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QUASI-SPIN SYMMETRIZED ORBITAL OPERATORS 
FOR $d^n$ CONFIGURATIONS

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Résumé. — Deux opérateurs de particules en orbite, ayant les propriétés de transformation des groupes quasi rotatifs et rotationnels $R_5$, sont construits. Les effets d'ordre secondaire produits par la corrélation électrostatique des inter-réactions orbitales d'une particule, sont écrites formellement en termes d'opérateurs symétriques. Le calcul des éléments de matrice est discuté ainsi que ses relations au problème du calcul des facteurs isoscalar.

L'application aux inter-réactions électriques quadripolaires infiniment fines est envisagée.

Abstract. — Two particle orbital operators having well-defined transformation properties under the quasi-spin group and the rotational group $R_5$ are constructed. The second-order effects produced by electrostatic correlation of one particle orbital interactions are formally written in terms of the symmetrized operators. The calculation of the matrix elements is discussed together with its relationship to the problem of calculating isoscalar factors. The possible application to electric quadrupole hyperfine interactions is considered.

Introduction. — The symmetrization of the interactions for many-electron systems into operators having well-defined transformation properties under the groups used to classify the many electron states is well established [1]. Judd [2] has discussed in some detail the analysis of the spin-spin and spin-other-orbit interactions for the d-shell, making particular use of quasi-spin methods [3]. Feneuille [4] has, in a similar fashion, considered the symmetrization of effective three-particle operators for the d-shell. These operators arise in the perturbative treatment of the configuration interaction produced by the Coulomb repulsion [5, 6].

In each of the above cases considered the Hamiltonian is rotationally invariant and hence scalar interactions arose. There are, however, a number of situations where the Hamiltonian, real or effective, is not rotationally invariant. This is indeed the case for an ion in an external electric or magnetic field or in the presence of a nuclear magnetic dipole or electric quadrupole.

In this paper we first establish the form of the effective operators required to represent electrostatically correlated single particle operators leading to the need to consider the evaluation of the matrix elements of effective two particle operators of the form

$$T^{(k_1 k_2)} = \sum_{i \neq j} \langle k_1 | i \rangle \langle k_2 | j \rangle \langle i | j \rangle .$$

The problem of representing these operators in terms of symmetrized operators of pure quasi-spin for the specific case of the $d^8$ configurations is then attacked. Problems related to the calculation of the matrix elements of the quasi-spin symmetrized operators and their application to problems in electric quadrupole hyperfine structure is considered.

I. Electrostatically Correlated Single Particle Interactions. — Any single particle interaction may be expressed in terms of double tensors [7],

$$T^{(KK)} = \sum_{i=1}^{N} t^{(KK)}_i .$$  

Consider the state $| A \alpha >$ of a configuration $A$ to be perturbed by the states $| B \beta >$ of a configuration $B$, then to second order we must replace each matrix element

$$\langle A \alpha \mid T^{(KK)} \mid A \alpha' \rangle$$

by

$$(1 + \delta) \langle A \alpha \mid T^{(KK)} \mid A \alpha' \rangle$$

In the case of spin-independent interactions, such as arise in crystal field and electric quadrupole hyperfine interactions, we must consider the matrix elements of the operators

$$T^{(k_1 k_2)} = \sum_{i \neq j} \langle k_1 | i \rangle \langle k_2 | j \rangle \langle i | j \rangle .$$

The problem of representing these operators in terms of symmetrized operators of pure quasi-spin for the specific case of the $d^8$ configurations is then attacked. Problems related to the calculation of the matrix elements of the quasi-spin symmetrized operators and their application to problems in electric quadrupole hyperfine structure is considered.
where
\[ A = - \sum_{j} (\langle A | Q | B \beta > < B \beta | T_{\text{eq}}^{(KK)} | A \alpha > ) + < A \alpha | T_{\text{eq}}^{(KK)} | B \beta > < B \beta | Q | A \alpha > ) \]
\[ / < A \alpha | T_{\text{eq}}^{(KK)} | A \alpha > > E \] (4)

where \( E \) is the positive excitation energy required to transfer a single electron from \( A \rightarrow B \) and \( Q \) designates the Coulomb interaction between electrons. If we identify the \( A \alpha \)'s with the states of a configuration \((nl)^N (n' l')^{4l+2}\) then we may distinguish three possible configurations \( B \), namely

1. \((nl)^N (n' l')^{4l+1} n'' l''\)
2. \((nl)^{N-1} (n' l')^{4l+2}\)
3. \((nl)^{N+1} (n' l')^{4l+1}\).

