensions. Representations are discussed.

I. INTRODUCTION

Theoretical analyses of atomic spectra enjoy two advantages. The contributions to the Hamiltonian are well defined, and the central-field approximation, on which the zero-order eigenfunctions are based, works extremely well. Such improvements as can be made to the theory are essentially improvements in technique; the basic framework of the theory remains today virtually the same as that described by Condon and Shortley in their classic work.[1] This is not to say that the theory is insusceptible of significant development; indeed, the work of Racah[2-4] has deeply influenced nuclear as well as atomic spectroscopy.

Conversely, progress in the treatment of the many-body problem in widely differing fields may be relevant to the theory of atomic spectra. It is the purpose of this article to explore the applicability to atomic spectroscopy of the method of second quantization, an approach which has proved extremely fruitful in the study of superconductivity[5] and nuclear pairing forces,[6] to name but two apparently unrelated topics. Interest in applying this method to nuclear-shell theory has been maintained since its value was pointed out by Brink and Satchler.[7] Recent articles by Watanabe[8] and by Lawson and Macfarlane[9] have shown how matrix elements of operators in different configurations can be related, thereby making transparent the origin of a number of formulae, that, by the conventional methods of Racah, emerge from a study of fractional parentage.[10]

Owing to the context of much of this work, it is not completely obvious how the method can be extended to atomic-shell theory, where the type of coupling prevailing often makes it desirable to keep properties of operators and eigenfunctions with respect to spin distinct from those with respect to orbit.

In what follows, the notation is chosen to be in line with that of atomic spectroscopy, and all the examples are selected from this field. It is hoped that this will emphasize the relevance of the method to the theory of atomic spectra.

II. BASIC FORMULAE

A. Annihilation and Creation Operators

The fundamental idea of the second-quantization method is the transference to operators of properties that are ordinarily thought of as being characteristic of eigenfunctions. Suppose $\{\alpha\,\beta\,\cdots\nu\}$ denotes a normalized N-electron determinantal product state, in which each Greek symbol is an abbreviation for the familiar quantum-number quartet $(n\ell m_s m_\ell)$. Such a state is replaced by a sequence of operators $a_\alpha^\dagger$, $a_\beta^\dagger$,... acting on the vacuum state $|0\rangle$. In other words, we make the identification

$$a_\alpha^\dagger a_\beta^\dagger \cdots a_\nu^\dagger |0\rangle \equiv \{\alpha\,\beta\,\cdots\,\nu\}. \tag{1}$$

The adjoint signs are put on the operators a to conform to the traditional definition; the adjoint of the equivalence (1) is

$$\langle 0|\, a_\nu \cdots a_\beta a_\alpha \equiv \{\alpha\,\beta\,\cdots\nu\}^*, \tag{2}$$

where the asterisk denotes the complex conjugate. If the operators $a^\dagger$ and a are to correctly reproduce the properties of the determinantal functions (which change sign if two rows or columns are interchanged), it is clear that they must separately anticommute:

$$a_\xi^\dagger a_\eta^\dagger + a_\eta^\dagger a_\xi^\dagger = 0 \tag{3}$$

$$a_\xi a_\eta + a_\eta a_\xi = 0$$

for all ξ and η. We must also require that our operators reproduce the orthonormality conditions of two determinantal product states. Now, the integral

$$\int \{\alpha\ \beta\ \cdots\ \nu\}^* \{\xi\eta\cdots\ \omega\}\ d\tau \tag{4}$$

contains not only the leading term

$$\delta(\alpha,\xi)\ \delta(\beta,\eta)\cdots\ \delta(\nu\omega),$$

but also terms of the type

$$-\delta(\alpha,\eta)\ \delta(\beta,\xi)\cdots\ \delta(\nu,\omega)$$

coming from all possible permutations of the quantum numbers with respect to the electrons. To generate such terms, we insist that, in addition to Eq. (3), the operators $a_\eta^\dagger$ and a_ξ satisfy the relations

$$a_\xi\ a_\eta^\dagger + a_\eta^\dagger\ a_\xi = \delta(\eta,\xi), \tag{5}$$

and also that

$$a_\xi|0\rangle = 0\ . \tag{6}$$

The term corresponding to (4) is

$$\langle 0|a_\nu\cdots\ a_\beta a_\alpha\ a_\xi^\dagger a_\eta^\dagger\cdots\ a_\omega^\dagger|0\rangle.$$

By a continual use of Eq. (5), each operator a_α, $a_\beta \cdots$ can be transferred gradually to the right, until at last it operates on $|0\rangle$, with a nul result. Each operation introduces a delta function, and the final sum corresponds exactly to that required from the orthonormality of the eigenfunctions.

Since $a_\alpha^\dagger|0\rangle$ corresponds to $\{\alpha\}$, we call $a_\alpha^\dagger$ a creation operator. The vacuum state is recovered if we operate on $a_\alpha^\dagger|0\rangle$ with a_α, owing to Eqs. (5) and (6); consequently a_α is called an annihilation operator. Equation (6) now appears as a statement that annihilation of an electron from the vacuum gives a nul result. The operators a_α and $a_\beta^\dagger$ are identical to $\bar{\eta}_\alpha$ and η_β of Dirac.[11]

A number of interesting properties follow from the anticommutation relations (3) and (5). By the process of transference of a_ξ to the right, we may show

$$(\Sigma\, a_\xi^\dagger a_\xi)\; a_\alpha^\dagger a_\beta^\dagger \cdots a_\nu^\dagger|0\rangle = N\, a_\alpha^\dagger a_\beta^\dagger \cdots a_\nu^\dagger|0\rangle,$$

where the sum runs over all possible states ξ. The operator $\Sigma\, a_\xi^\dagger a_\xi$ is therefore called the number operator. We also note that

$$a_\xi a_\xi = a_\eta^\dagger a_\eta^\dagger = 0,$$

so that any sequence of operators in which two identical operators occur side by side is automatically zero.

B. Representation of Operators

Two kinds of operators occur in atomic spectroscopy: single-particle operators of the type $F = \Sigma_i f_i$, and two-particle operators of the type $G = \Sigma_{i>j}\, g_{ij}$.[12] In the language of second quantization, the first is expressed as

$$F \equiv \sum_{\xi,\eta} a_\xi^\dagger \langle \xi|f|\eta\rangle a_\eta, \tag{7}$$

and the second as

$$G \equiv \frac{1}{2} \sum_{\xi,\eta,\zeta,\lambda} a_\xi^\dagger a_\eta^\dagger \langle \xi_1 \eta_2|g_{12}|\zeta_1 \lambda_2\rangle a_\lambda a_\zeta . \tag{8}$$

The subscripts 1 and 2 in the equivalence (8) refer to two electrons, making it clear how the quantum numbers ξ, η, ζ, and λ are assigned. Alternative prescriptions, in which $|\zeta\ \lambda\rangle$ and $\langle\xi\ \eta|$ are antisymmetrized states, have been given by Lane.[6] It is straightforward to convince oneself that the new representations for F and G reproduce the familiar expressions for their matrix elements. For example, the well known result[13]

$$\int \{\alpha\ \beta\}^* F\{\alpha\ \beta\}\, d\tau = \langle\alpha|f|\alpha\rangle + \langle\beta|f|\beta\rangle$$

can be equally well obtained from

$$\sum_{\xi,\eta} \langle 0|a_\beta a_\alpha a_\xi^\dagger a_\eta a_\alpha^\dagger a_\beta^\dagger|0\rangle \langle\xi|f|\eta\rangle$$

by repeated use of the anticommutation relations to transfer annihilation operators to the right.

III. CONFIGURATION INTERACTION

A. Core Polarization

As a first example of the methods described in the previous section, we study the distortions of closed shells of s electrons produced by an open shell of the type $(n\ell)^N$. This effect is important in hyperfine-structure calculations, since a small admixture of unpaired s electrons can produce a significant contribution to the hyperfine structure produced by the $n\ell$ electrons, particularly when $\ell > 0$. We proceed according to second-order perturbation theory, and fix our attention on the admixture into a closed shell $(n's)^2$ of the excited configuration $(n's)(n''s)$. The contribution of this effect to the hyperfine energy of a state $|X\rangle$ of $(n's)^2(n\ell)^N$ is given by

$$-2 \sum_Y \langle X|\Sigma e^2/r_{ij}|Y\rangle\langle Y|H_h|X\rangle/\Delta E, \tag{9}$$

where $|Y\rangle$ is a state of $(n's)(n''s)(n\ell)^N$, where ΔE is the energy required to excite an $n's$ electron into the $n''s$ shell, and where H_h is the magnetic-hyperfine operator $\underset{\sim}{Q}\cdot\underset{\sim}{I}$. For the present case we need take only the Fermi contact term, for which

$$\underset{\sim}{Q} = (16\pi\, \beta\beta_N\mu_N/3I) \sum_i \delta(\underset{\sim}{r}_i)\underset{\sim}{s}_i,$$

where β is the Bohr magneton, β_N the nuclear magneton, μ_N the nuclear moment (in nuclear magnetons), and I the nuclear spin. To evaluate (9) by conventional methods involves the calculation of two matrix elements, a process that necessitates a detailed knowledge of the states $|X\rangle$ and $|Y\rangle$. The use of annihilation and creation operators provides a striking short-cut in this procedure. To clarify the method as far as possible, we use a_ξ and $a_\xi^\dagger$

for annihilating and creating respectively an $n\ell$ electron; b_ξ and $b_\xi^\dagger$ for an n's electron; and c_ξ and $c_\xi^\dagger$ for an n"s electron. The Greek suffixes are now contractions only for $(m_s m_\ell)$.

The first step is to use the equivalences (7) and (8) to convert the operators $\underset{\sim}{\Omega}$ and $\Sigma e^2/r_{ij}$ to their second-quantized form. Since $\underset{\sim}{\Omega}$ is required to connect a bra of $(n's)(n''s)(n\ell)^N$ to a ket of $(n's)^2(n\ell)^N$, it must include one operator of the type $c_\xi^\dagger$, and one of the type b_η. This limits its form to the following:

$$\underset{\sim}{\Omega} \equiv (16\pi\,\beta\beta_N\mu_N/3I) \sum_{\xi,\eta} c_\xi^\dagger \langle n''s\xi|\delta(\underset{\sim}{r})\underset{\sim}{s}|n's\eta\rangle b_\eta .$$

The situation for the Coulomb interaction is a little more complicated. At least one operator of the type c_α must appear, and also one of the type $b_\beta^\dagger$, for otherwise we could not connect $|X\rangle$ to $|Y\rangle$. Since we are studying the polarization produced by the shell $(n\ell)^N$, the remaining operators must evidently be one of the type a_σ and one of the type $a_\tau^\dagger$, for this is the only point left to introduce the effect of the open shell. However, it should be noted in passing that we could equally well make up the full complement of four operators that appears in the equivalence (8) by introducing $d_\gamma^\dagger$ and d_ζ, where d_ζ annihilates a state ζ of a closed shell $(n'''\ell')^{4\ell'+2}$ present in the atom. This possibility leads to a nul result—which simply tells us that closed shells do not produce core polarization. The other possible combination, $b_\lambda^\dagger$ and b_μ, can also be ignored. So we may make the equivalence

$$\begin{aligned}\Sigma e^2/r_{ij} \cong\ & \tfrac{1}{2}\Sigma b_\beta^\dagger a_\tau^\dagger \langle (n's\beta)_1 (n\ell\tau)_2 | e^2/r_{12} | (n\ell\sigma)_1 (n''s\alpha)_2 \rangle c_\alpha a_\sigma \\ & + \tfrac{1}{2}\Sigma a_\tau^\dagger b_\beta^\dagger \langle (n\ell\tau)_1 (n's\beta)_2 | e^2/r_{12} | (n''s\alpha)_1 (n\ell\sigma)_2 \rangle a_\sigma c_\alpha \\ & + \tfrac{1}{2}\Sigma b_\beta^\dagger a_\tau^\dagger \langle (n's\beta)_1 (n\ell\tau)_2 | e^2/r_{12} | (n''s\alpha)_1 (n\ell\sigma)_2 \rangle a_\sigma c_\alpha \\ & + \tfrac{1}{2}\Sigma a_\tau^\dagger b_\beta^\dagger \langle (n\ell\tau)_1 (n's\beta)_2 | e^2/r_{12} | (n\ell\sigma)_1 (n''s\alpha)_2 \rangle c_\alpha a_\sigma \\ =\ & \Sigma a_\tau^\dagger b_\beta^\dagger \langle (n\ell\tau)_1 (n's\beta)_2 | e^2/r_{12} | (n''s\alpha)_1 (n\ell\sigma)_2 \rangle a_\sigma c_\alpha \\ & + \Sigma a_\tau^\dagger b_\beta^\dagger \langle (n\ell\tau)_1 (n's\beta)_2 | e^2/r_{12} | (n\ell\sigma)_1 (n''s\alpha)_2 \rangle c_\alpha a_\sigma\ .\end{aligned} \tag{10}$$

The second term, which can be dealt with by methods completely analogous to those that follow for the first term, leads to a nul result. We therefore drop it at this point. (It corresponds to an intermediate state of $(n's)(n''s)(n\ell)^N$ in which the two s electrons are coupled to ^1S.) The sum over the intermediate states can be carried out by means of the familiar closure procedure:[14]

$$\sum_Y |Y\rangle\langle Y| = 1.$$

The question whether the kets $|Y\rangle$ form a complete set or not is irrelevant, since missing components are not connected to $|X\rangle$ by our operators, and hence contribute nothing. Now that the intermediate states are eliminated, the creation and annihilation operators of the Coulomb interaction and the hyperfine operator $\underset{\sim}{\Omega}$ can be brought together. Using identifications of the type $\xi \equiv m_{s\xi} m_{\ell\xi}$, we find

$$-2 \sum_{Y}[\Sigma e^2/r_{ij}]|Y\rangle\langle Y|\underset{\sim}{Q}(\Delta E)^{-1}$$

$$\equiv -2 \overline{\sum_{\alpha,\beta,\sigma,\tau,\xi,\eta}} \delta(m_{s\tau},m_{s\alpha})\ \delta(m_{s\beta},m_{s\sigma})\ \delta(m_{\ell\tau},m_{\ell\sigma})(2\ell+1)^{-1} \qquad (11)$$

$$\times\ R^{\ell}(n\ell n's,n''sn\ell)(16\pi\ \beta\beta_N\mu_N/3I\Delta E)$$

$$\times\ \psi_{n's}(0)\psi_{n''s}(0)(\xi|\underset{\sim}{s}|\eta)\ a_\tau^\dagger b_\beta^\dagger a_\sigma c_\alpha c_\xi^\dagger b_\eta,$$

where $\psi_y(0)$ denotes the amplitude of the eigenfunction y at the nucleus, and R^ℓ is a Slater integral (see Condon and Shortley[1]).

