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Configuration Interaction Effects in ℓ^N Configurations*

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ABSTRACT

The effects of configuration interactions on the energy levels of configurations of the type ℓ^N 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. It has been found that by choosing suitable scalar interactions it is possible to include, to second-order, all electrostatic interactions with configurations having two electrons excited from the ℓ^N configuration. Using perturbation theory it has been found possible to derive explicitly the form of the scalar interactions together with the analytical form of their radial parts. Effective three-body interactions are introduced to account for the perturbations due to one-electron excitations. The physical significance of the parameters associated with the linear theory is clarified.

1. 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. Following the realization that the assumption of pure electron configurations was inadequate, numerous attempts have been made to include the effects of configuration interaction. The most obvious approach was to diagonalize energy matrices which included all the electrostatic interactions within and between several connected configurations. While this approach has met with some success it has been found to be a very cumbersome method requiring the construction of extremely large matrices, a great increase in the number of radial integrals and the assumption that only one or two perturbing configurations need to be considered.

In more recent times considerable attention has been directed towards the possibility of modifying the energy matrices of the principal electron configuration in such a way as to include the greater part of the effects of all the perturbing configurations. This approach has had the great advantage of requiring no increase in the dimensions of the energy matrices and relatively few additional parameters.

Particular attention has been given to the so called "linear" theory of configuration interaction following the observation of Bacher and Goudsmit[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.

2. 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 wave numbers.[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 treat the effects of configuration interaction in the doubly and triply ionized lanthanides by second-order perturbation theory. The analogous doubly and higher ionized actinides can undoubtedly be likewise treated. In the lower stages of ionization the spacings of the interacting configurations will be quite small and it will not always be appropriate to use second-order perturbation theory. However, in these cases it should be possible to construct energy matrices giving all the configuration interactions of the nearest configurations, diagonalize them, and then consider the effects of the higher perturbing configurations by second-order perturbation theory.

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 some interacting configuration (i.e., having the same parity and whose electron coordinates differ in not more than two electrons). If $|m\rangle$ lies above ℓ^N by an energy ΔE_m, the electrostatic matrix element $(\ell^N\psi|G|\ell^N\psi'')$ 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 configuration interaction, $\sum_{i<j} e^2/r_{ij}$. In general there may be several perturbing states and the total correction to $(\ell^N\psi|G|\ell^N\psi'')$ 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 configuration 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 be able 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 will be quite large and it becomes a reasonable approximation to assume the connected states are degenerate. Within this approximation Eq. (2) may be written as

$$C = \frac{-1}{\Delta E} \sum_m \langle\psi|G|m\rangle\langle m|G|\psi''\rangle \ . \qquad (3)$$

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 consider what possible configurations may interact with a configuration ℓ^N. There are only five basic types:

(a) $\ell^{N-2}(\ell')^2$ and $\ell^{N-2}\ell'\ell''$, (b) $(\ell')^{4\ell'}\ \ell^{N+2}$ and $(\ell')^{4\ell'+1}(\ell'')^{4\ell''+1}\ \ell^{N+2}$
(c) $(\ell)^{4\ell'+1}\ell^N\ell''$, (d) $\ell^{N-1}\ell'$, and (e) $(\ell')^{4\ell'+1}\ \ell^{N+1}$. 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.

3. CLOSED FORMULAS FOR CONFIGURATION INTERACTIONS

(a) ℓ^N with $\ell^{N-2}(\ell')^2$ or $\ell^{N-2}\ell'\ell''$.

We shall consider the interaction of states of the configuration $\ell^{N-2}(\ell')^2$ 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). A typical matrix element will be of the form[24]

$$(\ell^N\psi|\sum_k\sum_{i<j}^{N} e^2 \frac{r_<^k}{r_>^{k+1}} (\underset{\sim}{C}_i^k \cdot \underset{\sim}{C}_j^k)\,|\,\ell^{N-2}\tilde{\psi}, (\ell')^2\phi;SL) \tag{4}$$

where ϕ symbolizes the total spin (σ) and orbital (λ) quantum numbers of the states of $(\ell')^2$ and $\tilde{\psi}$ stands for the quantum numbers defining the particular state of ℓ^{N-2}.

Using a result due to Racah[5] (his Eq. 33c) we may write (4) as

$$\sum_k \left[\frac{N(N-1)}{2}\right]^{1/2} (\ell^N\psi\{|\ell^{N-2}\tilde{\psi},\ell^2\phi',SL)(\ell^2\phi|e^2\frac{r_<^k}{r_>^{k+1}} (\underset{\sim}{C}_N^k \cdot \underset{\sim}{C}_{N-1}^k)|(\ell')^2\phi). \tag{5}$$

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

$$(\ell^2\phi|e^2\frac{r_<^k}{r_>^{k+1}} (\underset{\sim}{C}_N^k \cdot \underset{\sim}{C}_{N-1}^k)|(\ell')^2\phi) = (-1)^{\ell+\ell'+\lambda}\begin{Bmatrix}\ell & \ell' & k\\ \ell' & \ell & \lambda\end{Bmatrix}(\ell||\underset{\sim}{C}^k||\ell')^2 G^k(\ell,\ell') \tag{6}$$

where $G^k(\ell,\ell')$ is the usual Slater radial integral arising from the radial parts of the left hand side. Inserting (6) in (5) we obtain

$$(\ell^N\psi|\sum_k\sum_{i<j}^{N} e^2\frac{r_<^k}{r_>^{k+1}}(\underset{\sim}{C}_i^k\cdot\underset{\sim}{C}_j^k)|\ell^{N-2}\tilde{\psi},(\ell')^2\phi;SL)$$

$$= \sum_k\left(\frac{N(N-1)}{2}\right)^{1/2}(\ell^N\psi\{|\ell^{N-2}\tilde{\psi},\ell^2\phi;SL)(-1)^{\ell+\ell'+\lambda}\begin{Bmatrix}\lambda & \ell & \ell\\ k & \ell' & \ell'\end{Bmatrix}(\ell||\underset{\sim}{C}^k||\ell')^2\,G^k(\ell,\ell'). \tag{7}$$

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

$$C = -\frac{N(N-1)}{2\,\Delta E}\sum_{kk'}\sum_{\tilde{\psi}\phi}(\ell^N\psi\{|\ell^{N-2}\tilde{\psi},\ \ell^2\phi;SL)$$

$$\times\ (\ell^N\psi'\{|\ell^{N-2}\tilde{\psi},\ell^2\phi;SL)\begin{Bmatrix}\lambda\ell & \ell\\ k\ell' & \ell'\end{Bmatrix}\begin{Bmatrix}\lambda & \ell & \ell\\ k' & \ell' & \ell'\end{Bmatrix}(\ell\|\underset{\sim}{C}^k\|\ell')^2(\ell\|\underset{\sim}{C}^{k'}\|\ell')^2G^k(\ell,\ell')G^{k'}(\ell,\ell'). \qquad (8)$$

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

$$C = -\frac{N(N-1)}{2\,\Delta E}\sum_{\tilde{\psi}\phi t}(\ell^N\psi\{|\ell^{N-2}\tilde{\psi},\ell^2\phi;SL)(\ell^N\psi'\{|\ell^{N-2}\tilde{\psi},\ell^2\phi;SL)\begin{Bmatrix}\ell\ell t\\ \ell\ell\lambda\end{Bmatrix}$$

$$\times\ [t]\ (-1)^{t+\lambda}\sum_{kk'}(-1)^{k+k'}\begin{Bmatrix}\ell\ell\ t\\ kk'\ell'\end{Bmatrix}^2(\ell\|\underset{\sim}{C}^k\|\ell')^2(\ell\|\underset{\sim}{C}^{k'}\|\ell')^2G^k(\ell,\ell')G^{k'}(\ell,\ell'), \qquad (9)$$

where λ now appears in only one 6-j symbol and the symbol $[t] \equiv 2t+1$ has been introduced. Noting that[5]

$$(\ell^N\psi|\sum_{i<j}^{N}(\underset{\sim}{U}_i{}^t\cdot\underset{\sim}{U}_j{}^t)|\ell^N\psi') = \frac{N(N-1)}{2}\sum_{\tilde{\psi}\cdot\phi}(\ell^N\psi\{|\ell^{N-2}\tilde{\psi},\ell^2\phi;SL)$$

$$\times\ (\ell^N\psi'\{|\ell^{N-2}\tilde{\psi},\ell^2\phi;SL)\ (-1)^\lambda\begin{Bmatrix}\lambda\ell\ell\\ t\ell\ell\end{Bmatrix}, \qquad (10)$$

we may now write Eq. (9) as

$$C = -\sum_t(\ell^N\psi|\sum_{i<j}^{N}(\underset{\sim}{U}_i^t\cdot\underset{\sim}{U}_j^t)|\ell^N\psi')\ [t]\ (-1)^t$$

$$\times\ \frac{1}{\Delta E}\sum_{k\,k'}\begin{Bmatrix}\ell\ell\ t\\ kk'\ell'\end{Bmatrix}^2(\ell\|\underset{\sim}{C}^k\|\ell')^2(\ell\|\underset{\sim}{C}^{k'}\|\ell')^2G^k(\ell,\ell')G^{k'}(\ell,\ell')$$

$$= -\sum_t X(t)\ (\ell^N\psi|\sum_{i<j}^{N}(\underset{\sim}{U}_i^t\cdot\underset{\sim}{U}_j^t)|\ell^N\psi')\ [t]\ (-1)^t\ , \qquad (11)$$

where the function X(t) is defined by

$$X(t) = \frac{1}{\Delta E} \sum_{kk'} \begin{Bmatrix} \ell \ell & t \\ kk' & \ell' \end{Bmatrix}^2 (\ell \| \underset{\sim}{C}^k \| \ell')^2 (\ell \| \underset{\sim}{C}^{k'} \| \ell')^2 G^k(\ell,\ell') G^{k'}(\ell,\ell'). \tag{12}$$