Case (1) has already been considered by Judd [7] who obtains the result

\[ \Delta^{(2)} = -4 \sqrt{2} \sum_{k,l} R^{(nlnl; n'l'n'l')} < l \parallel C^{(K)} \parallel l > < l \parallel C^{(K)} \parallel l' > < n'l' \parallel \tau^{(KK)} \parallel nsl > \]
\[ \times \left\{ \frac{k}{l} \frac{K}{l'} \right\} (1)^{K} \sqrt{\frac{l}{k}} < A \alpha \sum_{i<j} (\psi_{1}^{(K)} \psi_{2}^{(K)}) \parallel A \alpha > / E < A \alpha \parallel \psi^{(K)} \parallel A \alpha > . \] (7)

For the case of spin independent interactions \( K = 0 \) and eq. (7) becomes

\[ \Delta^{(2)} = -4 \sum_{k,l} R^{(nlnl; n'l'n'l)} < l \parallel C^{(K)} \parallel l > < l \parallel C^{(K)} \parallel l' > < n'l' \parallel \tau^{(K)} \parallel nsl > \]
\[ \times \left\{ \frac{k}{l} \frac{K}{l'} \right\} (1)^{K} \sqrt{\frac{l}{k}} < A \alpha \sum_{i<j} (\psi_{1}^{(K)} \psi_{2}^{(K)}) \parallel A \alpha > / E < A \alpha \parallel \psi^{(K)} \parallel A \alpha > . \] (8)

In each case \( l + K \) is even.

Case (3) gives

\[ \Delta^{(3)} = - \Delta^{(2)} - \Delta^{(3)} + \Delta^{(3)} \] (9)

where

\[ \Delta^{(3)} = \frac{\delta(l, l')}{(4l + 2)} \sum_{k} R^{(nlnl; n'l'n'l)} < l \parallel C^{(K)} \parallel l > \]
\[ \times < n'l' \parallel \tau^{(KK)} \parallel nsl > E < nsl \parallel \tau^{(KK)} \parallel nsl > \] (10a)

and

\[ \Delta^{(2)} = \delta(K, 0) \frac{R^{(nlnl; n'l'n'l)}}{(2K + 1)(2l + 1)} \sum_{i<j} (\psi_{i}^{(K)} \psi_{j}^{(K)}) \parallel A \alpha > / E < A \alpha \parallel \psi^{(K)} \parallel A \alpha > . \] (10b)

The last two terms in eq. (9) give rise to a simple scaling of the first order matrix elements. Here, our principal interest will be in the study of the properties of the terms \( \Delta \) which produce overt effects that cannot be accommodated by any simple scaling of the first order matrix elements.

The calculation of the electrostatic correlation of these purely orbital interactions necessitates the evaluation of the matrix elements of the two-particle orbital operators

\[ T^{(iK)} = \sum_{i<j} (\psi_{i}^{(K)} \psi_{j}^{(K)}) \] (11)
where \( k \) is necessarily even and \( t \) and \( K \) have the same parity.

In making practical calculations of the matrix elements of \( T^{(k)K} \) it is useful to be able to represent the operators in terms of operators of well-defined quasi-spin. The advantages gained include not only a simplification of the matrix element calculations but more importantly, a sharper and more descriptive analysis of the effects of the electrostatically correlated perturbations.

For the particular case of the d-shell we are interested in the matrix elements of \( T^{(22)K} \), \( T^{(42)K} \) and \( T^{(44)K} \) where \( K = 2 \) or 4. The operators \( T^{(k)0} \) all have matrix elements that are simply proportional to those of the Coulomb interaction and need not be considered here.