We are now in a position to manipulate the creation and annihilation operators with the aid of the anticommutation relations. This is the crux of the method. Thus

$$\begin{aligned} c_\alpha c_\xi^\dagger b_\eta^\dagger &= -c_\xi^\dagger c_\alpha b_\eta + \delta(\alpha,\xi)b_\eta \\ &= c_\xi^\dagger b_\eta c_\alpha + \delta(\alpha,\xi)b_\eta. \end{aligned}$$

Now there is no n"s electron in the configuration $(n's)^2(n\ell)^N$, and hence the operator c_α, acting to the right, gives a zero result. It follows that we may make the replacement

$$a_\tau^\dagger b_\beta^\dagger a_\sigma c_\alpha c_\xi^\dagger b_\eta \to a_\tau^\dagger b_\beta^\dagger a_\sigma b_\eta \delta(\alpha,\xi).$$

Similarly,

$$b_\beta^\dagger a_\sigma b_\eta = -a_\sigma b_\beta^\dagger b_\eta = a_\sigma b_\eta b_\beta^\dagger - a_\sigma \delta(\beta,\eta).$$

Since the shell $(n's)^2$ is full, the operator $b_\beta^\dagger$, acting to the right, also gives a zero result. Thus the final replacement is given by

$$a_\tau^\dagger b_\beta^\dagger a_\sigma c_\alpha c_\xi^\dagger b_\eta \rightarrow -a_\tau^\dagger a_\sigma \delta(\alpha,\xi)\delta(\beta,\eta).$$

The right-hand side of the equivalence (11) becomes

$$2\Gamma \sum_{\tau,\sigma} a_\tau^\dagger \langle\tau|\underset{\sim}{s}|\sigma\rangle a_\sigma, \tag{12}$$

where

$$\Gamma = [16\pi\, \beta\beta_N\mu_N/3I\Delta E(2\ell+1)]\ R^\ell(n\ell n's, n''sn\ell)\psi_{n's}(0)\psi_{n''s}(0).$$

The operator (12) is a single-particle operator acting within the $n\ell$ shell, and is, in fact, equivalent to $2\Gamma\underset{\sim}{S}$. Using the relations

$$\underset{\sim}{S} = \underset{\sim}{L} + 2\underset{\sim}{S} - \underset{\sim}{J} = \underset{\sim}{J}(g-1),$$

where g is the Landé g factor, we see that the contribution ΔA to the hyperfine constant A of the effective Hamiltonian $A\underset{\sim}{I}\cdot\underset{\sim}{J}$ for a given J level of $(n\ell)^N$ can be represented by

$$\Delta A = 2(g-1)\Gamma,$$

in agreement with the result found by conventional methods.[15]

B. The Rajnak-Wybourne Analysis

The most significant feature of the preceding section is the fact that it is never necessary to specify the state $|X)$ of $(n\ell)^N$. This advantage over conventional methods becomes especially valuable when more complicated examples of configuration interaction are considered. In a recent article,[16] Rajnak and Wybourne study the various perturbations on the positions of the terms of a configuration $(n\ell)^N$. To illustrate the approach being developed here, we choose as an example the perturbing effect of a configuration of the type $(n\ell)^{N-1}(n'\ell')$ on the terms of $(n\ell)^N$. The procedure of Rajnak and Wybourne is to calculate the general form for a matrix element of the Coulomb interaction between a term of $(n\ell)^N$ and one of $(n\ell)^{N-1}(n'\ell')$. This is squared and divided by the excitation energy ΔE. The resultant effect on the terms of $(n\ell)^N$ of all interactions of this kind is reproduced by an effective operator acting solely within the configuration. Their most striking result is that this effective operator must contain a three-particle operator (whose amplitude may vanish in exceptional circumstances) as well as a two-particle operator. However, the necessity of defining states of both interacting configurations involves the introduction of many quantum numbers (as well as fractional parentage coefficients) that subsequently disappear when the effective operator is constructed.

Progress in eliminating the superfluous mathematics in this calculation has been made by Stein.[17] However, his operators $\underset{\sim}{z}^{(k)}$, which are defined as being non-nul only when connecting $(n\ell)$ to $(n'\ell')$, are equivalent to a coupled product of an annihilation and a creation operator; so the treatment to be presented here can be regarded as underlying Stein's approach.

We use a_ξ and $a_\xi^\dagger$ for annihilating and creating respectively an $n\ell$ electron, b_ξ and $b_\xi^\dagger$ for an $n'\ell'$ electron, c_ξ and $c_\xi^\dagger$ for an $n''\ell''$ electron, etc. For the example in hand, an electron $n''\ell''$ belongs to a closed shell. As in Sec. III-A, a Greek suffix stands for the couple $(m_s m_\ell'')$. To connect a bra $\langle X|$ of $(n\ell)^N$ to a ket $|Z\rangle$ of $(n\ell)^{N-1}(n'\ell')$, the equivalence analogous to equivalence (10) is

$$\Sigma\, e^2/r_{ij} \equiv \Sigma\; a_\xi^\dagger a_\eta^\dagger \langle (n\ell\xi)_1 (n\ell\eta)_2 | e^2/r_{12} | (n'\ell'\zeta)_1 (n\ell\lambda)_2 \rangle a_\lambda b_\zeta, \qquad (13)$$

where the sum on the right-hand side runs over ξ, η, λ, and ζ. Terms that include operators of the type $a_\xi^\dagger c_\eta^\dagger c_\lambda b_\zeta$ can also connect $\langle X|$ to $|Z\rangle$. However, if the zero-order eigenfunctions are determined by the Hartree-Fock method, terms such as these that involve passive closed shells are taken into account in the central potential. They will therefore be considered no further. The operator connecting the bra $\langle Z|$ of $(n\ell)^{N-1}(n'\ell')$ to a ket $|X'\rangle$ of $(n\ell)^N$ is given by the equivalence

$$\Sigma\, e^2/r_{ij} \equiv \Sigma\, b_\alpha^\dagger a_\beta^\dagger \langle (n'\ell'\alpha)_1 (n\ell\beta)_2 | e^2/r_{12} | (n\ell\gamma)_1 (n\ell\epsilon)_2 \rangle a_\epsilon a_\gamma. \qquad (14)$$

The operator Ω that should be set between $\langle X|$ and $|X'\rangle$ to give the second-order correction to $\langle X|\Sigma\, e^2/r_{ij}|X'\rangle$ is given by

$$\Omega = - \sum_Z (\Delta E)^{-1}\; \Sigma\, e^2/r_{ij} |Z\rangle\langle Z| \Sigma\, e^2/r_{ij}.$$

When the sum over Z is carried out, the creation and annihilation operators of equivalences (13) and (14) are brought together, producing the sequence

$$a_\xi^\dagger a_\eta^\dagger a_\lambda b_\zeta b_\alpha^\dagger a_\beta^\dagger a_\epsilon a_\gamma.$$

By arguments similar to those used in Sec. III-A, we immediately see that this can be replaced by

$$a_\xi^\dagger a_\eta^\dagger a_\lambda a_\beta^\dagger a_\epsilon a_\gamma \; \delta(\alpha,\zeta),$$

that is, by

$$a_\xi^\dagger a_\eta^\dagger a_\epsilon a_\gamma \; \delta(\alpha,\zeta) \; \delta(\lambda,\beta) + a_\xi^\dagger a_\eta^\dagger a_\beta^\dagger a_\epsilon a_\lambda a_\gamma \; \delta(\alpha,\zeta). \tag{15}$$

Without any detailed study of the coefficients of these terms, it is clear that the first part represents a two-particle operator acting solely within $(n\ell)^N$; and the second part obviously corresponds to a three-particle operator. To actually find the coefficients, we use equations of the type

$$\begin{aligned} &\langle (n\ell m_{s\xi} m_{\ell\xi})_1 (n\ell m_{s\eta} m_{\ell\eta})_2 | e^2/r_{12} | (n'\ell' m_{s\zeta} m_{\ell\zeta})_1 (n\ell m_{s\lambda} m_{\ell\lambda})_2 \rangle \\ &= \sum_{k,q} (-1)^x \begin{pmatrix} \ell & k & \ell' \\ -m_{\ell\xi} & q & m_{\ell\zeta} \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ -m_{\ell\eta} & -q & m_{\ell\lambda} \end{pmatrix} (\ell \| C^{(k)} \| \ell')(\ell \| C^{(k)} \| \ell) \\ &\quad \times \; \delta(m_{s\xi}, m_{s\zeta}) \; \delta(m_{s\eta}, m_{s\lambda}) \; R^k(n\ell n\ell, n'\ell' n\ell), \end{aligned} \tag{16}$$

where $x = 2\ell - m_{\ell\xi} - m_{\ell\eta} - q$. The notation of Condon and Shortley[1] and Edmonds[18] is used. A similar expression is taken for the second Coulombic matrix element in the product. The 3-j symbols involving no other azimuthal quantum numbers but ℓ are left untouched; those that contain ℓ' are manipulated by standard tensor-operator techniques in order to transfer ℓ' from the 3-j symbols to higher-order coupling coefficients. To describe our results, we write

$$(\underset{\sim}{u}^{(k)} \cdot \underset{\sim}{u}^{(k')} \cdot \underset{\sim}{u}^{(k'')}) = \sum_{q,q',q''} \begin{pmatrix} k & k' & k'' \\ q & q' & q'' \end{pmatrix} u_q^{(k)} u_{q'}^{(k')} u_{q''}^{(k'')},$$

where the amplitude of the unit tensors is given by

$$(n\ell \| u^{(\lambda)} \| n\ell) = 1.$$

Following Rajnak and Wybourne,[16] we also introduce the abbreviation

$$P(kk';\ell\ell\ell\ell') = (\ell\|C^{(k)}\|\ell)(\ell\|C^{(k)}\|\ell')(\ell\|C^{(k')}\|\ell)(\ell\|C^{(k')}\|\ell')$$

$$\times\ R^k(n\ell n\ell, n\ell n'\ell')\ R^{k'}(n\ell n\ell, n\ell n'\ell')/\Delta E.$$

The final result can now be stated as follows. The effect of the configuration $(n\ell)^{N-1}(n'\ell')$ on the terms of $(n\ell)^N$ can be exactly reproduced to second-order perturbation theory by the operator Ω, given by

$$\begin{aligned} \Omega = & -\Sigma\,[k''] \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix} P(kk';\ell\ell\ell\ell') \\ & \times\ a_\xi^\dagger a_\eta^\dagger a_\beta^\dagger \langle (n\ell\xi)_1 (n\ell\eta)_2 (n\ell\beta)_3 | (\underset{\sim}{u}_1^{(k'')} \cdot \underset{\sim}{u}_2^{(k)} \cdot \underset{\sim}{u}_3^{(k')}) \\ & \qquad | (n\ell\gamma)_1 (n\ell\lambda)_2 (n\ell\epsilon)_3 \rangle a_\epsilon a_\lambda a_\gamma \\ & -\Sigma[k''] \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix} \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell \end{Bmatrix} P(kk';\ell\ell\ell\ell')(-1)^{k''} \\ & \times\ a_\xi^\dagger a_\eta^\dagger \langle (n\ell\xi)_1 (n\ell\eta)_2 | (\underset{\sim}{u}_1^{(k'')} \cdot \underset{\sim}{u}_2^{(k'')}) | (n\ell\gamma)_1 (n\ell\epsilon)_2 \rangle a_\epsilon a_\gamma, \end{aligned} \tag{17}$$

which acts solely within the states of $(n\ell)^N$. The traditional contraction

$[x] \equiv (2x+1)$ is used. The sums run over k, k', k'', and all the Greek symbols. At first sight, this result does not appear to agree with that of Rajnak and Wybourne. Their expression is written as the sum of three parts, and the last two [called by them $C(2)$ and $C(3)$] both include the delta function $\delta(\ell,\ell')$, which is completely absent from Eq. (17) above. However, a close examination reveals that these delta-function terms exactly cancel terms included in the first part [i.e., $C(1)$], and the residue turns out to be identical to Ω. Their statement of the result, which concludes Sec. III-D of their paper, is nevertheless incorrectly worded, and fails to account for terms of odd k'' in the second sum of Eq. (17).[19]

C. Graphical Methods

The examples of configuration interaction described in Secs. III-A and III-B are relatively straightforward. In higher orders of perturbation theory the situation becomes more complex, especially when excitations from closed shells are included. To get an overall view of a particular perturbation mechanism, it is often useful to draw out the corresponding Feynman graph. A prescription for doing this has been given by Goldstone.[20] The two graphs corresponding to the equivalences (13) and (14) are sketched in Fig. 1. The direction of increasing time is upwards. The first graph represents an interaction between two particles that are scattered from states $(n'\ell'\zeta)$ and $(n\ell\lambda)$ to the states $(n\ell\xi)$ and $(n\ell\eta)$; the interaction itself is represented by a horizontal dotted line. The direction of the arrows on the lines is appropriate to particles; holes in closed shells would be represented by lines in the opposite direction. The delta functions that result when the two quartets of operators are brought together imply the identity of pairs of states. This is represented graphically by the union of the corresponding lines. The graphs for the two terms in the expression (15) are drawn out in Fig. 2. The fact that the first graph corresponds to a two-particle operator is now obvious: two lines enter at the bottom of the graph and emerge at the top. The second graph corresponds equally obviously to a three-particle operator. The number and variety of the graphs increases when excitations from closed shells are considered. Safronova and Tolmachev have sketched all the 34 possible Feynman graphs that arise in second-order perturbation theory for two electrons outside closed shells.[21] Not all these graphs would appear in the reconstruction of the analysis of Rajnak and Wybourne[16] for the configuration $(n\ell)^N$, since the assumption of Hartree-Fock eigenfunctions automatically eliminates the effect of passive closed shells.

Apart from their use in representing in a succinct and striking way the interaction mechanism, the graphs contain sufficient information for a detailed quantitative analysis. In other words, we can find the coefficients of the operators in equations like Eq. (17) purely from a study of the graphs. This is possible because the Feynman graphs are topologically identical to the angular momentum diagrams of Jucys, Levinsonas, and Vanagas.[22] To see this in a simple case, we use the rules of these authors (Ref. 22, p.36) to draw out in Fig. 3 the diagram corresponding to

$$\sum_q (-1)^{k-q} \begin{pmatrix} \ell & k & \ell' \\ m_{\ell\xi} & -q & -m_{\ell\zeta} \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ m_{\ell\eta} & q & -m_{\ell\lambda} \end{pmatrix}. \qquad (18)$$

This expression occurs in Eq. (16), since for us k is even. It represents a term in the matrix element of the Coulomb interaction that corresponds to the first graph of Fig. 1. Apart from an undirected dotted horizontal line in the Feynman graph, the two figures are identical. Topological equivalences of this kind have been recognized for some time by Sandars;[23] an explicit statement of the property has recently appeared in the literature.[24] It follows that the technique for analyzing the angular-momentum graphs can be directly applied to the Feynman graphs.

