Configuration Interaction Effects in l^N Configurations*

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The effects of configuration interactions on the energy-level structure of l^N type configurations have been studied. In previous work the linear theory has sought to augment the usual Hamiltonian for an N-electron system with additional two-body scalar interactions. In the present study it is shown that by choosing suitable scalar interactions it is possible to include, to second order, all the electrostatic interactions with configurations having two electrons excited from the l^N configuration. The form of the scalar interactions, together with expressions for the interaction constants in terms of the radial integrals, has been derived explicitly using perturbation theory. Effective three-body interactions are introduced to account for the perturbations due to one-electron excitations. The physical significance of the interaction constants associated with the linear theory is clarified. Formulas are given for the matrix elements of the electrostatic interaction between the l^N configuration and the different species of perturbing configurations. An identity which greatly simplifies the summations arising from the second-order perturbation is established.

I. INTRODUCTION

THE theoretical understanding of complex spectra commenced with the classical paper of Slater.[1] In this paper he presented a method for calculating the electrostatic energies of the LS terms of electron configurations, expressing them as a linear function of a few radial integrals, usually considerably fewer than the number of terms of the configuration. The calculation of the energy levels of atoms and ions was further improved by Condon's[2] suggestion of including the effects of spin-orbit interactions. With the development of the powerful techniques of tensorial operators by Racah,[3–6] it became possible to calculate the complete electrostatic and spin-orbit interaction energy matrices of virtually any electron configuration.

It soon became evident that the diagonalization of the combined electrostatic and spin-orbit interaction energy matrices for a particular electron configuration yielded energy levels that deviated by several hundred to a thousand wave numbers from the observed energy levels, even when the radial integrals were treated as freely variable parameters.[7–13] These deviations were usually ascribed to the effects of configuration interaction. We may somewhat arbitrarily divide configuration interactions into two classes: (1) Strong configuration interactions where the perturbing configurations are energetically close to the perturbed configuration, and there is strong coupling of the configurations via the Coulomb field. (2) Weak configuration interactions where the perturbing configurations are well separated from the perturbed configuration, and the coupling of the configurations in the Coulomb field is weak. Where the configuration interaction is strong it becomes necessary to diagonalize energy matrices which include all the electrostatic interactions *within* and *between* the connected configurations. Clearly for complex configurations this method entails the construction of very large matrices and a substantial increase in the number of radial integrals to be determined.

Even when the strong interactions have been included there remain the perturbations produced by all the weakly interacting configurations. While individually their effects may be small, their cumulative influence may be considerable, due to the increasing density of states as the continuum is approached. It would be an impossible and physically meaningless task to construct individual matrix elements for each of these interactions. Rather, we should direct our attention towards modifying the energy matrices of the principal electron configuration in such a way as to include the greater part of the combined effects of *all* the weakly perturbing configurations. This approach has the advantage of requiring no increase in the dimensions of the energy matrices and relatively few additional interaction constants.

In recent years, considerable attention has been given to the so called "*linear*" theory of configuration interaction following the observation of Bacher and Goud-

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smit[14] that most configuration interactions which are second-order effects may be added linearly. In the linear theory the Hamiltonian of the N-electron system has been augmented with additional two-body *scalar* interaction terms.[14–21] Associated with each interaction is an adjustable constant which has been determined from the experimental data. In general, the number of additional interactions has been chosen so that the total number of adjustable parameters equals the number of allowed LS terms occurring in all distinct two-electron configurations formed by deleting $N-2$ of the electrons from the configuration under study.

While the linear theory has had some measure of success, the agreement with the observed energy levels has not been as good as would be desirable. There has been considerable confusion as to the physical significance of the additional two-body interactions and to the validity of the method.

In the present paper, a detailed study of the effects of configuration interactions on the energy levels of configurations of the type l^N is made. It is shown that both two- and three-body interactions must be considered and that the linear theory alone is insufficient. The physical significance of the effects of configuration interaction is clarified. Particular attention has been given to the treatment of configuration interactions in systems containing f^N configurations.

II. THE SECOND-ORDER THEORY OF CONFIGURATION INTERACTION

For the doubly and triply ionized lanthanides, the $4f^N$ configuration is generally isolated from the nearest interacting configurations by many thousands of wavenumbers.[22] The deviations between the calculated and experimentally determined energy levels are appreciable, though still quite small when expressed as a percentage of the width of the $4f^N$ configuration. Thus, it would appear justifiable to consider configuration interaction in the doubly and triply ionized lanthanides as weak and to treat its effects by second-order perturbation theory. The analogous doubly and higher ionized actinides can undoubtedly be likewise treated. On the other hand, in the lower stages of ionization the spacings of the interacting configurations will be quite small, giving rise to strong interactions that must be treated by construction of energy matrices containing complete expressions for the lowest energy configurations, and with the effects of the higher perturbing configurations given by second-order perturbation theory. At present we shall discuss only the case of weak interactions.

For generality we shall consider the effect of second-order configuration interaction perturbations on some configuration l^N. Let two particular states, $|\alpha SL\rangle$ and $|\alpha' SL\rangle$, of l^N be designated by $|\psi\rangle$ and $|\psi'\rangle$ and consider a perturbing state, $|m\rangle$, from a particular interacting configuration (i.e., one having the same parity and whose individual electron quantum numbers differ for not more than two electrons). If $|m\rangle$ lies above the center of gravity of l^N by an energy ΔE_m, the electrostatic matrix element $(l^N\psi|G|l^N\psi')$ is subject to the correction

$$C_m=-\frac{\langle\psi|G|m\rangle\langle m|G|\psi'\rangle}{\Delta E_m}, \tag{1}$$

where G is the operator representing the Coulomb energy of repulsion between electrons $\sum_{i<j} e^2/r_{ij}$. In general, there will be several perturbing states and the total second-order correction to $(l^N\psi|G|l^N\psi')$ for the effects produced by this particular perturbing configuration will be given by

$$C=-\sum_m \frac{\langle\psi|G|m\rangle\langle m|G|\psi'\rangle}{\Delta E_m}. \tag{2}$$

The summation in (2) is severely restricted since the matrix elements of the Coulomb interaction are diagonal in L and S. Nevertheless, for the complex configurations we shall be considering, there may be several perturbing states having the same L and S, and it is desirable to simplify the summation as much as possible. In most of the cases we shall be considering, the separation ΔE_m of the interacting terms is quite large and it becomes a reasonable approximation to assume the perturbing states degenerate. Within this approximation Eq. (2) may be written as

$$C=\frac{-1}{\Delta E_c}\sum_m\langle\psi|G|m\rangle\langle m|G|\psi'\rangle, \tag{3}$$

where ΔE_c is the average energy separation of the l^N configuration and the particular perturbing configuration. The placing of the energy denominator in Eq. (2) outside the summation over m, as in Eq. (3), makes it possible to search for explicit expressions for the sum over the perturbing states $|m\rangle$. Our task conveniently divides into two distinct steps: (i) Expressions must be obtained that will permit the evaluation of the matrix elements of the configuration interactions. (ii) Using these expressions in their simplest possible form, perform the sum over m in Eq. (3).