The expression $(\ell^N \psi | \sum_{i<j}^{N} (\underset{\sim}{U}_i^t \cdot \underset{\sim}{U}_j^t) | \ell^N \psi')$ appearing in Eq. (11) will contain both terms even in t 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

$$f_t = (\ell^N \psi | \sum_{i<j}^{N} (\underset{\sim}{C}_i^t \cdot \underset{\sim}{C}_j^t) | \ell^N \psi') = (\ell \| \underset{\sim}{C}^t \| \ell)^2 (\ell^N \psi | \sum_{i<j}^{N} (\underset{\sim}{U}_i^t \cdot \underset{\sim}{U}_j^t) | \ell^N \psi'), \tag{13}$$

and hence, for even t, Eq. (11) may be written as

$$C_{t\ \mathrm{even}} = - \sum_{t\ \mathrm{even}} X(t)\ f_t[t]/(\ell \| \underset{\sim}{C}^t \| \ell)^2. \tag{14}$$

Thus the corrections to the matrix elements of f^N arising from the 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]

$$(f^N \psi | \sum_{i<j}^{N} (\underset{\sim}{U}_i^1 \cdot \underset{\sim}{U}_j^1) | f^N \psi') = \delta(\psi,\psi') \left[\frac{L(L+1)}{12} - N \right] /14 \tag{15a}$$

$$(f^N \psi | \sum_{i<j}^{N} (\underset{\sim}{U}_i^3 \cdot \underset{\sim}{U}_j^3) | f^N \psi') = \delta(\psi,\psi') \left[5G(R_7) - 4\,G(G_2) - N \right] /14 \tag{15b}$$

and

$$(f^N \psi | \sum_{i<j}^{N} (\underset{\sim}{U}_i^5 \cdot \underset{\sim}{U}_j^5) | f^N \psi') = \delta(\psi,\psi') \left[28\,G(G_2) - \frac{L(L+1)}{56} - N \right] /14 \tag{15c}$$

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

$$((u_1u_2)|G(G_2)|(u_1u_2)) = [u_1^2 + u_1u_2 + u_2^2 + 5u_1 + 4u_2]/12 \quad (16a)$$

and $$((w_1w_2w_3)|G(R_7)|(w_1w_2w_3)) = [w_1(w_1+5) + w_2(w_2+3) + w_3(w_3+1)]/10, \quad (16b)$$

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

Inserting the results of Eq. (15) into Eq. (11) the corrections to the diagonal matrix elements due to the odd t terms may be written as

$$C_{t\ odd} = L(L+1)[X(1) - X(5)]/56 + 2G(G_2)\,[X(5) - X(3)] + \frac{5}{2}\,G(R_7)\,X(3)$$
$$- \frac{N}{14}\,[3X(1) - 7X(3) + 11\,X(5)] \quad (17)$$

$$= \alpha\,L(L+1) + \beta\,G(G_2) + \gamma G(R_7) + \delta \quad (18)$$

where $\alpha = [X(1) - X(5)]/56$ $\qquad \beta = 2[X(5) - X(3)]$

$\gamma = \frac{5}{2}\,X(3)$ $\qquad \delta = \frac{-N}{14}\,[3X(1) - 7X(3) + 11\,X(5)]$ (19)

and $X(t)$ is given by Eq. (12).

From Eqs. (14) and (18) 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 $f^{N-2}(\ell')^2$ configuration as

$$C = -\sum_{t\ even} X(t)\,f_t\,[^t]/(3\|C^t\|3)^2 + \delta(\psi,\psi')\left[\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \delta\right]. \quad (20)$$

δ shifts all terms of the f^N configuration by a constant amount as does the contribution for t = 0 in the summation. Where our interest is restricted to the relative shifts of terms within the f^N configuration we may write

$$C' = -\sum_t X(t) f_t [t]/(3\|\underset{\sim}{C}^t\|3)^2 + \delta(\psi,\psi')\left[\alpha L(L+1) + \beta G(G_2) + \gamma G(R_7)\right], \tag{21}$$

where t assumes the values 2, 4 and 6.

We note that for p^N configurations (ℓ=1) Eq. (21) has the form

$$C' = -3X(2) f_2/(1\|\underset{\sim}{C}^2\|1)^2 + \alpha' L(L+1),$$

where $\alpha' = \frac{X(1)}{2}$. (23)

For d^N configurations (ℓ=2) Eq. (21) assumes the form

$$C' = -\sum_t X(t) f_t [t]/(2\|\underset{\sim}{C}^t\|2)^2 + \delta(\psi,\psi')\left[\alpha'' L(L+1) + \beta' G(R_5)\right], \tag{24}$$

where t = 2 and 4 and

$$\alpha'' = [X(1) - X(3)]/10 \qquad \beta' = 3X(3), \tag{25}$$

where $G(R_5)$, is the eigenvalue of Casimir's operator for the group R_5. $G(R_5)$ is easily evaluated by means of Eqs. (18) and (19) of Racah.[6]

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

where Q is the seniority operator.

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

$$C = -Q(N,\nu)\left[G^{\ell}(\ell,0)/[\ell]\right]^2 \delta(\psi,\psi'), \tag{26}$$

where $Q(N,\nu) = (N-\nu)(4\ell+4-N-\nu)/4$ (27)

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

In a similar manner it can be shown that the energy shifts produced by interaction with the states of a configuration $\ell^{N-2}\ell'\ell''$ is identical with that of Eq. (11) apart from a redefinition of the functions X(t) which must now be written as

$$X'(t) = \frac{1}{\Delta E}\sum_{kk'}\begin{Bmatrix}\ell & \ell & t\\ k & k' & \ell\end{Bmatrix}\begin{Bmatrix}\ell & \ell & t\\ k & k' & \ell''\end{Bmatrix}(\ell\|C^k\|\ell')(\ell\|C^{k'}\|\ell')$$

$$\times\quad(\ell\|C^k\|\ell'')(\ell\|C^{k'}\|\ell'')\,R^k(\ell\ell,\ell'\ell'')\,R^{k'}(\ell\ell,\ell'\ell''). \tag{28}$$

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

These types of interaction 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 $(\ell')^{4\ell'}\ell^{N+2}$ may be written as $(\ell^N\gamma SL(\ell')^{4\ell'+2}\,{}^1S;SL|e^2\sum_k\sum_{i<j}^{N}\frac{r_<^k}{r_>^{k+1}}(C_i^k\cdot C_j^k)|$

$$\ell^{N+2}\gamma'S'L'(\ell')^{4\ell'}\sigma\lambda;SL) = \sum_k\sqrt{\frac{(N+2)(N+1)}{2}\frac{[L'][S']}{[L\;][S\;]}}$$

$$\times\quad(\ell^N\gamma SL\ell^2\sigma\lambda;\ S'L'|\}\,\ell^{N+2}\gamma'S'L')(-1)^{L+L'+S'-S+\lambda}$$

$$\times\begin{Bmatrix}\lambda & \ell' & \ell'\\ k & \ell & \ell\end{Bmatrix}(\ell'\|C^k\|\ell)^2G^k(\ell,\ell'). \tag{29}$$

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

$$C = -1/2(N+2)(N+1) \sum_{\substack{k\,k' \\ \psi'\sigma\lambda}} X(k,k')\frac{[S'][L']}{[S\ ][L\ ]}(\ell^N\psi\ell^2\sigma\lambda;S'L'|\}\ell^{N+2}\psi')$$

$$\times \quad (\ell^N\psi''\ell^2\sigma\lambda;S'L'|\}\ell^{N+2}\psi')\begin{Bmatrix}\lambda\ell'\ell' \\ k\ell\ \ell\end{Bmatrix}\begin{Bmatrix}\lambda\ \ell'\ell' \\ k'\ell\ \ell\end{Bmatrix}, \tag{30}$$

where ψ and ψ' stand for the quantum numbers γSL and $\gamma' S'L'$ respectively and $X(k,k')$ is defined by

$$X(k,k') = (1/\Delta E)G^k(\ell,\ell')G^{k'}(\ell,\ell')(\ell'\|\underset{\sim}{C}^k\|\ell)^2(\ell'\|\underset{\sim}{C}^{k'}\|\ell)^2. \tag{31}$$