As an example of the procedure, we verify the coefficient of the term

$$a_\xi^\dagger a_\eta^\dagger \langle (n\ell\xi)_1 (n\ell\eta)_2 | (\underset{\sim}{u}_1^{(k'')} \cdot \underset{\sim}{u}_2^{(k'')}) | (n\ell\gamma)_1 (n\ell\epsilon)_2 \rangle a_\epsilon a_\gamma , \tag{19}$$

which occurs in Eq. (17), by means of the rules of Jucys et al.[22] First, the analogous graph to Fig. 3 is constructed for the second Coulombic matrix element. The delta functions on the m_ℓ values and the sums over these quantities demand the union of these two graphs in just the same way as for the Feynman graphs. Thus, we arrive at the graph of Fig. 4. Now the 3-j symbols contained in the expression (19), summed over the projection q'' of k'', and with a phase factor $(-1)^{k''-q''}$, correspond to the graph of Fig. 5. In the language of Jucys et al., we contract the graph of Fig. 4 with the graph of Fig. 5 in order to find the coefficient. This involves changing the directions of the lines in the diagram of Fig. 5, and then attaching the four free ends to the correspondingly labelled lines of the diagram of Fig. 4. The result is given in Fig. 6. This is immediately identified (Ref. 22, p. 60) as the following product of 6-j symbols:

$$\begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix} \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell \end{Bmatrix} .$$

According to the rules, a factor $[k'']$ must also be included; and the neglected terms of the Coulombic matrix elements go to form $P(kk';\ell\ell\ell\ell')$. A phase factor $(-1)^{k''}$ is required to balance the similar factor introduced in the construction of the graph of Fig. 5. In this way, the second term on the right-hand side of Eq. (17) is obtained from the graphs.

Questions of phase have not been considered in complete detail in this brief description. The ordering of the columns of the 3-j symbols is nevertheless represented by the plus and minus signs against the vetices in Figs. 3, 4, and 5; and the prescription of Jucys et al. ensures that no phase information is lost in the working. The reader is referred to their book for details. By representing the three-particle interaction as the junction of three dotted lines (labelled k, k', and k" in the angular-momentum diagram), the first term on the right of Eq. (17) can be similarly checked.

IV. TENSOR OPERATORS

A. Definitions

The applications of the theory described in Sec. III depend only on the most elementary properties of the creation and annihilation operators. A large field for further study opens up when the tensorial character of these operators is examined. A convenient way to find the tensorial properties of any operator is to study its commutation relations with respect to the components of an angular-momentum vector (see Racah[2]). Two such vectors are of use to us: the total spin angular momentum $\underset{\sim}{S}$ and the total orbital angular momentum $\underset{\sim}{L}$. Of course, we must use equivalence (7) to put these momentum vectors into a convenient form. Letting the Greek symbols stand for the quartets of quantum numbers, and, in particular, setting $\sigma \equiv (n\ell m_s m_\ell)$, we find

$$[\sum_{\xi,\eta} a_\xi^\dagger \langle\xi|\ell_z|\eta\rangle\, a_\eta, a_\sigma^\dagger] = m_\ell a_\sigma^\dagger,$$

$$[\sum_{\xi,\eta} a_\xi^\dagger \langle\xi|\ell_\pm|\eta\rangle\, a_\eta, a_\sigma^\dagger] = \{\ell(\ell+1) - m_\ell(m_\ell \pm 1)\}^{1/2} a_\rho^\dagger,$$

$$[\sum_{\xi,\eta} a_\xi^\dagger \langle\xi|s_z|\eta\rangle\, a_\eta, a_\sigma^\dagger = m_s a_\sigma^\dagger,$$

$$[\sum_{\xi,\eta} a_\xi^\dagger \langle\xi|s_\pm|\eta\rangle\, a_\eta, a_\sigma^\dagger] = \{s(s+1) - m_s(m_s \pm 1)\}^{1/2} a_\tau^\dagger,$$

where $\rho \equiv (n\ell m_s m_\ell \pm 1)$ and $\tau \equiv (n\ell m_s \pm 1\, m_\ell)$. Comparison with the standard form for the commutation relations satisfied by a double tensor[25] reveal at once that for every n and ℓ, the $[s][\ell]$ operators $a_\sigma^\dagger\,(-\ell \leq m_\ell \leq \ell, -s \leq m_s \leq s)$ form the components of a double tensor of rank ℓ with respect to orbit and s with respect to spin. (Of course, we know that $s = 1/2$, but it is convenient to retain the symbol s so that the correspondence between spin and orbit is always kept in view.) As has been seen in Secs. III-A and III-B, it is often convenient to delete n and ℓ from the Greek suffix σ, changing from $a^\dagger$ to $b^\dagger$ when any distinction is necessary. If we do this, then we may follow the usual convention of tensor algebra by using bold-face suffix-free symbols $\mathbf{a}^\dagger$, $\mathbf{b}^\dagger$, etc., to stand for the double tensors.

The annihilation operators, as they stand, do not form the components of a double tensor. However, if we define

$$\tilde{a}_\sigma = (-1)^x a_\zeta, \tag{20}$$

where $\sigma \equiv (n\ell m_s m_\ell)$, $x = s+\ell-m_s-m_\ell$, and $\zeta \equiv (n\ell{-m_s}{-m_\ell})$, then it is found that for every n and ℓ, the $[s][\ell]$ operators $\tilde{a}_\sigma$ $(-\ell \leq m_\ell \leq \ell,\ -s \leq m_s \leq s)$ form the components of a double tensor of rank ℓ with respect to orbit and s with respect to spin. If we decide to suppress n and ℓ, then we may represent the double tensor whose components are $\tilde{a}_\sigma$ simply by $\mathbf{a}$.

B. Coupling Procedures

Our basic tensors $\mathbf{a}^\dagger$ and $\mathbf{a}$ can be coupled according to the familiar rules of the theory of angular momentum. Suppose we set $f = w_{\pi q}^{(\kappa k)}$ in equivalence (7), where $\mathbf{w}^{(\kappa k)}$ is a double tensor whose amplitude is defined by

$$(n\ell \| w^{(\kappa k)} \| n'\ell') = \delta(n,n')\, \delta(\ell,\ell')[\kappa]^{1/2}[k]^{1/2}.$$

The convention $[x] \equiv (2x+1)$ is maintained. Two 3-j symbols arise when the Wigner-Eckart theorem is used to evaluate $\langle \xi | f | \eta \rangle$, and a phase factor is introduced in replacing a_η by an operator of the type $\tilde{a}_\sigma$. These symbols and their associated phase factors can be immediately interpreted as coefficients that couple components of $\underset{\sim}{a}^\dagger$ to components of $\underset{\sim}{a}$, with the result that equivalence (7) now reads (for a given $n\ell$)

$$W_{\pi q}^{(\kappa k)} \equiv (-1)^{2s+2\ell}(\underset{\sim}{a}^\dagger \underset{\sim}{a})_{\pi q}^{(\kappa k)}. \qquad (21)$$

The operator $W_{\pi q}^{(\kappa k)}$ is defined by

$$\underset{\sim}{W}^{(\kappa k)} = \sum_i (\underset{\sim}{w}^{(\kappa k)})_i ,$$

and is identical to the operator introduced in Ref. 25. Since $2s+2\ell$ is always odd, and since the equivalence (21) is valid for all components π and q, we may write

$$\underset{\sim}{W}^{(\kappa k)} \equiv -(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(\kappa k)}, \qquad (22)$$

a remarkably simple result. By similar methods we may relate $(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(00)}$ to the number operator (see Sec. II-A), and hence show that the eigenvalues of $(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(00)}$ are

$$-N\,[s]^{-1/2}[\ell]^{-1/2}.$$

The anticommutation relations satisfied by the annihilation and creation operators lead to the result

$$(\underset{\sim}{a}\,\underset{\sim}{a}^\dagger)^{(\kappa k)} + (-1)^{2\ell+2s-\kappa-k}(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(\kappa k)} = \delta(\kappa,0)\,\delta(k,0)\,[s]^{1/2}[\ell]^{1/2}. \qquad (23)$$

C. Fractional Parentage Coefficients

In this section we restrict our attention to configurations of the type $(n\ell)^N$, where n and ℓ are fixed. A state $|\bar{\Theta}\rangle$ of $(n\ell)^{N-1}$ must be some linear combination of determinantal product states, say

$$\Sigma A_{\alpha\beta\cdots\nu}\{\alpha\ \beta\cdots\nu\}.$$

From the equivalence (1), we may evidently write

$$|\bar{\Theta}\rangle \equiv \Sigma A_{\alpha\beta\cdots\nu}\ a_\alpha^\dagger a_\beta^\dagger\cdots a_\nu^\dagger|0\rangle.$$

Operating on both sides with $a_\xi^\dagger$, we get

$$a_\xi^\dagger|\bar{\Theta}\rangle \equiv \Sigma A_{\alpha\beta\cdots\nu}\ a_\xi^\dagger a_\alpha^\dagger a_\beta^\dagger\cdots a_\nu^\dagger|0\rangle$$

$$\equiv \Sigma A_{\alpha\beta\cdots\nu}\ \{\xi\alpha\beta\cdots\nu\}.$$

Remembering that a determinantal product state for N particles contains a normalizing factor $(N!)^{-1/2}$, we obtain

$$\{\xi\alpha\beta\cdots\nu\} = (N)^{-1/2}\sum_i \{\alpha\beta\cdots\nu\}'\{\xi_i\}(-1)^{i-1}.$$

In this expression, the subscript i indicates that electron i is assigned the quantum numbers ξ; the prime denotes that the electrons are to be taken in the sequence

$$1,\ 2,\ldots,\ i-1,\ i+1,\ldots,\ N.$$

Hence

$$a_\xi^\dagger |\overline{\Theta}\rangle \equiv (N)^{-1/2} \sum_i (-1)^{i-1} |\overline{\Theta}', \xi_i\rangle,$$

and

$$\langle\Theta| a_\xi^\dagger |\overline{\Theta}\rangle = (N)^{-1/2} \sum_i (-1)^{i-1} \langle\Theta|\overline{\Theta}', \xi_i\rangle, \qquad (24)$$

where $\langle\Theta|$ is a bra of $(n\ell)^N$. Now $\langle\Theta|\overline{\Theta}', \xi_i\rangle$ is a number and must be invariant with respect to permutations of the electrons. On interchanging i and N, we find

$$\langle\Theta| \rightarrow -\langle\Theta|.$$

and

$$|\overline{\Theta}', \xi_i\rangle \rightarrow |\overline{\Theta}'', \xi_N\rangle = (-1)^{N-i-1} |\overline{\Theta}, \xi_N\rangle,$$

where the double prime implies the ordering

$$1,2,\ldots,i-1,\ i+1,\ldots,\ N-1,i.$$

The phase factor $(-1)^{N-i-1}$ represents the parity of this sequence with respect to the natural ordering. Thus

$$\langle\Theta|\overline{\Theta}', \xi_i\rangle = (-1)^{N-i} \langle\Theta|\overline{\Theta}, \xi_N\rangle,$$

and every term in the summation of Eq. (24) is the same. Hence

$$\langle\Theta| a_\xi^\dagger |\overline{\Theta}\rangle = (-1)^{N-1} (N)^{1/2} \langle\Theta|\overline{\Theta}, \xi_N\rangle.$$

The factor $\langle\Theta|\bar{\Theta},\xi_N\rangle$ is not quite a coefficient of fractional parentage (cfp), since it still contains a dependence on the M quantum numbers. We write $\Theta \equiv \psi M_S M_L$, $\bar{\Theta} \equiv \bar{\psi}\ \bar{M}_S \bar{M}_L$, and $\psi \equiv n\ell m_s m_\ell$ and factor out the vector-coupling (VC) coefficients by means of the equation

$$\langle\Theta|\bar{\Theta},\xi_N\rangle = (\psi\{|\bar{\psi})(\bar{L}\ell LM_L|\bar{L}\bar{M}_L\ell m_\ell)(\bar{S}_s SM_S|\bar{S}\bar{M}_S s m_s).$$

Precisely similar VC coefficients arise when the Wigner-Eckart theorem is applied to $\langle\Theta|a_\xi^{\dagger}|\bar{\Theta}\rangle$ (see Edmonds[18]). This operation introduces a phase $(-1)^{2s+2\ell}$ (which is replaced by -1) and a numerical factor. The cfp $(\psi\{|\bar{\psi})$ are finally found to satisfy the equation

$$(\psi\|a^{\dagger}\|\bar{\psi}) = (-1)^N\{N[S][L]\}^{1/2}(\psi\{|\bar{\psi}). \qquad (25)$$

If we take adjoints before using the Wigner-Eckart theorem, we get

$$(\bar{\psi}\|a\|\psi) = (-1)^x\{N[S][L]\}^{1/2}(\bar{\psi}|\}\psi), \qquad (26)$$

where $x = N+\bar{S}-s-S+\bar{L}-\ell-L$. Equation (25) corresponds exactly with the result obtained by Lawson and Macfarlane[9] for the configurations j^N when the replacement $[S][L] \rightarrow [J]$ is made.

Similar methods enable two-particle cfp to be related to the reduced matrix elements of pairs of creation or annihilation operators. The analog of Eq. (25) is

$$(\psi\|(\mathbf{a}^{\dagger}\mathbf{a})^{(\kappa k)}\|\tilde{\psi}) = \{N(N-1)[S][L]/2\}^{1/2}(\psi\{|\tilde{\psi},\ell^2(\kappa k)), \qquad (27)$$

where $\tilde{\psi}$ denotes a term of $(n\ell)^{N-2}$. The symbols κ and k stand for the total spin and total orbital quantum numbers for a term of $(n\ell)^2$.

V. EXAMPLES

A. Introduction

We are now ready to apply the techniques of the Racah algebra to evaluate the matrix elements of any operator involving $\underset{\sim}{a}^\dagger$ and $\underset{\sim}{a}$, since their reduced matrix elements are known from Eqs. (25) and (26). For the purpose of illustrating the theory, we limit ourselves to examples that can be obtained from the equation

$$(\psi\|\{\underset{\sim}{T}^{(\kappa'k')}\underset{\sim}{U}^{(\kappa''k'')}\}^{(\kappa k)}\|\psi')$$

$$= [\kappa]^{1/2}[k]^{1/2}(-1)^{S+\kappa+S'+L+k+L'} \tag{28}$$

$$\times \sum_{\psi''} \begin{Bmatrix} \kappa'' & \kappa & \kappa' \\ S & S'' & S' \end{Bmatrix} \begin{Bmatrix} k'' & k & k' \\ L & L'' & L' \end{Bmatrix} (\psi\|T^{(\kappa'k')}\|\psi'')(\psi''\|U^{(\kappa''k'')}\|\psi'),$$

where $\psi \equiv \gamma SL$, $\psi' \equiv \gamma' S' L'$, and $\psi'' \equiv \gamma'' S'' L''$. The symbols γ represent additional quantum numbers that may be necessary to define the terms unambiguously. Equation (28) is the extension to double tensors of Eq. (7.1.1) of Edmonds.[18]

B. Single-Particle Operators

As a first and very simple application of Eq. (28), we identify $\underset{\sim}{T}^{(\kappa'k')}$ with $\underset{\sim}{a}$; and we suppose that the states ψ and ψ' both belong to $(n\ell)^N$. The states of ψ'' must all belong to $(n\ell)^{N-1}$, and we write $\overline{\psi},\overline{S},\ldots$ in place of $\psi'',S'',\ldots$ to keep the notation in line with that of Sec. IV-C. The two reduced matrix elements in the summation of Eq. (28) become cfp, and, with the aid of the equivalence (22), we find

$$(\psi\|W^{(\kappa k)}\|\psi')$$

$$= N\{[S][\kappa][S'][L][k][L']\}^{1/2}$$

$$\times \sum_{\overline{\psi}} (\psi\{|\overline{\psi})(\overline{\psi}|\}\psi')(-1)^x \begin{Bmatrix} s & \kappa & s \\ S & \overline{S} & S' \end{Bmatrix} \begin{Bmatrix} \ell & k & \ell \\ L & \overline{L} & L' \end{Bmatrix} ,$$

where $x = \overline{S}+s+S+\kappa+\overline{L}+\ell+L+k$. This is identical to the result found by conventional methods.[26] Special cases of this equation have been used by Koster and Nielson[27] to evaluate matrix elements of $\underset{\sim}{V}^{(11)}$ ($\equiv \underset{\sim}{W}^{(11)}/3$) and of all tensors $\underset{\sim}{U}^{(k)}$ ($\equiv \{2/[k]\}^{1/2}\underset{\sim}{W}^{(0k)}$ for all configurations of the type p^N, d^N, and f^N.