The basic techniques for performing step (i) have been outlined in an earlier paper.[23] Before commencing to derive the explicit formulas of step (ii) we must

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consider what possible configurations may interact with a configuration l^N. There are only five basic types of interacting configurations that can modify the energy level structure of the l^N configuration:

(a) $l^{N-2}l'^2$ and $l^{N-2}l'l''$,

(b) $l'^{4l'}l^{N+2}$ and $l'^{4l'+1}l''^{4l''+1}l^{N+2}$,

(c) $l'^{4l'+1}l^Nl''$,

(d) $l^{N-1}l'$,

(e) $l'^{4l'+1}l^{N+1}$.

The interactions (b), (c), and (e) are core excitations where an electron is promoted from a closed shell to either an unfilled shell or to the partially filled l^N shell. The two-electron core excitations which involve the excitation of not more than one core electron into the l^N shell produce effects that are indifferent to the energy level structure of the l^N configuration and, at the most, give rise to a shift of the center of gravity of the entire configuration. As a result, we shall exclude them from our discussion.

In obtaining expressions for the correction C, we want to express our result as a sum of products of two factors. The first factor is to depend only on radial integrals, ΔE_c, and one-electron quantum numbers. This factor will, of course, vary with different perturbing configurations. The second factor represents the angular dependence of the second-order effects produced in the l^N configuration by the perturbing configuration and is a function of only the angular momenta of the states of the l^N configuration. We shall enumerate those few distinct angular factors that arise from second-order perturbations and that, therefore, represent the influence of all weakly interacting configurations upon the energy level structure of the l^N configuration.

In performing the summations it is convenient to define four quantities:

$$X(k;l_al_b,l_cl_d)\equiv(l_a\|\mathbf{C}^{(k)}\|l_c)(l_b\|\mathbf{C}^{(k)}\|l_d)R^k(l_al_b,l_cl_d), \quad (4)$$

$$P(kk';l_al_b,l_cl_d)\equiv X(k;l_al_b,l_cl_d)X(k';l_al_b,l_cl_d)/\Delta E_c, \quad (5)$$

$$M(t;l_cl_d)\equiv\sum_{kk'}\begin{Bmatrix}k & k' & t\\ l_a & l_b & l_c\end{Bmatrix}\begin{Bmatrix}k & k' & t\\ l_a & l_b & l_d\end{Bmatrix}P(kk';l_al_b,l_cl_d), \quad (6)$$

and

$$M(t)\equiv M(t;l_cl_d)[t]/(l\|\mathbf{C}^{(t)}\|l)^2, \quad (7)$$

which depend only on the radial integrals, ΔE_c, and functions of the one-electron quantum numbers.

III. CLOSED FORMULAS FOR CONFIGURATION INTERACTIONS

A. l^N with $l^{N-2}l'^2$ or $l^{N-2}l'l''$

We shall consider the interaction of states of the configuration $l^{N-2}l'^2$ with a particular state ψ of the l^N configuration as illustrative of the general method of obtaining closed formulas for the summations of Eq. (3).

Using a result due to Racah[5] [his Eq. (33c)], we may write a typical matrix element as

$$\left(l^N\psi\left|e^2\sum_k\frac{r_<^k}{r_>^{k+1}}\sum_{i<j}(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)})\right|l^{N-2}\tilde{\psi},l'^2\sigma\lambda;SL\right)$$
$$=\left[\frac{N(N-1)}{2}\right]^{1/2}(l^N\psi\{|l^{N-2}\tilde{\psi},l'^2\sigma\lambda;SL)$$
$$\times\left(l'^2\sigma\lambda\left|e^2\sum_k\frac{r_<^k}{r_>^{k+1}}(\mathbf{C}_N^{(k)}\cdot\mathbf{C}_{N-1}^{(k)})\right|l'^2\sigma\lambda\right), \quad (8)$$

where σ and λ are the total spin and orbital quantum numbers of the states of l'^2, and $\tilde{\psi}$ stands for the quantum numbers defining a particular state of l^{N-2}.

The two-electron matrix elements may be readily evaluated[24] to yield

$$\left(l^2\sigma\lambda\left|e^2\sum_k\frac{r_<^k}{r_>^{k+1}}(\mathbf{C}_N^{(k)}\cdot\mathbf{C}_{N-1}^{(k)})\right|l'^2\sigma\lambda\right)$$
$$=(-1)^{l+l'+\lambda}\sum_k\begin{Bmatrix}l & l & \lambda\\ l' & l' & k\end{Bmatrix}X(k;lll'l'). \quad (9)$$

Inserting (9) in (8) we obtain the right-hand side of Eq. (8) as

$$\left[\frac{N(N-1)}{2}\right]^{1/2}(l^N\psi\{|l^{N-2}\tilde{\psi},l^2\sigma\lambda;SL)(-1)^{l+l'+\lambda}$$
$$\times\sum_k\begin{Bmatrix}l & l & \lambda\\ l' & l' & k\end{Bmatrix}X(k;lll'l'). \quad (10)$$

Thus, for this particular configuration interaction, Eq. (3) becomes

$$C=-\frac{N(N-1)}{2}\sum_{\tilde{\psi},\sigma,\lambda}(l^N\psi\{|l^{N-2}\tilde{\psi},l^2\sigma\lambda;SL)$$
$$\times(l^{N-2}\tilde{\psi},l^2\sigma\lambda;SL|\}l^N\psi')\sum_{kk'}\begin{Bmatrix}l & l & \lambda\\ l' & l' & k\end{Bmatrix}$$
$$\times\begin{Bmatrix}l & l & \lambda\\ l' & l' & k'\end{Bmatrix}P(kk';lll'l'). \quad (11)$$

Using the Biedenharn-Elliott sum rule[24] we obtain

$$C=-\frac{N(N-1)}{2}\sum_{\tilde{\psi},\sigma,\lambda}(l^N\psi\{|l^{N-2}\tilde{\psi},l^2\sigma\lambda;SL)$$
$$\times(l^{N-2}\tilde{\psi},l^2\sigma\lambda;SL|\}l^N\psi')\sum_t[t](-1)^{t+\lambda}$$
$$\times\begin{Bmatrix}l & l & t\\ l & l & \lambda\end{Bmatrix}M(t;l'l'), \quad (12)$$

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where λ now appears in only one 6-j symbol and the symbol $[t]\equiv 2t+1$ has been introduced. The sum over the products of the two-particle coefficients of fractional parentage (c.f.p.) may be evaluated by noting that[5]

$$(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi')$$
$$=\frac{N(N-1)}{2}\sum_{\tilde{\psi},\sigma,\lambda}(l^N\psi\{|l^{N-2}\tilde{\psi},l^2\sigma\lambda;SL)$$
$$\times(l^{N-2}\tilde{\psi},l^2\sigma\lambda;SL|\}l^N\psi')(-1)^\lambda\begin{Bmatrix}\lambda & l & l\\ t & l & l\end{Bmatrix}. \quad (13)$$

Using this result Eq. (12) may be written as

$$C=-\sum_t(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi')$$
$$\times(-1)^t[t]M(t;l'l'). \quad (14)$$

The expression $(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi')$ appearing in Eq. (14) will contain terms even and odd in t. We consider first the even terms.

