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ELECTRONIC STRUCTURE OF f-BLOCK COMPOUNDS

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Introduction

The lanthanide and actinide series differ from the more widely studied d-transition metal series in that the 4f and 5f shells are inner electrons shielded by the $5s^2 5p^6$ (or $6s^2 6p^6$) closed shells. The result of this shielding is that the f shell interacts much less strongly with its environment than the d-transition series. Figures 1 and 2 illustrate the radial charge density for Pr^{3+} and U^{4+} . The electronic structure of an f^n ion is dominated by different interactions than for the more familiar d-transition ions. In this paper we will review the methods and nomenclature used to describe the electronic structure of f^n compounds.

Brief Review of Atomic Theory [1-4].

For an N electron atom with a nuclear charge Ze where e is the charge of the electron and Z is the atomic number, the non-relativistic Hamiltonian may be written (assuming the nuclear mass is infinite)

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} - \sum_{i=1}^N \frac{Ze^2}{r_i} + \sum_{i < j}^N \frac{e^2}{r_{ij}} \quad (1)$$

The first term in this equation represents the kinetic energy of all the electrons, the second term the potential energy of all the electrons in the electric field of the nucleus, and the third term the repulsive Coulomb potential between pairs of electrons.

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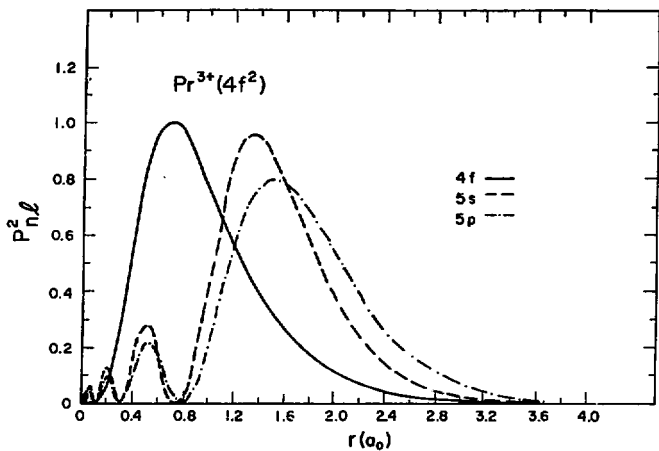


Figure 1. Radial charge density for Pr^{3+} .

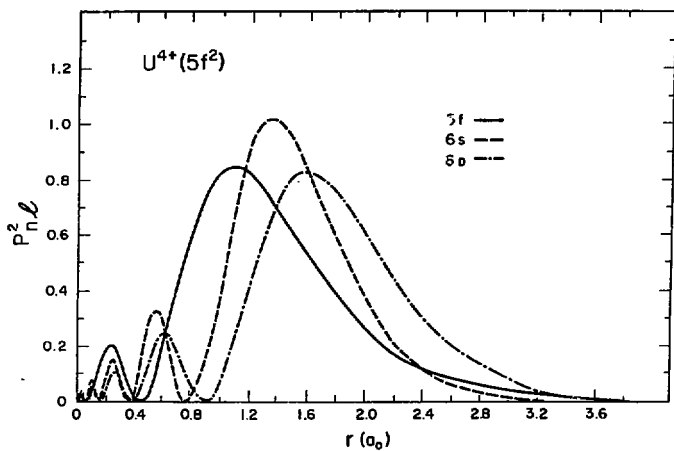


Figure 2. Radial charge density for U^{4+} .

