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ABSTRACT

Simplified expressions for the matrix elements of electrostatic interactions both within and between several types of complex electron configurations have been obtained by the application of angular-momenta recoupling techniques. The use of these recoupling techniques avoids the usual extensive calculation of the sums of products of the matrix elements of tensors of the types $V^{\kappa k}$ and U^{k}. The derived expressions involve the sums of products of coefficients of fractional parentage and n-j symbols, and as such are amenable to machine computation.

ELECTROSTATIC INTERACTIONS IN COMPLEX ELECTRON CONFIGURATIONS*

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INTRODUCTION

Studies of the complex spectra of rare-earth and actinide ions are complicated by the frequent requirement of a detailed knowledge of the structure of quite complex electron configurations, and in some cases a knowledge of the electrostatic interactions between the configurations is necessary. The configurations of greatest interest are typified by f^n, $f^n\ell'$, $f^n\ell'\ell''$, and $f^n\ell'^2$. The electrostatic matrices of all the f^n configurations are well known and will not be discussed. Of primary interest will be the interactions of the electrons outside the f^n core with those of the f^n core. The number of states occurring for these configurations is very large, and hence it is desirable to be able to compute the matrix elements on a high-speed computer. However, before calculations such as these are attempted, it is essential that the expressions for the matrix elements be put in as simple a form as is possible.

Racah[1] and Arima et al.[2] have given general procedures for calculating the matrix elements of "direct"-and "exchange"-type interactions between outer electrons and an equivalent electron core. Their treatment of exchange-type interactions requires the expanding of the exchange interactions into the sums of direct interactions. This approach--although equivalent, in its final results, to the method outlined in this paper--is complicated

by the appearance of sums of products of tensors of the types $V^{\kappa k}$ and U^k. In seeking simplifications of their formulae and in making the formulae amenable to machine computation, it is desirable to avoid having to evaluate the matrix elements of several tensorial quantities prior to the actual evaluation of the electrostatic matrix elements. In the present formulation of the problem the need to evaluate the matrix elements of the double tensors $V^{\kappa k}$ is overcome by suitably recoupling the angular momenta of the electrons involved in the electrostatic interactions. As a result the formulae may be expressed in a concise manner that displays clearly the properties of the angular momenta involved by the use of n-j symbols.[3]

$\ell^n \ell' \ell''$ CONFIGURATIONS

It will be assumed that the two inequivalent electrons are coupled together and then coupled to the ℓ^n core to form a total-orbital and a total-spin quantum number. For complete generality consider the matrix elements of the angular part of the electrostatic interaction between a configuration $\ell^n \ell' \ell''$ and a second configuration $\ell^n \ell''' \ell^{iv}$. We may write, for the matrix elements of the electrostatic interactions of the inequivalent electrons with the ℓ^n equivalent electron core,

$$\left(\ell^n S_1 L_1 (s\ell', s\ell'') S_1' L_1'; S_2 L_2 \Big| \sum_{i<j} (C_i^k \cdot C_j^k) \Big| \ell^n S_3 L_3 (s\ell''', s\ell^{iv}) S_3' L_3'; S_4 L_4\right)$$

$$= n \sum_{\overline{\psi}} (\psi_1 \{ | \overline{\psi}) (\psi_3 \{ | \overline{\psi})$$

$$\times \Big(\ell^{n-1} \overline{\alpha S L}, s\ell, S_1 L_1 (s\ell', s\ell'') S_1' L_1'; S_2 L_2 \big| (C_i^k \cdot C_j^k) \big| \ell^{n-1} \overline{\alpha S L}, s\ell,$$

$$S_3 L_3 (s\ell''', s\ell^{iv}) S_3' L_3'; S_4 L_4 \Big) , \qquad (1)$$

where the $(\psi\{|\overline{\psi})$ are the usual coefficients of fractional parentage[4,5] and the scalar products, $(C_i^k \cdot C_j^k)$, are tensorial sets of spherical harmonics.[6] The matrix element in (1) may now be examined. First a series of recouplings[6] of the type

$$\left((\overline{S}s)\, S_1, (ss)S_1'; S_2 \,|\, \overline{S}\,(sS_1')\sigma; S_2\right) = (-1)^{\overline{S}+s+S_1'+S_2} ([S_1][\sigma])^{1/2} \begin{Bmatrix} S_1' & S_2 & S_1 \\ \overline{S} & s & \sigma \end{Bmatrix} \quad (2)$$