The coefficients f_t of the Slater integrals F^t appearing in the electrostatic energy matrices of the l^N configuration are given by

$$f_t=(l^N\psi|\sum_{i<j}(\mathbf{C}_i^{(t)}\cdot\mathbf{C}_j^{(t)})|l^N\psi')$$
$$=(l\|\mathbf{C}^{(t)}\|l)^2(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi') \quad (15)$$

and, hence, for t even, Eq. (14) may be written as

$$C_{t_{\text{even}}}=-\sum_{t_{\text{even}}}M(t)f_t. \quad (16)$$

Thus, the corrections to the matrix elements of l^N arising from terms in even t are proportional to the coefficients of the Slater radial integrals F^t.

We now consider the terms odd in t. Limiting ourselves to f electrons ($l=3$) we may write[6]

$$(f^N\psi|\sum_{i<j}(\mathbf{U}_i^{(1)}\cdot\mathbf{U}_j^{(1)})|f^N\psi')$$
$$=\delta(\psi,\psi')\left[\frac{L(L+1)}{12}-N\right]\Big/14, \quad (17a)$$

$$(f^N\psi|\sum_{i<j}(\mathbf{U}_i^{(3)}\cdot\mathbf{U}_j^{(3)})|f^N\psi')$$
$$=\delta(\psi,\psi')[5G(R_7)-4G(G_2)-N]/14, \quad (17b)$$

and

$$(f^N\psi|\sum_{i<j}(\mathbf{U}_i^{(5)}\cdot\mathbf{U}_j^{(5)})|f^N\psi')$$
$$=\delta(\psi,\psi')\left[\frac{28G(G_2)}{11}-\frac{L(L+1)}{44}-N\right]\Big/14, \quad (17c)$$

where $G(R_7)$ and $G(G_2)$ are the eigenvalues of Casimir's operators for the groups R_7 and G_2, respectively. These eigenvalues are given by

$$((u_1u_2)|G(G_2)|(u_1u_2))$$
$$=\tfrac{1}{12}[u_1^2+u_1u_2+u_2^2+5u_1+4u_2] \quad (18a)$$

and

$$((w_1w_2w_3)|G(R_7)|(w_1w_2w_3))$$
$$=\tfrac{1}{10}[w_1(w_1+5)+w_2(w_2+3)+w_3(w_3+1)], \quad (18b)$$

where (u_1u_2) and $(w_1w_2w_3)$ are the integers used by Racah[6] to label the irreducible representations of the group G_2 and R_7, which in turn were used to classify the states ψ of the f^N configuration.

Inserting the results of Eq. (17) into Eq. (14) and adding the resultant to Eq. (16) we obtain the total correction to the matrix elements $(\psi|G|\psi')$ of the f^N configuration perturbed by all the interacting states of the $f^{N-2}l'^2$ configuration as

$$C=-\sum_{t_{\text{even}}}M(t)f_t+\delta(\psi,\psi')[\alpha L(L+1)$$
$$+\beta G(G_2)+\gamma G(R_7)+\delta], \quad (19)$$

where

$$\alpha=[M(1;l'l')-M(5;l'l')]/56,$$
$$\beta=2[M(5;l'l')-M(3;l'l')],$$
$$\gamma=\tfrac{5}{2}M(3;l'l'),$$

and

$$\delta=-N[3M(1;l'l')+7M(3;l'l')+11M(5;l'l')]/14.$$

δ has the effect of shifting all the terms of the f^N configuration by a constant amount, as does the $t=0$ term in the summation. Where our interest is restricted to the *relative* shift of terms within the f^N configuration we may write the correction as

$$C'=-\sum_t M(t)f_t+\delta(\psi,\psi')[\alpha L(L+1)$$
$$+\beta G(G_2)+\gamma G(R_7)], \quad (20)$$

where t assumes the values 2, 4, and 6.

For p^N configurations ($l=1$), Eq. (20) has the form

$$C'=-M(2)f_2+\alpha' L(L+1), \quad (21)$$

where $\alpha'=\frac{1}{2}M(1;l'l')$.

For d^N configurations ($l=2$), we obtain

$$C'=-[M(2)f_2+M(4)f_4]$$
$$+\delta(\psi,\psi')[\alpha''L(L+1)+\beta''G(R_5)], \quad (22)$$

where

$$\alpha''=\tfrac{1}{10}[M(1;l'l')-M(3;l'l')] \quad \text{and} \quad \beta''=3M(3;l'l').$$

$G(R_5)$ is the eigenvalue of Casimir's operator for the group R_5 and is readily evaluated using Eqs. (18) and (19) of Racah[6] to give

$$G(R_5)=\tfrac{1}{3}[\tfrac{1}{4}N(12-N)-Q-S(S+1)],$$

where Q is the seniority operator.

For the particular case of a configuration l^N interacting with a configuration $l^{N-2}s^2$, the correction to $(\psi|G|\psi')$ of l^N is given by

$$C=-Q(N,v)(G^1(l,0)/[l])^2\delta(\psi,\psi'), \tag{23}$$

where

$$Q(N,v)=\tfrac{1}{4}(N-v)(4l+4-N-v) \tag{24}$$

and v is the seniority number[5] of the state ψ of l^N.

In a similar manner it can be shown that the corrections to the matrix elements $(\psi|G|\psi')$ of l^N produced by interaction with the states of a configuration $l^{N-2}l'l''$ are identical to those of Eq. (14) if we make the substitution $M(t;l'l') \rightarrow M(t;l'l'')$.

B. l^N with $l'^{4l'}l^{N+2}$ and $l'^{4l'+1}l''^{4l''+1}l^{N+2}$

These types of configuration interactions correspond to "core excitations" where two electrons may be regarded as being promoted from closed shells into the partially filled l^N shell. The basic matrix element coupling a state of l^N with a state of $l'^{4l'}l^{N+2}$ may be written as

$$\left(l^N\gamma SLl'^{4l'+2}\,{}^1S;SL\left|e^2\sum_k\frac{r_<^k}{r_>^{k+1}}\sum_{i<j}(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)})\right|\right.$$
$$\left.\times l^{N+2}\gamma''S''L''l'^{4l'}\sigma\lambda;SL\right)$$
$$=\left[\frac{(N+2)(N+1)[S''][L'']}{2[S][L]}\right]^{1/2}(l^N\gamma SLl^2\sigma\lambda;S''L''|\}$$
$$\times l^{N+2}\gamma''S''L'')(-1)^{L+L''+S''-S+\lambda}$$
$$\times\sum_k\begin{Bmatrix}\lambda & l & l\\ k & l' & l'\end{Bmatrix}X(k;lll'l'). \tag{25}$$