II. \( R_5 \) Symmetrization of the Orbital Operators. —

The states of the d-shell may be profitably classified by their transformation properties under the chain of groups
\[
R_{21} \supseteq R_{20} \supseteq R_3^S \times (S_{P10} \supseteq R_3 \times R_5 \supseteq R_5^S \times R_3^S). \tag{12}
\]

The operators \( V^{(2)} \) and \( V^{(4)} \) transform together as the \([20]\) representation of \( R_5 \) and hence suitable linear combinations of the operators \( T^{(22)K} \), \( T^{(42)K} \) and \( T^{(44)K} \) must transform according to the representations of \( R_5 \) contained in the plethysm \([1]\),

Under restriction to the \( R^3 \) subgroup we find that only the \([20]\), \([22]\) and \([40]\) representations yield the representations \( D^{(K)} (K = 2 \text{ or } 4) \). Thus we wish to construct six \( R_5 \) symmetrized operators \( E^{[20]K} \), \( E^{[22]K} \), \( E^{[40]K} \) (\( K = 2 \text{ or } 4 \)) as linear combinations of the \( T^{(k)K} (t, k = 2, 4) \) operators. The linear combinations may be readily determined by writing
\[
E^{[k]K} = \sum_{t} T^{(k)K} | [20] t + [20] k | [\lambda\mu] K \rangle. \tag{13}
\]

The isoscalar factors may be readily determined \([1]\) from the known matrix elements of \( V^{(k)} \) tabulated by Nielson and Koster \([9]\) to give the results of Table I.

For later calculations it is also useful to construct the \( R_5 \) symmetrized operators \( O^{[20]K}, O^{[22]K} (K = 2, 4) \) from linear combinations of the operators \( T^{(k)K} \) where \( t, k = 1, 3 \). The appropriate isoscalar factors are given in Table II. The complete set of \( R_5 \) symmetrized operators appears in Table III. These results may then be readily inverted by either solving the linear equations or more simply by inversion of eq. (13) to give the operators \( T^{(k)K} \) as linear combinations of the \( R_5 \) symmetrized operators as given in Table IV. Thus we have a set of \( R_5 \) symmetrized two particle operators and must now study their properties with respect to the other groups appearing in eq. (12).

### Table I

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</tr>
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<tr>
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<td>( \frac{\sqrt{70}}{10} )</td>
<td>( \frac{\sqrt{30}}{10} )</td>
<td>( \frac{\sqrt{5}}{5} )</td>
</tr>
</tbody>
</table>
The operators $W_0$ and $W(k+1)$ ($k = 2, 4$) transform together as the $1_{22}$ representation of $Sp_{10}$ \[10, 11\] and hence the two-particle operators constructed from these operators must transform according to the representations of $Sp_{10}$ contained in the plethysm $\text{Sp}_{10} \rightarrow \mathbb{R} \times \mathbb{R}$. We find \[1\] that the $1_{22}$ representation occurs only with $2_{22}$, and hence the operators $E_{22}(K)$ have pure symplectic symmetry. The $1_{20}$ representation occurs in the reduction of both $1_{44}$ and $2_{22}$, while the $1_{22}$ representation occurs in the reduction of $1_{22}$, $1_{44}$, and $2_{22}$, and hence the operators $E_{22}(K)$ and $E_{20}(K)$ are not symmetrized with respect to $Sp_{10}$.

The operators $W(0k+1)$ and $W(1k)$ ($k = 0, 2, 4$) transform together as the $1_{2}$ representation of $Sp_{10}$, and hence two-particle operators constructed from them must transform according to representations of $Sp_{10}$ contained in the plethysm.

Operators transforming as $1_{2}$ will have vanishing matrix elements when evaluated between electron states and need not be considered further. The $1_{22}$ representation occurs only in the reduction of both $1_{44}$ and $2_{22}$, while the $1_{20}$ representation occurs in the reduction of both $1_{22}$, $1_{22}$, and $2_{22}$, and hence the operators $E_{22}(K)$ and $E(0K)$ are not symmetrized with respect to $Sp_{10}$.

The operators $W(0k+1)$ and $W(1k)$ ($k = 0, 2, 4$) transform together as the $2$ representation of $Sp_{10}$, and hence two particle operators constructed from them must transform according to representations of $Sp_{10}$ contained in the plethysm.
operators, together with certain additional operators, to give operators of well-defined symplectic symmetry it proves to be more useful to proceed directly to the construction of operators having pure quasi-spin.