We note that ψ and ψ'' may differ only in the quantum numbers γ. Using Eq. (32) of Racah[5] to evaluate the 2-particle c.f.p., Eq. (30) becomes

$$C = \frac{-1}{2}(N+2)(N+1)\sum_{\substack{kk' \\ \psi'\sigma\lambda \\ \bar{\psi}\,\bar{\psi}'}} X(k,k') \quad \frac{[S'][L']}{[S\ ][L\ ]}\,[\sigma][\lambda]\sqrt{[\bar{S}][\bar{L}][\bar{S}'][\bar{L}']}$$

$$\times \begin{Bmatrix}S\ s\ \bar{S} \\ s\ S'\sigma\end{Bmatrix}\begin{Bmatrix}S\ s\ \bar{S}' \\ s\ S'\sigma\end{Bmatrix}\begin{Bmatrix}L\ \ell\ \bar{L} \\ \ell\ L'\lambda\end{Bmatrix}\begin{Bmatrix}L\ \ell\ \bar{L}' \\ \ell\ L'\lambda\end{Bmatrix}(\ell^N\psi|\}\ell^{N+1}\bar{\psi})(\ell^N\psi''|\}\ell^{N+1}\bar{\psi}')$$

$$\times \quad (\ell^{N+1}\bar{\psi}|\}\ell^{N+2}\psi')(\ell^{N+1}\bar{\psi}'|\}\ell^{N+2}\psi')\begin{Bmatrix}\lambda\ \ell'\ell' \\ k\ \ell\ \ell\end{Bmatrix}\begin{Bmatrix}\lambda\ \ell'\ell' \\ k'\ell\ \ell\end{Bmatrix}. \tag{32}$$

By performing the sum over σ and using the Biedenharn-Elliott sum rule[24] on the 6-j symbols involving L and again to sum over λ, we obtain

$$C = -\frac{1}{2}(N+2)(N+1)\sum_{\substack{kk't\\ \psi'\bar{\psi}\bar{\psi}'}} X(k,k')\frac{[S'][L']}{[S][L]}[t]\sqrt{[\bar{L}][\bar{L}']}(-1)^{L'+L+\bar{L}+\bar{L}'}$$

$$\times \begin{Bmatrix} \ell & \bar{L} & L \\ \bar{L}' & \ell & t \end{Bmatrix} \begin{Bmatrix} \bar{L} & L' & \ell \\ \ell & t & \bar{L}' \end{Bmatrix} \begin{Bmatrix} t & k & k \\ \ell' & \ell & \ell \end{Bmatrix}^2 (\ell^N\psi|\}\ell^{N+1}\bar{\psi})(\ell^N\psi''|\}\ell^{N+1}\bar{\psi}')(\ell^{N+1}\bar{\psi}|\}\ell^{N+2}\psi')$$

$$\times (\ell^{N+1}\bar{\psi}'|\}\ell^{N+2}\psi')\ \delta(\bar{S},\bar{S}'). \qquad (33)$$

With Eq. (33) in this form the summation over the connected states $\ell^{N+2}\psi'$ cannot be carried out explicitly. However, if we note Eq. (19) of Racah,[5]

$$(\ell^N\psi\ell S'L'|\}\ell^{N+1}\psi') = \sqrt{\frac{(4\ell+2-N)[S][L]}{(N+1)[S'][L']}}\,(-1)^{L+L'+\ell+s-S-S'}$$

$$\times (\ell^{4\ell+1-N}\psi'\ell SL|\}\ell^{4\ell+2-N}\psi), \qquad (34)$$

we may convert the c.f.p. involving $(\ell^{N+1}|\}\ell^{N+2})$ 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 by making use of the relation

$$(\ell^N\psi''\|\underset{\sim}{U}^k\|\ell^N\psi) = (-1)^{k+1}(\ell^{4\ell+2-N}\psi''\|\underset{\sim}{U}^k\|\ell^{4\ell+2-N}\psi) \qquad (35)$$

which holds for all $k \neq 0$. Using Eqs. (34) and (35), Eq. (33) becomes

$$C = -(N+1)/2 \sum_{\substack{kk' \\ \bar{\psi}\,\bar{\psi}' \\ t\neq 0}} X(k,k')\, \frac{[t][\bar{S}]}{[S][L]} \sqrt{[\bar{L}][\bar{L}']}\, (-1)^{1+\ell+L+\bar{L}}$$

$$\times \begin{Bmatrix} t & k & k' \\ \ell' & \ell & \ell \end{Bmatrix}^2 \begin{Bmatrix} t & \ell & \ell \\ L & \bar{L} & L' \end{Bmatrix} (\ell^N\psi|\}\ell^{N+1}\bar{\psi})(\ell^N\psi''|\}\ell^{N+1}\bar{\psi}')(\ell^{N+1}\bar{\psi}\|U^t\|\ell^{N+1}\bar{\psi}').$$

The t = 0 term in the sum over t may be readily shown to give an additional correction

$$C' = -\frac{(4\ell+1-N)(4\ell+2-N)}{2[\ell]^2} \sum_k \frac{X(k,k)}{[k]}\, \delta(\psi,\psi'')$$

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

The identity (Eq. (68)) derived in the appendix can now be used to convert the matrix element involving states of ℓ^{N+1} to one involving states of ℓ^N. This gives

$$C = -\frac{1}{2}(N+1) \sum_{\substack{kk't\neq 0\\ \bar{\psi}}} X(k,k') \frac{[t][\bar{S}][\bar{L}]}{[S][L]} (-1)^{1+\ell+L+\bar{L}+t} \begin{Bmatrix} t & k & k' \\ \ell' & \ell & \ell \end{Bmatrix}^2$$

$$\times \Bigg[\sum_{\psi'''} (\ell^N\psi|\}\ell^{N+1}\bar{\psi}) (\ell^{N+1}\bar{\psi}\{|\ell^N\psi''') \begin{Bmatrix} \ell & \bar{L} & L \\ L''' & t & \ell \end{Bmatrix} (\ell^N\psi'''\|\underset{\sim}{U}^t\|\ell^N\psi'')$$

$$+ (-1)^{\ell+\bar{L}+L} (\ell^{N+1}\bar{\psi}\{|\ell^N\psi)(\ell^N\psi''|\}\ell^{N+1}\bar{\psi})/[\ell] \Bigg]. \quad (36)$$

Again converting to conjugate states, summing over $\bar{\psi}$, and reconverting to states ℓ^N we get

$$C = -\frac{1}{2} \sum_{kk't\neq 0} X(k,k')[t](-1)^t \begin{Bmatrix} t & k & k' \\ \ell' & \ell & \ell \end{Bmatrix}^2 \Bigg[\sum_{\psi'''} \frac{(-1)^{L+L'''}}{[L]} (\ell^N\psi\|\underset{\sim}{U}^t\|\ell^N\psi''')$$

$$\times (\ell^N\psi'''\|\underset{\sim}{U}^t\|\ell^N\psi'') - \frac{(4\ell+2-N)}{[\ell]} \delta(\psi,\psi'') \Bigg]. \quad (37)$$

Application of the closure property[4] gives

$$C = -\frac{1}{2} \sum_{kk't\neq 0} X(k,k')[t](-1)^t \begin{Bmatrix} t & k & k' \\ \ell' & \ell & \ell \end{Bmatrix}^2 \Big[(\ell^N\psi\|(\underset{\sim}{U}^t)^2\|\ell^N\psi'') - (4\ell+2-N)\delta(\psi,\psi'')/[\ell] \Big].$$

If we let

$$X(t) = \frac{1}{\Delta E} \sum_{kk'} G^k(\ell,\ell')G^{k'}(\ell,\ell')(\ell'\|\underset{\sim}{C}^k\|\ell)^2(\ell'\|\underset{\sim}{C}^{k'}\|\ell)^2 \begin{Bmatrix} t & k & k' \\ \ell' & \ell & \ell \end{Bmatrix}^2 ,$$

The total correction becomes

$$C + C' = - \sum_t X(t)(-1)^t[t] \left[(\ell^N\psi\|(\underset{\sim}{U}^t \cdot \underset{\sim}{U}^t)\|\ell^N\psi'') + (N-2\ell-1)\delta(\psi,\psi'')/[\ell] \right]$$

$$- \frac{(4\ell+1-N)(4\ell+2-N)}{2[\ell]^2} \sum_k \frac{X(k,k)}{[k]} \delta(\psi,\psi''). \qquad (38)$$

The first term is identical with Eq. (11), the expression for the depression of ℓ^N by $\ell^{N-2}(\ell')^2$. Thus, as in case (a) the terms even in t will scale the Slater integrals F^k while, for $\ell = f = 3$, the terms odd in t may be written as

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

(see Eq. (18)). The second and third terms in Eq. (38) merely produce a linear shift of all the terms of f^N.