The correction to the matrix element $(\psi|G|\psi')$ of l^N due to this interaction is then

$$C=-\frac{(N+2)(N+1)}{2}\sum_{\psi'',\sigma,\lambda}\frac{[S''][L'']}{[S][L]}$$
$$\times(l^N\psi l^2\sigma\lambda;S''L''|\}l^{N+2}\psi'')$$
$$\times(l^{N+2}\psi''\{|l^N\psi'l^2\sigma\lambda;S''L'')$$
$$\times\sum_{kk'}\begin{Bmatrix}\lambda & l & l\\ k & l' & l'\end{Bmatrix}\begin{Bmatrix}\lambda & l & l\\ k' & l' & l'\end{Bmatrix}P(kk';lll'l'). \tag{26}$$

The 2-particle c.f.p. may be evaluated using Eq. (32) of Racah[5] and then the Biedenharn-Elliott sum rule applied to those 6-j symbols involving L and to perform the sums over σ and λ to give

$$C=-\frac{(N+2)(N+1)}{2}\sum_{\psi',\bar{\psi},\bar{\psi}'}\delta(\bar{S},\bar{S}')\frac{[S''][L'']}{[S][L]}$$
$$\times([\bar{L}][\bar{L}'])^{1/2}(-1)^{L+L''+\bar{L}+\bar{L}'}(l^N\psi|\}l^{N+1}\bar{\psi})$$
$$\times(l^{N+1}\bar{\psi}'\{|l^N\psi')(l^{N+2}\psi''\{|l^{N+1}\bar{\psi})(l^{N+1}\bar{\psi}'|\}l^{N+2}\psi'')$$
$$\times\sum_t\begin{Bmatrix}\bar{L} & \bar{L}' & t\\ l & l & L\end{Bmatrix}\begin{Bmatrix}\bar{L} & \bar{L}' & t\\ l & l & L''\end{Bmatrix}[t]M(t;l'l'). \tag{27}$$

With Eq. (27) in this form the summation over the connected states $l^{N+2}\psi''$ cannot be carried out explicitly. However, if we note Eq. (19) of Racah,[5]

$$(l^N\psi l;S'L'|\}l^{N+1}\psi')=\left[\frac{(4l+2-N)[S][L]}{(N+1)[S'][L']}\right]^{1/2}$$
$$\times(-1)^{L+L'+l+s-S-S'}(l^{4l+1-N}\psi'l;SL|\}l^{4l+2-N}\psi), \tag{28}$$

we may convert the c.f.p. involving $(l^{N+1}|\}l^{N+2})$ to those involving their conjugate states in terms of which the sum over ψ' may be carried out explicitly. States of l^N or l^{N+1} may then be recovered using the relation

$$(l^N\psi'\|\mathbf{U}^{(k)}\|l^N\psi)$$
$$=(-1)^{k+1}(l^{4l+2-N}\psi'\|\mathbf{U}^{(k)}\|l^{4l+2-N}\psi), \tag{29}$$

which holds for $k>0$. Using Eqs. (28) and (29), Eq. (27) becomes

$$C=-\frac{(N+1)}{2}\sum_{\bar{\psi},\bar{\psi}'}\frac{[\bar{S}]}{[S][L]}([\bar{L}][\bar{L}'])^{1/2}(-1)^{L+\bar{L}+l+1}$$
$$\times(l^N\psi|\}l^{N+1}\bar{\psi})(l^{N+1}\bar{\psi}'\{|l^N\psi')\sum_{t>0}(l^{N+1}\bar{\psi}\|\mathbf{U}^{(t)}\|l^{N+1}\bar{\psi}')$$
$$\times[t]\begin{Bmatrix}t & l & l\\ L & \bar{L} & \bar{L}'\end{Bmatrix}M(t;l'l'). \tag{30}$$

The $t=0$ term gives an additional correction

$$C_0=-\frac{(4l+1-N)(4l+2-N)}{2[l]^2}$$
$$\times\sum_k\frac{P(kk;lll'l')}{[k]}\delta(\psi,\psi'), \tag{31}$$

which contributes a linear shift to all the terms of l^N.

The identity, Eq. (49), derived in the Appendix can now be used to convert the matrix element in Eq. (30) involving states of l^{N+1} to one involving states of l^N. By converting to conjugate states, summing over $\bar{\psi}$, and reconverting to states of l^N we may make use of the closure property[4] to obtain for Eq. (30) the result

$$C=-\sum_{t>0}\left[(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi')\right.$$
$$\left.-\frac{(2l+1-N)}{[l]}\delta(\psi,\psi')\right](-1)^t[t]M(t;l'l'), \tag{32}$$

which is essentially identical to Eq. (14). Thus, as in case (A), the terms even in t will "screen" the Slater F^t integrals, while for $l=3$ the terms odd in t may be written in the form

$$\alpha L(L+1)+\beta G(G_2)+\gamma G(R_7)+\delta.$$

The correction for the effects produced by interactions with the $l'^{4l'+1}l''^{4l''+1}l^{N+2}$ configuration are identical to those of Eqs. (31) and (32) if the substitutions $P(kk;ll'l')\rightarrow P(kk;ll'l'')$ and $M(t,l'l')\rightarrow M(t\,l'l'')$ are made.

C. l^N with $l'^{4l'+1}l^Nl''$

This is another "core excitation" and corresponds to the excitation of an electron l' from the closed $l'^{4l'+2}$ shell into some empty l'' shell. A typical matrix element coupling a state of l^N with $l^Nl'^{4l'+1}l''$ is given by

$$\left(l^N\gamma''S''L''[l'^{4l'+1}l'']\sigma t;SL\left|e^2\sum_k\frac{r_<^k}{r_>^{k+1}}\sum_{i<j}(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)})\right|l^N\gamma SLl'^{4l'+2}\,{}^1S;SL\right)$$

$$=\delta(k,t)\delta(\sigma,0)\left[\frac{[s]}{[L][t]}\right]^{1/2}(l^N\psi\|\mathbf{U}^{(t)}\|l^N\psi'')X(t;l''ll'l)+N\sum_{\bar\psi}(l^N\psi\{|l^{N-1}\bar\psi)(l^{N-1}\bar\psi|\}l^N\psi'')$$

$$\times([L'][S'][\sigma][t])^{1/2}\begin{Bmatrix}L&L''&t\\l&l&\bar L\end{Bmatrix}\begin{Bmatrix}S&S''&\sigma\\s&s&\bar S\end{Bmatrix}\sum_k(-1)^\gamma\begin{Bmatrix}l'&l''&t\\l&l&k\end{Bmatrix}X(k;ll''l'l),\quad(33)$$

where $\gamma=L+S+\bar L+\bar S+l+s+k+t+1$. The sum over $\bar\psi$ in the second term may be written as a matrix element of a double tensor $\mathbf{W}^{\sigma t}$ as defined by Judd,[25] $(l^N\psi\|\mathbf{W}^{(\sigma t)}\|l^N\psi'')$. However, the form given in Eq. (33) is more convenient for the present calculations.

