Coulomb and spin-orbit interaction matrix elements
in $d^2d'$ configuration

Edwin Lo‡

Henry A Rowland Department of Physics and Astronomy, The Johns Hopkins
University, Baltimore, Maryland 21218, USA

Abstract. The $d^2d'$ configuration is analysed in group-theoretical terms. Starting
from the table given by Condon and Odabasi for the configuration $d^2d'$, we determine
a set of convenient group-theoretical basis states, and rewrite the Coulomb matrix
elements in terms of this new basis. Linear combinations from the different parts of
the Coulomb operators are formed such that they have simple group transformation
properties in our scheme. The sequence of groups that we use is $U(20) \supset SO_T(3) \times
U(10) \supset SO_T(3) \times SO_S(3) \times U(5) \supset SO_T(3) \times SO_S(3) \times SO(5) \supset SO_T(3) \times SO_S(3) \times
SO_L(3)$, where $T$ denotes the isospin of Simonis et al., in which electrons with the same
angular momentum $l$ but different principle quantum numbers $n$ are accommodated by
introducing the eigenvalue $M_T$ of $T_0$. Using the Wigner-Eckart theorem and selection
rules on the higher symmetry groups, the tables of the Coulomb and spin-orbit matrix
elements for the reconstituted operators (with simple group transformation properties)
are much simplified in terms of these basis states.

1. Introduction

The configuration $d^2d'$ has been observed in the excited spectra of some rather common
atoms and ions. For instance, from the data of Sugar and Corliss (1985), Sc i, Ti ii, V iii and Cr iv all have excited levels with the configuration $3d^24d$ observed. In the
case of vanadium and chromium, almost all the 27 possible spectroscopic terms of the
configuration $3d^24d$ were found and their energies measured; for vanadium, a few $3d^25d$
levels were seen as well. In addition to the $d^2d'$ systems, the present work also applies
to commonly found systems of the type $d^8d'$. For example, $3d^84d$ has been observed in
Co i and Ni ii (Sugar and Corliss, 1985). For nickel, all 27 possible spectroscopic terms
of the configuration $3d^84d$ have been found, as well as some levels of $3d^85d, 3d^86d, 3d^87d$
and $3d^88d$.

Condon and Odabasi (1980) calculated the Coulomb matrix elements of $d^2d'$
using classical methods. Their basis couples the two equivalent electrons ($d^2$) to an
intermediate state $[^S]L'$, to which the $d'$ electron is coupled to give the final state $[^S]L$.
The basis is denoted by $|^S\rangle_{L'}^S \langle S|L$, where $|S| = 2S + 1$, the multiplicity. This basis is
quite good, as the $d'$ electron usually interacts rather weakly with the other $d$
electrons.

‡ e-mail: elo@pha.jhu.edu
As one can check from the data for V III and Cr IV (Sugar and Corliss, 1985), there is not a substantial mixing of the states in this basis except for $^2P$, $^2D$ and $^2F$.

Instead of this physical basis, we choose to use a different one that has simple transformation properties under higher symmetry groups. There are advantages in doing so, particularly when they are taken as intermediate states in a perturbation expansion (see, for example, Hansen et al 1997). In that case, the sum over intermediate states that appear render the choice of basis irrelevant to the physical properties being investigated. And certainly, if we introduce higher symmetry groups into the analysis, even though they might not give “good” quantum numbers, in the sense that they do not commute with the full Hamiltonian, they give simple results as far as the computation of matrix elements is concerned. The selection rules, and especially the Wigner-Eckart theorem, when applied to higher groups, strikingly reduce the amount of calculation and expose new mathematical structure.

Other than matrix elements among the states of the $d^2d'$ configuration itself, our interest in configuration interaction (CI) means that we will also need the matrix elements that connect $d^2d'$ to $d^3$. The physical basis that is commonly used for $d^3$ coincides with the group-theoretical basis that utilizes the higher unitary and symplectic groups $U(10)$ and $Sp(10)$. For this reason, it is best to use the same group-theoretical basis for the configuration $d^2d'$ as that needed to study the configuration interaction between $d^3$ and $d^2d'$. Once again, the Wigner-Eckart theorem and selection rules for the higher symmetry groups are invaluable.

The isospin formalism (Šimonis et al 1984, Kaniauskas et al 1987) that we will introduce into our work also provides a very useful setting for the study of CI. In the isospin formalism, the states in $d^3$ and $d^2d'$ that carry the same group labels belong to the same isospin multiplet, but with different isospin z-component $M_T$. We can therefore easily obtain the CI matrix elements from the ones for $d^2d'$ if everything, the states and the operators, have simple transformation properties under the symmetry groups. These considerations give us strong reasons to abandon the physical basis for $d^2d'$ and turn to the group-theoretical one instead.

2. The basis states

The classification used in Condon and Odabasi (1980), in group-theoretical language, is

$$SO_S^d(3) \times SO_L^d(3) \times SO_S^{d'}(3) \times SO_L^{d'}(3) \supset SO_S(3) \times SO_L(3).$$

(1)

As explained earlier, this provides a set of good physical states, but there are also good reasons to use an alternative basis which carries a set of simple group labels, that is, irreducible representations (irreps). The groups that we have chosen are

$$U(10) \supset SO_S(3) \times U(5) \supset SO_S(3) \times SO(5) \supset SO_S(3) \times SO_L(3).$$

(2)

The groups $U(5)$ and $SO(5)$ are based on the five orbital states of a $d$ (or $d'$) electron; the group $U(10)$ utilizes the spin of the electron as well. Another more common alternative
used in configurations of equivalent electrons is the sequence
\[ U(10) \supset Sp(10) \supset SO_S(3) \times SO(5) \supset SO_S(3) \times SO_L(3) \]
(3)
where the symplectic group \( Sp(10) \) is closely related to the seniority scheme widely used in atomic spectroscopy. It is, however, felt that the idea of seniority might not as useful in configurations with inequivalent electrons. At least not in the way we used it in configurations of equivalent electrons.

To simplify the notation, we use square brackets for unitary group labels, with a subscript to denote the order of the group. The zeros in the labels will either be omitted.

**Table 1.** Transformation between the new and old basis.

| New basis | Old basis in terms of \( |d^2(2S'+1L'),d'; 2S+1L⟩ \) |
|-----------|-------------------------------------------------|
| \([21][3][30]2S⟩ = | \( |1D⟩^2S⟩ \) | \( \frac{1}{\sqrt{3}} |1D⟩^2P⟩ + \frac{1}{\sqrt{3}} |3P⟩^2P⟩ - \frac{2}{\sqrt{3}} |3F⟩^2P⟩ \) |
| \([411][21][21]2P⟩ = \frac{1}{\sqrt{5}} |1D⟩^2P⟩ | \( \frac{1}{\sqrt{5}} |1D⟩^2D⟩ - \frac{2}{\sqrt{5}} |3P⟩^2D⟩ + \frac{1}{\sqrt{5}} |3F⟩^2D⟩ \) |
| \([21][111][11]2P⟩ = \frac{1}{\sqrt{2}} |1D⟩^2P⟩ | \( \frac{1}{\sqrt{2}} |1D⟩^2D⟩ - \frac{2}{\sqrt{2}} |3P⟩^2D⟩ + \frac{1}{\sqrt{2}} |3F⟩^2D⟩ \) |
| \([111][111][11]4P⟩ = -\frac{1}{\sqrt{6}} |3P⟩^4P⟩ | \( -\frac{1}{\sqrt{6}} |1D⟩^2D⟩ - \frac{2}{\sqrt{6}} |3P⟩^2D⟩ + \frac{1}{\sqrt{6}} |3F⟩^2D⟩ \) |
| \([21][21][21]2P⟩ = \frac{1}{\sqrt{15}} |1D⟩^2P⟩ | \( \frac{1}{\sqrt{15}} |1D⟩^2D⟩ - \frac{2}{\sqrt{15}} |3P⟩^2D⟩ + \frac{1}{\sqrt{15}} |3F⟩^2D⟩ \) |
| \([111][21][10]2D⟩ = \frac{1}{\sqrt{13}} |1S⟩^2D⟩ | \( \frac{1}{\sqrt{13}} |1D⟩^2D⟩ - \frac{2}{\sqrt{13}} |3P⟩^2D⟩ + \frac{1}{\sqrt{13}} |3F⟩^2D⟩ \) |
| \([21][11][10]2D⟩ = \frac{1}{\sqrt{6}} |1D⟩^2D⟩ | \( \frac{1}{\sqrt{6}} |1D⟩^2D⟩ - \frac{2}{\sqrt{6}} |3P⟩^2D⟩ + \frac{1}{\sqrt{6}} |3F⟩^2D⟩ \) |
| \([111][3][30]2D⟩ = \frac{1}{\sqrt{13}} |1D⟩^2D⟩ | \( \frac{1}{\sqrt{13}} |1D⟩^2D⟩ - \frac{2}{\sqrt{13}} |3P⟩^2D⟩ + \frac{1}{\sqrt{13}} |3F⟩^2D⟩ \) |
| \([111][21][21]2F⟩ = \frac{1}{\sqrt{15}} |1D⟩^2F⟩ | \( \frac{1}{\sqrt{15}} |1D⟩^2F⟩ - \frac{2}{\sqrt{15}} |3P⟩^2F⟩ + \frac{1}{\sqrt{15}} |3F⟩^2F⟩ \) |
| \([21][11][11]1F⟩ = \frac{1}{\sqrt{6}} |1D⟩^2F⟩ | \( \frac{1}{\sqrt{6}} |1D⟩^2F⟩ - \frac{2}{\sqrt{6}} |3P⟩^2F⟩ + \frac{1}{\sqrt{6}} |3F⟩^2F⟩ \) |
| \([21][21][21]2F⟩ = \frac{1}{\sqrt{15}} |1D⟩^2F⟩ | \( \frac{1}{\sqrt{15}} |1D⟩^2F⟩ - \frac{2}{\sqrt{15}} |3P⟩^2F⟩ + \frac{1}{\sqrt{15}} |3F⟩^2F⟩ \) |
| \([21][3][30]2F⟩ = \frac{1}{\sqrt{13}} |1D⟩^2F⟩ | \( \frac{1}{\sqrt{13}} |1D⟩^2F⟩ - \frac{2}{\sqrt{13}} |3P⟩^2F⟩ + \frac{1}{\sqrt{13}} |3F⟩^2F⟩ \) |
| \([411][111][11]4F⟩ = -\frac{1}{\sqrt{6}} |3P⟩^4F⟩ | \( -\frac{1}{\sqrt{6}} |1D⟩^2F⟩ + \frac{2}{\sqrt{6}} |3P⟩^2F⟩ + \frac{1}{\sqrt{6}} |3F⟩^2F⟩ \) |
| \([21][21][21]4F⟩ = \frac{1}{\sqrt{15}} |3P⟩^4F⟩ | \( \frac{1}{\sqrt{15}} |3P⟩^4F⟩ + \frac{1}{\sqrt{15}} |3F⟩^4F⟩ \) |
| \([111][21][21]2G⟩ = -\frac{1}{\sqrt{13}} |1D⟩^2G⟩ | \( -\frac{1}{\sqrt{13}} |1D⟩^2G⟩ + \frac{2}{\sqrt{13}} |3P⟩^2G⟩ + \frac{1}{\sqrt{13}} |3F⟩^2G⟩ \) |
| \([21][11][11]3G⟩ = -\frac{1}{\sqrt{13}} |1D⟩^2G⟩ | \( -\frac{1}{\sqrt{13}} |1D⟩^2G⟩ + \frac{2}{\sqrt{13}} |3P⟩^2G⟩ + \frac{1}{\sqrt{13}} |3F⟩^2G⟩ \) |
| \([21][3][30]3G⟩ = \frac{1}{\sqrt{13}} |1D⟩^2G⟩ | \( \frac{1}{\sqrt{13}} |1D⟩^2G⟩ + \frac{2}{\sqrt{13}} |3P⟩^2G⟩ + \frac{1}{\sqrt{13}} |3F⟩^2G⟩ \) |
| \([21][21][21]4G⟩ = |(3F)^4G⟩ | \( |(3F)^4G⟩ \) |
| \([411][111][21]2H⟩ = \frac{1}{\sqrt{6}} |1D⟩^2H⟩ | \( \frac{1}{\sqrt{6}} |1D⟩^2H⟩ - \frac{2}{\sqrt{6}} |3P⟩^2H⟩ + \frac{1}{\sqrt{6}} |3F⟩^2H⟩ \) |
| \([21][21][21]2H⟩ = \frac{1}{\sqrt{15}} |1D⟩^2H⟩ | \( \frac{1}{\sqrt{15}} |1D⟩^2H⟩ - \frac{2}{\sqrt{15}} |3P⟩^2H⟩ + \frac{1}{\sqrt{15}} |3F⟩^2H⟩ \) |
| \([111][21][21]3H⟩ = |(3F)^3H⟩ | \( |(3F)^3H⟩ \) |
| \([21][3][30]2I⟩ = |(1G)^2I⟩ | \( |(1G)^2I⟩ \) |

For states belonging to \([111]_{10} \), we use the same phases as in \( d^4 \); otherwise, we make an arbitrary phase choice when there is no precedent to guide us.
or abbreviated as a dash (–). Also, we write the negative values with an overline to save space. For example, the irreps $[210^8], [120^6 – 2]$ of $U(10)$ and $[11100]$ of $U(5)$ will be denoted as $[21]_{10}, [11 – \overline{1}]_{10}$ and $[111]_5$ respectively. The exponent form is retained if the same number (other than zero) occurs more than three times. The advantages of using such a notation will become clear when we discuss the generic branching rules of the type $U(2n) \rightarrow SU(2) \times U(n) \cong SO(3) \times U(n)$ in Table 3, as well as to tabulate Kronecker products for unitary groups of any order $n$ (see Table 6).