In order to solve this equation we make use of the central field approximation for which the following assumptions are made:

- 1) Each electron is assumed to move independently.
- 2) There is a central field made up of the spherically averaged potential fields of each of the other electrons and the nucleus; that is each electron is said to be moving in a spherically symmetric field (potential),
$$-\frac{U(r_i)}{e}.$$

Then we may write the central field Hamiltonian

$$\mathcal{H}_{CF} = \sum_{i=1}^N \left[\frac{p_i^2}{2m} + U(r_i) \right] \quad (2)$$

This central field Hamiltonian results in a Schrodinger equation which may be readily solved in polar coordinates with wavefunctions of the form

$$\psi = r^{-1} R_{n\ell}(r) Y_{\ell\ell_z}(\theta, \phi) \quad (3)$$

These wavefunctions are products of the radial functions $R_{n\ell}(r)$ times the spherical harmonics $Y_{\ell\ell_z}(\theta, \phi)$ and the energy levels are highly degenerate. The energy levels are labeled by the principal quantum number n and the orbital quantum number ℓ . This degeneracy is removed by considering a number of perturbing effects. An electronic configuration is described by a particular set of quantum numbers n and ℓ . For example, the electronic configuration of the U^{4+} ion is

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 5f^2$$

or as is commonly written $[Rn]5f^2$. Since the electrons in filled subshells ($n\ell^{4\ell+2}$) do not contribute to the electronic structure of the low-lying levels we consider in this paper only the properties of the electrons in the unfilled shell.

For f electrons the most important perturbation is the term obtained by subtracting equation 2 from equation 1:

$$\mathcal{H} - \mathcal{H}_{CF} = \sum_{i=1}^N \left[-\frac{Ze^2}{r_i} - U(r_i) \right] + \sum_{i < j}^N \frac{e^2}{r_{ij}} \quad (4)$$

The first summation shifts all the levels in a given configuration equally so we will not consider it. The second term

$$\mathcal{K}_1 = \sum_{i < j}^N \left(\frac{e^2}{r_{ij}} \right) \quad (5)$$

represents the electrostatic Coulomb repulsion between pairs of electrons.

It is convenient at this point to introduce the operators (note: throughout this paper all operators are typed in script;)

$$L = \sum_i \ell_i \quad \text{and} \quad S = \sum_i \delta_i$$

where ℓ_i and δ_i are the orbital and spin angular momentum operators of the i^{th} electron. \mathcal{K}_1 is diagonal in L and S which means we can label the eigenstates with particular eigenvalues of L and S in the form $2S+1L$. This type of coupling is called Russell-Saunders coupling or L-S coupling.

To allow for relativistic corrections in the Hamiltonian we introduce \mathcal{K}_2 , the spin-orbit interaction as

$$\mathcal{K}_2 = \sum_i \xi(r_i) \delta_i \cdot \ell_i \quad (6)$$

$$\text{or} \quad \mathcal{K}_2 = \zeta_{nl} S \cdot L$$

$$\text{where} \quad \xi(r) = \frac{\hbar^2}{2m^2 c^2 r} \frac{dU}{dr}$$

$$\text{and} \quad \zeta_{nl} = \int_0^\infty R_{nl}^2 \xi(r) dr$$

The term \mathcal{K}_2 becomes progressively more important as Z , the atomic number increases. This spin-orbit interaction is diagonal in J where $J = L + S$. The $2S+1L$ multiplet is split into levels labeled by their J eigenvalues; $J = |L+S|, |L+S-1|, \dots, |L-S|$ where each J level has a degeneracy of $2J+1$. The interaction \mathcal{K}_2 will couple $2S+1L$ states whose value of S and L differ by not more than one. The spin-orbit interaction is especially important for actinide ions because of their high values of Z . Then the L-S coupling scheme is no longer a valid approximation and we speak of intermediate coupling.

In a complex a transition metal ion is surrounded by a number of ligands. If we assume the ion of interest has purely electrostatic interactions with its surroundings we can write

$$\mathcal{H}_3 = -e \sum_1 V(r_1, \theta_1, \phi_1) \quad (7)$$

where the sum extends over all the electrons of the central ion. $V(r, \theta, \phi)$ is the potential at the central ion from the surrounding ligands. This potential may be expanded in a series of spherical harmonics and we obtain

$$\mathcal{H}_3 = \sum_{1, k, q} D_k^q(r_1^k) Y_k^q(\theta_1, \phi_1) \quad (8)$$

The number of terms that need to be considered in this series depends on the symmetry of the problem. This crystal-field or ligand field perturbation breaks the $2J+1$ degeneracy of a particular J level and the eigenvalues of the operator J_z are needed to label the states.