C. The Rajnak-Wybourne Identity

Making use of the anticommutation relations, we may show that

$$\{(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(\kappa k)}\underset{\sim}{a}^\dagger\}^{(\kappa'k')} = (-1)^{k+\kappa+s+\ell-k'-\kappa'}\{\underset{\sim}{a}^\dagger(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(\kappa k)}\}^{(\kappa'k')}$$

$$+ (-1)^{k+\kappa}\{[k][\kappa]/[s][\ell]\}^{1/2}\delta(k'\ell)\ \delta(\kappa',s)\underset{\sim}{a}^\dagger .$$

The operator on the left is set between the bra $\langle\psi|$ of $(n\ell)^N$ and the ket $|\bar{\psi}'\rangle$ of $(n\ell)^{N-1}$. This procedure is repeated for the operators on the right of the equation. We equate the results and pass to reduced matrix elements. Using the equivalence (22) and Eq. (28), we get, with some rearrangement,

$$\sum_{\psi''} (\psi\|W^{(\kappa k)}\|\psi'')(\psi''\{|\bar{\psi}')(-1)^{\kappa+k+\ell}\sqrt{\frac{[S''][L'']}{[S]\ [L]}} \begin{Bmatrix} L & L'' & k \\ \ell & k' & \bar{L}' \end{Bmatrix} \begin{Bmatrix} S & S'' & \kappa \\ s & \kappa' & \bar{S}' \end{Bmatrix}$$

$$= \sum_{\bar{\psi}} (\psi\{|\bar{\psi})(\bar{\psi}\|W^{(\kappa k)}\|\bar{\psi}')(-1)^{\kappa'+k'-s} \begin{Bmatrix} \bar{S} & \bar{S}' & \kappa \\ \kappa' & s & S \end{Bmatrix} \begin{Bmatrix} \bar{L} & \bar{L}' & k \\ k' & \ell & L \end{Bmatrix} \tag{29}$$

$$+ \ [k]^{1/2}[\kappa]^{1/2}(\psi\{|\bar{\psi}')\ \delta(k',\ell)\ \delta(\kappa',s)(-1)^y/[s][\ell],$$

where $y = \bar{S}'+\bar{L}'+S+L+s$. A special case of this equation was discovered empirically by Rajnak;[28] a proof by conventional methods appears in the appendix of the article with Wybourne.[16] Our parameters $(\kappa'k')$ correspond to the symbols $(s\ell')$ of Rajnak and Wybourne. Since s is limited to the value 1/2, whereas κ' can also take on the value 3/2, Eq. (29) is a slightly more general form for the identity.

D. Decomposition of Two-Particle cfp

Application of Eq. (28) to the left-hand side of Eq. (27) yields at once

$$(\psi\{|\tilde{\psi},\ell^2(\kappa k))$$

$$= -\sum_{\bar{\psi}}\{2[\kappa][k][\bar{S}][\bar{L}]\}^{1/2}\ (-1)^x(\psi\{|\bar{\psi})(\bar{\psi}\{|\tilde{\psi}) \begin{Bmatrix} s & \kappa & s \\ S & \bar{S} & \tilde{S} \end{Bmatrix} \begin{Bmatrix} \ell & k & \ell \\ L & \bar{L} & \tilde{L} \end{Bmatrix}$$

where $x = S+\tilde{S}+L+\tilde{L}$. This result expresses a two-particle cfp as a sum of products of single-particle cfp. The fact that for ℓ^2 the sum $\kappa+k$ must be even has been used to simplify the phase factor. The conventional derivation of the equation would be to break off the Nth particle and then the (N-1)th, recoupling their angular momenta to (κk). The minus sign that precedes the summation sign would appear as $(-1)^{2s+2\ell}$.

E. Redmond's Explicit cfp Formula

The power of our methods is well exemplified by the case with which a recursion formula for cfp due to Redmond[24] is derived. We merely put the operators that appear in Eq. (23) between the states $\langle\bar{\psi}|$ and $|\bar{\psi}'\rangle$ of $(n\ell)^{N-1}$, and evaluate their reduced matrix elements by means of Eq. (28). The result is

$$N \sum_{\psi'} (\bar{\psi}|\}\psi')(\psi'\{|\bar{\psi}')(-1)^x[S'][L'] \begin{Bmatrix} s & \kappa & s \\ \bar{S} & S' & \bar{S}' \end{Bmatrix} \begin{Bmatrix} \ell & k & \ell \\ \bar{L} & L' & \bar{L}' \end{Bmatrix}$$

$$= (N-1) \sum_{\tilde{\psi}} (\bar{\psi}|\}\tilde{\psi})(\tilde{\psi}\{|\bar{\psi}')(-1)^y$$

$$\times \{[\bar{S}][\bar{L}][\bar{S}'][\bar{L}']\}^{1/2} \begin{Bmatrix} s & \kappa & s \\ \bar{S} & \tilde{S} & \bar{S}' \end{Bmatrix} \begin{Bmatrix} \ell & k & \ell \\ \bar{L} & \tilde{L} & \bar{L}' \end{Bmatrix} \tag{30}$$

$$+ \delta(\kappa,0)\, \delta(k,0)\, \delta(\bar{\psi},\bar{\psi}')(-1)^z\{[s][\ell][\bar{S}][\bar{L}]\}^{1/2},$$

where $x = \bar{S}-s-S'+\bar{L}-\ell-L'$, $y = \tilde{S}-s-\bar{S}'+\tilde{L}-\ell-\bar{L}'+\kappa+k$, and $z = 2\bar{S}'+2\bar{L}'$. Both sides of Eq. (30) are now multiplied by

$$[\kappa][k](-1)^{S+L-S'-L'-x} \begin{Bmatrix} s & \kappa & s \\ \bar{S} & S & \bar{S}' \end{Bmatrix} \begin{Bmatrix} \ell & k & \ell \\ \bar{L} & L & \bar{L}' \end{Bmatrix}, \tag{31}$$

and sums over κ and k are carried out. Replacing ψ by the more detailed description γSL, we find that the left-hand side becomes

$$\sum_{\gamma} (\bar{\psi}|\}\gamma SL)(\gamma SL\{|\bar{\psi}')N. \tag{32}$$

Since

$$\sum_{\gamma} N(\gamma S'L'\{|\bar{\psi}')|\gamma SLM_SM_L\rangle$$

obviously represents a linear combination of states with unique values of S, L, M_S, and M_L, we can write it as

$$N'|\gamma' SLM_SM_L\rangle,$$

where, for real coefficients,

$$N'^2 = N^2 \sum_{\gamma} (\gamma SL\{|\bar{\psi}')^2. \tag{33}$$

The right-hand side of Eq. (30), multiplied by the expression (31), can be summed over κ and k without difficulty. The final result is

$$N'\ (\bar{\psi}|\}\gamma' SL)$$

$$= \delta(\bar{\psi},\bar{\psi}') + (N-1) \sum_{\tilde{\psi}} (\bar{\psi}\{|\tilde{\psi})(\tilde{\psi}|\}\bar{\psi}')(-1)^t \begin{Bmatrix} \bar{S} & s & S' \\ \bar{S}' & s & \tilde{S} \end{Bmatrix} \begin{Bmatrix} \bar{L} & \ell & L' \\ \bar{L}' & \ell & \tilde{L} \end{Bmatrix},$$

where $t = \bar{S}+\bar{S}'+\bar{L}+\bar{L}'$. This is equivalent to Redmond's result; it expresses a cfp for $(n\ell)^N$ in terms of cfp for $(n\ell)^{N-1}$. To use it, a godparent $\bar{\psi}'$ is selected and the products $N'(\bar{\psi}|\}\gamma' SL)$ are determined for all possible $\bar{\psi}$.

As Redmond showed for several configurations of equivalent nucleons, a judicious choice of godparent often forces γ' to assume the quality of a group-theoretical description; and from this starting point, orthogonal sets of cfp that have well-defined group-theoretical properties can be generated by choosing other suitable godparents. In Redmond's method, the number N' had to be determined from the condition

$$\sum_{\bar{\psi}} N'^2(\bar{\psi}|\}\gamma' SL)^2 = 1.$$

Our method gives Eq. (33) as an alternative, and it is readily verified for Redmond's examples that this equation is satisfied.[30] Not only has the use of annihilation and creation operators allowed us to perform a more complete analysis, but the extensive products of VC coefficients that Redmond introduces have been entirely circumvented. (At the same time, it should be mentioned that a more direct derivation of Redmond's result is given by Hassitt.[31]) It can also be understood now why the cfp for the terms $(210)(21)^2H$ and $(210)(11)^2H$ of f^3 can be obtained directly by choosing the respective godparents ^3H and ^3F of f^2, a curiosity noticed several years ago.[32] For, as may be immediately seen by examining the Kronecker products of the representations (u_1u_2) of G_2,

$$((210)(21)^2H\{|^3F) = ((210)(11)^2H\{|^3H) = 0.$$

It follows that for both H states, one of the two terms in the sum over γ in Eq. (32) is zero; hence the sequence of cfp generated is proportional to the term remaining.

VI. QUASI-SPIN

A. Seniority

The scope for further applications becomes greatly widened when a creation operator and the corresponding annihilation operator are regarded as two aspects of a single entity. As a preliminary step to making this interpretation, the following operators are introduced for a given $(n\ell)$:

$$Q_+ = \frac{1}{2}\{[s][\ell]\}^{1/2}(\underset{\sim}{a}^\dagger \underset{\sim}{a}^\dagger)^{(00)},$$

$$Q_- = -\frac{1}{2}\{[s][\ell]\}^{1/2}(\underset{\sim}{a}\,\underset{\sim}{a})^{(00)}, \tag{34}$$

$$Q_z = -\frac{1}{4}\{[s][\ell]\}^{1/2}\{(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(00)} + (\underset{\sim}{a}\,\underset{\sim}{a}^\dagger)^{(00)}\}.$$

By expanding the scalar products, we may show that the operators Q_+, Q_-, and Q_z are identical to the operators q_+, q_-, and q_o introduced by Flowers and Szpikowski.[33] The anticommutation relations can be used to derive the equations

$$[Q_+, Q_-] = 2Q_z,$$

$$[Q_z, Q_+] = Q_+,$$

$$[Q_z, Q_-] = -Q_-.$$

These are identical in form to the commutation relations satisfied by the components S_+, S_-, and S_z of the total spin $\underset{\sim}{S}$. To stress the correspondence, the operators Q_+, Q_-, and Q_z are said to form the components of the <u>quasi-spin</u> $\underset{\sim}{Q}$.

It has already been shown in Sec. IV-B that the eigenvalues of $(\underset{\sim}{a}^\dagger \underset{\sim}{a})^{(00)}$ are $-N[s]^{-1/2}[\ell]^{-1/2}$; and from Eq. (23) we may deduce that the eigenvalues of

$(\underset{\sim}{a}\,\underset{\sim}{a}^{\dagger})^{(00)}$ are $[s]^{1/2}[\ell]^{1/2}-N[s]^{-1/2}[\ell]^{-1/2}$. Setting $s = 1/2$, we conclude that the eigenvalues of Q_z, which we denote by M_Q, are given by

$$M_Q = -\frac{1}{2}(2\ell+1-N).$$

From Eq. (27) it can be seen that the operator Q_+ connects states of ψ and $\tilde{\psi}$ for which the cfp $(\psi\{|\tilde{\psi},\ell^2(00))$ is non-vanishing. Such cfp are precisely the ones that Racah introduced to connect states of the same seniority.[3] The seniority number v is defined as the number of electrons of the configuration $(n\ell)^N$ in which a member of a string of connected states first makes its appearance: a string begins with a state of $(n\ell)^v$ and ends with one of $(n\ell)^{4\ell+2-v}$. These configurations define the extrema of M_Q: and, denoting its maximum by Q, we see at once that

$$Q = \frac{1}{2}(2\ell+1-v).$$

Thus quasi-spin is merely another way of regarding seniority; and the specification (QM_Q) carries the same information as (vN).

B. Triple Tensors

The great advantage of the quasi-spin formalism over that of seniority is that various states and operators can be examined for their quasi-spin character by using the well-known rules for dealing with tensor operators. Following Lawson and Macfarlane,[9] we find that the two operators $a_\xi^\dagger$ and

$\tilde{a}_\xi$ (for a given ξ) behave under commutation with $\underset{\sim}{Q}$ like the two components of a tensor of rank 1/2. In particular, $a_\xi^\dagger$ corresponds to the component $m_q = +1/2$, and $\tilde{a}_\xi$ to $m_q = -1/2$. This is true for any choice of ξ. We may say that the [s][ℓ] components of $\underset{\sim}{a}^\dagger$ and the [s][ℓ] components of $\underset{\sim}{a}$ together form the [q][s][ℓ] components of the triple tensor $\underset{\sim}{a}^{(qs\ell)}$, where q = 1/2. The anticommutation relations [Eqs. (3) and (5)] are now completely described by the equation

$$a_\lambda^{(qs\ell)} a_\mu^{(qs\ell)} + a_\mu^{(qs\ell)} a_\lambda^{(qs\ell)} = (-1)^{x+1} \delta(m_q, -m_q') \delta(m_s, -m_s') \delta(m_\ell, -m_\ell') \tag{35}$$

where $\lambda \equiv (m_q m_s m_\ell)$, $\mu \equiv (m_q' m_s' m_\ell')$, and $x = s+\ell+m_q+m_s+m_\ell$.