IV. Quasi-spin Symmetrization. — If our operators are symmetrized with respect to the quasi-spin group $R^5$ then the dependence of their matrix elements upon the number of electrons $N$ and the seniority $v$ is simply proportional to a 3-j symbol involving $N$, $v$ and $l$. Judd [12] has shown that for $r$-particle operators we may restrict our attention to representations of $R_{S1+4}$ where $0 \leq x < r$. Thus in the case of the d-shell we may restrict our attention to the quasi-spin states arising in the reduction $R_{20} \rightarrow R_{5} \times S_{10}$. We then find that $a = -\sqrt{3}/3$.

The results of Tables I and II may be used to obtain the quasi-spin $Q = 2$ operator

$$X(22)_{(2)}^{(0)} = \frac{\sqrt{14}}{14} (3 T^{(22)0} - \sqrt{5} T^{(44)0}) + \frac{\sqrt{30}}{30} (\sqrt{7} T^{(11)0} - \sqrt{3} T^{(33)0}). \quad (17)$$

This operator is simply proportional to Judd’s $[8] e_2 + \Omega'$ operator, in fact

$$X(22)_{(2)}^{(0)} = \frac{\sqrt{70}}{420} (e_2 + \Omega'). \quad (18)$$

The operators $O(20)^{(K)}$ are of mixed quasi-spin 0 and 1. The single operators $V(K)$ (K even) are pure quasi-spin 1 operators. The operators $O(20)^{(K)}$ and $V(K)$ may be combined to form a pure quasi-spin zero operator

$$Y(20)^{(K)} = O(20)^{(K)} + b V(K), \quad (19)$$

where $b$ is independent of $K$. The constant $b$ may be readily determined by demanding that the reduced matrix element

$$<d^{2001}\Sigma || Y(20)^{(2)} || d^{201} D > = 0$$

to yield $b = -\sqrt{3}/4$. Finally we may construct a pure quasi-spin 2 operator by forming the linear combination

$$Z(20)^{(K)} = E(20)^{(K)} + dO(20)^{(K)} + e V(K). \quad (20)$$

The constants $d$ and $e$ are readily fixed by demanding that the reduced matrix elements

$$<d^{204} D || Z(20)^{(2)} || d^{204} D > = 0$$

and

$$<d^{4105} D || Z(20)^{(K)} || d^{4105} D > = 0$$

to give $d = \sqrt{5}/3$ and $e = 2 \sqrt{15}/15$. Thus we have the quasi-spin symmetrized operators of Table VI.

### Table VI

**Quasi-spin symmetrized orbital operators for the d-shell**

<table>
<thead>
<tr>
<th>Operator</th>
<th>Quasi-spin Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E(20)^{(K)}$</td>
<td>$&lt; 1^2 &gt;, &lt; 1^4 &gt;, &lt; 2^2 &gt;$</td>
</tr>
<tr>
<td>$E(22)^{(K)}$</td>
<td>$&lt; 1^4 &gt;, &lt; 2^2 &gt;$</td>
</tr>
<tr>
<td>$E(40)^{(K)}$</td>
<td>$&lt; 2^2 &gt;$</td>
</tr>
<tr>
<td>$O(20)^{(K)}$</td>
<td>$&lt; 1^2 &gt;, &lt; 2^2 &gt;$</td>
</tr>
<tr>
<td>$O(22)^{(K)}$</td>
<td>$&lt; 2^2 &gt;$</td>
</tr>
</tbody>
</table>

K. The value of $a$ may be readily fixed by demanding that the reduced matrix element

$$< d^{[00]} S || X(22)^{1} || d^{[22]} D > = 0.$$
V. Matrix Elements. — The reduced matrix elements of the operators $T^{(4)K}$ may be readily evaluated for a $l^2$ configuration using the result [13]

$$< l^2 SL \parallel T^{(4)K} \parallel l^2 SL' > = \frac{1}{2} [L, L', t, k, K]^{1/2} \left\{ \begin{array}{ccc} l & l & L \\ l & l & L' \\ t & k & K \end{array} \right\} . \quad (21)$$

Linear combinations were then formed to give the reduced matrix elements of the $R_5$ symmetrized operators (for $K = 2$) for the $d^2$ configuration shown in Table VII. The results of Table VI were then used to give the reduced matrix elements of the quasi-spin symmetrized operators given in Table VIII.