is made, where $[\sigma]$ etc., are understood as $(2\sigma+1)$ etc. Upon recoupling in both spin and orbital space, the matrix element in right-hand side (rhs) of (1) becomes

$$\sum_{\substack{\sigma,\lambda \\ \sigma'\lambda'}} (-1)^{S_1'+S_3'+L_1'+L_3'}\, \delta(\sigma,\sigma')\, \delta(\lambda,\lambda')\, \delta(S_2,S_4)\, \delta(L_2,L_4)$$

$$\times \left(([S_1][S_3][L_1][L_3])^{1/2} [\sigma][\lambda] \begin{Bmatrix} S_1' & S_2 & S_1 \\ \overline{S} & s & \sigma \end{Bmatrix} \begin{Bmatrix} S_3' & S_4 & S_3 \\ \overline{S} & s & \sigma' \end{Bmatrix}\right.$$

$$\left.\times \begin{Bmatrix} L_1' & L_2 & L_1 \\ \overline{L} & \ell & \lambda \end{Bmatrix} \begin{Bmatrix} L_3' & L_4 & L_3 \\ \overline{L} & \ell & \lambda' \end{Bmatrix} (\sigma\lambda \,|\, (C_i^k \cdot C_j^k) \,|\, \sigma'\lambda')\right), \quad (3)$$

where

$$\left(\sigma\lambda \,|\, (C_i^k \cdot C_j^k) \,|\, \sigma'\lambda'\right) = \left((sS_1')\sigma,\ (\ell L_1')\lambda \,|\, (C_i^k \cdot C_j^k) \,|\, (sS_3')\sigma',\ (\ell L_3')\lambda\right). \quad (4)$$

Thus there remains only to evaluate the matrix elements in (4) for three electrons and then perform the sum over σ and λ in (3). For direct interactions the calculation is quite straightforward,[6] and after application of the Biedenharn-Elliott sum rule[3] to the sum over λ, the matrix element on the

rhs of Eq. (1) becomes, for direct interactions,

$$(-1)^{L_1' + L_1 + L_2 + \ell + k} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} (L_1' || C_j^k || L_3') \begin{Bmatrix} L_3' & k & L_1' \\ L_1 & L_2 & L_3 \end{Bmatrix} (\psi_1 || U^k || \psi_3), \tag{5}$$

where

$$(\psi_1 || U^k || \psi_3) = n\,([L_1][L_3])^{1/2} \sum_{\overline{\psi}} (\psi_1 \{ | \overline{\psi}) (\psi_3 \{ | \overline{\psi}) \quad (-1)^{\overline{L} + L_1 + \ell + k} \begin{Bmatrix} \ell & L_1 & \overline{L} \\ L_3 & \ell^1 & k \end{Bmatrix}. \tag{6}$$

If the coefficients of the radial integral $R^k(\ell\ell'; \ell\ell''')$ are required, the matrix element in (5) is evaluated by putting

$$(\ell' \ell'' L_1' || C_1^k || \ell''' \ell^{iv} L_3') = (-1)^{\ell'' + L_3' + k} ([\ell'][\ell'''][L_1'][L_3'])^{1/2}$$

$$\times \begin{pmatrix} \ell' & k & \ell''' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L_1' & L_3' & k \\ \ell''' & \ell' & \ell'' \end{Bmatrix} \delta(\ell'', \ell^{iv}), \tag{7}$$

whereas if the coefficients of $R^k(\ell\ell''; \ell\ell^{iv})$ are required, we write

$$(\ell' \ell'' L_1' || C_2^k || \ell''' \ell^{iv} L_3') = (-1)^{\ell' + \ell'' + \ell^{iv} + L_1' + k} ([\ell''][\ell^{iv}][L_3'])^{1/2}$$

$$\times \begin{pmatrix} \ell'' & k & \ell^{iv} \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L_1' & L_3' & k \\ \ell^{iv} & \ell'' & \ell' \end{Bmatrix} \delta(\ell', \ell'''). \tag{8}$$