If we let

$$X^t=\text{coefficient of } X(t;l''ll'l),\quad Y^k=\text{coefficient of } X(k;ll''l'l),\quad\text{and}\quad M(k,t)=X(t;l''ll'l)X(k;ll''l'l)/\Delta E_c,$$

we may write the total correction to the matrix elements $(\psi|G|\psi')$ due to perturbations by the states of $l^Nl'^{4l'+1}l''$ in the form

$$C=-\sum_{\psi'',\sigma,k,k',t}[X^tX^tP(tt;l''ll'l)+Y^kY^{k'}P(kk';ll''l'l)+2X^tY^kM(k,t)].\quad(34)$$

Using the closure property to sum over ψ'', the first term in Eq. (34) becomes

$$C(1)=-\sum_t\left[2(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi')+\frac{N}{[l]}\delta(\psi,\psi')\right]\frac{[s]}{[t]}P(tt;l''ll'l),\quad(35)$$

where t is restricted to even values only.

To carry out the summation for the second term of Eq. (34), we first sum over σ and t and then convert to conjugate states to sum over ψ''. Upon application of the identity Eq. (49) the summation reduces to

$$C(2)=\sum_{x>0}[(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(x)}\cdot\mathbf{U}_j^{(x)})|l^N\psi')]2M(x;l'l'')-\frac{N(4l+3-N)}{[l]^2}\sum_k P(kk;ll''l'l)\delta(\psi,\psi')/[k],\quad(36)$$

where x may assume even and odd values.

The third term in Eq. (34) may be readily evaluated to yield

$$C(3)=\sum_t\left[2(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi')-\frac{N}{[l]}\delta(\psi,\psi')\right]\sum_k\begin{Bmatrix}l&l&t\\l'&l''&k\end{Bmatrix}M(k,t),\quad(37)$$

where t is restricted to even values.

The total correction to the matrix elements $(\psi|G|\psi')$ of l^N for the effects of the perturbations produced by $l^Nl'^{4l'+1}l''$ is given by the sum of Eqs. (35), (36), and (37). The net effect is to "screen" the Slater F^t integrals, introduce the parameters α, β, and γ (for f^N), and produce a linear shift of all the terms of the configuration. The relative corrections produced by this interaction have the same angular dependence as those of Eq. (14).

[25] B. R. Judd, J. Math. Phys. **3**, 557 (1962).

D. l^N with $l^{N-1}l'$

Wybourne[23] has shown that the matrix elements of this configuration interaction may be written as

$$\left(l^N\gamma SL\left|e^2\sum_k\frac{r_<^k}{r_>^{k+1}}\sum_{i<j}(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)})\right|l^{N-1}\gamma''S''L''l';SL\right)$$
$$=N^{1/2}\sum_k\sum_{\psi_1}(-1)^{L+L''+l}(l^N\psi\{|l^{N-1}\psi_1)(l^{N-1}\psi_1\|\mathbf{U}^{(k)}\|l^{N-1}\psi'')\begin{Bmatrix}L_1 & L'' & k\\ l' & l & L\end{Bmatrix}X(k;lll'l'). \quad (38)$$

Using the identity in the Appendix, Eq. (49), to perform the sum over ψ_1, the r.h.s. of Eq. (38) becomes

$$=N^{1/2}\sum_k\Bigg[\sum_{\bar\psi}(-1)^{l+l'+k}([\bar L]/[L])^{1/2}(l^N\bar\psi\{|l^{N-1}\psi'')(l^N\psi\|\mathbf{U}^{(k)}\|l^N\bar\psi)\begin{Bmatrix}\bar L & L & k\\ l' & l & L''\end{Bmatrix}$$
$$-\delta(l,l')(-1)^{L+L''+l}(l^N\psi\{|l^{N-1}\psi'')/[l]\Bigg](-1)^{L+L''+l}X(k'lll'). \quad (39)$$

For $l\neq l'$ the second term in Eq. (39) is zero and after performing the summation over the states of $l^{N-1}l'$ we may write the correction to the matrix elements $(\psi|G|\psi')$ of l^N as

$$C(1)=\sum_{k,k',k''}\sum_{\bar\psi,\bar\psi'}[k'']/[L]\begin{Bmatrix}k & k' & k''\\ \bar L' & \bar L & L\end{Bmatrix}\begin{Bmatrix}k & k' & k''\\ l & l & l'\end{Bmatrix}(l^N\psi\|\mathbf{U}^{(k)}\|l^N\bar\psi)(l^N\bar\psi\|\mathbf{U}^{(k'')}\|l^N\bar\psi')(l^N\bar\psi'\|\mathbf{U}^{(k')}\|l^N\psi')P(kk';lll'). \quad (40)$$

Using a result due to Racah[4] (his Eq. 33) we note

$$(\psi|(\{\mathbf{U}^{(k)}\mathbf{U}^{(k'')}\}^{(k')}\mathbf{U}^{(k')})^{(0)}|\psi')=\sum_{\bar\psi,\bar\psi'}\begin{Bmatrix}k & k' & k''\\ \bar L' & \bar L & L\end{Bmatrix}(\psi\|\mathbf{U}^{(k)}\|\bar\psi)(\bar\psi\|\mathbf{U}^{(k'')}\|\bar\psi')(\bar\psi'\|\mathbf{U}^{(k')}\|\psi')/[L].$$

Equation (40) can now be rewritten as

$$C(1)=-\sum_{k,k',k''}(l^N\psi|(\{\mathbf{U}^{(k)}\mathbf{U}^{(k'')}\}^{(k')}\mathbf{U}^{(k')})^{(0)}|l^N\psi')[k'']\begin{Bmatrix}k & k' & k''\\ l & l & l'\end{Bmatrix}P(kk';lll'). \quad (41)$$

We note that Eq. (41) contains three-particle terms of the type

$$(l^N\psi|\sum_{i\neq j\neq h}(\{\mathbf{u}_i^{(k)}\mathbf{u}_j^{(k'')}\}^{(k')}\mathbf{u}_h^{(k')})^{(0)}|l^N\psi'). \quad (41a)$$

When $l\equiv l'$ two additional terms must be added to $C(1)$. The first is given by

$$C(2)=2\sum_{k,k'}\sum_{\psi'',\bar\psi}(-1)^{l+k+L+L''}([\bar L]/[L])^{1/2}(l^N\bar\psi\{|l^{N-1}\psi'')(l^{N-1}\psi''|\}l^N\psi')\begin{Bmatrix}L & \bar L & k\\ l & l & L''\end{Bmatrix}(l^N\psi\|\mathbf{U}^{(k)}\|l^N\bar\psi)P(kk';lll')/[l].$$

Evaluating the sum over ψ'', and then using the closure property to sum over $\bar\psi$ we obtain

$$C(2)=\delta(l,l')\sum_{k,k'}\Bigg[2(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(k)}\cdot\mathbf{U}_j^{(k)})|l^N\psi')+\frac{N}{[l]}\delta(\psi,\psi')\Bigg]\frac{2P(kk';lll')}{[l]}, \quad (42)$$

where k is restricted to even values only. The second term for $l\equiv l'$ is simply

$$C(3)=-\delta(l,l')N\sum_{\psi''}(l^N\psi\{|l^{N-1}\psi'')(l^{N-1}\psi''|\}l^N\psi')/[l]^2\sum_k P(kk';lll')=-\delta(l,l')N[\sum_{kk'}P(kk';lll')/[l]^2]\delta(\psi,\psi'). \quad (43)$$

Thus, for $l\equiv l'$, the effects of the interaction of l^N with $l^{N-1}l'$ may be represented by a three-body interaction, plus a scalar two-body interaction proportional to the coefficients of the Slater integrals F^k and a linear shift of all the terms of l^N.