The correction for the effects produced by interactions with the $(\ell')^{4\ell'+1}(\ell'')^{4\ell''+1}\ell^{N+2}$ configuration are identical to those of Eq. (38) if the substitution

$$X(t) = \frac{1}{\Delta E} R^k(\ell\ell,\ell'\ell'') R^{k'}(\ell\ell,\ell'\ell'')(\ell\|\underset{\sim}{C}^k\|\ell')(\ell\|\underset{\sim}{C}^k\|\ell'')$$

$$\times (\ell\|\underset{\sim}{C}^{k'}\|\ell')(\ell\|\underset{\sim}{C}^{k'}\|\ell'') \begin{Bmatrix} t & k & k' \\ \ell' & \ell & \ell \end{Bmatrix} \begin{Bmatrix} t & k & k' \\ \ell'' & \ell & \ell \end{Bmatrix}$$

is made.

c) $(\ell')^{4\ell'+2}\ \ell^N$ with $(n'\ell')^{4\ell'+1}\ \ell^N\ell''$

This is another "core excitation" corresponding to an electron ℓ' being promoted from the closed $(n'\ell')^{4\ell'+2}$ shell to some empty $n''\ell''$ shell. A typical matrix element coupling ℓ^N with $\ell^N(n'\ell')^{4\ell'+1}n''\ell''$ is given by

$$((n\ell)^N \gamma' S' L' [(n'\ell')^{4\ell'+1} n''\ell''] \, S_2 L_2; \, SL \mid \sum_k \sum_{i<j}^{N} \frac{e^2 r_<^k}{r_>^{k+1}} (\underset{\sim}{C}_i^k \cdot \underset{\sim}{C}_j^k) \mid$$

$$(n\ell)^N \, \gamma SL \, (n'\ell')^{4\ell'+2} \, {}^1S; SL)$$

$$= N \sum_{\substack{\bar{\psi} k \\ \mathcal{L}\mathcal{S} \\ \sigma\lambda}} (\ell^N \psi \{ | \ell^{N-1} \bar{\psi})(\ell^N \psi' \{ | \ell^{N-1} \bar{\psi}) \, [\mathcal{L}][\mathcal{S}][\lambda][\sigma] \, ([s][\ell'])^{1/2}$$

$$\times \; ([L][L'][L_2][S][S'][S_2])^{1/2} \, (-1)^{\ell} \begin{Bmatrix} \bar{L} & \ell & L' \\ \ell' & \ell'' & L_2 \\ \mathcal{L} & \lambda & L \end{Bmatrix} \begin{Bmatrix} \bar{S} & s & S' \\ s & s & S_2 \\ \mathcal{S} & \sigma & S \end{Bmatrix} \begin{Bmatrix} \bar{L} & \ell & L \\ \ell' & \ell' & 0 \\ \mathcal{L} & \lambda & L \end{Bmatrix} \begin{Bmatrix} \bar{S} & s & S \\ s & s & 0 \\ \mathcal{S} & \sigma & S \end{Bmatrix}$$

$$\times \left[(-1)^{\ell''+\lambda} \begin{Bmatrix} \lambda & \ell & \ell'' \\ k & \ell' & \ell \end{Bmatrix} E_1 + (1)^{\ell'+\sigma} \begin{Bmatrix} \lambda & \ell'' & \ell \\ k & \ell' & \ell \end{Bmatrix} E_2 \right], \tag{39}$$

where

$$E_1 = (\ell''\|\underset{\sim}{C}^k\|\ell')\ (\ell\|\underset{\sim}{C}^k\|\ell)\ R^k(\ell''\ell,\ell'\ell)$$

$$E_2 = (\ell\|C^k\|\ell')\ (\ell''\|C^k\|\ell)\ R^k(\ell\ell'',\ell'\ell).$$

Carrying out the summs except those over k and $\bar{\psi}$, the right hand side of Eq. (39) becomes

$$\sum_k (-1)^t \frac{\delta(k,t)\delta(S_2,0)}{[L]\ \ [t]}\sqrt{[s]}\,(\ell^N\psi\|U^t\|\ell^N\psi')\ E_1 + N\sum_{k\bar{\psi}} (\ell^N\psi\{|\ell^{N-1}\bar{\psi})$$

$$\times\ (\ell^N\psi'\{|\ell^{N-1}\bar{\psi})\ \sqrt{[L'][t][S'][S_2]}\ (-1)^{\gamma} \begin{Bmatrix} L' & L & t \\ \ell & \ell & \bar{L} \end{Bmatrix} \begin{Bmatrix} s & S_2 & s \\ S' & \bar{S} & S \end{Bmatrix} \begin{Bmatrix} \ell & \ell'' & k \\ \ell' & \ell & t \end{Bmatrix} E_2, \tag{40}$$

where $\gamma = L + \bar{L} + \ell + s + S + \bar{S} + 1 + k + t$, $t \equiv L_2$ and t is even. Each value of t corresponds to a different perturbing state. The sum over $\bar{\psi}$ in the second term may be written as a matrix element of a double tensor $W^{S_2L_2}$ as defined by Judd,[25] $(\ell^N\psi\|W^{S_2L_2}\|\ell^N\psi')$. However, the form given in Eq. (40) is more convenient for the present calculations.

If we let

$$X^k = \text{coefficient of } E_1$$

$$Y^k = \text{coefficient of } E_2,$$

the total correction to the matrix elements of ℓ^N due to states of $\ell^N(n'\ell')^{4\ell'+1}n''\ell''$ is of the form

$$C = -\frac{1}{\Delta E} \sum_{\substack{\psi' S_2 t \\ kk'}} \left[X^k X^{k'}\, E_1^k E_1^{k'} + \sum_{\bar{\psi}\ \bar{\psi}'} \left(Y^k Y^{k'}\, E_2^k E_2^{k'} + 2X^k Y^{k'}\, E_1^k E_2^{k'} \right) \right] \tag{41}$$

Using the closure property to sum over ψ', the first term in Eq. (41) may readily be shown to be

$$C(E_1) = -\frac{1}{\Delta E}\sum_t \left[2(\ell^N\psi\|\underset{\sim}{U}^t\cdot\underset{\sim}{U}^t\|\ell^N\psi'') + \frac{N}{[\ell]}\,\delta(\psi,\psi'')\right]\frac{(E_1^t)^2[s]}{[t]}. \qquad (42)$$

Carrying out the sums over S_2 and t, the term in $Y^kY^{k'}$ becomes

$$C(E_2) = \frac{-N^2}{\Delta E}\sum_{\substack{kk'\\ \bar\psi\,\bar\psi'\\ \psi' x}}\delta(S,S')(\ell^N\psi\{|\ell^{N-1}\bar\psi)(\ell^N\psi''\{|\ell^{N-1}\bar\psi')\quad [x]\quad (-1)^{k+k'}$$

$$\times\begin{Bmatrix}x & \bar L' & \bar L\\ L & \ell & \ell\end{Bmatrix}\begin{Bmatrix}\ell & k & \ell'\\ k' & \ell & x\end{Bmatrix}\begin{Bmatrix}k & \ell'' & \ell\\ \ell & x & k'\end{Bmatrix}\sum_{\psi'}N(\ell^N\psi'\{|\ell^{N-1}\bar\psi)(\ell^N\psi'\{|\ell^{N-1}\bar\psi')$$

$$\times\frac{[L'][S'](-1)^{L+L'}}{[S]}\begin{Bmatrix}x & \bar L' & \bar L\\ L' & \ell & \ell\end{Bmatrix}E_2^kE_2^{k'}. \qquad (43)$$

Again changing to conjugate states in order to carry out the sum on ψ', we obtain

$$C(E_2) = -N\sum_{\substack{\bar\psi\,\bar\psi'\\ kk'\\ x\neq 0}}F(x)(\ell^{N-1}\bar\psi\|\underset{\sim}{U}^x\|\ell^{N-1}\bar\psi')(\ell^N\psi\{|\ell^{N-1}\bar\psi)(\ell^N\psi''\{|\ell^{N-1}\bar\psi')$$

$$\times(-1)^{L+\bar L'+\ell+1}\begin{Bmatrix}\bar L & \bar L' & x\\ \ell & \ell & L\end{Bmatrix} - \frac{N(4\ell+3-N)}{\Delta E\,[\ell]^2}\sum_k\frac{(E_2^k)^2}{[k]}\,\delta(\psi,\psi''), \qquad (44)$$

where F(x) is given by

$$F(x) = \frac{1}{\Delta E}\,[x]\begin{Bmatrix}x & \ell & \ell\\ \ell' & k & k'\end{Bmatrix}\begin{Bmatrix}x & \ell & \ell\\ \ell'' & k & k'\end{Bmatrix}E_2^kE_2^{k'} \qquad (45)$$

and k + k' is even.