The mapping of states from the classical basis to the new basis was worked out by Judd (1997) and the author, and is given in Table 1. The reader should for the moment disregard the first superscript labeling each state. That is the isospin label which will be introduced later in section 4. If the alternative scheme involving the symplectic group $Sp(10)$ is used instead, almost all of the states in the first column of Table 1 corresponds to a single state in that scheme. The only mixing comes from a pair of $2^D$ states that share the same labels in $U(10)$ and $SO_S(3) \times SO(5)$. They are given on the last two lines in Table 4.

3. The Coulomb interaction matrix elements

The matrix element table given in Condon and Odabasi (1980) can be transformed to the new basis without difficulty. At the same time, we also followed Judd (1998) and Racah (1954) and take specific linear combinations of the two-electron Coulomb operators so that they transform irreducibly under the action of the group $SO(5)$.

The full two-body Coulomb interaction contains three distinct parts. One involves only the $d$-electrons (or only the $d'$-electrons, if we had more than one $d'$-electron.) The other two are the direct and exchange parts that involve one $d$ and one $d'$ electron.

We can write the perturbing Hamiltonian as

$$H_1 = \sum_k f_k(d, d') F^k(d, d) + f_k(d, d') F^k(d, d') + g_k(d, d') G^k(d, d')$$

$$= \sum_i e_i E^i + f_i F^i + g_i G^i$$

(4)

where the sums run over $k = 0, 2, 4$ and $i = 0, 1, 2$. The $F^k$ and $G^k$ are the usual direct and exchange radial integrals, and the matrix elements of $f_k(d, d')$ and $g_k(d, d')$ in $d^2d'$ in the classical basis are tabulated by Condon and Odabasi (1980). The operators $e_0, e_1$ and $e_2$ on the second line, constructed from the operators $f_k(d, d)$ by Judd (1998) and Racah (1954) independently, transform irreducibly as (00), (00) and (22) of $SO(5)$ respectively. They are given by

$$e_0 = f_0(d, d)$$
$$e_1 = \frac{7}{5}[f_0(d, d) + 5f_2(d, d) + 9f_4(d, d)]$$
$$e_2 = 63[f_2(d, d) - f_4(d, d)]$$

(5)

§ A negative sign for the matrix element $\langle (1^3F)^2H|g_0(1^3G)^2H \rangle$ is missing in their table; its correct value should be -105.
and the corresponding $E^i$ are

\[
E^0 = F_0(d, d) - \frac{7}{2} F_2(d, d) - \frac{63}{2} F_4(d, d) \\
E^1 = \frac{5}{2} F_2(d, d) + \frac{45}{2} F_4(d, d) \\
E^2 = \frac{1}{2} F_2(d, d) - \frac{5}{2} F_4(d, d)
\]

(6)

where $F_0 = F^0$, $F_2 = F^2/49$ and $F_4 = F^4/441$ as defined by Condon and Shortley (1953). Replacing $f_k(d, d)$ by $f_k(d, d')$ and $g_k(d, d')$ in equation (6), we arrive at the operators $\tilde{F}_i$ and $\overline{F}_i$ respectively; and they transform as (00) and (22) in $SO(5)$ just like the operators $e_i$. Similar substitution in equation (6) gives us the relation between $F$ and the direct radial integrals $F^k(d, d')$; and likewise, the relation between $\overline{F}$ and $G^k(d, d')$.

In terms of the creation and annihilation operators, or rather in terms of $\nu_{dd}^{(k)} = \sqrt{2} \omega_{dd}^{(ok)} = -\sqrt{2}(d'd')(ok)$, the operators $e_i$ are given by

\[
e_0 = \frac{5}{2} : \nu_{dd}^{(0)} \cdot \nu_{dd}^{(0)} : = \frac{1}{2} (d'_\mu d_\mu) \cdot (d'_\nu d_\nu) = \frac{1}{2} (d'_\mu d'_\nu d_\mu d_\nu) = \frac{1}{2} (d'_\mu d_\nu d'_\nu d_\mu).
\]

(7a)

\[
e_1 = \frac{7}{2} : \nu_{dd}^{(0)} \cdot \nu_{dd}^{(0)} : + : \nu_{dd}^{(2)} \cdot \nu_{dd}^{(2)} : + : \nu_{dd}^{(4)} \cdot \nu_{dd}^{(4)} :
\]

(7b)

\[
e_2 = 9 : \nu_{dd}^{(2)} \cdot \nu_{dd}^{(2)} : - 5 : \nu_{dd}^{(4)} \cdot \nu_{dd}^{(4)} :
\]

(7c)

where colons denote normal ordering. For instance, with Einstein summation convention over repeated Greek indices ($\mu, \nu$ etc.) used throughout the paper, the operator $e_0$ from the above can be written as

\[
e_0 = \frac{5}{2} : \nu_{dd}^{(0)} \cdot \nu_{dd}^{(0)} : = \frac{1}{2} (d'_\mu d_\mu) \cdot (d'_\nu d_\nu) = \frac{1}{2} (d'_\mu d'_\nu d_\mu d_\nu).
\]

(8a)

The direct and exchange operators, $\tilde{F}_i$ and $\overline{F}_i$, also admit similar expressions in terms of the operators $\nu_{dd}^{(k)} (= -\sqrt{2}(d'd')(ok))$, $\nu_{dd'}^{(k)}$ and $\nu_{dd'}^{(k)}$. For example, $\tilde{F}_0$ and $\overline{F}_0$ are given as

\[
\tilde{F}_0 = 5 : \nu_{dd}^{(0)} \cdot \nu_{dd'}^{(0)} : = (d'_\mu d_\mu)(d'_\nu d_\nu)
\]

(8b)

\[
\overline{F}_0 = 5 : \nu_{dd}^{(0)} \cdot \nu_{dd'}^{(0)} : = (d'_\mu d_\mu)(d'_\nu d_\nu).
\]

(8c)

The extra factor $\frac{1}{2}$ in equations (7d) and (8d) is to allow for the pairwise interaction between the identical d-electrons being counted twice. The other direct and exchange operators $\tilde{F}_i$ and $\overline{F}_i$ are similarly given as in equations (7d) and (8d), with an extra factor of two. As a note, normal ordering removes the self-interaction terms in $e_i$; and it takes cares of the ambiguity that arises in the case of the exchange operators $\overline{F}_i$, in which $\nu_{dd}^{(k)} \cdot \nu_{dd'}^{(k)}$ and $\nu_{dd'}^{(k)} \cdot \nu_{dd'}^{(k)}$ are both legitimate but distinct forms, if not normal ordered.

In terms of the new basis states given in table II, the matrix elements of the operators $e_i$, $\tilde{F}_i$ and $\overline{F}_i$ can be easily obtained from the table by Condon and Odabasi (1980). We
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Table 2. Matrix elements in the new basis.

| $e_0$ | $f_0$ | $g_0$ | $e_1$ | $f_1$ | $g_1$ |
|-------|-------|-------|-------|-------|-------|
| $^2[21][3][30]2S$ | 1 | 2 | -1 | 4 | -2 |
| $^4[11][2][1][2][1]2P$ | 1 | 2 | 2 | $\begin{bmatrix} 0 & 0 & 2 \sqrt{7} \sqrt{3} \end{bmatrix}$ | $\begin{bmatrix} 14/3 & 0 & -7/3 & -2 \sqrt{7}/3 \end{bmatrix}$ | $\begin{bmatrix} 14/3 & 0 & -7/3 & -2 \sqrt{7}/3 \end{bmatrix}$ |
| $^2[21][1][1][1][2][1]2P$ | 1 | 2 | -1 | 0 | 0 | 0 |
| $^2[21][1][2][1][1][1]2P$ | 1 | 2 | -1 | 0 | 0 | 0 |
| $^4[11][1][1][1][1][1][1]4P$ | 1 | 2 | 2 | $\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ | $\begin{bmatrix} 14/3 & 0 & -7/3 & -2 \sqrt{7}/3 \end{bmatrix}$ | $\begin{bmatrix} 14/3 & 0 & -7/3 & -2 \sqrt{7}/3 \end{bmatrix}$ |
| $^2[21][2][1][1][1][1][1][1][1]4P$ | 1 | 2 | -1 | 0 | 0 | 0 |

The matrix elements $g_0$ from Condon and Odabasi’s table possess a variety of values. In the new basis, the corresponding $\overline{g}_0$ matrix elements are diagonal and only take the values 2 and -1.

simply transform their matrix elements\footnote{Notice that the matrix elements of $f_k(d,d)$ in the table of Condon and Odabasi (1980) are simply taken from the configuration $d^2$.} of $f_k(d,d)$, $f_k(d',d')$ and $g_k(d,d')$ into the new basis, then take the corresponding linear combinations as given in equation (3). In this way, we arrive at table 4.

3.1. The irreps of the Coulomb operators

As can be seen from table 4, all the states have definite group labels with respect to the symmetry groups in (3). We have now to determine the transformation properties of the nine operators $e_i$, $f_i$ and $g_i$. Of course, we know that they are scalars in the spin and orbital spaces. As mentioned in the previous section, these nine operators thus...
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| $e_2$ | $\overline{f}_2$ | $\overline{g}_2$ |
|-------|------------------|------------------|
| -9    | -18              | 9                |
| $\begin{bmatrix} -2 & 4\sqrt{7} & -7 \\ 4\sqrt{7} & 7 & -4\sqrt{7} \\ -7 & -4\sqrt{7} & -2 \end{bmatrix}$ | $\begin{bmatrix} -4 & -4\sqrt{7} & 7 \\ -4\sqrt{7} & 14 & 4\sqrt{7} \\ 7 & 4\sqrt{7} & -4 \end{bmatrix}$ | $\begin{bmatrix} -4 & -4\sqrt{7} & 7 \\ -4\sqrt{7} & -7 & -8\sqrt{7} \\ 7 & -8\sqrt{7} & 2 \end{bmatrix}$ |
| $\begin{bmatrix} -4\sqrt{14} & -7 \\ 7 & -4\sqrt{14} \end{bmatrix}$ | $\begin{bmatrix} 14 & 4\sqrt{14} \\ 4\sqrt{14} & -11 \end{bmatrix}$ | $\begin{bmatrix} 14 & 4\sqrt{14} \\ 4\sqrt{14} & 16 \end{bmatrix}$ |
| $\begin{bmatrix} 0 & 2\sqrt{21} & -\sqrt{21} & 0 & 0 \\ 2\sqrt{21} & 4 & -8 & -\sqrt{21} & -2\sqrt{3} \\ -\sqrt{21} & -8 & 4 & 2\sqrt{21} & -2\sqrt{3} \\ 0 & -\sqrt{21} & 2\sqrt{21} & 0 & 0 \\ 0 & -2\sqrt{3} & -2\sqrt{3} & 0 & 0 \end{bmatrix}$ | $\begin{bmatrix} 0 & 4\sqrt{21} & \sqrt{21} & 0 & 0 \\ 4\sqrt{21} & 8 & 8 & \sqrt{21} & 2\sqrt{3} \\ \sqrt{21} & 8 & 8 & 4\sqrt{21} & 2\sqrt{3} \\ 0 & \sqrt{21} & 4\sqrt{21} & 0 & 0 \\ 0 & 2\sqrt{3} & 2\sqrt{3} & 0 & 0 \end{bmatrix}$ | $\begin{bmatrix} 0 & 4\sqrt{21} & \sqrt{21} & 0 & 0 \\ 4\sqrt{21} & 8 & 8 & \sqrt{21} & 2\sqrt{3} \\ \sqrt{21} & 8 & 8 & 4\sqrt{21} & 2\sqrt{3} \\ 0 & \sqrt{21} & 2\sqrt{21} & 0 & 0 \\ 0 & 2\sqrt{3} & -4\sqrt{3} & 0 & 0 \end{bmatrix}$ |
| $\begin{bmatrix} 8 & 6\sqrt{2} & -7 & 2\sqrt{5} \\ 6\sqrt{2} & -3 & -6\sqrt{2} & 0 \\ -7 & -6\sqrt{2} & 8 & 2\sqrt{5} \\ 2\sqrt{5} & 0 & 2\sqrt{5} & -5 \end{bmatrix}$ | $\begin{bmatrix} 16 & -6\sqrt{2} & 7 & -2\sqrt{5} \\ -6\sqrt{2} & -6 & 6\sqrt{2} & 0 \\ 7 & 6\sqrt{2} & 16 & -2\sqrt{5} \\ -2\sqrt{5} & 0 & -2\sqrt{5} & -10 \end{bmatrix}$ | $\begin{bmatrix} 16 & -6\sqrt{2} & 7 & -2\sqrt{5} \\ -6\sqrt{2} & 3 & -12\sqrt{2} & 0 \\ 7 & -12\sqrt{2} & -8 & 4\sqrt{5} \\ -2\sqrt{5} & 0 & 4\sqrt{5} & 5 \end{bmatrix}$ |
| $\begin{bmatrix} -3 & -12 \\ -12 & 15 \end{bmatrix}$ | $\begin{bmatrix} -6 & 12 \\ 12 & 9 \end{bmatrix}$ | $\begin{bmatrix} -6 & 12 \\ 12 & 6 \end{bmatrix}$ |
| $\begin{bmatrix} -16 & 11 & 2\sqrt{55} \\ 11 & -16 & 2\sqrt{55} \\ 2\sqrt{55} & 2\sqrt{55} & -7 \end{bmatrix}$ | $\begin{bmatrix} -32 & -11 & -2\sqrt{55} \\ -11 & -32 & -2\sqrt{55} \\ -2\sqrt{55} & -2\sqrt{55} & -14 \end{bmatrix}$ | $\begin{bmatrix} -32 & -11 & -2\sqrt{55} \\ -11 & -16 & 4\sqrt{55} \\ -2\sqrt{55} & 4\sqrt{55} & 7 \end{bmatrix}$ |
| $\begin{bmatrix} -9 \\ -2 & 7 \\ 7 & -2 \\ -9 \\ 5 \end{bmatrix}$ | $\begin{bmatrix} -4 & 7 \\ -7 & -4 \\ 3 \\ 10 \\ -5 \end{bmatrix}$ | $\begin{bmatrix} -4 & 7 \\ -7 & 2 \\ -12 \\ -7 & 2 \\ -5 \end{bmatrix}$ |

