

# COMPUTER CALCULATION OF MATRIX ELEMENTS OF ELECTRON REPULSION FOR A $d^n$ -ELECTRON SYSTEM IN STRONG LIGAND FIELD APPROXIMATION

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An algorithm for a symbolic calculation of matrix elements of electron repulsion for  $d^n$ -electron systems in the approximation of a strong ligand field of any symmetry is described. The algorithm, based on the knowledge of the corresponding wave functions, gives the matrix elements in the form  $(a_1 \sqrt{a_2/a_3}) A + (b_1 \sqrt{b_2/b_3}) B + (c_1 \sqrt{c_2/c_3}) C$ , where  $a_i$ ,  $b_i$  and  $c_i$  are integers and  $A$ ,  $B$ ,  $C$  Racah parameters.

The technique of calculations performed in the theory of ligand field has been dealt with in detail in many classical papers and monographs<sup>1-12</sup>. All preliminary calculations needed for explanation of optical and magnetic properties that can be interpreted in terms of the theory of ligand field of symmetry  $O_h$  or  $T_d$  were already made. However, it turns out that a cubic symmetry cannot be ascribed to all systems; on the contrary, many optical or other properties can be well explained only on the assumption that the system has another symmetry than cubic. The intricacy of complete interpretative calculations in such cases depends on the intricacy of the calculation of matrix elements of electron repulsion. In a weak ligand field approximation, the matrix elements are available in the literature; for calculations of matrix elements of single or double one-electron operators, the method of irreducible tensor operators<sup>13-19</sup> can be used with advantage. In the approximation of a strong field of another symmetry than  $O_h$  or  $T_d$ , the "manual" calculation of matrix elements of electron repulsion (performed either by the direct method<sup>10-12,19,20</sup> or by the method of recurrent formula<sup>6,11,21</sup> or directly by the method of irreducible tensor operators<sup>8,15</sup>) is tedious and time-consuming, hence more effective techniques are desirable.

The present work deals with the algorithm for computer calculation of matrix elements of electron repulsion in the approximation of a strong ligand field of an arbitrary symmetry. The algorithm is based on a direct method of calculation of matrix elements and on the assumption that they can be expressed as a linear combination of Racah parameters  $A$ ,  $B$  and  $C$ <sup>9,11,12</sup>.

## DESCRIPTION OF THE ALGORITHM

$n$ -Electron wave functions  $|\Psi\rangle$  and  $|\Phi\rangle$  forming the basis for calculation of matrix elements of electron repulsion,  $V = \sum_{i < j}^n e^2/r_{ij}$ , in a field of a given symmetry, are

composed from real wave functions<sup>10-12</sup>

$$d_{z^2}, d_{x^2-y^2}, d_{xy}, d_{xz}, d_{yz} \quad (1)$$

and can be calculated by the known methods<sup>8,10-12,14,15</sup>. Mainly the generalized Racah method for composing the  $d^n$ -electron functions<sup>8,11,14,15</sup> is very effective since both the coefficients of fractional percentage<sup>6,11,14,15</sup> and the Clebsch-Gordon coefficients<sup>6,9,11,14</sup> are known for most point groups. To enable calculation with these wave functions, a set of  $n$  whole numbers,  $[k_1, k_2, \dots, k_n]$ ,  $0 \leq k_i < 10$ , is ascribed to every  $n$ -electron Slater determinant according to the scheme\* in Table I. Thus, every  $n$ -electron function  $|\Psi(S\Gamma M_S M_T)\rangle$  can be expressed as a sum of terms of the form

$$\alpha\beta^{1/2}\gamma^{-1} \sum_{i=1}^m c_i [k_1^i k_2^i \dots k_n^i], \quad (2)$$

where  $\alpha, \beta, \gamma$  and  $c_i$  are whole numbers;  $\beta, \gamma \geq 1$ . Obviously, if  $|\Psi\rangle = \sum_{i=1}^p |\Psi_i\rangle$  and  $|\Phi\rangle = \sum_{i=1}^q |\Phi_i\rangle$ , where  $|\Psi_i\rangle$  and  $|\Phi_i\rangle$  have the form of (2), then

$$\begin{aligned} \langle \Psi | V | \Phi \rangle &= \sum_{i=1}^p \sum_{j=1}^q \langle \Psi_i | V | \Phi_j \rangle, \\ \langle \Psi | V | \Psi \rangle &= \sum_{i=1}^p \langle \Psi_i | V | \Psi_i \rangle + 2 \sum_{i < j}^p \langle \Psi_i | V | \Psi_j \rangle. \end{aligned} \quad (3)$$