E. l^N with $l'^{4l'+1}l^{N+1}$

This type of configuration interaction corresponds to a "core excitation" where an electron l' from a closed $l'^{4l'+2}$ shell is excited into the partially filled l^N shell.

A typical matrix element coupling a state of l^N with a state of $l'^{4l'+1}l^{N+1}$ will be of the form

$$\left(l^N\gamma SLl'^{4l'+2}\,{}^1S;SL\left|e^2\sum_k\frac{r_<^k}{r_>^{k+1}}\sum_{i<j}(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)})\right|l^{N+1}\gamma''S''L''l'^{4l'+1};SL\right)=(-1)^{S''-S-s}\left[\frac{(N+1)[S'']}{[S]}\right]^{1/2}$$
$$\times\sum_k\Bigg[\sum_{\bar\psi}(l^{N+1}\psi''\{|l^N\bar\psi)(l^N\bar\psi\|\mathbf{U}^{(k)}\|l^N\psi)\begin{Bmatrix}\bar L & L & k\\ l' & l & L''\end{Bmatrix}-\frac{\delta(l,l')}{[l]}(l^{N+1}\psi''\{|l^N\psi)(-1)^{L''+l+L}\Bigg]X(k';lll'). \quad (44)$$

We may perform the summation using the properties of conjugation to obtain for $l \neq l'$ the correction

$$C(1) = -\sum_{k,k',k''>0} (l^N\psi|(\{\mathbf{U}^{(k)}\mathbf{U}^{(k'')}\}^{(k')}\mathbf{U}^{(k')})^{(0)}|l^N\psi') \begin{Bmatrix} k & k' & k'' \\ l & l & l' \end{Bmatrix} (-1)^{k''+1}[k'']P(kk';llll') - \frac{(4l+2-N)}{[l]}\sum_k \left[2(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(k)}\cdot\mathbf{U}_j^{(k)})|l^N\psi') - \frac{N}{[l]}\delta(\psi,\psi')\right]P(kk';llll')/[k], \quad (45)$$

where k and k' are even.

The first term of Eq. (45) is identical to the expression for the interaction of l^N with $l^{N-1}l'$ [Eq. (41)] apart from the phase factor $(-1)^{k''+1}$. The last two terms give rise to a "screening" of the Slater F^k integrals and a linear shift of all the terms of l^N.

When $l \equiv l'$ we must add to Eq. (45) the expression

$$C' = -\sum_{k,k'} [4(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(k)}\cdot\mathbf{U}_j^{(k)})|l^N\psi') + (N+4l+2)\delta(\psi,\psi')/[l]]P(kk';llll')/[l], \quad (46)$$

where again k and k' are even.

The two-body interactions contributions to C' only affect the screening of the Slater F^k integrals and make no contributions to the additional two-body interaction constants α, β, and γ.

IV. EVALUATION OF THE RADIAL PARAMETERS

The expressions obtained in Sec. III contain a radial part and an angular part. Were radial functions available for both the ground state and excited state orbitals it would be possible to calculate the radial parts of the expressions for particular perturbing configurations. Clearly, the full correction will only be attained if the effects of many perturbing configurations are considered. In making calculations such as these, it will be important to ensure that the perturbation to be calculated has not already been built into the radial functions.

The use of perturbation theory starting from Hartree-Fock functions has been discussed in detail by Nesbet.[26] His method of symmetry and equivalence restrictions includes configuration interaction involving the promotion of any one electron to another state of the same symmetry, e.g., $4f$ to $5f$, $5p$ to $6p$, etc. Because the angular part of each function is fixed and only the radial parts are allowed to vary, one-electron excitations to states of different symmetry, which would be included in an unrestricted Hartree-Fock calculation, must be treated as a perturbation on these functions.

The Hartree-Fock calculations of Watson and Freeman[27] make no use of symmetry and equivalence restrictions but still include effects of one-electron excitations to states of the same symmetry. Their functions could in principle be used in making a perturbation calculation if they were supplemented by similar functions for the perturbing configurations.

V. CONCLUSIONS

It has been shown that, to second order, in the approximation that the weakly perturbing configurations are well separated from the perturbed l^N configuration, the effects of all two-particle interactions with the l^N configuration may be represented by a linear shift of all the terms of the configuration and $(2l+1)$ scalar two-body interactions. The effects of one-electron excitations, either from the core or the unfilled l^N shell, are representable by an effective three-body interaction, a linear shift of all the terms of l^N and, in some cases, $(2l+1)$ scalar two-body interactions of the same angular form as those arising from the two-electron excitations.

In general, the effect of any perturbing configuration acting upon the states of an l^N configuration, to second-order, may be taken into account by adding to the electrostatic matrix elements calculated for the l^N configuration a correction term of the form

$$C = -\sum_{t_{\text{even}}} P(t)f_t + \delta(\psi,\psi')\sum_{t_{\text{odd}}} P(t)(l^N\psi|\sum_{i<j}(\mathbf{U}_i^{(t)}\cdot\mathbf{U}_j^{(t)})|l^N\psi') - \sum_{k,k',k''>0} P(k,k',l')[k'']\begin{Bmatrix} k & k' & k'' \\ l & l & l' \end{Bmatrix}(l^N\psi|(\{\mathbf{U}^{(k)}\mathbf{U}^{(k'')}\}^{(k')}\mathbf{U}^{(k')})^{(0)}|l^N\psi') + \sum_{k,k',k''>0} P'(k,k',l')[k''](-1)^{k''}\begin{Bmatrix} k & k' & k'' \\ l & l & l' \end{Bmatrix}(l^N\psi|(\{\mathbf{U}^{(k)}\mathbf{U}^{(k'')}\}^{(k')}\mathbf{U}^{(k')})^{(0)}|l^N\psi'), \quad (47)$$

[26] R. K. Nesbet, Rev. Mod. Phys. **33**, 28 (1961).
[27] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

where $P(t)$, $P(k,k',l')$, and $P'(k,k',l')$ depend only on the radial integrals, the average energy separation ΔE_c between l^N and the particular perturbing configuration, and the one-electron quantum numbers, and in no way do they involve the angular dependence of the states of l^N.

The first term in Eq. (47) has the effect of "screening" the Slater F^t radial integrals. Thus, the F^t integrals are reduced by an amount $P(t)$ for a particular configuration interaction. The amount of the reduction will be different for different values of t and for different perturbing configurations. Thus, an $s \rightarrow d$ excitation will "screen" the F^2 radial integral, but not the F^4 or F^6 integrals.