constructed belong to either (00) or (22) of $SO(5)$. We will now find the $U(5)$ and $U(10)$ labels of these operators.

The two-body operators contain two creation and two annihilation operators. As the creation operators ($d^1$ or $d'^1$) transform as $[1]_5$, while annihilation operators $[\overline{T}]_5$, the product

$[1]_5 \times [1]_5 \times [\overline{T}]_5 \times [\overline{T}]_5 = 2[0]_5 + 4[1 - \overline{T}]_5 + [2 - \overline{T}]_5 + [11 - \overline{\overline{T}}]_5 + [11 - \overline{T}]_5 + [2 - \overline{T}]_5$

must contain the appropriate labels for the two-body operators. We only need to pick out those $U(5)$ irreps from the Kronecker product above that contain either (00) or (22) of $SO(5)$. The branching rules $U(5) \rightarrow SO(5)$ are given by Wybourne (1970)\textsuperscript{+}, for instance. We are then left with $[0]_5$, $[11 - \overline{T}]_5$ and $[2 - \overline{T}]_5$ where the first irrep contain

\textsuperscript{+} The table by Wybourne (1970) does not include $U(5)$ irreps with negative values. But if we look at the reduction $U(5) \rightarrow SU(5) \rightarrow SO(5)$ instead, the fact that $[a_1, a_2, \cdots]$ and $[a_1 + c, a_2 + c, \cdots]$ of $U(5)$ reduce to the same $SU(5)$ multiplet tells us they must contain the same $SO(5)$ components. So, we can easily remove the negative numbers in each irrep of $U(5)$ without changing its $SO(5)$ content.
Table 3. Branching rule $U(2n) \rightarrow SO(3) \times U(n)$.

| $U(2n)$ | $SO(3) \times U(n)$ |
|---------|---------------------|
| $[1]_{2n}$ | $2[1]_{n}$ |
| $[11]_{2n}$ | $3[11]_{n} + 1[2]_{n}$ |
| $[2]_{2n}$ | $1[11]_{n} + 3[2]_{n}$ |
| $[21]_{2n}$ | $2[111]_{n} + 2[21]_{n} + 2[3]_{n}$ |
| $[1 - \Gamma]_{2n}$ | $3[0]_{n} + 1, 3, 5[1 - \Gamma]_{n} + 1, 3, 5[2 - \Gamma]_{n} + 1, 3, 5[2 - \Gamma]_{n}$ |
| $[11 - \Pi]_{2n}$ | $1, 5[0]_{n} + 1, 3, 5[1 - \Pi]_{n} + 1, 3, 5[11 - \Pi]_{n} + 1, 3, 5[2 - \Pi]_{n} + 1, 3, 5[2 - \Pi]_{n}$ |
| $[2 - \Pi]_{2n}$ | $1, 5[0]_{n} + 1, 3, 5[1 - \Pi]_{n} + 1, 3, 5[11 - \Pi]_{n} + 1, 3, 5[2 - \Pi]_{n} + 1, 3, 5[2 - \Pi]_{n}$ |

(00) of $SO(5)$, the second one contain (22) and the last one both.

On the $U(10)$ level, we use the branching rules given in table 3 and pick out the irreps in the Kronecker product $[1]_{10} \times [1]_{10} \times [\Pi]_{10} \times [\bar{\Pi}]_{10}$ that contain either $1[0]_{5}$, $1[11 - \Pi]_{5}$ or $1[2 - \bar{\Pi}]_{5}$ of $SO(5) \times U(5)$. (The Coulomb operators are spin scalars.) The eligible ones are $[0]_{10}$, $[11 - \Pi]_{10}$ and $[2 - \bar{\Pi}]_{10}$.

The group labels for the nine operators $e_i$, $\mathcal{F}_i$ and $\mathcal{G}_i$ can thus be written down rapidly as given in table 4. (Once again, the reader can ignore the isospin superscript for the time being.) The only ones that need explanation are the three $e_i$ operators as well as $\mathcal{F}_0$ and $\mathcal{G}_0$. The three equivalent electron operators $e_i$ do not contain the irrep $[2 - \bar{\Pi}]_{10}$ of $U(10)$ because the two creation operators (and likewise, the annihilation operators) must form an antisymmetric product in $U(10)$. So no $[2 - \bar{\Pi}]_{10}$ appears. In fact, they were examined by Judd and Leavitt (1986), and it is found that $e_0$ belongs to $[0]_{10}$ of $U(10)$, $e_2$ belongs to $[11 - \Pi]_{10}$, and $e_1$ is a mixture of $[0]_{10}$ and $[11 - \Pi]_{10}$.

For the operators $e_0$, $\mathcal{F}_0$ and $\mathcal{G}_0$, they can be shown to be $U(10)$ scalars rather easily. From the expressions (27) through (29), it is a simple exercise to show that they commute with all the 100 generators $d_0^\mu d_\nu + d_0^\mu d_\nu$ of the group $U(10)$. (See section 4 for further discussion of the group generators.) Hence, they are all $U(10)$ scalars.

3.2. Selection rules and the Wigner-Eckart Theorem

With the group labels for the operators worked out, we are now in a position to appreciate the use of the new group-theoretical basis. We can look at the situation on different group levels. First of all, the six $SO(5)$ scalars operators $e_0, e_1, \mathcal{F}_0, \mathcal{F}_1, \mathcal{G}_0$ and $\mathcal{G}_1$ cannot connect states with different $SO(5)$ labels. And for the other three operators $e_2, \mathcal{F}_2$ and $\mathcal{G}_2$ which belong to (22), the Kronecker products for $SO(5)$ account for all the vanishing matrix elements one can find in table 3 on those three columns.

When we apply the Wigner-Eckart theorem on the group $U(10)$, we expect a lot of simple proportionality relations among the different operators. Between the operators
\[ \langle [111]_{10}^\beta | \bar{f}_i | [111]_{10}^\gamma \rangle = 2 \langle [111]_{10}^\beta | e_i | [111]_{10}^\gamma \rangle \] \hspace{1cm} (9a) \\
\[ \langle [111]_{10}^\beta | \bar{g}_i | [21]_{10}^\gamma \rangle = \langle [111]_{10}^\beta | e_i | [111]_{10}^\gamma \rangle \] \hspace{1cm} (9b)

for \( i = 0, 1 \) and 2; and \( \beta, \gamma \) denotes the rest of the quantum numbers needed to specify the state. As for the relations with the operators \( e_i \), we have

\[ \langle [111]_{10}^\beta | \bar{f}_i | [111]_{10}^\gamma \rangle = 2 \langle [111]_{10}^\beta | e_i | [111]_{10}^\gamma \rangle \] \hspace{1cm} (10a) \\
\[ \langle [111]_{10}^\beta | \bar{g}_i | [21]_{10}^\gamma \rangle = - \langle [111]_{10}^\beta | e_i | [21]_{10}^\gamma \rangle \] \hspace{1cm} (10b) \\
\[ \langle [21]_{10}^\beta | \bar{f}_i + \bar{g}_i | [21]_{10}^\gamma \rangle = \langle [21]_{10}^\beta | e_i | [21]_{10}^\gamma \rangle \] \hspace{1cm} (10c)

Most of the proportionality relations above are the result of the Wigner-Eckart theorem at work on the group \( U(10) \). To demonstrate, let us use a few examples. For \( i = 2 \) in equation (10c), since \( \Pi \Pi |_{10} \times [111]_{10} \) contains \( [11 - \Pi]_{10} \) once and no \( [2 - \Pi]_{10} \) appears (see table 3), only the \( [11 - \Pi]_{10} \) part (but not the \( [2 - \Pi]_{10} \) part) of the operators \( \bar{f}_2 \) and \( \bar{g}_2 \) contributes to their matrix elements. Hence, by the Wigner-Eckart theorem, they should be proportional to each other, and the proportionality constant turns out to be unity. Analogous argument applies to explain the proportionality relations in (10a), (10d) and (10f) for \( i = 0, 2 \). The \( i = 1 \) operators contain the irreps \( [0]_{10} \) and \( [11 - \Pi]_{10} \), which both contribute to the matrix elements in general. So, the

Table 4. Group labels of the Coulomb interaction operators.

| operator | \( SO_\tau(3) \times U(10) \) | \( U(5) \) | \( SO(5) \) |
|----------|-----------------|-------|---------|
| \( e_0, \bar{e}_0 \) | \( 1.5[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( e_1, \bar{e}_1 \) | \( 1.5[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( e_2, \bar{e}_2 \) | \( 1.5[11 - \Pi]_{10} \) | \( [11 - \Pi]_{5} + [2 - \Pi]_{5} \) | (22) |
| \( \bar{f}_0, \bar{g}_0 \) | \( 1.5[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( \bar{f}_1, \bar{g}_1 \) | \( 1.5[11 - \Pi]_{10} \) | \( [0]_{5} + [2 - \Pi]_{5} \) | (00) |
| \( \bar{f}_2, \bar{g}_2 \) | \( 1.5[2 - \Pi]_{10} \) | \( [11 - \Pi]_{5} + [2 - \Pi]_{5} \) | (22) |
| \( \bar{e}_0 \) | \( 1[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( \bar{e}_1 \) | \( 1[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( \bar{e}_2 \) | \( 1[2 - \Pi]_{10} \) | \( [0]_{5} + [2 - \Pi]_{5} \) | (00) |
| \( \bar{e}_0 + e_0 \) | \( 1[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( \bar{e}_1 + e_1 \) | \( 1[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( \bar{e}_2 + e_2 \) | \( 1[11 - \Pi]_{10} \) | \( [0]_{5} + [2 - \Pi]_{5} \) | (00) |
| \( 2\bar{e}_0 - e_0 \) | \( 5[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( 2\bar{e}_1 - e_1 \) | \( 5[0]_{10} \) | \( [0]_{5} \) | (00) |
| \( 2\bar{e}_2 - e_2 \) | \( 5[11 - \Pi]_{10} \) | \( [0]_{5} + [2 - \Pi]_{5} \) | (00) |

The work on the group \( U(10) \) for the state. As for the relations with the operators \( e_i \), we have
Wigner-Eckart theorem fails to provide an explanation for these \( i = 1 \) cases in \( [10] \) and \( [11] \); although it works well with \( [0] \) and \( [10] \) where the scalar part \( [0]_{10} \) does not contribute to the matrix elements. But in any case, it cannot explain why the proportionality constants are the same for \( i = 0, 1 \) and 2.