The identity (Eq. (68)) again allows us to convert the sum over reduced matrix elements of states of ℓ^{N-1} to a similar sum over states of ℓ^N. Eq. (44) then becomes

$$C(E_2) = N \sum_{\substack{\bar{\psi}' \\ kk' \\ x\neq 0}} F(x)(\ell^N\psi''\{|\ell^{N-1}\bar{\psi}')\left[\sum_{\psi'''}(-1)^{\bar{L}'+L+\ell+x}\sqrt{\frac{[L'']}{[L]}}(\ell^N\psi'''\{|\ell^{N-1}\bar{\psi}')\right.$$

$$\left.\times\begin{Bmatrix}\ell & L''' & \bar{L}' \\ L & \ell & x\end{Bmatrix}(\ell^N\psi\|\underset{\sim}{U}^x\|\ell^N\psi''') - (\ell^N\psi\{|\ell^{N-1}\bar{\psi}')/[\ell]\right] - \frac{N(4\ell+3-N)}{\Delta E' \quad [\ell]^2}\sum_k (E_2^{\,k})^2/[k]\ \delta(\psi,\psi'')$$

$$= \sum_{\substack{kk' \\ x\neq 0}} 2F(x)(\ell^N\psi\|\underset{\sim}{U}^x\cdot\underset{\sim}{U}^x\|\ell^N\psi'') - \frac{N(4\ell+3-N)}{\Delta E' \quad [\ell]^2}\sum_k (E_2^{\,k})^2/[k]\delta(\psi,\psi'') \quad (46)$$

where x may be even or odd.

The third term in Eq. (41) is given by

$$C(E_1E_2) = -N\sum_{\psi'k't}\frac{X(k',t)}{[L]}\sum_{\bar{\psi}}\sqrt{[L][L']}\,(-1)^{L+\bar{L}+\ell+1+k'}\begin{Bmatrix}L & L' & t \\ \ell & \ell & \bar{L}\end{Bmatrix}(\ell^N\psi''\{|\ell^{N-1}\bar{\psi})$$

$$\times \quad (\ell^N\psi'\{|\ell^{N-1}\bar{\psi})(\ell^N\psi\|\underset{\sim}{U}^t\|\ell^N\psi'), \quad (47)$$

where $X(k',t) = \frac{2}{\Delta E} \begin{Bmatrix}\ell & \ell' & k' \\ \ell'' & \ell & t\end{Bmatrix} E_1^{\,k}E_2^{\,k'}$.

Carrying out the sums on $\bar{\psi}$ and ψ', Eq. (47) may readily be rewritten as

$$C(E_1E_2) = \sum_{k't} X(k',t)(-1)^{k'}\left[2(\ell^N\psi\|\underset{\sim}{U}^t\cdot\underset{\sim}{U}^t\|\ell^N\psi'') + (N/[\ell])\,\delta(\psi,\psi'')\right] \quad (48)$$

The total correction to the matrix elements of ℓ^N by $\ell^N(\ell')^{4\ell'+1}n''\ell''$ is then given by the sum of Eqs. (42), (46) and (48). The net effect of this interaction is to modify the Slater integrals F^k, introduce the parameters α, β and γ (for f^N) and produce a linear shift of all the levels of the configuration. The relative correctior produced by this interaction are then of the same form as the corrections to the matrix elements of ℓ^N produced by interaction with $\ell^{N-2}\ell'\ell''$, Eqs. (11) and (28).

(d) ℓ^N with $\ell^{N-1}\ \ell'$

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

$$(\ell^N \gamma SL| \sum_{i<j}^{N} \frac{e^2 r_<^k}{r_>^{k+1}} \left(\underset{\sim}{C}_i^{\,k} \cdot \underset{\sim}{C}_j^{\,k}\right) |\ell^{N-1}\gamma' S' L' \ell' SL)$$

$$= \sum_k (-1)^{L+L'+\ell} \sqrt{N}\, (\ell\|\underset{\sim}{C}^k\|\ell)(\ell\|\underset{\sim}{C}^k\|\ell')\, R^k(\ell\ell,\ell\ell') \sum_{\psi_1} (\ell^N\psi\{|\ell^{N-1}\psi_1)$$

$$\times\ (\ell^{N-1}\psi_1\|\underset{\sim}{U}^k\|\ell^{N-1}\psi') \begin{Bmatrix} L' & k & L_1 \\ \ell & L & \ell' \end{Bmatrix} . \qquad (49)$$

If the summation over ψ_1 is evaluated by means of the identity in Appendix I (Eq. (68)), the right hand side of Eq. (49) becomes

$$= \sum_k (-1)^{L+L'+\ell} \sqrt{N}\, (\ell\|\underset{\sim}{C}^k\|\ell)(\ell\|\underset{\sim}{C}^k\|\ell')\, R^k(\ell\ell,\ell\ell') \Bigg[(-1)^{\ell+\ell'+k} \sum_{\bar{\psi}} ([\bar{L}]/[L])^{1/2}$$

$$\times\ (\ell^N\bar{\psi}\{|\ell^{N-1}\psi') \begin{Bmatrix} \ell & \bar{L} & L' \\ L & \ell' & k \end{Bmatrix} (\ell^N\psi\|\underset{\sim}{U}^k\|\ell^N\bar{\psi})$$

$$-\ \delta(\ell,\ell')\, (-1)^{\ell+L+L'} (\ell^N\psi\{|\ell^{N-1}\psi')/[\ell] \Bigg] . \qquad (50)$$

For $\ell \neq \ell'$ when the second term in Eq. (50) is zero, we may write the corrections to the matrix elements of ℓ^N as

$$C = -N \sum_{k\,k'} \sum_{\substack{\psi' \\ \bar{\psi}\ \bar{\psi}'}} X(k,k')([\bar{L}][\bar{L}'])^{1/2}/[L])(\ell^N\bar{\psi}\{|\ell^{N-1}\psi')$$

$$\times\ (\ell^N\bar{\psi}'\{|\ell^{N-1}\psi') \begin{Bmatrix} \ell & \bar{L} & L' \\ L & \ell' & K \end{Bmatrix} \begin{Bmatrix} \ell & \bar{L}' & L' \\ L & \ell' & k' \end{Bmatrix} (\ell^N\psi\|\underset{\sim}{U}^k\|\ell^N\bar{\psi})$$

$$\times \quad (\ell^N\psi''\|\underset{\sim}{U}^{k'}\|\ell^N\bar{\psi}'), \tag{51}$$

where

$$X(k,k') = (\ell\|\underset{\sim}{C}^k\|\ell)(\ell\|\underset{\sim}{C}^k\|\ell')(\ell\|\underset{\sim}{C}^{k'}\|\ell)(\ell\|\underset{\sim}{C}^{k'}\|\ell')$$

$$\times \quad R^k(\ell\ell,\ell\ell')\, R^{k'}(\ell\ell,\ell\ell')/\Delta E. \tag{52}$$

Performing the summation over the states of $\ell^{N-1}\ell'$ which connect a particular state ψ of ℓ^N we obtain

$$C = -\sum_{kk'k''}\sum_{\bar{\psi}\,\bar{\psi}'} X(k,k')[k'']/[L] \begin{Bmatrix} k & k'' & k' \\ \bar{L}' & L & \bar{L} \end{Bmatrix} \begin{Bmatrix} k & k'' & k' \\ \ell & \ell' & \ell \end{Bmatrix}$$

$$\times \quad (\ell^N\psi\|\underset{\sim}{U}^k\|\ell^N\bar{\psi})(\ell^N\bar{\psi}\|\underset{\sim}{U}^{k''}\|\ell^N\bar{\psi}')(\ell^N\bar{\psi}'\|\underset{\sim}{U}^{k'}\|\psi''). \tag{53}$$

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

$$(\psi|(\{\underset{\sim}{U}^k\underset{\sim}{U}^{k''}\}^{k'}\cdot\underset{\sim}{U}^{k'})|\psi'')$$

$$= \sum_{\bar{\psi}'} (-1)^{L-\bar{L}'}(\psi\|\{\underset{\sim}{U}^k\,\underset{\sim}{U}^{k''}\}^{k'}\|\bar{\psi}')\,(\bar{\psi}'\|\underset{\sim}{U}^{k'}\|\psi'')/[L]$$

$$= \sum_{\bar{\psi}\,\bar{\psi}'} (-1)^{k'}([k'])^{1/2} \begin{Bmatrix} k & k'' & k' \\ \bar{L}' & L & \bar{L} \end{Bmatrix} (\psi\|\underset{\sim}{U}^k\|\bar{\psi})(\bar{\psi}\|\underset{\sim}{U}^{k''}\|\bar{\psi}')(\bar{\psi}'\|\underset{\sim}{U}^{k'}\|\psi'')/[L].$$