The last perturbation to be discussed will be the Zeeman operator

$$\mathcal{H}_4 = \beta(L+2S) \cdot H \quad (9)$$

To first order this operator can be replaced by

$$\mathcal{H}_4 = g_J \beta H \cdot J \quad (10)$$

where g_J is the Landé g value which depends on L , S , and J for a particular free ion multiplet, H is the external magnetic field, and β is the Bohr magneton. This term is important for the discussion of magnetic susceptibility and electron paramagnetic resonance (EPR) results.

We can picture the results of this discussion in Figure 3. Here we show the energy levels of the f^2 configuration and schematically show the results of successively applying the perturbation Hamiltonians \mathcal{H}_1 , \mathcal{H}_2 , \mathcal{H}_3 to this configuration.

Ligand Field and Spin Orbit Hamiltonians for f^1 .

In this section we will discuss in some detail the application of \mathcal{H}_2 and \mathcal{H}_3 to a configuration consisting of one f electron outside a closed shell. We shall use as an example a ligand field of axial symmetry such as one might find in uranocene-type molecules.

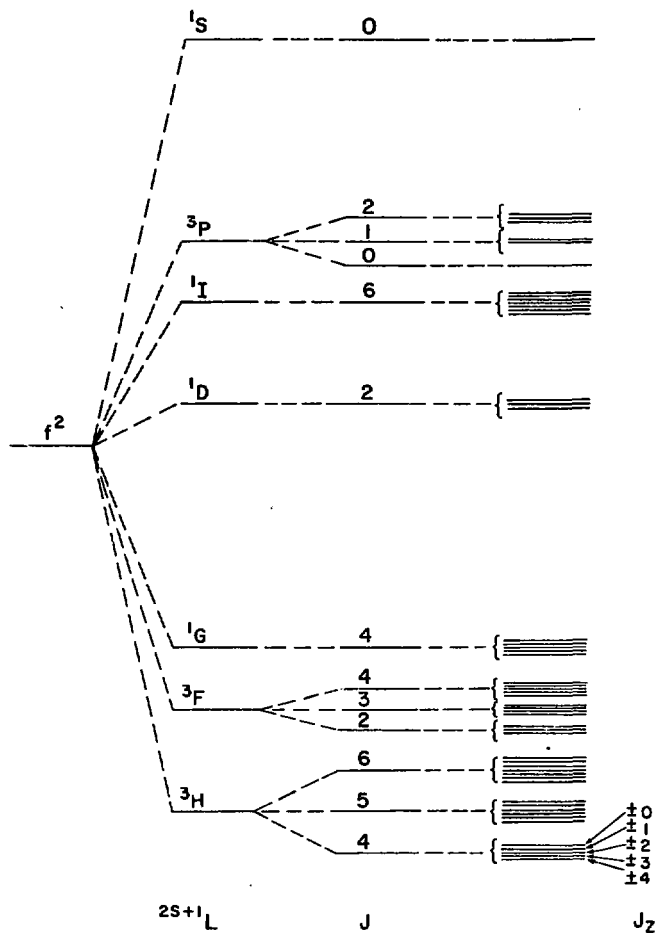


Figure 3. Energy levels of the f^2 configuration with the perturbations \mathcal{K}_1 , \mathcal{K}_2 , and \mathcal{K}_3 applied successively.

The ligand-field Hamiltonian was written as (equation 8)

$$\mathcal{H}_3 = \sum_{l,k,q} D_k^q(r_1^l) V_k^q(\theta, \phi)$$

for an f electron. The value of k is restricted to be $k \leq 2l$ where l is the value of the orbital angular momentum for the electrons. For f electrons $k \leq 6$. Furthermore, from a consideration of the parity of the matrix elements involving the crystal field potential, k must be even. This further restricts values of k to be 2, 4, or 6 for f electrons. Values allowed for q are restricted by the rule $|q| \leq k$. Further restrictions on q are determined by the symmetry of the ligand field. If the highest symmetry axis (the quantization axis) contains an n -fold rotation axis then $|q| = \lambda n$, $\lambda = 0, 1, 2, \dots$. If q is non-zero, then only J_z eigenstates with eigenvalues that differ by $\pm q$ can be mixed by the crystal-field interaction. For the C_3 axis found in uranocene type molecules only $q = 0$ is allowed. Therefore, the non-zero crystal field parameters are D_2^0 , D_4^0 , and D_6^0 . We shall later assume that D_2^0 is the dominant term, i.e., $D_2^0 \gg D_4^0$ or D_6^0 , and determine the energy levels for an f^1 system.