The last relation \( [10] \) is a little bit different. Since \( [21]_{10} \times [21]_{10} \) contain both \( [11 - 11]_{10} \) and \( [2 - 2]_{10} \), we do not have a simple relation as we had before. For \( i = 2 \), if we write equation \( [10] \) as \( g_2 = e_2 - (f_2) \), we can interpret \( e_2 \) and \( f_2 \) as two independent sets of isoscalar factors; hence \( g_2 \) can be written as a linear combinations of the two sets of isoscalars. Once again, the argument does not apply to the \( i = 1 \) case; and for \( i = 0 \), the three sets of matrix elements \( e_0 \), \( f_0 \) and \( g_0 \) are proportional to each other as the operators are all \( U(10) \) scalars. Despite these differences between the \( i = 0, 1 \) and 2 cases, they display the same relation as given in \( [10] \). We will explain the above relations in a more elegant way in the next few sections. Relations \( [10] \) and \( [21] \) will be explained in section 3.3 and relations \( [10] = [10] \) in section 4.4 making use of the isospin structure.

Before we go on any further, let us pause and reflect on what we have achieved so far. We are trying to find all the matrix elements of the nine operators \( e_i \), \( f_i \) and \( g_i \) for the configuration \( d^2 d' \). The matrix elements \( e_i \) are rather well known, as they come strictly from the \( d^2 \) matrix elements (see Condon and Odabasi, 1980). Now with equations \( [0] \), \( [7] \) and \( [10] \), the \( g_i \) matrix elements can be easily obtained from those of \( f_i \) and \( e_i \). Furthermore, with equations \( [10] \) and \( [0] \), the matrix elements \( [11]_{10} \beta \) \( f_i \) \( [11]_{10} \gamma \) and \( [11]_{10} \beta \) \( f_i \) \( [21]_{10} \gamma \) are readily obtained from the \( e_i \) matrix elements; we are only left with \( [21]_{10} \beta \) \( f_i \) \( [21]_{10} \gamma \) to work on. Is there an easy way to find these matrix elements? By observation, we find that the matrix elements of \( \tilde{e}_i \equiv e_i + f_i \) are surprisingly simple. For \( i = 0 \), the sum \( e_0 + f_0 \) is always 3; for \( i = 1 \), the sum \( e_1 + f_1 \) is diagonal, and the value depends only on the \( U(5) \) and \( SO(5) \) irreps, but not the \( U(10) \) label nor the spin and orbital ranks. For the case \( i = 2 \), the sum is almost diagonal, with the three exceptions

\[
\langle d^2 d' [^T] U[21](21)^{[S]} D | e_2 + f_2 | d^2 d' [^T] U[21](10)^{[S]} D \rangle = 6 \sqrt{21}
\]

The diagonal values once again do not depend on the \( U(10) \) irrep and the spin, although they do depend on the orbital rank. These properties, which will be addressed in section 3, greatly simplify our task of finding the \( f_i \) matrix elements. With these simple relations, (almost) all the matrix elements can be related to the known \( e_i \) matrix elements. We will elaborate this further in section 3.

### 3.3. The operators \( \overline{c} \) and \( \tilde{e}_i \) with simpler \( U(10) \) transformation properties

As mentioned before, the ten creation operators \( d_{\mu}^i \) belong to the irrep \( [1]_{10} \) of \( U(10) \); so do the ten components \( d_{\mu}^{i*} \). When we form products from the two independent sets, we can get \( [2]_{10} \) or \( [11]_{10} \). From the knowledge of unitary groups and their representations, we know that \( [2]_{10} \) corresponds to the symmetric product, while \( [11]_{10} \) the antisymmetric one. More precisely, \( (d_{\mu}^i d_{\nu}^{i*} + d_{\nu}^i d_{\mu}^{i*}) \) and \( (d_{\mu}^i d_{\nu}^{i*} - d_{\nu}^i d_{\mu}^{i*}) \) have 45 components each; they
are the antisymmetric products and belong \([11]_{10}\) and \([\Pi]_{10}\) respectively. The other combination \((d^i_\mu d^j_\nu - d^j_\mu d^i_\nu)\) belongs to \([2]_{10}\), has 55 components; and \((d^\mu d^\nu - d^\nu d^\mu)\) belongs to \([2]_{10}\). Of course, the symmetric product \([2]_{10}\) is identically zero for two equivalent electrons.

In terms of creation and annihilation operators, \(\overline{f}_i\) and \(\overline{g}_i\) can be written as

\[
\overline{f}_i = \sum_k 2a_{ik} :v^{(k)}_{dd} :v^{(k)}_{d'd'} : \sim \sum C_{\mu\nu}C_{\eta\xi}d^\mu_\eta d^\nu_\xi d^\nu_\eta d^\mu_\xi \]
\[
\overline{g}_i = \sum_k 2a_{ik} :v^{(k)}_{dd} :v^{(k)}_{d'd'} : \sim \sum C_{\mu\nu}C_{\eta\xi}d^\nu_\eta d^\mu_\xi d^\nu_\xi d^\mu_\eta \tag{11}
\]

where \(a_{ik}\) are the corresponding coefficients as given in equations \((7)\) to \((7)\), and \(C_{\mu\nu}\) are the appropriate Clebsch-Gordan (CG) coefficients. They are invariant under the simultaneous interchange of \(d^\mu\) with \(d^\nu\) and \(d\) with \(d'\). But they are neither symmetric nor antisymmetric with respect to the interchange of the creation operators alone. In fact, if we interchange \(d^\mu\) and \(d^\nu\) (or \(d\) and \(d'\)) alone, \(\overline{f}_i\) becomes \(\overline{g}_i\), and vice versa. If we take the combination

\[
\tilde{e}_i = \frac{1}{2}(\overline{f}_i + \overline{g}_i) \sim \sum C_{\mu\nu}C_{\eta\xi}d^\mu_\eta d^\nu_\xi (d^\mu_\xi d^\nu_\eta + d^\nu_\xi d^\mu_\eta)
\]

we first note that the annihilation operators within the parenthesis transform as the antisymmetric product \([\Pi]_{10}\). With a little algebraic manipulation, we can obtain a similar expression with the creation operators grouped as a \([11]_{10}\) product. This tells us the new operators \(\tilde{e}_i\) belong to \([11 - \Pi]_{10}\) of \(U(10)\). Similarly, \(\tilde{e}_0 = \frac{1}{2}(\overline{f}_0 - \overline{g}_0)\) is the symmetric product, and belongs to \([2 - \Pi]_{10}\). There are flaws in the above argument; namely, we ignored the scalar parts. The arguments above do not exclude the possibility that the operators can be \(U(10)\) scalars. As we already know, \(\overline{f}_0\) and \(\overline{g}_0\) are both \(U(10)\) scalars, so the sum or difference \((\tilde{e}_0\) or \(\tilde{e}_0\)) must also be \(U(10)\) scalars; although their expressions look as if they belong to \([11 - \Pi]_{10}\) and \([2 - \Pi]_{10}\) respectively. Similarly, \(\tilde{e}_1\) and \(\tilde{e}_1\) can contain a scalar part and, in fact, they do. The transformation properties of these new operators \(\tilde{e}_i\) and \(\tilde{e}_i\) are summarized in table \(\text{[4]}\). In terms of these six new operators, the perturbative Hamiltonian in \(\text{[4]}\) becomes

\[
H_1 = \sum_i e_i E_i + \frac{\overline{f}_i F_i}{2} + \frac{\overline{g}_i G_i}{2}
\]

\[
= \sum_i e_i E_i + \frac{\overline{f}_i + \overline{g}_i}{2}(F_i + G_i) + \frac{\overline{f}_i - \overline{g}_i}{2}(F_i - G_i)
\]

\[
\equiv \sum_i e_i E_i + \overline{e}_i E_i + \tilde{e}_i \tilde{E}_i \tag{12}
\]

From a group-theoretical point of view, it is more convenient to use these new operators, \(\overline{e}_i\) and \(\tilde{e}_i\), with simpler transformation properties, rather than the distinct direct and exchange operators, \(\overline{f}_i\) and \(\overline{g}_i\). Notice that the operators \(\overline{e}_i\) have the same transformation properties as \(e_i\). The matrix elements of \(\overline{e}_i\) and \(\tilde{e}_i\) are given in table \(\text{[3]}\), in which we copied down the \(e_i\) matrix elements from table \(\text{[3]}\) to make it complete. These new operators transform irreducibly in \(U(10)\), makes applying the Wigner-Eckart theorem as well as the selection rules on the \(U(10)\) level so much easier and more elegant.
Coulomb and spin-orbit interaction matrix elements in $d^2d'$ configuration

**Table 5.** Matrix elements for the operators $e_i$, $\overline{e}_i$, $\tilde{e}_i$ and $\tilde{e}_i$.

| $e_i$ | $\overline{e}_i$ | $\tilde{e}_i$ | $\tilde{e}_i$ |
|-------|------------------|--------------|--------------|
| $^2[21][3(30)2S$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | 2 | 1 | 3 | 6 |
| $^4[111][21](21)^2P$ | 1 2 0 3 | $\left[\begin{array}{c} 1 0 1 \\ 0 0 0 \\ 1 0 1 \end{array}\right]$ | $\left[\begin{array}{c} 2 0 \frac{1}{2} \\ 0 0 0 \\ -1 0 \frac{1}{2} \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 \\ 0 0 0 \\ 0 0 \frac{3}{2} \end{array}\right]$ | 3 |
| $^2[21][21](21)^2P$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 \\ 0 0 0 \\ 0 \frac{3}{2} \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 \\ 0 0 0 \\ 0 \frac{3}{2} \end{array}\right]$ | 3 |
| $^4[111][111](11)^4P$ | 1 2 0 3 | $\left[\begin{array}{c} 0 0 0 \\ 0 \frac{3}{2} \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 \\ 0 \frac{3}{2} \end{array}\right]$ | 0 |
| $^2[21][21](21)^4P$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 \\ 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 \\ 0 0 0 \end{array}\right]$ | 3 |
| $^4[111][21](10)^2D$ | 1 2 0 3 | $\left[\begin{array}{c} \frac{7}{9} 0 0 \frac{2 \sqrt{7}}{3} \\ \frac{1}{9} 0 \frac{2 \sqrt{7}}{3} \frac{7}{9} \\ \frac{7}{9} 0 \frac{2 \sqrt{7}}{3} \frac{7}{9} \end{array}\right]$ | $\left[\begin{array}{c} 0 0 \frac{3}{2} \frac{3}{2} \frac{7}{9} \frac{2 \sqrt{7}}{3} \frac{7}{9} \\ 0 \frac{3}{2} \frac{3}{2} \frac{7}{9} \frac{2 \sqrt{7}}{3} \frac{7}{9} \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \frac{3}{2} \frac{3}{2} \frac{7}{9} \frac{2 \sqrt{7}}{3} \frac{7}{9} \\ 0 0 0 0 \frac{3}{2} \frac{3}{2} \frac{7}{9} \frac{2 \sqrt{7}}{3} \frac{7}{9} \end{array}\right]$ | 13 |
| $^2[21][21](10)^4D$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 \\ 0 0 0 \\ 0 \frac{3}{2} \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 \\ 0 0 0 \\ 0 \frac{3}{2} \end{array}\right]$ | 3 |
| $^4[111][21](10)^2F$ | 1 2 0 3 | $\left[\begin{array}{c} 1 0 1 0 \\ 0 0 0 0 \\ 1 0 1 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 0 |
| $^2[21][21](10)^2F$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 3 |
| $^2[21][21](10)^4F$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 3 |
| $^4[111][111](11)^4F$ | 1 2 0 3 | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 0 |
| $^2[21][21](11)^2G$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 3 |
| $^2[21][21](11)^4G$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 3 |
| $^4[111][21](21)^2H$ | 1 2 0 3 | $\left[\begin{array}{c} 1 1 \\ 1 1 \\ 1 1 \end{array}\right]$ | $\left[\begin{array}{c} 2 -1 \\ 2 -1 \\ 2 -1 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 \\ 0 0 \\ 0 0 \end{array}\right]$ | 3 |
| $^2[21][21](21)^4H$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 3 |
| $^2[21][21](21)^2I$ | 1 $\frac{3}{2}$ $\frac{3}{4}$ 3 | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | $\left[\begin{array}{c} 0 0 0 0 \\ 0 0 0 0 \\ 0 0 0 0 \end{array}\right]$ | 6 |

For example, equations (94) and (114) are now written as

$$\langle [111]_0^{10} | \beta \tilde{e}_i | [111]_0^{10} \rangle = 0$$  \hspace{1cm} (13a)

$$\langle [111]_0^{10} | \beta \tilde{e}_i | [21]_0^{10} \rangle = 0$$  \hspace{1cm} (13b)

From the Kronecker products given in table 4 neither $[33]_{10} \times [111]_{10}$ nor $[33]_{10} \times [21]_{10}$ contains $[2 - \frac{7}{2}]_{10}$. Therefore, equation (134) as well as the $i = 2$ case in (134) come from the $U(10)$ group selection rule. The matrix elements $\langle \tilde{e}_0 | 0 \rangle$ in (13a) can be obtained using the derived eigenvalue expression for $\tilde{e}_0$ in section 4.6 after we introduce the isospin structure. And $\langle \tilde{e}_0 | 0 \rangle$ in (134) can be verified using the results in section 5. Most of the Wigner-Eckart relations we had before are now re-interpreted as the selection rule on the group $U(10)$. This also explains why the proportionality constants are the same for all $i$, and why they are 1.