Equation (53) can now be rewritten as

$$C = -\sum_{kk'k''} X(k,k')[k''][[k']]^{1/2} \begin{Bmatrix} k & k'' & k' \\ \ell & \ell' & \ell \end{Bmatrix}$$

$$\times \quad (\ell^N\psi|(\{\underset{\sim}{U}^k\underset{\sim}{U}^{k''}\}^{k'}\cdot\underset{\sim}{U}^{k})|\ell^N\psi''). \tag{54}$$

We note that Eq. (54) contains 3-particle terms of the type

$$(\ell^N\psi|\sum_{i<j<h}((\underset{\sim}{U}_i^k \cdot \underset{\sim}{U}_j^{k''})^{k'} \underset{\sim}{U}_h^{k'})|\ell^N\psi'').$$

When $\bar{\ell} \equiv \ell'$ two additional terms must be added to C. The first is given by

$$C_1 = 2\sum_{k\,k'\psi'\,\bar{\psi}} X(k,k')/[\ell](-1)^{\ell+k+L+L'}\,([\bar{L}]/[L])^{1/2}(\ell^N\bar{\psi}\{|\ell^{N-1}\psi')$$

$$\times\;(\ell^N\psi''\{|\ell^{N-1}\psi')\begin{Bmatrix}\ell & \bar{L} & L'\\ L & \ell & k\end{Bmatrix}(\ell^N\psi\|\underset{\sim}{U}^k\|\ell^N\bar{\psi}),$$

where X(k,k') is given by Eq. (47). Evaluating the summation over ψ' and then using the closure property to sum over $\bar{\psi}$, we obtain

$$C_1 = \sum_{k\,k'} X(k,k')/[\ell]\left[4(\ell^N\psi\|\underset{\sim}{U}^k\cdot\underset{\sim}{U}^k\|\ell^N\psi'') + \frac{2N}{[\ell]}\,\delta(\psi,\psi'')\right]. \tag{55}$$

The second term is merely

$$C_2 = -N\sum_{k\,k'} X(k,k')\sum_{\psi'}(\ell^N\psi'\{|\ell^{N-1}\psi')(\ell^N\psi''\{|\ell^{N-1}\psi')/[\ell]^2 = -N\sum_{k\,k'}\frac{X(k,k')}{[\ell]}\,\delta(\psi,\psi'') \tag{56}$$

Adding Eqs. (55) and (56) we obtain

$$C' = \sum_{k\,k'} X(k,k')/[\ell]\left[4(\ell^N\psi\|\underset{\sim}{U}^k\cdot\underset{\sim}{U}^k\|\ell^N\psi'') + \frac{N}{[\ell]}\;\delta(\psi,\psi'')\right] \tag{57}$$

Thus we see that when $\ell \equiv \ell'$, interaction of ℓ^N with $\ell^{N-1}\ell'$ is represented by a 3-body interaction, plus a scalar 2-body interaction proportional to the coefficients of the Slater integral F^k and a linear shift of all the terms in the configuration.

(e) ℓ^N with $(\ell')^{4\ell+1}\ell^{N+1}$

This type of interaction corresponds to a "core excitation" where an electron ℓ' from a closed $(\ell')^{4\ell'+2}$ shell is regarded as being promoted into the partially filled ℓ^N shell. A typical matrix element coupling a state of the ℓ^N configuration with a state of $(\ell')^{4\ell'+1}\ell^{N+1}$ configuration will be of the form

$$(\ell^N\gamma SL;[(\ell')^{4\ell'+2}\ ]^1S;SL|\sum_k \sum_{i<j}^N e^2 \frac{r_<^k}{r_>^{k+1}}(\underset{\sim}{C}_i^k \cdot \underset{\sim}{C}_j^k)|\ell^{N+1}\gamma'S'L';(\ell')^{4\ell'+1}SL)$$

$$= (N+1)^{1/2}(-1)^{S'-S-1/2}\left[\frac{[S'][L']}{[S][L]}\right]^{1/2}(\ell\|\underset{\sim}{C}^k\|\ell)\left[\sum_{\bar{\psi}}(\ell^{N+1}\psi'\{|\ell^N\bar{\psi})\right.$$

$$\times (\ell^N\bar{\psi}\|\underset{\sim}{U}^k\|\ell^N\psi)\begin{Bmatrix}\bar{L} & k & L\\ \ell' & L' & \ell\end{Bmatrix}(\ell'\|\underset{\sim}{C}^k\|\ell)-\delta(\ell,\ell')(\ell^{N+1}\psi'\{|\ell^N\psi)$$

$$\left.\times (\ell\|\underset{\sim}{C}^k\|\ell)(-1)^{L'+\ell+L}/[\ell]\right]R^k(\ell\ell,\ell\ell')\ , \qquad (58)$$

where the principal quantum numbers are of course always different.

In order to obtain an expression for C, we again consider first the case of $\ell \neq \ell'$. The total correction is then

$$C = -(N+1)\sum_{kk'}\sum_{\substack{\psi'\ \bar{\psi}\\ \bar{\psi}'}} X(k,k')\ \frac{[S'][L']}{[S][L]}(\ell^{N+1}\psi'\{|\ell^N\bar{\psi})(\ell^{N+1}\psi'\{|\ell^N\bar{\psi}')$$

$$\times (\ell^N\bar{\psi}\|\underset{\sim}{U}^k\|\ell^N\psi)(\ell^N\bar{\psi}'\|\underset{\sim}{U}^{k'}\|\ell^N\psi'')\begin{Bmatrix}\bar{L} & k & L\\ \ell' & L' & \ell\end{Bmatrix}\begin{Bmatrix}\bar{L}' & k' & L\\ \ell' & L' & \ell\end{Bmatrix}\ , \qquad (59)$$

where X(k,k') is again given by Eq. (52). We may now use Eq. (34) to convert to conjugate states and carry out the sums over ψ', $\bar{\psi}$, and $\bar{\psi}'$. Converting back to states of ℓ^N and ℓ^{N+1} by means of Eq. (35), for $k''\neq 0$, Eq. (59) becomes

$$C = -\sum_{\substack{kk'\\k''\neq 0}} X(k,k') \frac{(-1)^{k'+k''+1}[k'']}{\sqrt{[k']}} \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix} \tag{60}$$

$$\times \; (\ell^N\psi\|(\{\underset{\sim}{U}^k\underset{\sim}{U}^{k''}\}^{k'} \cdot \underset{\sim}{U}^{k'})\|\ell^N\psi'') - \sum_k \frac{(4\ell+2-N)X(k,k)}{[k][\ell]} \Big[2(\ell^N\psi\|\underset{\sim}{U}^k \cdot \underset{\sim}{U}^k\|\ell^N\psi'')$$
$$+ \frac{N}{[\ell]}\delta(\psi,\psi'')\Big]$$

where k and k' are even and $\ell \neq \ell'$. The first term differs only by some multiplicative factors from the interaction of ℓ^N with $\ell^{N-1}\ell'$, Eq. (54), while the last two terms give a scalar two-body interaction and a linear shift of all terms of ℓ^N.

When $\ell = \ell'$ we again have two additional terms.

$$C_1 = 2\sum_{kk'} X(k,k') \sum_{\psi'\bar{\psi}} \frac{(N+1)[S'][L']}{[\ell]\,[S][L]} (\ell^{N+1}\psi'\{|\ell^N\bar{\psi})(\ell^{N+1}\psi'\{|\ell^N\psi'')$$

$$\times \quad (-1)^{L'+\ell+L} \begin{Bmatrix} \bar{L} & k & L \\ \ell' & L' & \ell \end{Bmatrix} (\ell^N\bar{\psi}\|\underset{\sim}{U}^k\|\ell^N\psi). \tag{61}$$

Again converting to conjugate states to carry out the sum on ψ' and using the closure property, we obtain

$$C_1 = -\sum_{kk'} \frac{X(k,k')}{[\ell]} \Big[4(\ell^N\psi\|(\underset{\sim}{U}^k \cdot \underset{\sim}{U}^k)\|\ell^N\psi'') + (2N/[\ell])\delta(\psi,\psi'')\Big]. \tag{62}$$

Using Eq. (20) of Racah,[5] C_2 is readily seen to be

$$C_2 = -\frac{(4\ell+2-N)}{[\ell]^2} \sum_{kk'} X(k,k'). \tag{63}$$

For the case of $\ell \equiv \ell'$ we must then add to Eq. (60) the expression

$$C' = -\sum_{kk'} \frac{X(k,k')}{[\ell]} \Big[4(\ell^N\psi\|(\underset{\sim}{U}^k \cdot \underset{\sim}{U}^k)\|\ell^N\psi'') + (N+4\ell+2)/[\ell]\delta(\psi,\psi'')\Big]. \tag{64}$$

The total correction then has the same form as Eq. (57). Thus when $\ell \equiv \ell'$ the interaction of ℓ^N with $(\ell')^{4\ell'+1}\ell^{N+1}$ may be represented in the same way as the interaction of ℓ^N with $\ell^{N-1}\ell'$, i.e., as a 3-body interaction plus a scalar 2-body interaction and a linear shift of all the terms of ℓ^N.