**TABLE VII**

<table>
<thead>
<tr>
<th>Matrix elements of the $R_5$ symmetrized orbital operators for $d^2$</th>
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<tbody>
<tr>
<td><strong>E[20]$$^{(2)}$$</strong></td>
</tr>
<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>1S</td>
</tr>
<tr>
<td>1D</td>
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<tr>
<td>3P</td>
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<tr>
<td>3F</td>
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<tr>
<td><strong>O[20]$$^{(2)}$$</strong></td>
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<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>1S</td>
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<tr>
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<tr>
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**TABLE VII (Contd)**

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<th><strong>E[22]$$^{(2)}$$</strong></th>
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<table>
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<td>1G</td>
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<td>$-\frac{5\sqrt{6}}{14}$</td>
<td>$\frac{\sqrt{165}}{14}$</td>
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<td>$\frac{\sqrt{70}}{10}$</td>
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<td>$\frac{3\sqrt{5}}{10}$</td>
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The reduced matrix elements given in Table VIII form the basis for calculating the matrix elements for all $d^N$ matrix elements since if $T^{(K)}$ is an arbitrary two particle operator we have the well known results [13, 14].
TABLE VIII
Reduced Matrix Elements of $X^{[22]}(2)$, $Y^{[20]}(2)$ and $Z^{[20]}(2)$ for $d^2$

where in (22a) the sum is over the two-particle coefficients of fractional parentage (c. f. p.) and in (22b) over the one-particle c. f. p. Tables of both types of c. f. p. are available for the $d^N$ configurations [9, 13, 15].

Equations (22a) and (22b) are strictly valid only for two particle operators whereas some of the operators in Table VI include one particle operators. These cases may be readily handled by assuming eq. (22a) and (22b) are valid for one- and two-particle operators and then subtracting from the result the matrix elements of the one particle operators.

Equation (22b) may be readily used to evaluate the matrix elements for the states of maximum multiplicity to give, for example, the results of Table IX. The matrix elements all vanish for the $6S$ state of $d^5$ while for the 'D state of $d^4$ the only non-zero two-particle quasi-spin symmetrized matrix element with $K = 2$ is

$$< d^4 \, ^4D \parallel Y^{[20]}(2) \parallel d^4 \, ^4D > = \frac{3\sqrt{15}}{4}.$$  

TABLE IX
Reduced matrix elements for $d^3$

There is, in principle, no difficulty in calculating the matrix elements of the quasi-spin symmetrized orbital operators for all the states of the d-shell. Such a calculation would provide a rich source of isoscalar factors [16].
VI. Isoscalar Factors. — The Wigner-Eckart theorem leads to substantial simplifications in the calculation of the reduced matrix elements of the quasi-spin symmetrized operators. Application of the Wigner-Eckart theorem gives

\[
< d^0[\lambda] \sum L | T[\lambda']^\dagger(K) d^0[\lambda'] SL' > = \sum A_\lambda < \lambda(L) \sum K + [\lambda'] L' >
\]

where \( A_\lambda \) is independent of \( K, L \) and \( L' \) and \( \lambda \) distinguishes those cases where \([\lambda] \) occurs more than once in the Kronecker product \([\lambda'] \times [\lambda'] \). Thus the entire dependence upon \( L, L' \) and \( K \) of the reduced matrix elements is contained in the \( R_\lambda \) isoscalar factor

\[
< \lambda(L) \sum K + [\lambda'] L' > .
\]

Judd [8, 12] has discussed a number of applications of isoscalar factors in atomic shell theory. For example, since the Kronecker product \([11] \times [11]\) contains just once we conclude immediately that the reduced matrix elements of \( Y[20](K), V(K), Z[20](K), \) and of \( O[22](K) \) and \( X[22](K) \) among the states of maximum multiplicity of \( d^2 \) and \( d^3 \) differ by at most a proportionality constant. In a similar fashion the matrix elements for \( d^2 \) of the operators with \( K = 4 \) have been obtained from those found for \( K = 2 \) by use of the isoscalar factors of Tables I and II.