The l scalar two-body interactions occurring in the second term of Eq. (47) are the same as those arising from the "linear" theory. The validity of Racah[19] and Trees'[17] treatment of the two-body scalar interactions is established and, in addition, the interaction constants associated with these interactions have been expressed in terms of the radial integrals of particular configuration interactions. Racah[19] and Trees[17] have introduced two scalar interactions to be added to the energy matrices of d^N, one proportional to $L(L+1)$ and the other proportional to the eigenvalues of the seniority operator Q. We prefer to use the eigenvalues of Casimir's operator for the group R_5 in place of the seniority operator, since the radial parameters have a simpler form. It will be noted that different choices of scalar interactions will yield different corrections to the Slater F^t integrals. In general, we need only introduce l two-body scalar interactions in addition to the $l+1$ electrostatic two-body interactions to account for the effects of the two-electron excitations. Racah and Shadmi[28] have made a detailed study of the Q correction in d^N configurations and failed to obtain a substantial improvement in their energy level calculations. This we believe is due to their neglect of the effective three-body interact ions contained in the third and fourth parts of Eq. (47).

The third and fourth terms of Eq. (47) are the effective *nonlinear* three-body interactions that take into account the effects of one-electron excitations. The third term arises when there are one-electron excitations from the l^N shell, while the fourth term arises when there are one-electron excitations from a single closed shell into the l^N shell. These three-body terms may be further simplified, however, by noting that for k'' odd the triple scalar product is antisymmetric and as a result may be reduced to effective two-body interactions that are absorbed by parts 1 and 2 of Eq. (47).[29] Thus, the last two terms of Eq. (47) may be combined to give a correction

$$\sum_{kk'k''\text{even}} \mathcal{P}(kk',l')[k'']\begin{Bmatrix} k & k' & k'' \\ l & l & l' \end{Bmatrix} \times (l^N\psi|\,(\{\mathbf{U}^{(k)}\mathbf{U}^{(k'')}\}\mathbf{U}^{(k')})^{(0)}\,|l^N\psi'), \quad (47a)$$

where

$$\mathcal{P}(kk',l') = P'(kk',l') - P(kk',l'). \quad (47b)$$

It should be noted that in addition to the actual three-body terms of (41a), this correction still contains some terms that behave as two-particle interactions. If these two-body terms are removed and incorporated into the parameters of parts 1 and 2 of Eq. (47), the matrix element in Eq. (47a) may be rewritten as

$$(l^N\psi|\sum_{h\neq i\neq j}(\{\mathbf{U}_h^{(k)}\mathbf{U}_i^{(k'')}\}^{(k')}\mathbf{U}_j^{(k')})^{(0)}\,|l^N\psi'),$$

where k, k', and k'' are all even. The triple scalar product is now completely symmetric with respect to k, k', and k'', and, hence, for f^N, the complete parametrization of *all* three-particle interactions occurs by taking ten distinct combinations of k, k', and k'', viz., (222), (422), (442), (444), (644), (664), (666), (622), (662), (642). The parameters then become extremely complicated functions of k, k', and k'' and l', but their magnitude is a true indication of the importance of including three-body interactions. However, if this formulation is used for f^3, the number of parameters becomes equal to the number of terms.

For d^N configurations the effects of single s-electron excitations may be taken into account by the addition of one parameter $P(2,2,0)$. This parameter is of the type recently used by Trees[30] to take into account the effect of $3s3d^7$ on $3s^2d^6$.

While we have given the parameters associated with the additional two- and three-body interactions in terms of explicit functions of the radial integrals for particular configurations, the parameters derived from experimental data will represent the weighted contributions of many configurations, since the *angular* part of the corrections are independent of the principal quantum numbers $n'l'$ of the excited electrons. Not only do the parameters absorb the effects of the bound states, but also the states of the continuum, making it very difficult to assess the agreement between the experimentally derived parameters and those calculated from Hartree-Fock calculations. Thus, in Trees[30] calculations of the effect of $3s3d^7$ on $3s^23d^6$, the contributions of all single s excitations have automatically been included. We note that since Trees obtained a substantial improvement in the energy level calculation by including what is clearly the parametrization of a three-body interaction we may consider his results as establishing the importance of the three-body interactions in atomic spectra. We also note that in second-order perturbation theory interactions of a higher order than the three-body interactions are not possible for an l^N configuration. Only in going to higher orders of perturbation do higher order n-body interactions arise.

The appearance of l' in the 6-j symbol associated with the three-body terms of Eq. (47a) makes para-

[28] G. Racah and Y. Shadmi, Phys. Rev. **119**, 156 (1960).

[29] We are grateful to Professor Racah for drawing our attention to this result.

[30] R. E. Trees, Phys. Rev. **129**, 1220 (1963).

metrization of the three-body terms more difficult than for the two-body interactions. However, it should, in some cases, be possible to parametrize these three-body terms for the most significant excitations ($l'=1$ and 3 for f^N) and determine these parameters from experimental data on systems of sufficient complexity. For the f^N configurations, two additional parameters are required to take into account the effects of the p excitations. For f excitations, six additional parameters are required. If the formulation of Eq. (47b) is used, however, *all* one-electron excitations may be accounted for with the inclusion of ten additional parameters. For the $4f^N$ configuration of the lanthanides both two- and one-electron excitations could be included by adding thirteen parameters to supplement the usual Slater parameters.

Since the total correction for two-electron excitations is given by the $(2l+1)$ scalar interactions of the first two terms of Eq. (47), it is essential that all the $(2l+1)$ interactions be included in the parametrization.

In the case of low-energy perturbing configurations it will still be necessary to take into account interactions explicitly. However, there will normally only be a few such configurations and we may parametrize the effects of all higher configurations. If, for example, there was appreciable interaction between the l^N and $l^{N-1}l'$ configuration, we would construct the energy matrix for the states belonging to these two configurations, and in addition to the results obtained here for the l^N configuration we would need to consider the summations

$$\sum_m \langle l^N \alpha SL|G|m\rangle\langle m|G|l^{N-1}\bar{\psi}l'SL\rangle$$

and

$$\sum_m \langle l^{N-1}\bar{\psi}l'|G|m\rangle\langle m|G|l^{N-1}\bar{\psi}'l'SL\rangle.$$

The expressions derived for the effects of configuration interaction upon the l^N configuration will also hold for configurations containing electrons outside of an l^N core with some restrictions; the effects, to second-order, of perturbing configurations in which the quantum numbers of the added electrons do not change will be taken into account if the corrections given here are applied to the states of the l^N core. Thus, for the $f^N p$ configuration, the effects of the perturbations produced by the $f^{N-2}d^2p$ configuration would be included, but not those produced by the $f^N f'$ configuration. The latter type of perturbations involve summations of the type

$$\sum_{\bar{\psi}} (l^N\psi l'SL|G|l^N\bar{\psi}l''SL)(l^N\bar{\psi}l''SL|G|l^N\psi'l'SL).$$

Starting with the equations of Wybourne,[23] it can be readily shown that, for the *direct* part of the interaction, the above summation contains a term of the form

$$(l^N\psi\|\{\mathbf{U}^{(k)}\mathbf{U}^{(k')}\}^{(k'')}\|l^N\psi'),$$

which is a nonscalar two-body interaction.

The use of effective interactions has also been discussed by Talmi[31] in connection with the nuclear shell model, and the remarks of this paper should have equivalent analogs where configurations of nucleons are encountered.