4. EVALUATION OF THE RADIAL PARAMETERS

If radial functions were available for both the ground state and excited orbitals it would now be possible to calculate the perturbation due to the various excited configurations. One must, however, be sure that the perturbation to be calculated has not already been included in the calculation of the wave functions used. The use of perturbation theory starting from Hartree-Fock functions has been discussed in some detail by Nesbet.[26] His method of symmetry and equivalence restrictions, used by Watson and Freeman[27] in their HF calculations for the rare earths, includes configuration interaction involving promotion of any 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 HF calculation, must be treated as a perturbation on these functions. Similarly the SCF calculation of Ridley[28] includes one-electron excitations to states of the same symmetry. No two-electron excitations are included, even in the unrestricted HF functions. HF functions calculated for a particular S and L can contain configuration interaction only with states of the same S and L in an excited configuration. Such functions may be appropriate for estimating perturbations due to a one-electron excitation to another state of the same symmetry but, of different S and L. A function which is an average for a configuration must, in some average way, take into account all one-electron excitations of the same symmetry, but it is difficult to say exactly what has been included. Thus, in computing the interactions due to various configurations one must be very careful that all or part of that interaction has not already been included in the computation of the radial wave functions.

5. CONCLUSIONS

It has been shown that, to second-order, in the approximation that the configurations are well separated, all two-particle interactions with the configuration ℓ^N may be represented by a linear shift of all the terms of the configuration and a scalar two-body interaction. One-electron excitations, either from the core or the unfilled ℓ^N shell, are represented by an effective three-body interaction, a linear shift of all the terms of ℓ^N and, in some cases, a scalar two-body interaction.

The scalar two-body interactions are those arising from the linear theory. The validity of Racah[19] and Trees'[17] treatment of the two-body scalar interaction has been established and, in addition, the analytical form of the radial parts of the interactions determined. Racah[19] and Trees[17] have introduced two scalar interactions to be added to the matrices of d^N, one proportional to $L(L+1)$ and the other 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 (Eqs. (12) and (25)) are of a simpler form. It will be noted that different choices of scalar interactions will yield different corrections to the Slater F^k radial integrals. In general we need only introduce ℓ parameters in addition to the $\ell+1$ Slater parameters to include the effects of the two-particle interactions with the ℓ^N configuration. Racah and Shadmi[29] 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 interactions.

The three-body interactions are of a non-linear type. For d^N configurations where there is the excitation of a single s electron they may be reduced to the addition of a single parameter of the type recently used by Trees[30] to take into account the effect of $3s3d^7$ on $3s^2 3d^6$. For f^N the total correction to the electrostatic matrix element is given by a change in the Slater integrals

F^k plus a term of the form

$$C = \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) + \sum_{kk'k''\ell'} X(k,k',\ell') \begin{Bmatrix} k & k' & k'' \\ \ell & \ell & \ell' \end{Bmatrix}$$

$$\times \quad (f^N\psi \| \{ \underset{\sim}{U}^k \underset{\sim}{U}^{k''} \}^{k'} \cdot \underset{\sim}{U}^{k'} \| f^N\psi''), \tag{65}$$

where $X(k,k',\ell')$ is a constant for a given k, k' and ℓ'. The appearance of ℓ' in the 6-j symbol makes parametrization of the three-body terms more difficult than for the two-body interactions. However, it should be possible to parametrize these three-body terms for the most significant interactions, $\ell' = 1$ and 3 for f^N, and determine the parameters $X(k,k',\ell')$, from experiment. For the p excitations only two additional parameters, $X(2,2,p)$ and $X(4,4,p)$, are needed while for the f excitations six additional parameters, $X(2,2,f)$, $X(4,4,f)$, $X(6,6,f)$, $X(6,2,f)$, $X(4,2,f)$ and $X(6,4,f)$, are required. Thus for the f^N configurations both the two- and one-electron excitations could be included by adding ten parameters to supplement the usual Slater parameters.

Since the total correction for two electron excitations is given by the sum of ℓ additional parameters, it is meaningless to perform a least aquares analysis without including all of them. Thus, for f^N it is unwise to consider only a term $\alpha L(L+1)$ as this is only part of the correction. We have also seen that the addition of the parameters α, β and γ is <u>always</u> associated with a modification of Slater integrals F^k. Therefore, one should never do a least squares analysis for these parameters without allowing the Slater integrals to vary at the same time.

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 <u>angular</u> part of the interactions is independent of the principal quantum numbers $n'\ell'$ of the excited electrons. Not only will 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] calculation of the effects of $3s3d^7$ on $3s^23d^6$, the effects of $3s^23d^54s$ have automatically been included.

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.

It should be pointed out that the above conclusions hold only for ℓ^N type configurations and do not necessarily hold for other configurations. For example, starting from the equations of Wybourne,[23] it can readily be shown that the direct part of the interaction of $\ell^N\ell'$ with $\ell^N\ell''$ contains a term of the form

$$(\ell^N\psi\|\{\underset{\sim}{U}^k\underset{\sim}{U}^{k'}\}^{k''}\|\ell^N\psi'')$$

which is a non-scalar two-body interaction. Such non-scalar terms may be important when considering the interactions of such configurations as d^Np.

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 analogues where configurations of equivalent nucleons are encountered.

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Alternate Expression for the Interaction between the Configurations ℓ^N and $\ell^{N-1}\ell'$

If we make use of the technique used by Racah to calculate the interaction between the configurations d^n and $d^{n-1}s$, another expression, equivalent to Eq. (22), may be obtained for the interaction between the configurations ℓ^N and $\ell^{N-1}\ell'$. These results lead to an interesting identity[32] which can be shown to be generally true, even in the case of double tensors.

Following Racah,[5] we may write

$$(\ell^N\gamma SL|\sum_{i<j}\frac{r_<^k}{r_>^{k+1}}(\mathbf{C}_i^k\cdot\mathbf{C}_j^k)|\ell^{N-1}\psi'\ell'SL)$$

$$= \Bigg\{\frac{1}{2[L]}\Bigg[\sum_{\psi''}(-1)^{L-L''}(\ell^N\gamma SL\|\sum_i\mathbf{C}_i^k\|\ell^N\gamma''SL'')(\ell^N\gamma''SL''\|\sum_i\mathbf{C}_i^k\|\ell^{N-1}\psi'\ell'SL)$$

$$+\sum_{\psi_1 L'''}(-1)^{L-L'''}(\ell^N\gamma SL\|\sum_i\mathbf{C}_i^k\|\ell^{N-1}\psi_1\ell'SL''')(\ell^{N-1}\psi_1\ell'SL'''\|\sum_i\mathbf{C}_i^k\|\ell^{N-1}\psi'\ell'SL)\Bigg]$$

$$-\sqrt{N}\,(\ell^N\psi\{|\ell^{N-1}\psi')(\ell\|\mathbf{C}^k\|\ell')^2\,\delta(\ell,\ell')/[\ell]\Bigg\}R^k(\ell\ell,\ell\ell') \qquad (66)$$

The last term in this expression arises from the fact that Racah's technique of replacing the $\sum_{i<j}(\mathbf{C}_i^k\cdot\mathbf{C}_j^k)$ by $(\sum_i\mathbf{C}_i^k)^2$ introduces extra terms which are non zero for $\ell=\ell'$ and must therefore be subtracted out.