The other three new operators $\overline{e}_i$ have identical group labels with the corresponding
But introducing these new operators do not come from the Wigner-Eckart theorem. In a sense, we are just rewriting those three equations without adding much understanding to the problem we are facing.

\[ \begin{align*}
\langle |111|_{10}\beta |\bar{e}_i| |111|_{10}\gamma \rangle &= 2\langle |111|_{10}\beta |e_i| |111|_{10}\gamma \rangle \\
\langle |111|_{10}\beta |\bar{e}_i| |21|_{10}\gamma \rangle &= -\langle |111|_{10}\beta |e_i| |21|_{10}\gamma \rangle \\
\langle |21|_{10}\beta |\bar{e}_i| |21|_{10}\gamma \rangle &= \frac{1}{2}\langle |21|_{10}\beta |e_i| |21|_{10}\gamma \rangle
\end{align*} \]

which are the same as equations (10d) to (10d). Once again, the \( i = 1 \) cases in (14d) and (14d) do not come from the Wigner-Eckart theorem. In a sense, we are just rewriting those three equations without adding much understanding to the problem we are facing. But introducing these new operators \( \bar{e}_i \) and \( \bar{e}_i \) is a very crucial step towards the full understanding of the underlying group structure to the problem on hand.

4. Isospin and the group \( U(20) \)

Simonis et al (1984) first introduced the idea of isospin into the theory of atomic
Coulomb and spin-orbit interaction matrix elements in $d^2d'$ configuration

Table 6. Some Kronecker products for Unitary Groups $U(n)$.

| Product | Expression |
|---------|------------|
| $[1] \times [1]$ | $[2] + [11]$ |
| $[1] \times [1]_t$ | $[1 - \overline{1}] + [0]$ |
| $[11] \times [11]$ | $[22] + [211] + [1]^4$ |
| $[11] \times [\overline{11}]$ | $[11 - \overline{11}] + [1 - \overline{1}] + [0]$ |
| $[11] \times [2]$ | $[31] + [211]$ |
| $[11] \times [2]_t$ | $[11 - \overline{2}] + [1 - \overline{1}]$ |
| $[2] \times [2]$ | $[4] + [31] + [22]$ |
| $[2] \times [\overline{2}]$ | $[2 - \overline{2}] + [1 - \overline{1}] + [0]$ |
| $[111] \times [111]$ | $[222] + [2211] + [21]^4 + [1]^6$ |
| $[111] \times [\overline{111}]$ | $[111 - \overline{111}] + [11 - \overline{11}] + [1 - \overline{1}] + [0]$ |
| $[111] \times [21]$ | $[321] + [3111] + [2211] + [21]^4$ |
| $[111] \times [21]_t$ | $[111 - \overline{21}] + [11 - \overline{2}] + [11 - \overline{11}] + [1 - \overline{1}]$ |
| $[111] \times [3]$ | $[411] + [3111]$ |
| $[111] \times [\overline{3}]$ | $[111 - \overline{3}] + [11 - \overline{2}]$ |
| $[21] \times [21]$ | $[42] + [411] + [33] + 2[321] + [3111] + [2211] + [2211]$ |
| $[21] \times [\overline{21}]$ | $[21 - \overline{21}] + [11 - \overline{2}] + [2 - \overline{2}] + [2 - \overline{1}] + [21 - \overline{11}] + [21 - \overline{1}] + [0]$ |
| $[21] \times [3]$ | $[51] + [42] + [411] + [321]$ |
| $[21] \times [\overline{3}]$ | $[21 - \overline{3}] + [11 - \overline{2}] + [2 - \overline{2}] + [1 - \overline{1}]$ |
| $[3] \times [3]$ | $[6] + [51] + [42] + [33]$ |
| $[3] \times [\overline{3}]$ | $[3 - \overline{3}] + [2 - \overline{2}] + [1 - \overline{1}] + [0]$ |

The above products are obtained using the method of Young’s tableaux. When negative integers are involved in the irrep, we first add a constant to it so that all integers becomes non-negative; then use the standard Young’s method to find the Kronecker product, and finally subtract the same constant from the resulting irreps.

The Kronecker products are valid for large enough $n$. For instance, $[111 - \overline{111}]_5$ contains at least six entries and is identically zero for $U(5)$.

spectroscopy. The idea, borrowed from nuclear spectroscopy, is to treat two electrons with different principal quantum numbers $n$ as two states ($\uparrow$ or $\downarrow$) of a generic $d$-electron in the isospin space. This gives an elegant explanation to the simple relations observed in the previous sections, as well as providing new results such as the closed-form expressions for the scalar operators. Furthermore, putting $d$ and $d'$ electrons on the same footing lets us conveniently switch between configurations $d^3$, $d^2d'$ and so forth; hence CI can be taken into account in a natural manner.

4.1. Motivation

In an attempt to exploit the orthogonality relation (Judd and Leavitt, 1986 and Judd et al 1982) between the nine operators we are looking at (either the set $e_i$, $\overline{f_i}$, $\overline{g_i}$ or $e_i$, $\overline{c_i}$ and $\overline{e_i}$), it becomes clear that the situation we are now facing is very different from the equivalent-electron case. In the latter one, the operators in question ($e_i$) belong solely to a single irrep $[11 - \overline{11}]_{10}$ of $U(10)$, with the exception of a complete scalar operator, $e_0$ (see table 4). The three operators $e_0$, $e'_1 = e_1 - \frac{7}{3}e_0$ and $e_2$ are orthogonal to each other. Orthogonality requires summing over all states with the irrep $[1^N]_{10}$ (all
the states in $d^3$, for instance). But now, the states in $d^2d'$ belong to two different irreps $[111]_{10}$ and $[21]_{10}$. Another very important aspect about orthogonality is, operators with different transformation properties are necessarily orthogonal. For this reason, the $i = 2$ operators are orthogonal to the $i = 0, 1$ operators, as they transform as $(22)$ and $(00)$ in $SO(5)$ respectively. Similarly, $\tilde{e}_2$ is orthogonal to $e_2$ and $\overline{e}_2$ as they have different $U(10)$ irreps. But $e_1$ and $\overline{e}_1$, as well as $\overline{f}_i$ and $\overline{g}_i$, have the same transformation properties. Can we find a higher symmetry group to distinguish them? We also like to have a group such that all the states in $d^2d'$ belong to a single irrep.

4.2. The group $U(20)$, its generators and its subgroup

The 100 generators of the group $U(10)$ in terms of the creation and annihilation operators are $d^\dagger_\mu d_\nu + d^{\dagger \mu \nu}$. They can be re-expressed as $(d^\dagger d)^{(SL)} + (d^{\dagger \mu \nu})^{(SL)}$, where $S = 0, 1$ and $L = 0, \cdots, 4$. This group transforms the states in the configuration $d^N d^{N'}$ among themselves. If we drop the scalar operators for which $S = L = 0$, we are left with the $SU(10)$ generators. The other subgroups that we use, $SO_S(3)$ and $U(5)$, are generated by $(d^\dagger d)^{(10)} + (d^{\dagger \mu \nu})^{(10)}$ and $(d^\dagger d)^{(0L)} + (d^{\dagger \mu \nu})^{(0L)}$ respectively.

One can however consider a more general transformation group. If we take the 20 one-electron states $(d^\dagger_\mu$ or $d^\dagger_\mu$ acting on the vacuum $|0\rangle$) as the basis vector space, the most general transformation among them constitute the unitary group $U(20)$, which has 400 generators of the form $d^\dagger_\mu d_\nu, d^{\dagger \mu \nu}, \sum d^\dagger_\mu d_\nu$ and $d^\dagger_\mu d_\nu$. These operators preserve electron number, but they connect states in different configurations, like $d^2d'$ with $d^3$ and so forth. The nine operators $(e_i, \overline{e}_i$ and $\tilde{e}_i$) now belong to a single irrep $[11 - \overline{1}1]_{20}$ of this higher group plus the scalar $[0]_{20}$.

A more elegant formulation is given below. Following Šimonis et al (1984) and Kaniauskas et al (1987), we introduce the operators $d^{(t s l)}_{m_s m_l}$ where $t = \frac{1}{2}$ is the isospin rank, with $d^{(t s l)}_{m_s m_l} = d^{(s l)}_{m_s m_l}, d^{(t s l)}_{s l} = d^{(s l)}_{m_s m_l}$, $d^{(t s l)}_{m_s m_l} = d^{(s l)}_{m_s m_l}$ and $d^{(t s l)}_{m_s m_l} = d^{(s l)}_{m_s m_l}$. In this notation, the 400 generators of $U(20)$ can be written as $w^{(TSL)} = (d^T d)^{(TSL)}$, where $T, S = 0, 1$ and $L = 0, \cdots, 4$. One can immediate see that the operators $(d^T d)^{(TSL)}$ with isospin $T = 0$ are simply the $U(10)$ operators described above; and those for which $T = S = 0$ correspond to the $U(5)$ generators. The three components of $-\sqrt{10}(d^T d)^{(100)}$ are recognized as the pure isospin generators $T_+, T_0$ and $T_-$. In terms of creation and annihilation operators,

$$T_+ = d^\dagger_\mu d_\mu$$
$$T_- = d^{\dagger \mu \nu}$$
$$T_0 = \frac{1}{2} (d^\dagger_\mu d_\mu - d^{\dagger \mu \nu}).$$

(15)

Obviously, the group $U(20)$ contains $SO_T(3) \times U(10)$ as a formal subgroup. The subgroup structure $U(20) \rightarrow SO_T(3) \times U(10)$ goes exactly the same way as $U(10) \rightarrow SO_S(3) \times U(5)$. Augmenting equation (12), we can now use the full chain of subgroups

$U(20) \supset SO_T(3) \times U(10) \supset SO_T(3) \times SO_S(3) \times U(5)$.
\[ SO_T(3) \times SO_S(3) \times SO(5) \supset SO_T(3) \times SO_S(3) \times SO_L(3) \]  

4.3. Isospin ranks for states and operators

Since fermions obey the Pauli exclusion principle, no two electrons occupy the same quantum state (spin and orbital quantum numbers \( m_s, m_l, \) and isospin \( z \)-component \( m_i \)), which is the same as principal quantum number \( n \) in a certain sense). Therefore, any state with \( r \) electrons (\( d \) or \( d' \)) belongs to \([1^r]_{20}\) of \( U(20) \). Using the branching rule given in table 3, \([1^r]_{20} \rightarrow r+1[1^r]_{10} + r-1[21^{r-2}]_{10} + \cdots\), we can quickly write down the isospin rank for all the states. Using the same notation as for regular spin, we put the multiplicity \([T] = 2T + 1\) as a superscript preceding the \( U(10) \) label. They are given in table 4. Notice that the isospin ranks are uniquely determined by the \( U(10) \) labels for atomic states. (This is not true for operators, however.) As for the isospin \( z \)-component \( M_T\), it is simply given by the configuration type. From equation (15), we can see that for the configuration \( d^N \cdot d'^{N'} \), \( M_T = \frac{1}{2}(N - N')\).

Let us now look at the isospin rank of the Coulomb operators. The operators we have considered so far, which do not include CI, all have \( M_T = 0 \). This can be verified by evaluating the commutator \([T_0, \epsilon_0] = 0\) for example (using equations (13) and (8d)). From now on, we will omit the commutator brackets, knowing that the adjoint action (group generators acting on operators) always means taking the commutator; and the above equation reads \( T_0 \epsilon_0 = 0 \). Since we know that all Coulomb operators belong to \([11 - \Pi]_{20}\) and \([0]_{20}\) of \( U(20) \), the branching rules \( U(20) \rightarrow SO_T(3) \times U(10) \) (from table 3) will give us the possible ranks for the operators. The branching rules uniquely determine the isospin rank of the operator \( \tilde{\epsilon}_2 \), which belongs to \([22 - \Pi]_{10}\). In fact, we can easily show that \( \tilde{\epsilon}_0 \) and \( \tilde{\epsilon}_1 \) are also isospin scalars as well. From equation (11), we have \( \tilde{\epsilon}_i \sim \sum C_{\mu\nu} \xi_{\mu
u}(d_\mu^l d_\mu^\eta d_\nu^\mu d_\nu^\nu - d_\mu^\eta d_\mu^l d_\nu^\nu) \). Together with equation (13), we find \( T_+ \tilde{\epsilon}_i = 0 \) for all \( i \). So, they are all isospin scalars.