Since $\underset{\sim}{Q}$ is totally scalar with respect to S and L, properties of operators with respect to quasi-spin are quite independent of their ordinary tensorial properties. Hence we can easily extend our coupling techniques to embrace the quasi-spin description. The simplest compound tensor to construct is the following:

$$\underset{\sim}{X}^{(K\kappa k)} = (\underset{\sim}{a}^{(qs\ell)} \underset{\sim}{a}^{(qs\ell)})^{(K\kappa k)}.$$

Special cases can be readily found by uncoupling the two tensors $\underset{\sim}{a}^{(qs\ell)}$. Thus, we find

$$\underset{\sim}{X}^{(100)} = -2[\ell]^{-1/2} \underset{\sim}{Q} ,$$

and

$$\underset{\sim}{X}^{(010)} = -2[\ell]^{-1/2} \underset{\sim}{S} ,$$

thereby demonstrating the close correspondence between spin and quasi-spin. We also find

$$\underset{\sim}{X}^{(001)} = -\underset{\sim}{L}\{3/\ell(\ell+1)(2\ell+1)\}^{1/2}.$$

For the hypothetical case of $\ell = 1/2$, the coefficient of $\underset{\sim}{L}$ becomes the same as that of $\underset{\sim}{S}$ or $\underset{\sim}{Q}$ in the two previous equations. In the more general case, we find, from the equivalence (21), that

$$X_{0\pi q}^{(K\kappa k)} = -2^{-1/2}\{1-(-1)^{K+\kappa+k}\}W_{\pi q}^{(\kappa k)}$$
$$-(-1)^{K}[\ell]^{1/2}\delta(\kappa,0)\delta(k,0)\delta(\pi,0)\delta(q,0). \qquad (36)$$

For $K+\kappa+k$ even,

$$\underset{\sim}{X}^{(K\kappa k)} = -[\ell]^{1/2}\delta(K,0)\delta(\kappa,0)\delta(k,0).$$

This result can be regarded as a statement of the anticommutation relations of Eq. (35) in tensorial form.

C. Conjugation

Let us postulate the existence of an operator C for which

$$C\, a_{\xi}^{(qs\ell)}C^{-1} = (-1)^{y}\, a_{\eta}^{(qs\ell)}, \qquad (37)$$

where $\xi \equiv (m_q m_s m_\ell)$, $\eta = (-m_q m_s m_\ell)$, and $y = q-m_q$. The part $-m_q$ of y is crucial in preserving the anticommutation relations (35) under the transformation C; the part q is included to avoid imaginary coefficients and also because it leads to analogous transformation equations for other operators. For example, it can be shown from Eq. (35) that

$$C\, X^{(K\kappa k)}_{\rho\pi q}\, C^{-1} = (-1)^{K-\rho}\, X^{(K\kappa k)}_{-\rho\pi q} \ . \tag{38}$$

The transformation of states under C can be found by considering the eigenvalues of Q_z and the effect of Q_+ and Q_-. It is convenient to impose the unitary condition $C^\dagger C = 1$ so that normalization is preserved. We find

$$C|\Theta Q M_Q\rangle = (-1)^x\, |\Theta Q {-M_Q}\rangle, \tag{39}$$

where $x = Q-M_Q$. Just as in Eq. (37), the phase is to some extent arbitrary. The effect of C on a state of ℓ^N is thus to produce a state of $\ell^{4\ell+2-N}$ with the same set Θ ($\equiv \psi M_S M_L$) of quantum numbers. This is the operation of conjugation; it has been introduced from a slightly different standpoint by Bell.[34] Our operator C corresponds to the reciprocal of Bell's operator, as can be seen by rewriting Eq. (37) in the form

$$\begin{aligned} C\, \underset{\sim}{a}^\dagger C^{-1} &= \underset{\sim}{a} \\ C\, \underset{\sim}{a}\, C^{-1} &= -\underset{\sim}{a}^\dagger \end{aligned} \tag{40}$$

and comparing these equations to Eqs. (5) and (6) of Bell.

Setting $\kappa = k = \pi = q = 0$ and $K = 1$ in Eq. (38), we at once obtain the results

$$\begin{aligned} C\, Q_+ C^{-1} &= -Q_- \\ C\, Q_z C^{-1} &= -Q_z \\ C\, Q_- C^{-1} &= -Q_+ \ . \end{aligned}$$

In other words, for Cartesian components Q_u of $\mathbf{Q}$,

$$C\, Q_u C^{-1} = -Q_u \;;$$

furthermore,

$$C\, i\, C^{-1} = -i.$$

The first equation shows that the conjugation operator C is completely analogous to the time-reversal operator T, for which $T\, L_u T^{-1} = -L_u$ and $T\, S_u T^{-1} = -S_u$; and the second equation shows that C, like T, is an antilinear operator (see Wigner[35] or Messiah[36]). Thus we have the interesting result that time-reversal is to spin what conjugation is to quasi-spin. For time-reversal, the analog of Eq. (39) is

$$T|\gamma SLM_SM_L\rangle = (-1)^w|\gamma SL\text{-}M_S\text{-}M_L\rangle,$$

where $w = S+L-M_S-M_L$.

D. Reduced Matrix Elements

Equation (39) can be regarded as establishing the correspondence between particle states and hole states. With the aid of Eq. (38), we may make precise the connection between matrix elements. All we have to do is to insert the unit operators $C^\dagger C$ and $C^{-1}C$ before and after the operator $X^{(K\kappa k)}_{0\pi q}$ in a typical (real) matrix element. On transforming the operator and also allowing $C^\dagger$ and C to act on the bra and the ket respectively, we obtain

$$(\Theta Q M_Q | X^{(K\kappa k)}_{0\pi q} | \Theta' Q' M_Q)$$

$$= (-1)^x (\Theta Q\text{-}M_Q | X^{(K\kappa k)}_{0\pi q} | \Theta' Q' \text{-}M_Q), \tag{41}$$

where $x = Q-M_Q+\kappa+Q'-M_Q$. For $K+\kappa+k$ odd (the only interesting case), we may use Eq. (36) to convert the operator to the more familiar form $W^{(\kappa k)}_{\pi q}$. The Wigner-Eckart theorem is now used to remove the dependence on M_S, M_L, π, q, M_S', and M_L', and we arrive at the result

$$(\ell^N\psi \| W^{(\kappa k)} \| \ell^N\psi')$$

$$= (-1)^y (\ell^{4\ell+2-N}\psi \| W^{(\kappa k)} \| \ell^{4\ell+2-N}\psi') + \delta(\psi,\psi')\delta(\kappa,0)\delta(k,0)\{[S][L][s][\ell]\}^{1/2}, \tag{42}$$

where $y = \kappa+k+\frac{1}{2}(v'-v)+1$. Apart from the term $\frac{1}{2}(v'-v)$ in the phase angle, Eq. (42) agrees with the corresponding equation of Racah.[2] The discrepancy is rather interesting, since a phase angle identical to y is used by Jucys and his collaborators.[37] As they point out, the difference arises because Racah defined phases for states in the second half of a shell in terms of holes rather than of particles.

A similar manipulation with $a_\xi^{(qs\ell)}$ instead of $X^{(K\kappa k)}_{0\pi q}$ leads in a straightforward way to an equation relating a reduced matrix element of $\underset{\approx}{a}^\dagger$ to one of $\underset{\approx}{a}$. Interpreting these reduced matrix elements as cfp through Eqs.(25) and (26), we immediately obtain

$$(\ell^{N-1}\psi\{|\ell^N\psi')$$

$$= (-1)^z \left\{\frac{(4\ell+2-N)[S'][L']}{(N+1)[S][L]}\right\}^{1/2} (\ell^{4\ell+1-N}\psi|\}\ell^{4\ell+2-N}\psi'), \tag{43}$$

where $z = S+S'-s+L+L'-\ell+\frac{1}{2}(v+v'+1)$. Like Eq. (42), this equation agrees with the corresponding formula of Racah to within a phase.[38]

E. The Wigner-Eckart Theorem

The most striking success of the quasi-spin formalism is the case with which the dependence of matrix elements on N, the number of equivalent electrons in a shell, can be determined. Instead of interpreting M_Q simply as a quantum number from which N can be found, we can regard it in the same way as we are accustomed to regard M_S and M_L. In complete analogy to the usual use of the Wigner-Eckart theorem, we see, for example, that the dependence on N of the matrix element

$$(\Theta Q M_Q | X^{(K\kappa k)}_{0\pi q} | \Theta' Q' M_Q')$$

is contained in the product P given by

$$P = (-1)^x \begin{pmatrix} Q & K & Q' \\ -M_Q & 0 & M_Q \end{pmatrix},$$

where $x = Q-M_Q$. Two special cases of interest immediately arise: (i) K=0, and κ+k odd; (ii) K=1, with κ+k even. In the first case, $P = \delta(Q,Q')[Q]^{-1/2}$. From Eq. (36), we deduce that all matrix elements of $W^{(\kappa k)}$ for κ+k odd are diagonal with respect to seniority and independent of N. The second case admits of two distinct possibilities: either Q'=Q or Q'=Q±1. Taking the first possibility as an example, we see, for κ+k even, that

$$\frac{(\ell^N\psi\|W^{(\kappa k)}\|\ell^N\psi')}{(\ell^v\psi\|W^{(\kappa k)}\|\ell^v\psi')} = (-1)^{\frac{1}{2}(N-v)} \frac{\begin{pmatrix} \frac{1}{2}(2\ell+1-v) & 1 & \frac{1}{2}(2\ell+1-v) \\ \frac{1}{2}(2\ell+1-N) & 0 & -\frac{1}{2}(2\ell+1-N) \end{pmatrix}}{\begin{pmatrix} \frac{1}{2}(2\ell+1-v) & 1 & \frac{1}{2}(2\ell+1-v) \\ \frac{1}{2}(2\ell+1-v) & 0 & -\frac{1}{2}(2\ell+1-v) \end{pmatrix}}$$

$$= (2\ell+1-N)/(2\ell+1-v).$$

The second possibility can be treated in an analogous fashion. These results were first obtained by Racah;[3] derivations employing annihilation and creation operators have been given by Watanabe[8] and by Lawson and Macfarlane.[9]

Two-particle operators can be handled with similar ease. We can couple the operators that appear in the equivalence (8), so that the form G takes (for a shell of equivalent electrons) is

$$-\frac{1}{2}\sum_{\kappa,k}\{(\underset{\sim}{a}^\dagger\,\underset{\sim}{a}^\dagger)^{(\kappa k)}(\underset{\sim}{a}\,\underset{\sim}{a})^{(\kappa k)}\}^{(00)}(\ell^2\kappa k|g_{12}|\ell^2\kappa k).$$

Now, $(\underset{\sim}{a}^\dagger\,\underset{\sim}{a}^\dagger)^{(\kappa k)}$ and $(\underset{\sim}{a}\,\underset{\sim}{a})^{(\kappa k)}$ are the components $\rho = +1$ and -1 respectively of $\underset{\sim}{X}^{(K\kappa k)}$. On making a detailed expansion, we find

$$\{(\underset{\sim}{a}^\dagger\,\underset{\sim}{a}^\dagger)^{(\kappa k)}(\underset{\sim}{a}\,\underset{\sim}{a})^{(\kappa k)}\}^{(00)}$$
$$= 6^{-1/2}(\underset{\sim}{X}^{(1\kappa k)}\underset{\sim}{X}^{(1\kappa k)})^{(200)}_{000} + 2^{-1/2}(\underset{\sim}{X}^{(1\kappa k)}\underset{\sim}{X}^{(1\kappa k)})^{(100)}_{000}$$
$$+ 3^{-1/2}(\underset{\sim}{X}^{(1\kappa k)}\underset{\sim}{X}^{(1\kappa k)})^{(000)}_{000}.$$

The second term in the sum can be simplified by using the basic anticommutation relations that the operators $\underset{\sim}{a}^{(qs\ell)}$ satisfy. The result is

$$(\underset{\approx}{X}^{(1\kappa k)}\underset{\approx}{X}^{(1\kappa k)})^{(100)}_{000} = -[1+(-1)^{\kappa+k}]\{2[\kappa][k]\}^{1/2}Q_z[\ell]^{-1}.$$

Since Q_z must be diagonal with respect to Q, we have the interesting result that matrix elements of scalar two-particle operators that are off-diagonal with respect to seniority are proportional to an operator of rank 2 with respect to quasi-spin. They must thus show a dependence on N contained in

$$(-1)^x \begin{pmatrix} Q & 2 & Q' \\ -M_Q & 0 & M_Q \end{pmatrix},$$

where $x = Q-M_Q$. Setting $Q = \frac{1}{2}(2\ell+1-v)$ and $Q' = \frac{1}{2}(2\ell+5-v)$, we find with the aid of Edmond's tables[18] for 3-j symbols, for example, that

$$(\ell^N\psi|G|\ell^N\psi')$$

$$= \left[\frac{(4\ell+4-v-N)(4\ell+6-v-N)(N-v+4)(N-v+2)}{32(2\ell+2-v)(2\ell+3-v)}\right]^{1/2} (\ell^v\psi|G|\ell^v\psi'),$$

where ψ and ψ' refer to states with seniorities v and $v-4$ respectively. An equivalent relation is given by de-Shalit and Talmi.[10] Their results for $\Delta v=0$ and 2 can be obtained by an analogous method. The most important example of G in atomic spectroscopy is the Coulomb interaction.

Since cfp can be regarded as the reduced matrix elements of the tensor $\underset{\approx}{a}^{(qs\ell)}$, the dependence on N of these quantities can be obtained by very similar methods. For example, if ψ and $\overline{\psi}$ refer to states with seniorities v and $v+1$ respectively,

$$\frac{(\ell^N\psi\{|\ell^{N-1}\bar{\psi})}{(\ell^{v+2}\psi\{|\ell^{v+1}\bar{\psi})}$$

$$= (-1)^{\frac{1}{2}(N-v)+1} \frac{\begin{pmatrix} \frac{1}{2}(2\ell+1-v) & \frac{1}{2} & \frac{1}{2}(2\ell-v) \\ \frac{1}{2}(2\ell+1-N) & \frac{1}{2} & -\frac{1}{2}(2\ell+2-N) \end{pmatrix}}{\begin{pmatrix} \frac{1}{2}(2\ell+1-v) & \frac{1}{2} & \frac{1}{2}(2\ell-v) \\ \frac{1}{2}(2\ell+1-v) & \frac{1}{2} & -\frac{1}{2}(2\ell-v) \end{pmatrix}} \left(\frac{v+2}{N}\right)^{\frac{1}{2}}$$

$$= [(N-v)(v+2)/2N]^{1/2},$$

in exact agreement with Eq. (58c) of Racah.[3] Two-particle cfp can be treated in an analogous fashion.

F. The Half-Filled Shell

When $N=2\ell+1$, we may readily show that C commutes with

$$\{(\underset{\sim}{a}^\dagger \underset{\sim}{a}^\dagger)^{(\kappa k)}(\underset{\sim}{a}\,\underset{\sim}{a})^{(\kappa k)}\}^{(00)},$$

the operational part of the Coulomb interaction. Hence the eigenvalues of C may be used as additional labels to distinguish the terms of $(n\ell)^{2\ell+1}$. For the half-filled shell, $M_Q=0$. Thus, from Eq. (39), the eigenvalues of C are +1 for states for which $v \equiv 2\ell+1$ (mod 4) and -1 for states for which $v \equiv 2\ell-1$ (mod 4).