If we use the Biedenharn-Elliott sum rule and the orthogonality properties of 6-j symbols to evaluate the sum over L''', the righthand side of Eq. (66) may be rewritten as

$$\Bigg[\frac{1}{2} \sum_{\psi''} \sqrt{\frac{N[L'']}{[L]}} (-1)^{L+L'+\ell'+k} (\ell^N\psi''\{|\ell^{N-1}\psi') \begin{Bmatrix} \ell & L'' & L' \\ L & \ell' & k \end{Bmatrix} (\ell\|\underset{\sim}{C}^k\|\ell)$$

$$\times (\ell|\underset{\sim}{C}^k\|\ell')(\ell^N\gamma SL\|\underset{\sim}{U}^k\|\ell^N\gamma''SL'') + \frac{1}{2} \sum_{\psi_1} (-1)^{L+L'+\ell} \sqrt{N} (\ell^N\psi\{|\ell^{N-1}\psi_1)$$

$$\times (\ell\|\underset{\sim}{C}^k\|\ell')(\ell\|\underset{\sim}{C}^k\|\ell) \begin{Bmatrix} \ell' & L & L' \\ L_1 & k & \ell \end{Bmatrix} (\ell^{N-1}\psi_1\|\underset{\sim}{U}^k\|\ell^{N-1}\psi')$$

$$- \frac{1}{2} \delta(\ell,\ell') \sqrt{N} (\ell^N\psi\{|\ell^{N-1}\psi')(\ell\|\underset{\sim}{C}^k\|\ell')^2/[\ell] \Bigg] R^k(\ell\ell,\ell\ell') \tag{67}$$

Since they are two different expressions for the same matrix element, Eq. (67) must be identically equal to the righthand side of Eq. (49). A slight rearrangement of terms then leads to the identity

$$\sum_{\psi_1} (\ell^N\psi\{|\ell^{N-1}\psi_1) \begin{Bmatrix} \ell' & L & L' \\ L_1 & k & \ell \end{Bmatrix} (\ell^{N-1}\psi_1\|\underset{\sim}{U}^k\|\ell^{N-1}\psi')$$

$$\equiv \sum_{\psi''} ([L'']/[L])^{1/2} (-1)^{\ell+\ell'+k} (\ell^N\psi''\{|\ell^{N-1}\psi') \begin{Bmatrix} \ell & L'' & L' \\ L & \ell' & k \end{Bmatrix}$$

$$\times (\ell^N\gamma SL\|\underset{\sim}{U}^k\|\ell^N\gamma''SL'') - \delta(\ell,\ell')(-1)^{\ell+L+L'}(\ell^N\psi\{|\ell^{N-1}\psi')/[\ell] \tag{68}$$

A similar expression for the more general case of double tensors may be generated in the following manner. Take the tensors $\underset{\sim}{U}^{\kappa k} = \sum_1 (\underset{\sim}{U}^{\kappa k})_i$ where $(s\ell\|\underset{\sim}{U}^{\kappa k}\|s'\ell') = \delta(s,s')\delta(\ell,\ell')$. Since the U^k's stay within a configuration ℓ^N a complete set of states is $|\ell^N\psi''M_S''M_L'')$ where $\psi'' \equiv \gamma''S''L''$.

Thus

$$\sum_{\substack{\psi''\psi'''M_S''\\ M_S'''M_L''M_L'''}} (\ell^{N-1}\bar{\psi}\|\}\ell^N\psi'')(\bar{S}\ \bar{M}_S s m_s|\bar{S}\ sS''M_S'')(\bar{L}\ \bar{M}_L\ \ell m_\ell|\bar{L}\ell L''M_S'') \tag{69}$$

$$\times \quad (\psi''M_S''M_L''|U^{\kappa k}_{\pi q}|\psi'''M_S'''M_L''')(\ell^N\psi'''\{|\ell^{N-1}\bar{\psi}')$$

$$\times \quad (\bar{\bar{S}}'s\ S'''M_S'''|\bar{\bar{S}}'\bar{\bar{M}}_S'\ s\ m_s')(\bar{\bar{L}}'\ell L'''\ M_S'''|\bar{\bar{L}}'\bar{\bar{M}}_L'\ \ell m_\ell')$$

$$= \quad (\bar{\bar{\psi}}\ \bar{\bar{M}}_S\bar{\bar{M}}_L,\ s\ell m_s m_\ell|U^{\kappa k}_{\pi q}|\bar{\psi}'\ \bar{M}_S'\ \bar{M}_L',\ s\ell m_s' m_\ell').$$

The states with bars over them are all states of ℓ^{N-1}. We now multiply both sides by $(\bar{\bar{L}}\ell LM_L|\bar{L}\ \bar{M}_L\ell m_\ell)$ $(\bar{\bar{L}}'\bar{\bar{M}}_L'\ell m_\ell'|\bar{L}\ \ell\ L'M_L')$ $(\bar{\bar{S}}sSM_S|\bar{S}\ \bar{\bar{M}}_S s\ m_s)(\bar{S}'\bar{\bar{M}}_S' s\ m_s'|\bar{\bar{S}}sS'M_S')$ and sum over $\bar{\bar{M}}_L, \bar{M}_S$, m_ℓ, m_s, $\bar{\bar{M}}_L, \bar{\bar{M}}_S'$, m_ℓ', m_s'. Using the Wigner-Eckart theorem[24] on the matrix elements we get,

$$\sum_{\psi''\psi'''} (\ell^{N-1}\bar{\psi}|\}\ell^N\psi'')(\ell^N\psi''\|\underset{\sim}{U}^{\kappa k}\|\ell^N\psi''')(\ell^N\psi'''\{|\ell^{N-1}\bar{\psi}')\ \delta(L',L''')\ \delta(S',S''') \tag{70}$$

$$\times \quad \delta(L,L'')\ \delta(S,S'') \ = \ (\ell^{N-1}\bar{\psi},s\ell,\psi\|\underset{\sim}{U}^{\kappa k}\|\ell^{N-1}\bar{\psi}',s\ell,\psi').$$

Because of the delta functions in S and L, we can multiply by $(\ell^N\psi|\ell^{N-1}\bar{\psi})$ and sum over $\bar{\psi}$. This gives

$$\sum_{\psi'''} (\ell^N\psi\|\underset{\sim}{U}^{\kappa k}\|\psi'')(\ell^N\psi'''\{|\ell^{N-1}\overline{\psi}') \, \delta(L',L'') \, \delta(S',S''')$$

$$= \sum_{\overline{\psi}} (\ell^N\psi\{|\ell^{N-1}\overline{\psi})(\ell^{N-1}\overline{\psi}, \, s\ell, \, SL\|\underset{\sim}{U}^{\kappa k}\|\ell^{N-1}\overline{\psi}', \, s\ell, S'L')$$

$$= \sum_{\overline{\psi}} (\ell^N\psi\{|\ell^{N-1}\overline{\psi})(-1)^{\overline{L}+\ell+L'+k+\overline{S}+s+S'+\kappa} ([L][L'][S][S'])^{1/2} \tag{71}$$

$$\times \quad \begin{Bmatrix} L & k & L' \\ \overline{L}' & \ell & \overline{L} \end{Bmatrix} \begin{Bmatrix} S & \kappa & S' \\ \overline{S}' & s & \overline{S} \end{Bmatrix} (\ell^{N-1}\overline{\psi}\|\underset{\sim}{U}^{\kappa k}\|\ell^{N-1}\overline{\psi}')$$

$$+ \quad (\ell^N\psi\{|\ell^{N-1}\overline{\psi}')(-1)^{\overline{L}'+\ell+L+k+\overline{S}'+s+S+\kappa} ([L][L'][S][S'])^{1/2}$$

$$\times \quad \begin{Bmatrix} L & k & L' \\ \ell & \overline{L}' & \ell \end{Bmatrix} \begin{Bmatrix} S & \kappa & S' \\ s & \overline{S}' & s \end{Bmatrix} (s\ell\|\underset{\sim}{U}^{\kappa k}\|s\ell).$$

If we now multiply by

$$\begin{Bmatrix} L & k & L' \\ \ell & \overline{L}' & \ell' \end{Bmatrix} \begin{Bmatrix} S & \kappa & S' \\ s & \overline{S}' & s' \end{Bmatrix} \sqrt{\frac{[S'][L']}{[S]\,[L\ ]}}$$

and sum over S' and L', we obtain

$$\sum_{\psi'''} (\ell^N\psi\|\underset{\sim}{U}^{\kappa k}\|\ell^N\psi''')(\ell^N\psi'''\{|\ell^{N-1}\bar{\psi}) \sqrt{\frac{[L'''][S''']}{[L\ ][S\ ]}}$$

$$\times \begin{Bmatrix} L & k & L''' \\ \ell & \bar{L}' & \ell' \end{Bmatrix} \begin{Bmatrix} S & \kappa & S''' \\ s & \bar{S}' & s' \end{Bmatrix} \qquad (72)$$

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

$$\times (\ell^{N-1}\bar{\psi}\|\underset{\sim}{U}^{\kappa k}\|\ell^{N-1}\bar{\psi}') + (\ell^N\psi\{|\ell^{N-1}\bar{\psi}')(-1)^{\bar{L}+\ell+\bar{S}'+s+S+k+L+\kappa}$$

$$\times \delta(\ell,\ell')\ \delta(s,s')/([\ell][s]).$$

This is the same as (68) for the more general case of double tensors.

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