For the other six operators \( \epsilon_i \) and \( \overline{\epsilon}_i \), the possible isospin ranks as given by the branching rules are \( [1, 5, 0]_{10} \) and \( [1, 3, 5, 11 - \Pi]_{10} \). The immediate question that comes to mind is whether we can separate the various spin rank components from these operators. Repeatedly applying the raising operator \( T_+ \) to them should eliminate the lower rank components. One of the results that we find is \( T_- T_+^2 \overline{\epsilon}_i \) is proportional to \( T_+ \overline{\epsilon}_i \). This tells us that the operators \( \overline{\epsilon}_i \) do not have a rank 1 component. So, they belong only to \( [1, 5, 0]_{10} \) and \( [1, 5, 11 - \Pi]_{10} \). The results are summarized in table 4.

4.4. Operators with pure isospin rank

We will now continue our effort to separate the \( \overline{\epsilon}_i \) (and \( \epsilon_i \)) operators into various isospin components. The rank 2 component of \( \overline{\epsilon}_i \) is given by \( \frac{1}{2} T_+ T_+^2 \tilde{\epsilon}_i \); as we already know there is no spin 1 component, the remaining piece must be the isospin scalar part. From equation (11),

\[ \overline{\epsilon}_i = \frac{1}{2}(\overline{\tau}_i + \tau_i) = \sum_k a_{ik} \{ : \mathbf{v}_{dd}^{(k)} \cdot \mathbf{v}_{dd'}^{(k)} : + : \mathbf{v}_{dd}^{(k)} \cdot \mathbf{v}_{d'd}^{(k)} : \} \]
Comparing this result to equation (17), we see that our definition of $e_i$ is the analogous term for the problem as we have only one state, with the only difference in isospin $z$. The first term within the parenthesis is recognized as $2C_{\mu \nu}C_{\eta \xi}d_{\xi}^\dagger d_{\eta}^\dagger d_{\nu}d_{\mu} + d_{\mu}^\dagger d_{\nu}^\dagger d_{\eta}d_{\xi}$.

Let us take the simplest one, $\tau_0 = \frac{1}{2}(d_{\mu}^\dagger d_{\nu}^\dagger d_{\xi}d_{\mu} + d_{\mu}^\dagger d_{\nu}d_{\eta}^\dagger d_{\mu})$, as an example. After taking four consecutive commutations on $\tau_0$, we find

$$T_+^2 T_-^2 \tau_0 = 16\tau_0 - 4(d_{\mu}^\dagger d_{\nu}d_{\mu} + d_{\mu}^\dagger d_{\nu}^\dagger d_{\mu}).$$

The first term within the parenthesis is recognized as $2e_0$ (see equation [111]). The second one is the analogous term for the $d'$-electron, which does not contribute in our problem as we have only one $d'$-electron. We would like to absorb the second term into our definition of $e_0$, and $e_i$ in general, and so we write

$$e_i = \sum_k a_{ik}\{ : \psi_{dd}^{(k)} \cdot \psi_{dd}^{(k)} : + : \psi_{d'd'}^{(k)} \cdot \psi_{d'd'}^{(k)} : \}$$

$$\sim \sum C_{\mu \nu}C_{\eta \xi}d_{\xi}^\dagger d_{\eta}^\dagger d_{\mu} + d_{\mu}^\dagger d_{\eta}^\dagger d_{\xi}d_{\mu}.$$  

Comparing this result to equation (17), we see that $e_i$ and $\tau_i$ are almost the same; after all, they have the same group transformation properties. Of course, in the complete analysis of configurations with at least two $d'$ and two $d$-electrons, one should include three new operators of the kind $d_{\mu}^\dagger d_{\nu}d_{\eta} + d_{\mu}d_{\nu}^\dagger d_{\mu}^\dagger$, as in equation (14). The underlying reasons are as follows. The combination $2\tau_i - e_i$ has isospin rank 2. We can now separate $\tau_i$ as $\frac{1}{2}(2\tau_i - e_i) + \frac{1}{2}(\tau_i + e_i)$, with the first term purely isospin rank 2, and the second one an isospin scalar. One can also verify $T_+(\tau_i + e_i) = 0$ easily.

In principle, we can re-tabulate the matrix elements using these six new operators $\tau_i + e_i$ and $2\tau_i - e_i$ that have simpler transformation properties in place of $e_i$ and $\tau_i$. However, we also feel that the relatively simple expressions of $e_i$ and $\tau_i$ (as in equations (17) and (13)) have their merits. Moreover, the $e_i$ matrix elements are easily obtained from the $d^2$ matrix elements. We would rather leave them untouched. The new combinations, with pure isospin ranks, can nevertheless give us a lot of useful information and insight into the problem we are facing.

Recall that we have found some simple proportionality relations in equations (14a)–(14d). The underlying reasons are as follows. The combination $2\tau_i - e_i$, with isospin rank 2, must have vanishing matrix elements if sandwiched between a pair of $2[21]_{10}$ states, since two $T = \frac{1}{2}$ states cannot be stretched to $T = 2$. Therefore, $\langle \tau_i \rangle = \frac{1}{2}\langle e_i \rangle$ for these matrix elements, and thus we arrive at relation (14a). And the other combination $\tau_i + e_i$, being an isospin scalar, must be diagonal in isospin space. So, it vanishes between a pair of $4[111]_{10}$ and $2[21]_{10}$ states. In other words, $\langle \tau_i \rangle = -\langle e_i \rangle$, as in equation (14d). From our new perspective, the two Wigner-Eckart relations we had before are now interpreted as selection rules on the isospin group.

To explain relation (14a) requires a more elaborate analysis. First notice that the $4[111]_{10}$ states also appear in the configuration $d^3$. In fact, they are almost the same state, with the only difference in isospin $z$-component. Recall that states in $d^3$ have
isospin $M_T = \frac{3}{2}$, while the $d^2d'$ states have $M_T = \frac{1}{2}$. It is well-known that matrix elements can be factored as

$$\langle \alpha T M_T | U^{(k)}_q | \alpha' T' M'_T \rangle = (-1)^{T-M_T} \left( \begin{array}{c} T \cr -M_T \end{array} \right) \left( \begin{array}{c} k \cr q \end{array} \right) (\alpha T) || U^{(k)} || \alpha' T'$$

where the last factor is the reduced matrix element. So, for the isospin scalar operator $\overline{e}_i + e_i$, we have

$$\langle d^2d' | d^2d' [111]_{10} | \overline{e}_i + e_i | d^2d' [111]_{10} \rangle = - \left( \begin{array}{cc} 3/2 & 0 \cr -1/2 & 0 \end{array} \right) \left( \begin{array}{cc} 3/2 & 0 \cr -1/2 & 0 \end{array} \right)^{-1} = 1,$$

while for the isospin rank 2 operator $2\overline{e}_i - e_i$, we have

$$\langle d^2d' | d^2d' [111]_{10} | 2\overline{e}_i - e_i | d^2d' [111]_{10} \rangle = - \left( \begin{array}{cc} 3/2 & 2 \cr -1/2 & 0 \end{array} \right) \left( \begin{array}{cc} 3/2 & 2 \cr -1/2 & 0 \end{array} \right)^{-1} = -1.$$  

But $\langle d^3 | d^3 [111]_{10} | d^3 [111]_{10} \rangle = 0$ in $d^3$ since there is no $d'$ electron. Therefore from these two equations, we can solve for $\langle d^3 | d^3 [111]_{10} | e_i | d^3 [111]_{10} \rangle$ and $\langle d^2d' | d^2d' [111]_{10} | e_i | d^2d' [111]_{10} \rangle$ in terms of $\langle d^2d' | d^2d' [111]_{10} | e_i | d^2d' [111]_{10} \rangle$ which are assumed known; and the answer is

$$\langle d^2d' | d^2d' [111]_{10} | e_i | d^2d' [111]_{10} \rangle = 2 \langle d^2d' | d^2d' [111]_{10} | e_i | d^2d' [111]_{10} \rangle$$

and

$$\langle d^3 | d^3 [111]_{10} | e_i | d^3 [111]_{10} \rangle = 3 \langle d^3 | d^3 [111]_{10} | e_i | d^3 [111]_{10} \rangle.$$  

The first one is of course relation (14b) that we are aiming at; the second one is a bonus, that relates the $d^2d'$ matrix elements to the ones in $d^3$. Of course, the $d^3$ matrix elements are also available in the literature (see Nielson and Koster 1963 for instance), so the second equation can be served as a consistency check.

### 4.5. Configuration mixing via Coulomb interaction

The isospin arguments used above can relate the $d^3$ Coulomb matrix elements to those in $d^2d'$. In the same way, we can obtain the mixed matrix elements between configurations $d^3$ and $d^2d'$. The first point to note is that the Coulomb operators which connect $d^3$ with $d^2d'$ necessarily have $M_T = 1$; so no isospin scalar Coulomb operator can be responsible for CI. Let us write $\langle \hat{A}_i \rangle^{(2)}_q$ as the isospin rank 2 Coulomb operator, such that

$$\langle \hat{A}_i \rangle^{(2)}_0 = \sqrt{2/3} (2\overline{e}_i - e_i)$$

$$\langle \hat{A}_i \rangle^{(2)}_1 = \sum C_{\mu\nu} C_{\eta\xi} (d^1_{\mu} d^1_{\nu} d^1_{\xi} d^1_{\eta} - d^1_{\mu} d^1_{\nu} d^1_{\eta} d^1_{\xi} - 1/2 d^1_{\mu} d^1_{\eta} d^1_{\xi} d^1_{\nu})$$

$$\langle \hat{A}_i \rangle^{(2)}_2 = - \sum C_{\mu\nu} C_{\eta\xi} (d^1_{\mu} d^1_{\nu} d^1_{\xi} d^1_{\eta} - d^1_{\mu} d^1_{\nu} d^1_{\eta} d^1_{\xi} - d^1_{\xi} d^1_{\nu} d^1_{\eta} d^1_{\xi})$$

With the notation developed before, the above operators are simply the components of the tensor operator $10(w^{(10k)} \cdot w^{(10k)})^{(200)}$. Parallel to equations (21) and (22), we have

$$\langle d^3 | d^3 [111]_{10} | \langle \hat{A}_i \rangle^{(2)}_1 | d^2d' [111]_{10} \rangle = - \left( \begin{array}{cc} 3/2 & 2 \cr -1/2 & 0 \end{array} \right) \left( \begin{array}{cc} 3/2 & 2 \cr -1/2 & 0 \end{array} \right)^{-1} = 1/\sqrt{2}$$

(24a)
That is to say, states in \( l \) is coupled to the Coulomb interaction, if the HF solution for the HF says, the Hartree-Fock (HF) solution \( \Psi \) start from the simplest operator \( e \). From equations (8a) and (19), we can see that \( e \) is a \( \gamma \) operator eigenvalue \( 2 \). This is important because it allows us to calculate the coefficients \( \bar{c}_{0} \) and \( \bar{g}_{0} \) in (19). In the configurations with no more than one \( d' \) electron, they have the same matrix elements as the \( e \). So in this manner, we can determine all the configuration-interaction Coulomb matrix elements between \( d^3 \) and \( d^2 d' \) from the known ones in \( d^2 d' \). We can similarly write down the other matrix elements between \( d^3 \) and \( dd^2 \), \( d^2 d' \) and \( dd^2 \) and so forth.

Before we close this section, we should mention the relevance of Brillouin’s theorem (see Bauche and Klapisch 1972, and Godefroid et al 1987) in our analysis. The theorem says, the Hartree-Fock (HF) solution \( \Psi_{HF} \) of the configuration \( l^N \) has vanishing matrix elements with a class of states in \( l^{N-1} l' \). They are the states in which the l’ electron is coupled to the \( l^{N-1} \) state via the ordinary fractional parentage coefficients as in \( l^N \). That is to say, states in \( l^{N-1} l' \) and \( l^N \) with the same angular form will not mix via Coulomb interaction, if the HF solution for the \( l^N \) configuration is used. In our case, \( \langle d^3 \ 4[111]_{10}\beta} | \text{Coulomb} | d^2 d' \ 4[111]_{10}\beta} \rangle \) will have a vanishing radial integral. That does not make our work less useful, however. In order to apply Brillouin’s theorem in our situation, one has to first find out the HF solution \( \Psi_{HF} \) for each single \( LS \) term in the configuration \( l^N \), which might be straightforward, but definitely not easy. Only then, equation (24a) will rendered irrelevant, as Brillouin’s theorem predicts zero radial integrals in those cases. All other results are otherwise unaffected.