From Sec. VI-E, the matrix elements of $\underset{\sim}{X}^{(K\kappa k)}$ are seen to depend on

$$\begin{pmatrix} Q & K & Q' \\ 0 & 0 & 0 \end{pmatrix}.$$

Such a 3-j symbol is zero for Q+K+Q' odd. Excluding the special case of the totally scalar operator (for which κ=k=0), it can be seen from Eq. (36) that this condition is equivalent to the condition that $\frac{1}{2}(v+v') + \kappa + k$ be odd. We thus obtain the familiar result[39] that for no change of seniority (v=v') all tensors for which κ+k is even have nul matrix elements; and that for a simple change of seniority (v-v'=±2), all tensors for which κ+k is odd have nul matrix elements. The quasi-spin approach makes this remarkable result quite transparent.

G. Complementarity

The various components of the tensor $\underset{\sim}{a}^{(qs\ell)}$ can be related by the conjugation operator C (which changes the sign of m_q) or by the time-reversal operator T (which changes the sign of m_s and m_ℓ). In view of the close parallelism between spin and quasi-spin, a third connection between the components of $\underset{\sim}{a}^{(qs\ell)}$ irresistably suggests itself. This corresponds to the interchange $m_s \leftrightarrow m_q$, and is represented formally by an operator R for which

$$R\, a_\xi^{(qs\ell)} R^{-1} = a_\eta^{(qs\ell)}, \tag{44}$$

where $\xi \equiv (m_q m_s m_\ell)$ and $\eta \equiv (m_s m_q m_\ell)$. Unlike the corresponding equation for C, no phase factor is necessary to maintain the anticommutation relations (35).

The implications of Eq. (44) are not difficult to work out. Thus, we see immediately that

$$R\, X_{\rho\pi q}^{(K\kappa k)} R^{-1} = X_{\pi\rho q}^{(\kappa K k)}.$$

When studying the effect of R on kets, it is convenient to impose the unitary condition $R^\dagger R=1$. An examination of the eigenvalues of $\underset{\sim}{X}^{(100)}$ and $\underset{\sim}{X}^{(010)}$ leads to the result

$$R|\gamma QM_Q SM_S\rangle = (-1)^t |\gamma SM_S QM_Q\rangle . \tag{45}$$

It is to be stressed that this transformation does not correspond to a mere reordering of the quantum numbers; the quasi-spin for the ket onthe right is S and the real spin is Q. For example, on setting $\gamma \equiv IM_L$, $Q=M_Q=0$, and $S=M_S=5/2$, Eq. (45) becomes

$$R|f^7\,{}^6IM_L, v=7, M_S=5/2\rangle = (-1)^t |f^2\,{}^1IM_L, v=2, M_S=0\rangle . \tag{46}$$

Since R commutes with $\underset{\sim}{X}^{(00k)}$, the phase angle t is independent of the purely orbital description γ. Operation with $X^{(100)}_{100}$ and $X^{(010)}_{010}$ reveals that t must also be independent of M_S and M_Q. Hence $t = t(S,Q)$. Further precision is impossible without a knowledge of the choice of phase made for the cfp.

The recognition of correspondences of the kind represented by Eq. (46) dates back to the work of Racah.[4] He observed that to every γ there corresponds two couples v and S which are related by the equations

$$v_1 + 2S_2 = v_2 + 2S_1 = 2\ell+1.$$

If we replace the seniority numbers by the corresponding quasi-spin quantum numbers, these equations become simply $S_2=Q_1$ and $S_1=Q_2$. In other words, if (QS) is one couple corresponding to a given γ, then the other is (SQ). This is precisely the kind of relationship represented in Eq. (45).

Just as Eq. (41) comes about by using the conjugation operator C, the use of the operator R leads to the result

$$(\gamma Q M_Q S M_S | X^{(K\kappa k)}_{\rho\pi q} | \gamma' Q' M_Q' S' M_S')$$
$$= (-1)^y (\gamma S M_S Q M_Q | X^{(\kappa K k)}_{\pi\rho q} | \gamma' S' M_S' Q' M_Q'), \tag{47}$$

where $y = y(Q,S,Q',S')$. We now set $\rho=\pi=0$ and use Eq. (36) to introduce the familiar tensors $\underset{\sim}{W}^{(\kappa k)}$. The sum $K+\kappa+k$ is taken to be odd, and the scalar $\kappa=k=0$ is excluded. We use the Wigner-Eckart theorem to separate out the dependence of the matrix elements of Eq. (47) on the magnetic quantum numbers of the real spin (M_S and M_S' on the left-hand side, M_Q and M_Q' on the right). The result is

$$\frac{(\gamma Q M_Q S \| W^{(\kappa k)} \| \gamma' Q' M_Q' S')}{(\gamma S M_S Q \| W^{(Kk)} \| \gamma' S' M_S' Q')} = (-1)^z \frac{\begin{pmatrix} Q & K & Q' \\ -M_Q & 0 & M_Q \end{pmatrix}}{\begin{pmatrix} S & \kappa & S' \\ -M_S & 0 & M_S \end{pmatrix}},$$

where $z = y+Q-M_Q-S+M_S$. We note that S, as well as representing the real spin of one state, defines the quasi-spin of another; so that we may write $Q= \frac{1}{2}(2\ell+1-v_1)$ for the first state, and $S= \frac{1}{2}(2\ell+1-v_2)$ for the second. This permits the result to be expressed in a more striking fashion:

$$\frac{(\ell^N \gamma v_1 S_1 \| W^{(\kappa k)} \| \ell^N \gamma' v_1' S_1')}{(\ell^{N'} \gamma v_2 S_2 \| W^{(Kk)} \| \ell^{N'} \gamma' v_2' S_2')}$$
$$= (-1)^z \frac{\begin{pmatrix} \frac{1}{2}(2\ell+1-v_1) & K & \frac{1}{2}(2\ell+1-v_1') \\ \frac{1}{2}(2\ell+1-N) & 0 & -\frac{1}{2}(2\ell+1-N) \end{pmatrix}}{\begin{pmatrix} \frac{1}{2}(2\ell+1-v_2) & \kappa & \frac{1}{2}(2\ell+1-v_2') \\ \frac{1}{2}(2\ell+1-N') & 0 & -\frac{1}{2}(2\ell+1-N') \end{pmatrix}},$$

where $K+\kappa+k$ is odd, and the case when $K=\kappa=0$ is excluded. An equation of precisely this form has been derived from a detailed examination of determinantal product states,[40] and subsequently used[15] to evaluate the matrix elements of the hyperfine operator $W^{(12)}$ for PuI $5f^6$ from the existing tables[27] of $U^{(2)}$ for f^5. The derivation given here avoids a great deal of tedious algebra and makes the origin of the final result more understandable.

VII. GROUPS

A. Root Figures

Lie's fundamental condition that must be satisfied if a collection of operators are to form the infinitesimal operators of a continuous group is that the commutator of any two of the operators be equivalent to some linear combination of the operators of the set. The $8\ell+4$ operators $a_\xi^\dagger$ and a_η for a shell of equivalent electrons do not fulfill this requirement. However, if we add to these the $(4\ell+2)(8\ell+3)$ distinct non-zero commutators that can be formed from the basic annihilation and creation operators, then the augmented set is closed with respect to commutation among its members. The simplest way to prove this result is to adopt the triple-tensor formalism of Sec. VI-B and use Eq. (35) repeatedly to simplify the commutators.

To find the group corresponding to the complete set of $(4\ell+2)(8\ell+5)$ operators, we first select the $4\ell+2$ operators that are given by

$$H_\xi = \frac{1}{2}[a_\xi^\dagger, a_\xi],$$

where $\xi \equiv (m_s m_\ell)$. The quantum numbers $n\ell$ that define the shell are implicit in all Greek suffixes. The operators H_ξ commute among themselves, and correspond to the abstract operators H_i of Weyl.[41] The remaining operators correspond to his E_α. The relations

$$[H_i, E_\alpha] = \alpha_i E_\alpha$$

define the covariant components α_i of the roots $\underset{\sim}{\alpha}$, which can be regarded as vectors in the weight space spanned by the H_i. For us, the weight space is $(4\ell+2)$-dimensional. We now take the operators of the set, and test the commutation with each of the H_ξ in turn. For the simple annihilation and creation operators, we find

$$[H_\xi, a_\eta^\dagger] = \delta(\xi,\eta)a_\eta^\dagger, \tag{48}$$

$$[H_\xi, a_\eta] = -\delta(\xi,\eta)a_\eta. \tag{49}$$

For the others,

$$[H_\xi,[a_\eta^\dagger,a_\nu^\dagger]] = \{\delta(\xi,\eta) + \delta(\xi,\nu)\}[a_\eta^\dagger,a_\nu^\dagger],$$

$$[H_\xi,[a_\eta^\dagger,a_\nu]] = \{\delta(\xi,\eta) - \delta(\xi,\nu)\}[a_\eta^\dagger,a_\nu],$$

$$[H_\xi,[a_\eta,a_\nu]] = \{-\delta(\xi,\eta) -\delta(\xi,\nu)\}[a_\eta,a_\nu].$$

For the weight space, the metric tensor g_{ik} is just $\Sigma_\alpha \alpha_i \alpha_k$ (see Weyl[41]). The components α_i can be immediately read off from the five commutation relations given above; the result is

$$g_{ik} = \delta(i,k)(16\ell+6).$$

The inverse tensor g^{ik} is therefore given by

$$g^{ik} = \delta(i,k)(16\ell+6)^{-1}.$$

The reason for introducing this quantity is to allow us to form scalar products of the type $\underset{\sim}{\alpha}\cdot\underset{\sim}{\beta} = \alpha_i\beta_k g^{ik}$ (summation over i and k implied). The $4\ell+2$ roots corresponding to the creation operators $a_\eta^\dagger$ can now be seen from Eq. (48) to be mutually orthogonal in as much as for any two of them $\underset{\sim}{\alpha}\cdot\underset{\sim}{\beta} = 0$. They thus form a system of $4\ell+2$ orthogonal vectors, which we write as $\underset{\sim}{e}_i$ ($i = 1,2,\ldots,4\ell+2$). If $a_\eta^\dagger$ corresponds to a certain vector $\underset{\sim}{e}_k$, then a_η corresponds to the vector $-\underset{\sim}{e}_k$, from Eq. (49). Similarly, the remaining commutation relations lead to the roots $\pm\underset{\sim}{e}_i \pm \underset{\sim}{e}_k$ ($i \neq k$, all possible combinations of sign). Now van der Waerden has shown that to every root figure there corresponds only one Lie group.[42] To find the group for our case, we have merely to refer to van der Waerden's paper (or to the lecture notes of Racah[43]) and see what group corresponds to the system $\pm\underset{\sim}{e}_i$, $\pm\underset{\sim}{e}_i\pm\underset{\sim}{e}_k$. It turns out that the group is $R_{8\ell+5}$, the rotation group in $8\ell+5$ dimensions. (In Cartan's notation,[44] it is $B_{4\ell+2}$.) This, then, is the group for which we have been searching.

B. Subgroups

Suppose that the $8\ell+4$ simple operators of the type $a_\xi^\dagger$ and a_μ are discarded from the complete set of operators for $R_{8\ell+5}$. The remaining $(8\ell+3)(4\ell+2)$ operators are commutators of the type $[a_\eta^\dagger, a_\nu^\dagger]$, $[a_\eta^\dagger, a_\nu]$, and $[a_\eta^\dagger, a_\nu]$. These also satisfy the basic condition that the commutator of any two of them, such as

$$[[a_\eta^\dagger, a_\nu^\dagger], [a_\xi^\dagger, a_\nu]],$$

can be expressed as a linear combination of the operators of the set. They therefore form the operators for a subgroup of $R_{8\ell+5}$. The operators H_ξ again play the role of Weyl's operators H_i, and the roots are all of the type $\pm e_i \pm e_k$ ($i \neq k$, all combinations of sign). As before, we turn to the work of van der Waerden or Racah, and immediately find that the subgroup is $R_{8\ell+4}$, the rotation group in $8\ell+4$ dimensions. (In Cartan's notation, it is $C_{4\ell+2}$.) To indicate that $R_{8\ell+4}$ is a subgroup of $R_{8\ell+5}$, we write $R_{8\ell+5} \supset R_{8\ell+4}$.

From Sec. VI-B, we may readily show that $a_\xi^{(qs\ell)} a_\eta^{(qs\ell)}$ can be expressed as a linear combination of the components of the triple tensors $X^{(K\kappa k)}$. The inverted product $a_\eta^{(qs\ell)} a_\xi^{(qs\ell)}$ can be similarly expressed; in fact, the vector coupling coefficients can be made identical by a simple interchange of magnetic quantum numbers. This introduces the phase $(-1)^x$, where $x = 2s+2q+2\ell - K-\kappa-k$. The commutator $[a_\xi^{(qs\ell)}, a_\eta^{(qs\ell)}]$, which includes all the operators of $R_{8\ell+4}$, can thus be expressed as a linear combination of the components of $X^{(K\kappa k)}$; but, owing to the phase factor, only those tensors occur for which $K+\kappa+k$ is odd. Since they are linearly independent, we may equally well regard these tensors as the operators for $R_{8\ell+4}$. The reason for making this change is that among the components $X_{\rho\pi q}^{(K\kappa k)}$ are all the tensors that Racah used for his celebrated analysis[4] of the configurations $(n\ell)^N$, so that we are now in a position to consider subgroups of $R_{8\ell+4}$ that can be immediately identified with Racah's groups. Before beginning, it is convenient to write down the commutator of two of our operators for reference purposes:

$$[X^{(K\kappa k)}_{\rho\pi q} \; , \; X^{(K'\kappa' k')}_{\rho'\pi' q'}]$$

$$= 2\,\Sigma\,(-1)^{K''+\kappa''+k''+\rho''+\pi''+q''}\{(-1)^{K+K'+K''+\kappa+\kappa'+\kappa''+k+k'+k''}-1\}$$

$$\times \begin{pmatrix} K & K' & K'' \\ \rho & \rho' & -\rho'' \end{pmatrix} \begin{pmatrix} \kappa & \kappa' & \kappa'' \\ \pi & \pi' & -\pi'' \end{pmatrix} \begin{pmatrix} k & k' & k'' \\ q & q' & -q'' \end{pmatrix} \tag{50}$$

$$\times \begin{Bmatrix} K & K' & K'' \\ q & q & q \end{Bmatrix} \begin{Bmatrix} \kappa & \kappa' & \kappa'' \\ s & s & s \end{Bmatrix} \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell \end{Bmatrix}$$

$$\times \{[K][K'][K''][\kappa][\kappa'][\kappa''][k][k'][k'']\}^{1/2} \; X^{(K''\kappa''k'')}_{\rho''\pi''q''} \; .$$

This result can be obtained from a straightforward application of the anti-commutation relations (35). In the first 6-j symbol, it is to be noted that q stands for the quasi-spin (and, like s, is equal to 1/2); elsewhere q refers to the projection of k.