The coefficients of $R^k(\ell\ell'';\ \ell'''\ell^{iv})$ are trivial and need not be considered here.[6] If the electrons external to the core are equivalent, we need only replace the matrix element $(L_1' \| C_j^k \| L_3')$ in (5) by

$$(-1)^{\ell'}[\ell'] \begin{pmatrix} \ell' & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} (L_1' \| U^k \| L_3'), \tag{9}$$

where

$$(L_1' \| U^k \| L_3') = 2([L_1'][L_3'])^{1/2} (-1)^{L_1'+k} \begin{Bmatrix} L_1' & L_3' & k \\ \ell' & \ell' & \ell' \end{Bmatrix}. \tag{10}$$

If the direct interactions between $\ell^n\ell'^2$ and $\ell^n\ell'''\ell^{iv}$ are of interest, we may evaluate the coefficients of the radial integrals $R^k(\ell\ell';\ \ell\ell''')$ and $R^k(\ell\ell';\ \ell\ell^{iv})$ by putting $\ell' \equiv \ell''$ in Eq. (7) and (8).

The exchange-type interactions may be treated by performing a recoupling of the angular momentum such as to interchange the positions of two particles. The angular part of the interactions will give rise to the coefficients of three basic types of radial integrals $R^k(\ell\ell';\ \ell'''\ell)$, $R^k(\ell\ell'';\ \ell^{iv}\ell)$, and $R^k(\ell'\ell'';\ \ell^{iv}\ell'')$. The third type is amenable to the usual two-electron treatment[6] and will not be discussed. The calculation of the matrix elements of the exchange interactions proceeds, in a manner similar to that used for the direct interactions, by first performing a recoupling on the right-hand side of (4), summing over and eliminating the new angular momenta (spin and orbit) that enter the expression, returning the result to equation (3), and performing the summation over σ and λ. The procedure is lengthy though quite straightforward, and hence only the results are given.

For $R^k(\ell\ell'; \ell'''\ell)$, the matrix elements on the rhs of Eq. (1) are given by

$$n[\ell]\,([\ell'][\ell''']\,[L_1][L_3][L_1'][L_3'][S_1][S_3][S_1'][S_3'])^{1/2}(-1)^{\ell'''+k+\ell'}$$

$$\times \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell''' & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \delta(\ell'', \ell^{iv})$$

$$\times \sum_{\overline{\Psi}} (\psi_1\{|\overline{\Psi})(\psi_3\{|\overline{\Psi}) \begin{Bmatrix} \overline{S} & S_3 & 1/2 \\ S_1 & S_2 & S_1' \\ 1/2 & S_3' & 1/2 \end{Bmatrix} \begin{Bmatrix} \ell'' & \ell''' & L_3' & L_3 \\ \ell' & k & \ell & L_1 \\ L_1' & \ell & L_2 & \overline{L} \end{Bmatrix}, \qquad (11)$$

while for $R^k(\ell\ell''; \ell^{iv}\ell)$, the matrix elements on the rhs of Eq. (1) are given by

$$n[\ell]\,([\ell''][\ell^{iv}][L_1][L_3][L_1'][L_3'][S_1][S_3][S_1'][S_3'])^{1/2}$$

$$\times (-1)^{S_1'+S_3'+L_1'+L_3'+k} \begin{pmatrix} \ell & k & \ell'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell^{iv} & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \delta(\ell', \ell''')$$

$$\times \sum_{\overline{\Psi}} (\psi_1\{|\overline{\Psi})(\psi_3\{|\overline{\Psi}) \begin{Bmatrix} \overline{S} & S_3 & 1/2 \\ S_1 & S_2 & S_1' \\ 1/2 & S_3' & 1/2 \end{Bmatrix} \begin{Bmatrix} \ell' & \ell^{iv} & L_3' & L_3 \\ \ell'' & k & \ell & L_1 \\ L_1' & \ell & L_2 & \overline{L} \end{Bmatrix}, \qquad (12)$$

where the last factor in each expression is a standard 12-j symbol.[3]

In the case in which the electrons added to the ℓ^n core are all equivalent (though $\ell' \neq \ell$), the expression

$$2n[\ell][\ell'] ([L_1][L_3][L_1'][L_3'][S_1][S_3][S_1'][S_3'])^{1/2} (-1)^k \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times \sum_{\overline{\Psi}} (\psi_1 \{|\overline{\Psi}) (\psi_3\{|\overline{\Psi}) \begin{Bmatrix} \overline{S} & S_3 & 1/2 \\ S_1 & S_2 & S_1' \\ 1/2 & S_3' & 1/2 \end{Bmatrix} \begin{Bmatrix} \ell' & \ell' & L_3' & L_3 \\ \ell' & k & \ell & L_1 \\ L_1' & \ell & L_2 & \overline{L} \end{Bmatrix} \tag{13}$$

results.