### 4.6. Eigenvalues for the scalar operators

From table [4], there are a few complete scalar operators. We can now find closed-form expressions for each \( U(10) \) scalar operator; that is, the \( i = 0 \) operators. Let us start from the simplest operator \( \epsilon_0 \). From equations (8a) and (19), we can see that

| operator | eigenvalue |
|----------|------------|
| \( \epsilon_0 \) | \( \frac{1}{2} N(N - 1) + \frac{1}{2} N'(N' - 1) \) |
| \( \bar{F}_0 \) | \( NN' \) |
| \( \bar{g}_0 \) | \( : T_+ T_- = T^2 - T_0^2 + T_0 - N \) |
|               | \( = T^2 - (\frac{N + N'}{2})^2 (\frac{N + N'}{2} + 1) + NN' \) |
| \( \bar{c}_0 \) | \( \frac{1}{2}(T^2 - (\frac{N + N'}{2})^2 (\frac{N + N'}{2} + 1)) + NN' \) |
| \( \bar{e}_0 \) | \( \frac{1}{2}(T^2 - (\frac{N + N'}{2})^2 (\frac{N + N'}{2} + 1)) \) |
| \( 2\bar{e}_0 - \epsilon_0 \) | \( T^2 - 3T_0^2 \) |

\[
\frac{\langle d^3 \ 4[111]_{10}\beta} | \tilde{A}_i \rangle | d^2 d' \ 2[21]_{10}\gamma} \rangle}{\langle d^2 d' \ 4[111]_{10}\beta} | \tilde{A}_i \rangle | d^2 d' \ 2[21]_{10}\gamma} \rangle} = - \left( \frac{3}{2} \ 2 \ \frac{1}{2} \right) \left( \frac{3}{2} \ 2 \ \frac{1}{2} \right)^{-1} = \sqrt{2} . \tag{24b}
\]
the eigenvalue for $e_0$ is simply given by $\frac{1}{2}N(N-1) + \frac{1}{2}N'(N'-1)$. For $\mathcal{F}_0$, from equations (8d), it is equals to $NN'$. For the next one, $\mathcal{F}_0$, from equations (8d) and (13), we find $\mathcal{G}_0 = :T_+T_- = T_+T_- - N$. None of these three operators $e_0$, $\mathcal{F}_0$ and $\mathcal{G}_0$ is an isospin scalar. The other two operators $\mathcal{C}$ and $\mathcal{C}'$ are just linear combinations of $\mathcal{F}_0$ and $\mathcal{G}_0$. The results are summarized in the table [4]. Note that the operator $\mathcal{C}_0$ is an isospin scalar, so is the combination $\mathcal{C}_0 + e_0$. Their expressions from table [4] certainly verify that fact; as $T^2$ is a scalar in $SO_T(3) \times U(10)$ and the total electron number $N_T = N + N'$ is, in fact, a scalar in $U(20)$ and hence scalar in all its subgroups.

5. The operator sum $\hat{e}_i = e_i + \mathcal{F}_i = e_i + \mathcal{C} + \hat{e}_i$

Recall that at the end of section 1.2, we mentioned a simple result on the operators $\hat{e}_i \equiv e_i + \mathcal{F}_i$. In terms of the new operators, the sum is $\hat{e}_i \equiv e_i + \mathcal{C}_i + \hat{e}_i'$; whose matrix elements are included in table [4]. As a brief summary of our work up to this point, the $e_i$ matrix elements of $d^2d'$ are obtained easily from the ones in the configuration $d^2$. The $\mathcal{C}_i$ matrix elements can be related to $e_i$ by just three constants using the isospin structure as in (14d) - (14d). For the last operator $\hat{e}_i$, selection rules on $SO_T(3) \times U(10)$ give us a lot of vanishing matrix elements (equations (13a) and (13b)); the rest involving a pair of $[21]_{10}$ states are yet to be found. A thorough understanding on the simple result for the operator $\hat{e}_i$ will definitely help to accomplish our plan for finding the remaining matrix elements.

Let us look at the three different cases separately. For $i = 0$, $\hat{e}_0$ always equals 3 in $d^2d'$. From table [4], one can see that the operator sum equals $\frac{1}{2}N_T(N_T - 1)$, which is scalar in $U(20)$. Since all the states belong to the same $U(20)$ multiplet $[111]_{20}$, they must have the same matrix element.

The next one $\hat{e}_1$ is also diagonal; with matrix elements 0,3,6,7 and 13 only, which are determined by the $U(5)$ and $SO(5)$ irreps. To explain this, we write down the operator in terms of $v^{(k)} = v^{(k)}_{dd} + v^{(k)}_{d'd'} = 2w^{(00k)}$. Using the extended version of equations (7a) (recall that we have added the identical terms involving the $d'$-electron to the operators $e_i$ in section 1.3), the operator $\hat{e}_1$ takes the simple form

$$\frac{7}{2} : v^{(0)} \cdot v^{(0)} + : v^{(2)} \cdot v^{(2)} : + : v^{(4)} \cdot v^{(4)} :$$

which is reminiscent of the (quadratic) Casimir operators for the groups $SU(2l)$ and $SO(2l+1)$; they are given by $C(SU_{2l+1}) = \sum_{k>0} v^{(k)} \cdot v^{(k)}$ and $C(SO_{2l+1}) = \sum_{odd k} v^{(k)} \cdot v^{(k)}$ respectively. For the irrep $[\lambda_1, \lambda_2, \cdots]_{2l+1}$ of $U(2l+1)$, the eigenvalue of $C(SU_{2l+1})$ is (see Judd 1998, §5.9)

$$\sum_{i=1}^{2l+1} \lambda_i(\lambda_i + 2 + 2l - 2i) - \frac{n^2}{[l]}$$

(25)

where $n = \sum \lambda_i$. One can check that $[\lambda_1, \lambda_2, \cdots]_{2l+1}$ and $[\lambda_1 + \alpha, \lambda_2 + \alpha, \cdots]_{2l+1}$ both have the same eigenvalue as they should since they possess the same $SU(2l+1)$ content.
The eigenvalue of $C(SO_{2l+1})$ on the irrep $(w_1, w_2, \cdots)$ of $SO(2l + 1)$ is
\[
\frac{1}{2} \sum_{i=1}^{l} w_i (w_i + 1 + 2l - 2i).
\]
(26)

We can remove the normal ordering using the relation:
\[
\mathbf{v}^{(k)} \cdot \mathbf{v}^{(k)} : = \mathbf{v}^{(k)} \cdot \mathbf{v}^{(k)} - \frac{[k]}{[l]} N_T,
\]
where $l = 2$ in our case. Putting these together with $\mathbf{v}^{(0)} \cdot \mathbf{v}^{(0)} = N_T^2/[l]$, we find
\[
\tilde{e}_1 = \frac{7}{10} : N_T^2 : + : C(SU_5) - C(SO_5) : \\
= \frac{7}{10} N_T^2 - \frac{7}{2} N_T + C(SU_5) - C(SO_5).
\]
This explains why $\tilde{e}_1$ is diagonal, and gives the correct eigenvalues. As we know $\langle e_1 \rangle$ and $\langle \overline{e}_1 \rangle$ already, this simple result can also be used to determine $\langle \tilde{e}_1 \rangle = 0$ in equation (132), where vanishing matrix elements cannot be explained by $U(10)$ selection rule.

Finally, the operator $\tilde{e}_2$ is almost diagonal, with the three exceptions
\[
\langle d^2d' [^T]U[21](21)[^5]D|\tilde{e}_2|d^2d' [^T]U[21](10)[^5]D \rangle = 6\sqrt{21}.
\]
Since the operators $e_2 + \overline{e}_2$ and $\overline{e}_2$ are both isospin scalars, clearly the sum must also be diagonal in isospin space. With a little hindsight, we can further conclude that it is diagonal in the $U(5)$ space as well; so that the $[21]_5$ states will not mix with $[111]_5$ or $[3]_5$ states\footnote{The operator is not a $U(5)$ scalar however; $U(5)$ scalars do not give (22) of $SO(5)$.}. The above three exceptions are the only possible off-diagonal entries we can have. Furthermore, the matrix elements for a set of $L$ states do not depend on the spin, isospin or $U(10)$ irreps; they depend only on their respective $SO(5)$ irreps. All these can be explained using the spin-isospin supermultiplet group $SU(4)$ of Wigner (1937).

To explain these, let us first introduce an alternative branching scheme $U(20) \supset SO_S(3) \times U'(10) \supset SO_S(3) \times SO_T(3) \times U(5)$ as oppose to the one in (119). The $U'(10)$ group acts on the isospin-orbital space, which is analogous but different from the spin-orbital $U(10)$ group that we had before; however, the $U(5)$ group is the same in both schemes. To better display the symmetry, in the original scheme, we label a state with its spin superscript $[S]$ put before the $U(5)$ label. For example, we now write the first of the doublet $F$ states and the last of the quartet $F$ states as $[^4[111]_1^0[21]_5(21)F]$ and $[^2[21]_5(21)F]$; which become $[^2[21]_5^4(21)F]$ and $[^4[111]_1^0(21)F]$ respectively in the new scheme. With a mere spin-isospin exchange, the doublet $F$ state switches with the quartet $F$ state; on the other hand, the operator $\tilde{e}_2$ is invariant. This explain why the two states have the same matrix element. But there is yet another doublet $F$ state, $[^2[21]_5(21)F]$, that has the same diagonal matrix element. To accommodate this, we should promote the idea of spin-isospin exchange to a more general transformation in the spin-isospin space. This leads us to introduce the $SU(4)$ supermultiplet group due to Wigner (1937). The three $F$ states now fall into a single supermultiplet $[21]_4 \otimes [21]_5$ of $SU(4) \times U(5) \subset U(20)\footnote{We use the simpler $U(4)$ irreps rather than $SU(4)$ irreps throughout the paper, which should not affect the validity of our arguments and results.}$. The other possible multiplets in $d^2d'$ are $[111]_4 \otimes [3]_5$ and $[3]_4 \otimes [111]_5$. The operator $\tilde{e}_2$, being a $SU(4)$ scalar, is
diagonal in the $SU(4)$ space; which appears as if it is diagonal in the orbital $U(5)$ space
since each $U(5)$ irrep is paired with a unique $SU(4)$ irrep in the problem on hand. This
also explain why the matrix elements are independent of spin or isospin ranks, as they
belong to the same multiplet in $SU(4) \times SO(5)$.

As explained before, $\langle d^2d^2[21]_{10}\beta|e_2|d^2d^2[21]_{10}\gamma \rangle$ are the only matrix elements for
which we have not yet found a simple way to deduce the values. With this latest result,
we can obtain those matrix elements easily if $\beta,\gamma$ do not contain the irreps $[3]_5(30)$ of
$U(5)$ and $SO(5)$. To fill in the last piece of puzzle, we make use of the following operator
introduced by Judd (1998, p 222):

$$\Omega' = 7\mathbf{v}^{(1)} \cdot \mathbf{v}^{(1)} - 3\mathbf{v}^{(3)} \cdot \mathbf{v}^{(3)} = -3\mathcal{C}(SO_5) + L^2.$$ 

It transforms as (22) in $SO(5)$, just like the $i = 2$ operators; and its eigenvalue is easy
to compute. So for the $[^2[21]_{10}[3]_5(30)^2SGHI]$ states, since $(30) \times (30)$ contains (22)
only once, we can apply the Wigner-Eckart theorem and find

$$\langle ^2[21][3](30)^2L|\tilde{e}_2|^2[21][3](30)^2L \rangle = \langle ^2[21][3](30)^2L|\Omega'|^2[21][3](30)^2L \rangle.$$ 

In other words, we only need to calculate the matrix element for one of the four terms
$SGHI$ to determine the proportionality constant (which turns out to be unity). The
other three can be determined from the above relation easily. Usually, the calculation
on the fully stretched state ($^2I$) is reasonably easy. In the end, we find that $\langle ^2I|\mathbf{f}_2|^2I \rangle
is the only matrix element we need to calculate. All other $d^2d'$ matrix elements are
related to $e_i$ ones via some simple arithmetic relations. This is a truly surprising result
from the present analysis.