As a preliminary step, we consider only those components $X^{(K\kappa k)}_{\rho\pi q}$ for which $\rho = 0$. On putting $\rho=\rho''=0$ in Eq. (50), we see that $\rho''=0$ for the first 3-j symbol not to vanish. Hence these components form the operators for a subgroup of $R_{8\ell+4}$. They do not shift the quasi-spin quantum number M_Q, and hence act within a single configuration. There are $(4\ell+2)^2$ of them, and they can be regarded as the operators for $U_{4\ell+2}$. We may reproduce Racah's decomposition of this group by first selecting the three components $X^{(010)}_{0\pi 0}$ and the $(2\ell+1)^2$ components $X^{(K0k)}_{00q}$. These form the operators for $SU_2 \times U_{2\ell+1}$; this direct product corresponds to the separation of the spin and orbital spaces. The components $X^{(K0k)}_{00q}$ for which K=0 are the operators for $R_{2\ell+1}$, and the three operators of this collection for which k=1 span a further subgroup, R_3. The entire decomposition runs as follows:

$$R_{8\ell+5} \supset R_{8\ell+4} \supset U_{4\ell+2} \supset SU_2 \times U_{2\ell+1}$$
$$\supset SU_2 \times R_{2\ell+1} \supset SU_2 \times R_3. \tag{51}$$

Alternatively, we may select from the components $X^{(K\kappa k)}_{0\pi q}$ those for which K=0. These form the operators for the symplectic group $Sp_{4\ell+2}$. On limiting κ to 1, we recover the operators for $SU_2 \times R_{2\ell+1}$. This alternative decomposition may be represented by replacing $SU_2 \times U_{2\ell+1}$ by $Sp_{4\ell+2}$ in the sequence (51).

The use of the tensors $\underset{\sim}{X}^{(K\kappa k)}$ considerably widens the choice of decomposition. In the first place, all the steps of the previous paragraph can be repeated with spin and quasi-spin interchanging roles. The new group-theoretical labelling of states that results from this is not of any special interest, however, since we have already introduced in Sec. VI-G the operator R to exploit this interchange. But we can carry out a different and essentially symmetrical reduction of $R_{8\ell+4}$ by limiting the operators $X^{(K\kappa k)}_{\rho\pi q}$ to $X^{(100)}_{\rho 00}$, $X^{(010)}_{0\pi 0}$, and $X^{(00k)}_{00q}$ (where k is odd). This decomposition separates the quasi-spin space, the spin space, and the orbital space at a single stroke. It is represented by

$$R_{8\ell+4} \supset SU_2 \times SU_2 \times R_{2\ell+1}.$$

Thus γ of Eq. (45) can be interpreted as $W\tau LM_L$, where W stands for an irreducible representation of $R_{2\ell+1}$. The symbol τ is an additional quantum number that must be included when two or more identical L values occur in the reduction of W.

C. Representations

Since $U_{4\ell+2}$ and its subgroups coincide with the groups used by Racah, our interest centers on the two new groups $R_{8\ell+5}$ and $R_{8\ell+4}$. The first contains as its operators all the creation operators for a shell. Since all the states of the configurations $(n\ell)^N$ $(0 \leq N \leq 4\ell+2)$ can be reproduced by some combination of creation operators acting on $|0\rangle$, it follows that this collection of states, comprising every state of the shell, can be regarded as the basis for a representation of $R_{8\ell+5}$. This representation corresponds to an ensemble of points in the weight space. To find the co-ordinates of the point corresponding to the determinantal product state $\{\alpha\beta\cdots\nu\}$, we follow the usual procedure[45] and operate with each of the operators H_ξ in turn. The eigenvalues give the required co-ordinates. We begin by writing

$$\frac{1}{2}[a_\xi^\dagger, a_\xi]\{\alpha\beta\cdots\nu\} \equiv (a_\xi^\dagger a_\xi - \frac{1}{2})a_\alpha^\dagger a_\beta^\dagger \cdots a_\nu^\dagger |0\rangle.$$

The operator a_ξ is gradually worked through the sequence of creation operators so that it can act on $|0\rangle$ and give a nul result. If ξ is not contained in the set $(\alpha\beta\cdots\nu)$, this procedure can be immediately carried out. The eigenvalue of H_ξ in this case is simply -1/2. However, if ξ is contained in the set $(\alpha\beta\cdots\nu)$, we can pass the product $a_\xi^\dagger a_\xi$ through the sequence of creation operators until it stands just to the immediate left of the operator $a_\xi^\dagger$. The equation $a_\xi^\dagger a_\xi a_\xi^\dagger = a_\xi^\dagger$ follows at once from the anticommutation relations. In this case the eigenvalue of H_ξ is 1- 1/2, that is, + 1/2. Thus every determinantal product state corresponds to a point (or weight) of the type

$$(\pm 1/2, \pm 1/2, \ldots, \pm 1/2).$$

There are $2^{4\ell+2}$ weights of this kind, one for every state of the shell. The highest weight (1/2, 1/2,...1/2) serves to label the representation. In the language of Murnaghan,[46] this representation is the simplest spin representation of $R_{8\ell+5}$; that is, the representation has the smallest dimensionality of those whose weights fall on the half-integral (rather than the integral) co-ordinates. The representation is therefore irreducible.

Under the reduction $R_{8\ell+5} \to R_{8\ell+4}$, the representation (1/2, 1/2,...,1/2) decomposes into two irreducible representations (1/2, 1/2,...,1/2,1/2) and (1/2, 1/2,...,1/2,-1/2) of $R_{8\ell+4}$. The first comprises those weights ($\pm$ 1/2, $\pm$ 1/2,...,$\pm$ 1/2) for which the number of positive signs is even; the second for which the number is odd. If the number of positive signs is even, the states corresponding to the weights must be generated from the vacuum by an even number of creation operators. In other words, the representation (1/2, 1/2,...,1/2) comprises the states of $(n\ell)^0$, $(n\ell)^2$, $(n\ell)^4$, etc.; whereas the representation (1/2, 1/2,...,1/2,-1/2) comprises the states of $(n\ell)$, $(n\ell)^3$. There is no way of connecting the two systems, since the operators for $R_{8\ell+4}$ either create a pair of electrons, annihilate a pair, or leave the number of electrons invariant.

The results of this section and of Sec. VII-A are illustrated in Fig. 7 for an s shell. The four possible states of such a shell form the representation (1/2,1/2) of R_5. This decomposes into the two representations (1/2,1/2) and (1/2,-1/2) of R_4. The former embraces the two points (1/2, 1/2) (for $|s^2\,{}^1S\rangle$) and (-1/2,-1/2) (for $|s^0\,{}^1S\rangle$); the latter the points (1/2,-1/2) and (-1/2,1/2) (for $|s, m_s = \pm 1/2\rangle$). It is clear why the representation of $R_{8\ell+5}$ spanned by the states of a shell must be as compact as it is, since the condition $a_\xi^\dagger a_\xi^\dagger = 0$ implies that two steps in the same direction in the weight space cannot lead to another point of the representation. The fact that electrons are fermions therefore plays a crucial role in determining the representation in question.

D. Concluding Remarks

It is hoped that the preceding sections have given some idea of the power of methods involving annihilation and creation operators. Not only are they useful in deriving algebraic relations between matrix elements, fractional parentage coefficients, and various coupling coefficients, but they are particularly valuable in perturbation-theory studies. The extension of the techniques of Section II to third and higher order of perturbation theory is straightforward, and the qualitative effect of a particular mechanism on the ground configuration can be immediately grasped by constructing the appropriate Feynman diagram. The applications that have been discussed in detail have been for configurations of equivalent electrons of the type $(n\ell)^N$. Mixed configurations would provide an extensive field for further developments.

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FOOTNOTES AND REFERENCES

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19. The interaction $(n\ell)^N \longleftrightarrow (n\ell)^{N-1}(n'\ell')$ discussed above is case D of the five types of configuration interaction (A,B,C,D, and E) studied by Rajnak and Wybourne. The four other cases can also be treated by methods

similar to that used above for D. In carrying this out, a number of numerical and typographical errors were found. For cases A and B, the substitution $M(t;\ell'\ell') \to M(t;\ell'\ell'')$ on pp. 284 and 285 should read $M(t;\ell'\ell') \to 2M(t;\ell'\ell'')$; and, also on p. 285, $P(kk;\ell\ell\ell'\ell') \to P(kk;\ell\ell\ell'\ell'')$ should similarly be augmented by a factor of 2 on the right. The term C(3) for case C [given in Eq. (37)] should be multiplied by 2, the factor $(-1)^k$ inserted in the summation over k, and $-N/[\ell]$ replaced by $+N/[\ell]$. The matrix element of the Coulomb interaction for case E [given in Eq. (44)] is incorrect, the radial integral multiplying $\delta(\ell,\ell')$ being properly given by $X(k;\ell'\ell'\ell'\ell)$ rather than $X(k';\ell\ell\ell\ell')$. These functions are distinct even when $k=k'$ and $\ell=\ell'$, since the principal quantum numbers n and n' associated with ℓ and ℓ' are implicit and necessarily different. A factor $\{1-2[\ell]\delta(k,0)\}$ should also multiply $X(k;\ell'\ell'\ell'\ell)$. Consequently Eq. (46), which depends on this term, is incorrect. Two minor errors also occur in Eq. (45): the term $-N/[\ell]$ should be $+N/[\ell]$, and $P(kk';\ell\ell\ell\ell')$ must be replaced by $P(kk;\ell\ell\ell\ell')$. The qualitative statements made in the last paragraph of Sec. III-E nevertheless still hold. The error in $X(k;\ell'\ell'\ell'\ell)$ vitiates the result of Sec. II-3 of a subsequent paper by Rajnak and Wybourne [J. Chem. Phys. 41, 565 (1964)].

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Figure Captions

Fig. 1. Feynman graphs corresponding to $a_\xi^\dagger a_\eta^\dagger a_\lambda b_\zeta$ and $b_\alpha^\dagger a_\beta^\dagger a_\epsilon a_\gamma$.

Fig. 2. Graphs corresponding to the two terms of expression (15) in the text.

Fig. 3. Angular-momentum diagram corresponding to expression (18) in the text. The signs against the vertices carry phase information.

Fig. 4. Angular-momentum diagram for the product of two pairs of 3-j symbols.

Fig. 5. Angular-momentum diagram corresponding to expression (19) in the text.

Fig. 6. The result of contracting the diagram of Fig. 4 with that of Fig. 5.

Fig. 7. The representation (1/2,1/2) of R_5 superposed on the root figure. The roots connect the weights of the representation; the subscripts α and β are contractions for $m_s = 1/2$ and $m_s = -1/2$ respectively. For example, the operator $a_\alpha^\dagger$ acting on $|s^0\,{}^1S\rangle$ connects the point (-1/2,-1/2) to (1/2,-1/2), corresponding to the ket $|s, m_s = 1/2\rangle$.