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APPENDIX

Following Racah,[5] we may write

$$(l^N\gamma SL|\sum_{i<j}(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)})|l^{N-1}\psi'l'SL)=\frac{1}{2[L]}[\sum_{\psi''}(-1)^{L-L''}(l^N\psi\|\sum_i \mathbf{C}_i^{(k)}\|l^N\psi'')(l^N\psi''\|\sum_i \mathbf{C}_i^{(k)}\|l^{N-1}\psi'lSL)$$
$$+\sum_{\psi_1,L'''}(-1)^{L-L'''}(l^N\psi\|\sum_i \mathbf{C}_i^{(k)}\|l^{N-1}\psi_1l'SL''')(l^{N-1}\psi_1l'SL'''\|\sum_i \mathbf{C}_i^{(k)}\|l^{N-1}\psi'l'SL)]$$
$$-N^{1/2}(l^N\psi\{|l^{N-1}\psi')(l\|\mathbf{C}^{(k)}\|l')^2\delta(l,l')/[l]. \quad (48)$$

The last term in Eq. (48) arises from the replacement of $\sum_{i<j}(\mathbf{C}_i^{(k)}\cdot\mathbf{C}_j^{(k)})$ by $(\sum \mathbf{C}_i^{(k)})^2$ which introduces extra terms which are nonzero for $l\equiv l'$ and must be subtracted out.[32]

Using the Biedenharn-Elliott sum rule and the orthogonality properties of 6-j symbols to evaluate the sum over L''' and then comparing the result with the angular part of Eq. (38) leads to the identity

$$\sum_{\psi_1}(l^N\psi\{|l^{N-1}\psi_1)\begin{Bmatrix} L' & L_1 & k \\ l & l' & L\end{Bmatrix}(l^{N-1}\psi_1\|\mathbf{U}^{(k)}\|l^{N-1}\psi')\equiv\sum_{\psi''}\left(\frac{[L'']}{[L]}\right)^{1/2}(-1)^{l+l'+k}\begin{Bmatrix} L & L'' & k \\ l & l' & L'\end{Bmatrix}$$
$$\times(l^N\psi''\{|l^{N-1}\psi')(l^N\psi\|U^{(k)}\|l^N\psi'')-\delta(l,l')(-1)^{l+L+L'}(l^N\psi\{|l^{N-1}\psi')/[l]. \quad (49)$$

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[31] I. Talmi, Rev. Mod. Phys. **34**, 704 (1962).
[32] K. Rajnak, University of California Lawrence Radiation Laboratory Report, UCRL-10460, 1962 (unpublished).

A similar identity for the more general case of double tensors may be generated in the following manner. Consider the tensors $\mathbf{U}^{(\kappa k)}=\sum_i(\mathbf{U}^{(\kappa k)})_i$, where $(sl\|\mathbf{U}^{(\kappa k)}\|s'l')=\delta(s,s')\delta(l,l')$. Since the $\mathbf{U}^{(k)}$'s stay within the l^N configuration $|l^N\psi''M_S''M_L'')$ form a complete set of states, where $\psi''=\gamma''S''L''$.

Thus,

$$\sum_{\substack{\psi'',\psi''',M_S'',\\ M_S''',M_L'',M_L'''}}(l^N\psi''\{|l^{N-1}\bar{\psi})(l^{N-1}\bar{\psi}'|\}l^N\psi''')(\psi''M_S''M_L''|\mathbf{U}_{\pi q}^{(\kappa k)}|\psi'''M_S'''M_L''')$$

$$\times(\bar{S}\bar{M}_S sm_s|\bar{S}sS''M_S'')(\bar{S}'sS'''M_S'''|\bar{S}'\bar{M}_S'sm_s)(\bar{L}\bar{M}_L lm_l|\bar{L}lL''M_S'')(\bar{L}'lL'''M_S'''|\bar{L}'\bar{M}_L'lm_l')$$

$$=(\bar{\psi}\bar{M}_S\bar{M}_L,slm_sm_l|\mathbf{U}_{\pi q}^{(\kappa k)}|\bar{\psi}'\bar{M}_S'\bar{M}_L',slm_s'm_l'). \quad (50)$$

Upon multiplying both sides by $(\bar{L}lLM_L|\bar{L}\bar{M}_Llm_l)(\bar{L}'\bar{M}_Llm_l|\bar{L}lL'M_L')(\bar{S}sSM_S|\bar{S}\bar{M}_Ssm_s)(\bar{S}'\bar{M}_Ssm_s'|\bar{S}sS'M_S')$, summing over $\bar{M}_L,\bar{M}_S$, m_l, m_s, $\bar{M}_L'$, $\bar{M}_S'$, m_l', m_s' and using the Wigner-Eckart theorem[24] on the matrix elements we obtain

$$\sum_{\psi'',\psi'''}(l^{N-1}\bar{\psi}|\}l^N\psi'')(l^N\psi'''\{|l^{N-1}\bar{\psi}')(l^N\psi''\|\mathbf{U}^{(\kappa k)}\|l^N\psi''')\delta(L',L''')\delta(S',S''')\delta(L,L'')\delta(S,S'')$$

$$=(l^{N-1}\bar{\psi},sl,\psi\|\mathbf{U}^{(\kappa k)}\|l^{N-1}\bar{\psi}',sl,\psi'). \quad (51)$$

Because of the delta functions in S and L we can multiply by $(i^N\psi\{|l^{N-1}\bar{\psi})$ and sum over $\bar{\psi}$. On multiplying the result by

$$\begin{Bmatrix}L & L' & k\\ l & l' & \bar{L}'\end{Bmatrix}\begin{Bmatrix}S & S' & \kappa\\ s & s & \bar{S}'\end{Bmatrix}\left[\frac{[S'][L']}{[S][L]}\right]^{1/2},$$

and summing over S' and L' we obtain the identity for double tensors as

$$\sum_{\psi'''}(l^N\psi\|\mathbf{U}^{(\kappa k)}\|l^N\psi''')(l^N\psi'''\{|l^{N-1}\bar{\psi}')\begin{Bmatrix}L & L''' & k\\ l & l' & \bar{L}'\end{Bmatrix}\begin{Bmatrix}S & S''' & \kappa\\ s & s & \bar{S}'\end{Bmatrix}\left[\frac{[S'''][L''']}{[S][L]}\right]^{1/2}(-1)^{l+\kappa+k}$$

$$=\sum_{\bar{\psi}}(l^N\psi\{|l^{N-1}\bar{\psi})(l^{N-1}\bar{\psi}\|\mathbf{U}^{(\kappa k)}\|l^{N-1}\bar{\psi}')\begin{Bmatrix}\bar{S} & \bar{S}' & \kappa\\ s & s & S\end{Bmatrix}\begin{Bmatrix}\bar{L} & \bar{L}' & k\\ l' & l & L\end{Bmatrix}(-1)^{l'}$$

$$+(l^N\psi\{|l^{N-1}\bar{\psi}')\delta(l,l')(-1)^{\bar{L}'+\bar{S}'+S+L+s}/([l][s]). \quad (52)$$