6. Spin-Orbit interaction

From a group-theoretical point of view, the spin-orbit interaction is much simpler than
the Coulomb interaction. The interaction Hamiltonian, in second quantized form, is:

$$H_2 = \zeta_{dd} \, w_{dd}^{(11)0} + \zeta_{d'd'} \, w_{d'd'}^{(11)0},$$

where the $\zeta_{dd}$ and $\zeta_{d'd'}$ are the corresponding radial integrals; the symbol $\kappa$ following
the ranks ($SL$) for the coupled tensor $w_{dd}^{(SL)\kappa} = -(d^\dagger d)^{(SL)\kappa}$ is the rank to which $S$ and
$L$ coupled (see Judd 1967). The radial integral $\zeta_{dd}$ is related to the classic parameter $\zeta
of Condon and Shortley (1953) by $\zeta_{dd} = -\sqrt{15}\zeta$. In the same manner, we can include
CI into our analysis by introducing the perturbing Hamiltonian

$$H_2^{mix} = \zeta_{dd'} \, w_{dd'}^{(11)0} + \zeta_{d'd} \, w_{d'd}^{(11)0}.$$ 

The operators $w_{dd'}^{(11)0}$ and $w_{d'd}^{(11)0}$ are simply hermitian conjugate to each other. Each
of the above four operators belongs to $[1 - \mathbf{T}]_{20}$, the adjoint representation of $U(20)$;
since the nine components of $w^{(11)}$ are the $SU(20)$ group generators (see section 4.2),
the coupled scalar operator must also belong to the adjoint representation. Using the
branching rule $U(20) \rightarrow SO_5(3) \times U(10)$ given in table [3], $[1 - \mathbf{T}]_{20}$ gives
$^13[1 - \mathbf{T}]_{10} + 13[0]_{10}$. Only the irreps $^13[1 - \mathbf{T}]_{10}$ can eventually give us a $S = L = 1$ ($^3P$) tensor in
the ordinary spin and orbital spaces, to which the spin-orbit operators belong; hence the $U(10)$ scalar irreps can be dropped. Then from $U(10) \to SO_S(3) \times U(5)$, $[1-\frac{11}{2}]_{10}$ gives us $1^3[1-\frac{3}{2}]_{5} + 1^3[0]_{5}$; once again, the $U(5)$ scalar irreps can be dropped. And this time we only want the spin 1 part, so $^3[1-\frac{3}{2}]_{5}$ is the only permissible label for the spin-orbit operators on the $SO_S(3) \times U(5)$ level.

Finally, on the $SO(5)$ level, using the branching rules $U(5) \to SO(5)$, $[1-\frac{11}{2}]_{5}$ gives us $(11) + (20)$ of $SO(5)$, but $(20)$ contains only $S, D$ and $G$ terms in $SO_L(3)$ while we are looking for a $P$ term. So, we can conclude that the spin orbit operators belong to $[1-\frac{11}{2}]_{20}^1 \cdot 3^2[1-\frac{3}{2}]_{10}^0 [1-\frac{11}{2}]_{5}^3 (11)_3^P$ in our branching scheme.

6.1. Relations between various spin-orbit matrix elements on the $U(10)$ level

Using the Wigner-Eckart theorem, we can take advantage of the known spin-orbit interaction matrix elements of the configuration $d^3$ (see Nielsen and Koster 1963, for instance), in which all the states belong to $^4[111]_{10}$ of $SO_T(3) \times U(10)$. Since $[\frac{111}{10}] \times [111]_{10}$ contains the adjoint irrep $[1-\frac{11}{2}]_{10}$ once, on the $U(10)$ level we can write down several direct proportionalities. With the numerical constants, they run

\begin{align}
(d^3 \cdot 4[111]_{10}\beta\|w^{(11)}_{dd}\|d^3 \cdot 4[111]_{10}\gamma) &= 3(d^{2}d' \cdot 4[111]_{10}\beta\|w^{(11)}_{dd'}\|d^{2}d' \cdot 4[111]_{10}\gamma) \\
&= \frac{3}{2}(d^{2}d' \cdot 4[111]_{10}\beta\|w^{(11)}_{dd'}\|d^{2}d' \cdot 4[111]_{10}\gamma) \\
&= \sqrt{3}(d^3 \cdot 4[111]_{10}\beta\|w^{(11)}_{dd'}\|d^{2}d' \cdot 4[111]_{10}\gamma). \\
\end{align}

Since these involve reduced matrix elements, no components of $u^{(11)}$ or magnetic quantum numbers $M_S$ and $M_L$ appear; hence the extra information $\kappa = 0$ is rendered irrelevant. So, with just three constants, we can determine all the spin-orbit matrix elements between a pair of $^4[111]_{10}$ states in $d^2d'$, as well as the CI matrix elements between $d^2d'$ and $d^3$.

For matrix elements involving the $^2[21]_{10}$ states, there are no such corresponding states in the $d^3$ configuration. But still, for matrix elements between the $^4[111]_{10}$ and $^2[21]_{10}$ states, since $[\frac{111}{10}] \times [21]_{10}$ contains the adjoint only once, we can relate the reduced matrix elements by direct proportionalities, which turn out to be

\begin{align}
(d^{2}d' \cdot 4[111]_{10}\beta\|w^{(11)}_{dd'}\|d^{2}d' \cdot 2[21]_{10}\gamma) &= -(d^{2}d' \cdot 4[111]_{10}\beta\|w^{(11)}_{dd'}\|d^{2}d' \cdot 2[21]_{10}\gamma) \\
&= -\frac{1}{\sqrt{3}}(d^3 \cdot 4[111]_{10}\beta\|w^{(11)}_{dd'}\|d^{2}d' \cdot 2[21]_{10}\gamma) \\
\end{align}

Lastly, for matrix elements between a pair of $^2[21]_{10}$ states, the simple version of the Wigner-Eckart theorem does not apply, since $[\frac{21}{10}] \times [21]_{10}$ contains the adjoint $[1-\frac{11}{2}]_{10}$ twice. The above equations are all we can get from the Wigner-Eckart theorem on the $U(10)$ level. One direction to proceed is to seek for similar relations on the $U(5)$ and $SO(5)$ levels, so that most of the remaining matrix elements can eventually be related to the ones in $d^3$. We can also look at the use of isospin in the spin-orbit analysis.
6.2. The use of isospin in spin-orbit interaction matrix interaction

In order to take advantage of the underlying isospin structure in the spin-orbit interaction, we should first decompose the spin-orbit interaction operators into components with definite isospin ranks. The four operators $w_{dd}^{(11)}$, $w_{dd'}^{(11)}$, $w_{dd}^{(11)}$, and $w_{dd'}^{(11)}$, belong to $1, 3 [1 - T]_{10}$ in $SO_T(3) \times U(10)$. Among them, $w_{dd}^{(11)}$ and $w_{dd'}^{(11)}$ has $M_T = 1$ and $-1$ respectively; so they must belong solely to $3 [1 - T]_{10}$. For the other two operators, $w_{dd}^{(11)}$ and $w_{dd'}^{(11)}$, with $M_T = 0$, one can check that $w_{dd}^{(11)} + w_{dd'}^{(11)}$ is an isospin scalar (i.e. commutes with $T_{+/ -}$); and $w_{dd}^{(11)} - w_{dd'}^{(11)}$ has an isospin rank 1. More precisely, $-w_{dd}^{(11)}, \frac{1}{\sqrt{2}}(w_{dd}^{(11)} - w_{dd'}^{(11)})$ and $w_{dd'}^{(11)}$ are the three components $M_T = 0, \pm 1$ of the operator $3w_{dd}^{(11)} = 3(d^dd^d)^{(11)}$; while $-\sqrt{2}w_{dd}^{(11)} = (w_{dd}^{(11)} + w_{dd'}^{(11)})$ is the isospin scalar operator.

We can now easily deduce equations (27d) to (27d) from isospin arguments. First of all, the scalar operator just mentioned is diagonal in isospin space, therefore we have

$$(d^2d' \ 4[111]_{10}\beta||w_{dd}^{(11)} + w_{dd'}^{(11)}||d^2d' \ 2[21]_{10}\gamma) = 0$$

which proves relation (27d). Then, using equation (20) to remove the $M_T$ dependence of the two matrix elements

$$(d^3 \ 4[111]_{10}\beta||w_{dd}^{(11)}||d^2d' \ 2[21]_{10}\gamma) = -\frac{1}{\sqrt{6}}(4[111]_{10}\beta||w_{dd}^{(11)}||d^2d' \ 2[21]_{10}\gamma)$$

we can easily get relation (27d). Similarly, we can express

$$(d^3 \ 4[111]_{10}\beta||w_{dd}^{(11)}||d^2d' \ 4[111]_{10}\gamma)$$

$$(d^2d' \ 4[111]_{10}\beta||w_{dd}^{(11)}||d^2d' \ 4[111]_{10}\gamma)$$

$$(d^3 \ 4[111]_{10}\beta||w_{dd}^{(11)}||d^2d' \ 4[111]_{10}\gamma)$$

$$(d^2d' \ 4[111]_{10}\beta||w_{dd}^{(11)}||d^2d' \ 4[111]_{10}\gamma)$$

in terms of their matrix elements reduced with respect to $S, L$ and $T$. The first four matrix elements, together with the fact that $w_{dd}^{(11)} = 0$ in $d^3$, give equations (27d) and (27d). The last one gives the remaining relation (27d).

7. Concluding remarks

We started with this relatively simple configuration $d^2d'$ as the subject of the present work. The ideas and techniques introduced in this paper can certainly be applied to other configurations like $d^nd'$ and $d^N'd^{N'}$. Of course, it is a different question whether these configurations are experimentally observed, or simply of theoretical interest. Another obvious extension is to apply it to the $f$-shell electrons. The $f$-shell is known
to have a richer group structure. We are aware that similar analysis on the f-shell might reveal more surprises calling for explanations.

Another direction for further research is to introduce the idea of quasispin into the analysis. Quasispin generators are of the type \((d'd')(00)\) and \((dd)(00)\) in the case of ordinary d-electrons. These operators, together with \((d'd')(00) + (dd)(00)\), generate the SO_Q(3) quasispin group. But in the case where the electrons have an extra spin structure, namely the isospin, it is known that the analogous quasispin group is qualitatively different (see Flowers and Szpikowski 1964, Feng and Judd 1982). The full quasispin group is SO(8) rather than merely SO(3). This extra group structure may give us some new selection rules and proportionality relations, as we know it does in the case of configurations of equivalent electrons.

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**References**

Bauche J and Klapisch M 1972 *J. Phys. B: At. Mol. Phys.* **5** 29-36
Condon E U and Odabasi H 1980 Atomic Structure (Cambridge: Cambridge University Press) pp 583-4
Condon E U and Shortley G H 1953 The Theory of Atomic Spectra (Cambridge: Cambridge University Press)
Feng C T and Judd B R 1982 *J. Phys. A: Math. Gen.* **15** 2273-84
Flowers B H and Szpikowski S 1964 *Proc. Phys. Soc.* **84** 673-9
Godefroid M, Lievin J and Metz Y 1987 *J. Phys. B: At. Mol. Phys.* **20** 3283-96
Hansen J E, Judd B R, Raassen A J J and Uylings P H M 1997 *Phys. Rev. Lett.* **78** 3078-81
Judd B R 1967 Second Quantization and Atomic Spectroscopy (Baltimore: Johns Hopkins Press) p 33
—1968 Group Theory in Atomic Spectroscopy in Group Theory and its Applications ed E M Loebl (New York: Academic Press)
—1997 Private communication
—1998 Operator Techniques in Atomic Spectroscopy (Princeton: Princeton University Press)
Judd B R, Hansen J E and Raassen A J J 1982 *J. Phys. B: At. Mol. Phys.* **15** 1457-72
Judd B R and Leavitt R C 1986 *J. Phys. B: At. Mol. Phys.* **19** 485-99
Kaniauskas J M, Šimonis V Č and Rudzikas Z B 1987 *J. Phys. B: At. Mol. Phys.* **20** 3267-81
Lindgren I and Morrison J 1981 Atomic Many-Body Theory (New York: Springer-Verlag) §11.2
Nielson C W and Koster G F 1963 Spectroscopic Coefficients for the p\(^n\), d\(^n\) and f\(^n\) configurations (Cambridge, MA: MIT Press)
Racah G 1954 Bulletin of the Research Council of Israel **3** 290-8
Šimonis V Č, Kaniauskas J M and Rudzikas Z B 1984 *Int. J. Quantum Chem.* **25** 57-62
Sugar J and Corliss C 1985 Atomic Energy Levels of the Iron-Period Elements: potassium through nickel *J. Phys. Chem. Ref. Data* **14**
Weinberg S 1995 The Quantum Theory of Fields vol I (New York: Cambridge University Press) p 200
Wigner E P 1937 *Phys. Rev.* **51** 106-19
Wybourne B G 1970 Symmetry Principles and Atomic Spectroscopy (New York: Wiley-Interscience) table C-3