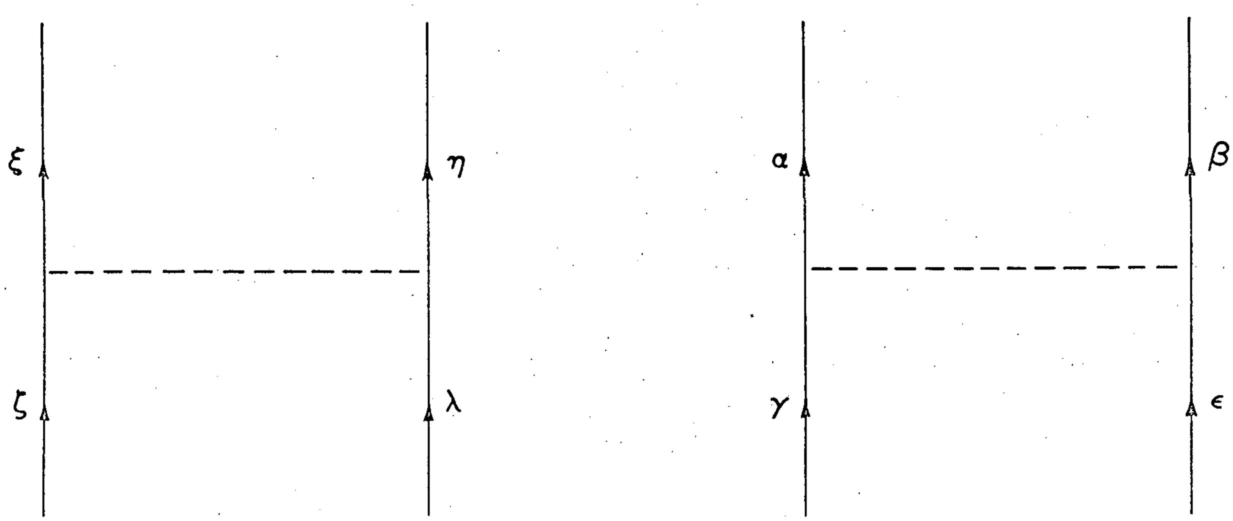

Fig. 1

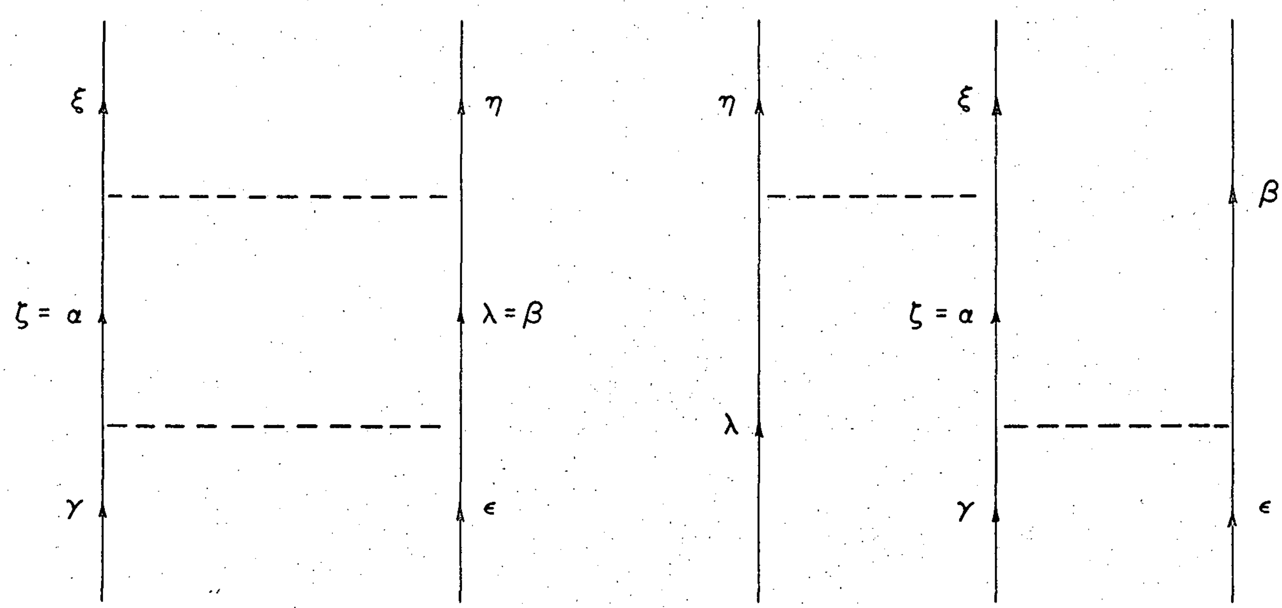

Fig. 2

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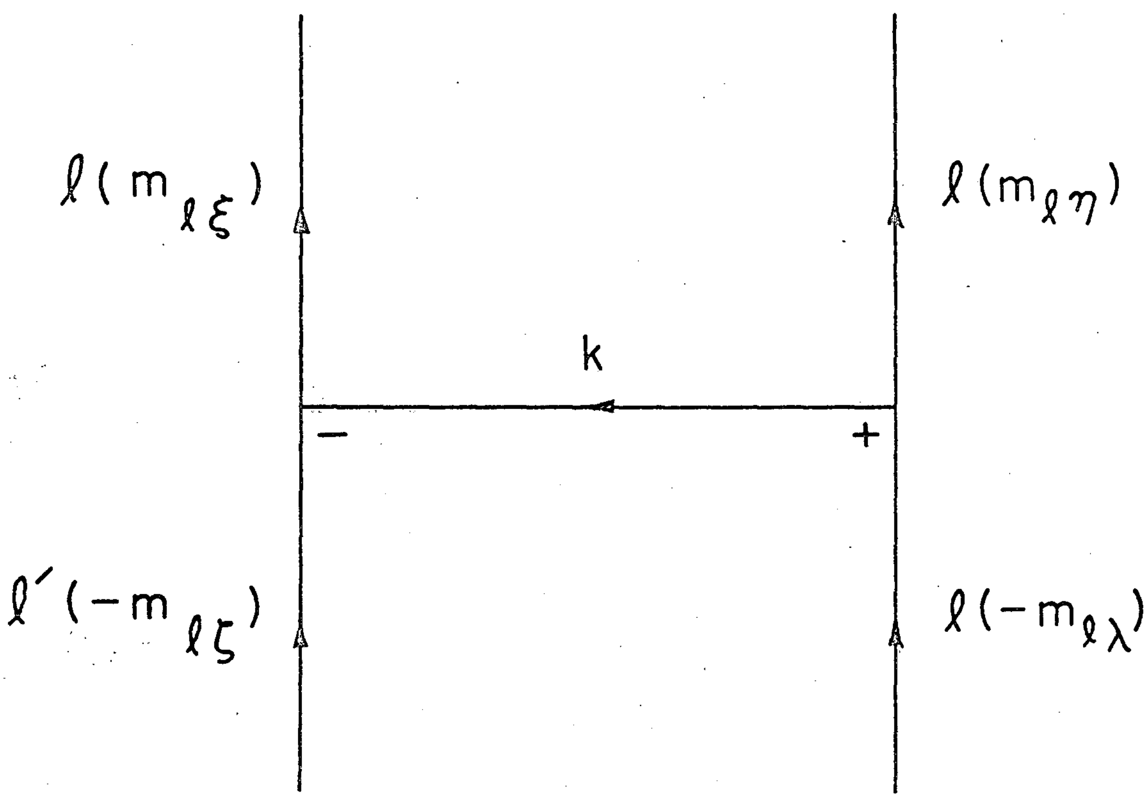

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Fig. 3

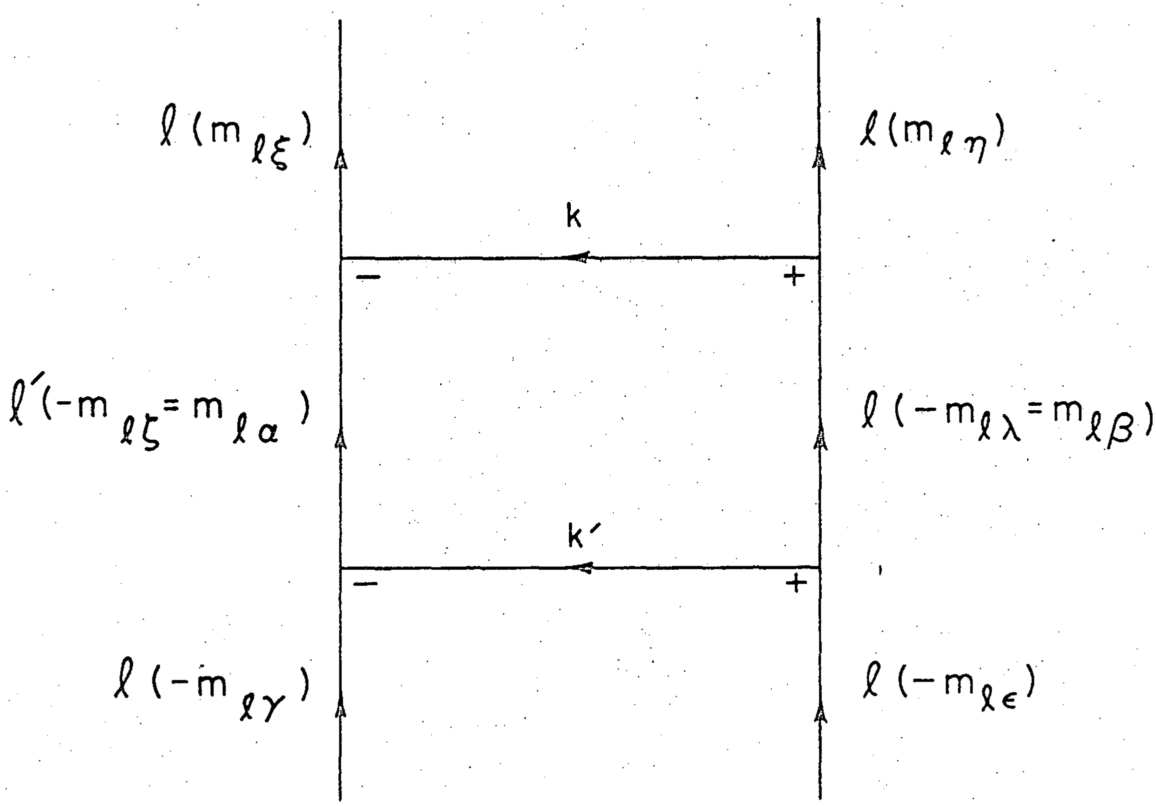

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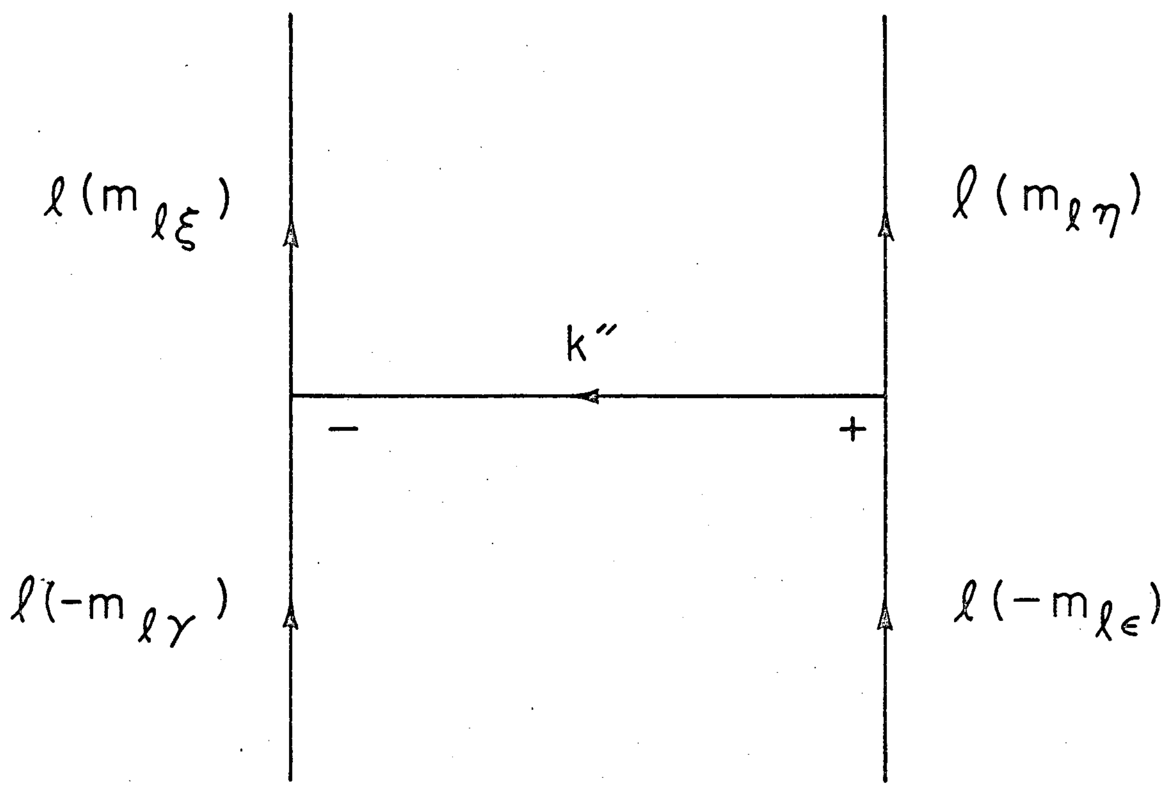
Fig. 4



MUB-6223

Fig. 5

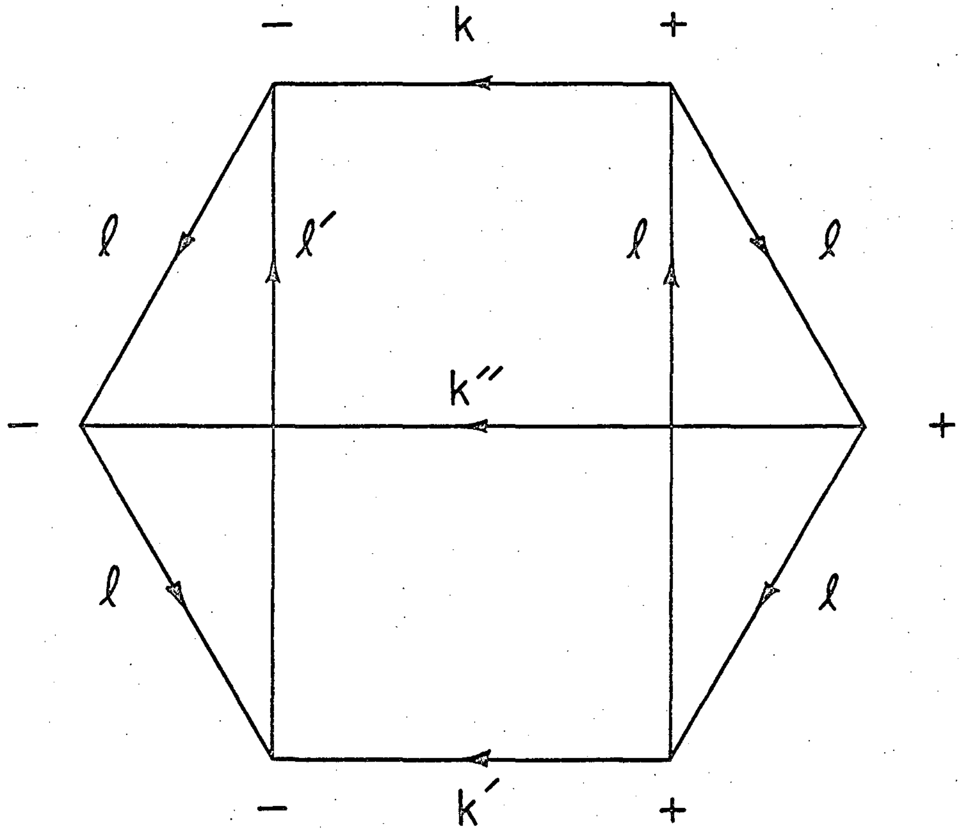


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Fig. 6

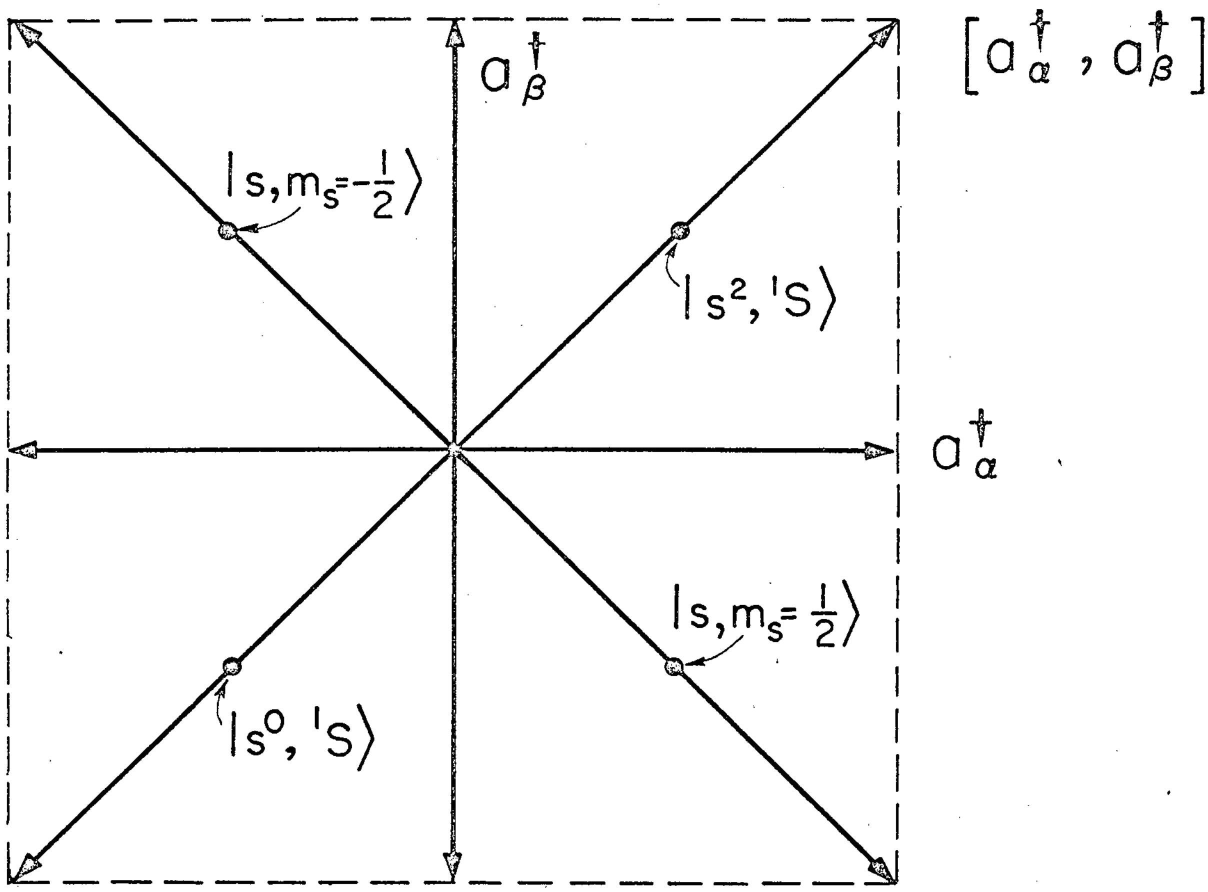

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Fig. 7