While the matrix elements of the tensor operators \( V(K) \) provide a rich source of isoscalar factors their range is limited by the fact that the operators all transform under \( R_5 \) as \([11] \) (\( K \) odd) or \([20] \) (\( K \) even). Furthermore, since we only have one species of operator of a given symmetry type we do not have a natural means of distinguishing those isoscalar factors where there is a multiplicity problem. Calculations of Kronecker products [1] of \( R_5 \) for those representations describing the transformation properties of \( d^N \) electron states never involve multiplicities of \( >3 \), the multiplicity 3 occurring only for the \([21] \) and \([31] \) representations that arise in the Kronecker product \([21] \times [21]\). For the \( d^N \) shell we are limited to one-electron excitations where \( l' = s, d \) or \( g \). The relevant operators, to within an obvious proportionality constant, are listed in Table X together with their expansion into \( R_5 \) symmetrized operators. The corresponding expansion into quasi-spin symmetrized operators follows directly from Table VI.

Contributions from single electron excitations of the type \( d^N \rightarrow d^{N-1}s \) and \( d^N \rightarrow d^{N+1}s^{-1} \) are likely to be dominant throughout the transition elements. For states of maximum multiplicity the matrix elements of \( E[40]^{(2)} \) must vanish leaving just those of \( E[20]^{(2)} \). But the representation \([20] \) occurs at most once in the relevant Kronecker product and hence the matrix elements of \( E[20]^{(2)} \) must be simply proportional to

\[
\begin{align*}
\text{TABLE X} \\
\text{Electrostatically Correlated Operators} \\
\text{for Electric Quadrupole Hyperfine Structure}
\end{align*}
\]

\[
\begin{align*}
d^N \rightarrow d^{N-1}s \sqrt{5} T^{(22)2} + 3 T^{(42)2} &= \\
&= \frac{\sqrt{3}}{6} (2 E[20]^{(2)} + \sqrt{10} E[40]^{(2)})
\end{align*}
\]

\[
\begin{align*}
d^N \rightarrow d^{N-1}d' \sqrt{5} T^{(22)2} - 4 T^{(42)2} &= \\
&= - (\sqrt{3} E[20]^{(2)} + \sqrt{10} E[22]^{(2)})
\end{align*}
\]

\[
\begin{align*}
4 \sqrt{5} T^{(42)2} + 5 \sqrt{22} T^{(44)2} &= \\
&= (6 \sqrt{15} E[20]^{(2)} - 5 \sqrt{22} E[22]^{(2)})
\end{align*}
\]

\[
\begin{align*}
d^N \rightarrow d^{N-1}g \sqrt{12} \sqrt{5} T^{(22)2} + T^{(42)2} &= \\
&= - \frac{1}{6} (16 \sqrt{3} E[20]^{(2)} + 30 \sqrt{10} E[22]^{(2)} - \sqrt{330} E[40]^{(2)})
\end{align*}
\]

\[
\begin{align*}
\sqrt{110} T^{(42)2} + 3 T^{(44)2} &= \frac{1}{3} (\sqrt{330} E[20]^{(2)} - \\
&+ 3 \sqrt{11} E[22]^{(2)} + 7 \sqrt{3} E[40]^{(2)})
\end{align*}
\]
those of $V^{(2)}$ which arises in the calculation of the unperturbed electric quadrupole hyperfine structure [17]. Thus if the $d \leftrightarrow s$ excitations are dominant it should still be possible to fit the electric quadrupole hyperfine structure associated with the states of maximum multiplicity with a single value of $<r^{-3}>$. However, detailed calculations must await the computation of the relevant energy denominators and radial integrals.

VIII. Conclusion. — Quasi-spin symmetrized orbital operators have been constructed to aid the calculation of electrostatically correlated orbital interactions and their matrix elements computed for the $d^2$ configuration and the states of maximum multiplicity for $d^3$ and $d^4$. The calculation of the matrix elements of the symmetrized operators for the d-shell will provide a new source of isoscalar-factors which in turn could give more light on the subject of atomic shell theory.

References