For the interaction between $\ell^n \ell'^2$ and $\ell^n \ell''' \ell^{iv}$ we put $\ell' \equiv \ell''$ in Eqs. (11) and (12).

These formulae undergo considerable simplification when one or more of the angular momenta in the n-j symbols are zero.

CONFIGURATION INTERACTION BETWEEN $\ell^n \ell'$ and $\ell^n \ell''$

Judd[7] has already treated the electrostatic interaction within the configuration $\ell^n \ell'$. His expressions may be readily generalized to give for the direct interaction the coefficients of $R^k(\ell\,\ell'; \ell\,\ell'')$ as

$$\left(\ell^n S_1 L_1 s \ell'; S_2 L_2 \Big| \sum_{i<j} (C_i^k \cdot C_j^k) \Big| \ell^n S_3 L_3 s \ell''; S_4 L_4\right) = ([\ell'][\ell''])^{1/2} \delta(S_2, S_4) \delta(L_2, L_4)$$

$$\times \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell' & k & \ell'' \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell'' & k & \ell' \\ L_1 & L_2 & L_3 \end{Bmatrix} (\psi_1 || U^k || \psi_3) , \tag{14}$$

whereas for the exchange interaction the coefficients of $R^k(\ell\ell'; \ell''\ell)$ are given by

$$n[\ell]([\ell'][\ell''][S_1][S_3][L_1][L_3])^{1/2} (-1)^{S_1+S_3} \begin{pmatrix} \ell' & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell'' & k & \ell \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_{\overline{\Psi}} (\psi_1\{|\overline{\Psi}) (\psi_3\{|\overline{\Psi}) \begin{Bmatrix} s & \overline{S} & S_3 \\ s & S_2 & S_1 \end{Bmatrix} \begin{Bmatrix} \overline{L} & \ell & L_3 \\ \ell & k & \ell'' \\ L_1 & \ell' & L_2 \end{Bmatrix} . \tag{15}$$

CONFIGURATION INTERACTION BETWEEN ℓ^n and $\ell^{n-1}\ell'$

Racah[1] has obtained an expression for the matrix elements of the electrostatic interaction between d^n and $d^{n-1}s$. This result may be considerably simplified to give, for the coefficients of $R^k(\ell\ell; \ell\ell')$,

$$\left(\ell^n S_2 L_2 \,|\, \sum_{i<j} (C_i^k \cdot C_j^k) \,|\, \ell^{n-1} S_3 L_3 \ell' S_4 L_4\right)$$

$$= (-1)^{L_2+L_3+\ell} \delta(S_1, S_3)\, \delta(S_2, S_4) \delta(L_2, L_4) [\ell](n[\ell][\ell'])^{1/2} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_{\psi_1} (\psi_2\{|\psi_1)(\psi_1 || U^k || \psi_3) \begin{Bmatrix} L_3 & k & L_1 \\ \ell & L_2 & \ell' \end{Bmatrix} , \tag{16}$$

where ψ_1 are the parents of the $S_2\, L_2$ state of ℓ^n.

CONCLUSIONS

The application of simple recoupling techniques results in formulae that are considerably more amenable to machine calculation. The appearance of the 9-j and 12-j symbols in (9) and (10) need not disturb us, as they may be readily evaluated by standard programming techniques. The present formulae possess the advantage of requiring a minimum use of the sums over coefficients of fractional parentage with the emphasis placed on the coupling of the electrons. It might be hoped that these formulae could be further simplified. However, except for the trivial cases in which one (or more of the inequivalent electrons is an s electron, no fundamental simplification seems possible without explicit formulae for the coefficients of fractional parentage.

These results are presented with hope that they will eventually lead to the machine computation of the energy matrices of many of the configurations discussed in this paper.

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FOOTNOTES AND REFERENCES

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