The table of integrals<sup>11,12</sup>  $\langle ab | 1/r_{12} | cd \rangle$  is put into the memory of the computer;  $a, b, c$  and  $d$  denote one-electron real wave functions (1) according to Table I. The integrals are identified by numbers of the form

$$1000a + 100b + 10c + d, \quad (4)$$

which are included in the table together with the coefficients before the Racah parameters  $A, B$  and  $C$ . Symmetrical properties of the integrals enable to reduce their number from 506 to 111, for which

$$a \geq b \geq d, \quad a \geq c. \quad (5)$$

In the calculation proper, sets of  $n$  numbers corresponding to functions  $|\Psi_i\rangle$  are in turn compared with sets of  $n$  numbers corresponding to  $|\Phi_i\rangle$ . For a matrix element

\* If an increasing series of numbers is not formed in the given set of  $n$  numbers, it is necessary to interchange the rows or columns of the Slater determinant so as to make the mentioned series increasing and to observe the change of the sign of the determinant.

TABLE I  
Indexing of Real Wave Functions by Whole Numbers<sup>a</sup>

$d_{x^2-y^2}^+$	$d_{x^2-y^2}^-$	$d_{xy}^+$	$d_{xy}^-$	$d_{z^2}^+$	$d_{z^2}^-$	$d_{xz}^+$	$d_{yz}^-$	$d_{yz}^+$	$d_{yz}^-$
0	1	2	3	4	5	6	7	8	9

<sup>a</sup> + or - denotes the orientation of spin.

$\langle \Psi_i | V | \Phi_j \rangle$ , an identification number is constructed according to (4) and (5), after which the corresponding coefficients before  $A$ ,  $B$  and  $C$  are selected from the table of integrals and their multiples are added to the sums of coefficients stored in the memory. After finishing the cycle, the partial square root is calculated and the numerator and denominator of the corresponding sum are divided by their largest common divisor, so far as possible. The described algorithm can be simply generalized in two senses: a) By a change of the table of integrals  $\langle ab | 1/r_{12} | cd \rangle$  stored in the memory of the computer it would be possible to compute matrix elements in dependence on general parameters characterizing repulsion in a field of a given symmetry (e.g., for  $O_h$  symmetry<sup>9,11</sup>). b) The principle of the algorithm could be utilized also in programming the calculation of matrix elements of electron repulsion in a field of a given symmetry in the case of  $f$ -electrons.

#### EXAMPLES OF CALCULATION

Based on the described algorithm, a program was elaborated in Elliott Algol\* and its considerable effectiveness was demonstrated on two examples where the matrix elements of electron repulsion are known, namely on a matrix of the terms  ${}^2A_{1g}$  of a  $d^3$ -electron system in a field of axial symmetry<sup>19</sup>  $D_{\infty h}$  and on a matrix of the terms  ${}^1E_g$  of a  $d^4$ -electron system in a field of symmetry  $O_h$  (ref.<sup>11</sup>).\*\* In both cases the obtained matrix elements were identical with those given in the literature<sup>11,19</sup>.

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\* Available by the author on request. The program applies for the case where the function contains only one term of the form (2). Its possible generalization for the case where the function is a sum of several such terms is based on Eqs (3). However, since the wave functions forming the bases of irreducible representations of the point group  $D_{\infty h}$  and its subgroups (for which the matrix elements of electron repulsion are not yet known) consist of only one term of the form (2), the generalization was not considered in the mentioned program.

\*\* Since the functions corresponding to the configurations  $t_2^3({}^2E) e$  and  $t_2^2({}^1E)e^2({}^1E)$  are sums of two terms of the form (2), Eqs (3) were used in the calculation of matrix elements.

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