A straightforward method for evaluating crystal field matrix elements was developed by Stevens [5], the operator-equivalent method. The basis for this method is derived from the Wigner-Eckart theorem from which it can be shown that within a particular J (or L) manifold all operators of the same rank have matrix elements which are proportional to one another. The matrix elements of these operators have been tabulated along with the proportionality constants for the ground terms of the f^n ions. A convenient source for these tables is the appendices of Abragam and Bleaney [6].

The usual way of writing the matrix element is

$$\begin{aligned} \langle J, J_z | \mathcal{H}_3 | J, J_z \rangle &= \sum_{k,q} D_k^q(r^k) \langle J, J_z | V_k^q | J, J_z \rangle \\ &= \sum_{k,q} K_k A_k^q(r^k) \langle J, J_z | O_k^q | J, J_z \rangle \end{aligned}$$

The O_k^q 's are the equivalent operators which are proportional to the spherical harmonic tensors of Eq. (8) with the proportionality constants K_k being α, β , and γ ; the second, fourth, sixth order operator equivalent factors, respectively. The A_k^q 's are usually treated as crystal field parameters.

We will now evaluate the second order crystal field matrix elements for an f^1 ion. The equivalent operator is $O_2^0 = 3J_z^2 - J^2$.

Table 1

Matrix elements of the type $\langle \ell, \ell_z | O_k^0 | \ell, \ell_z \rangle$ for $L = 3$ ($\ell = 3$ for a single f electron) from Abragam and Bleaney. Each matrix element must be multiplied by $(-2/45)A_2^0 \langle r^{-2} \rangle$.

ℓ_z	0	± 1	± 2	± 3
0	-12	0	0	0
± 1	0	-9	0	0
± 2	0	0	0	0
± 3	0	0	0	15

From Table 17 of Appendix B in Abragam and Bleaney we find $J = 3$ (or L in our case) and the L_z states 0, ± 1 , ± 2 , ± 3 . The matrix is shown in Table 1. From Table 18 (Abragam and Bleaney) the second rank operator equivalent for an f electron is $-2/45$.

The energy levels may then be listed as

$$E_{\pm 3} = -\frac{2}{45} \times 15 \times A_2^0 \langle r^{-2} \rangle = -\frac{2}{3} A_2^0 \langle r^{-2} \rangle$$

$$E_{\pm 2} = -\frac{2}{45} \times 0 \times A_2^0 \langle r^{-2} \rangle = 0$$

$$E_{\pm 1} = -\frac{2}{45} \times (-9) \times A_2^0 \langle r^{-2} \rangle = +\frac{2}{5} A_2^0 \langle r^{-2} \rangle$$

$$E_0 = -\frac{2}{45} \times (-12) \times A_2^0 \langle r^{-2} \rangle = +\frac{8}{15} A_2^0 \langle r^{-2} \rangle \quad (12)$$

The factor $\langle r^{-2} \rangle$ is the expectation value of the radial wavefunction. Since A_2^0 and $\langle r^{-2} \rangle$ are functions of the radial wavefunctions, the usual practice is to evaluate these parameters empirically. The matrix elements and factors we have found are dependent only on the angular parts of the wavefunction and may be evaluated exactly. The energy levels in terms of the second, fourth, and sixth order crystal field parameters are given later in Appendix C.

The other interaction which is important for the f^1 case is the spin-orbit interaction \mathcal{H}_2 . We may use the ℓ, ℓ_z basis set described above and evaluate exactly the angular part of this interaction. This is described in detail in Appendix A. We may

also use the J, J_z basis set which is diagonal in J to calculate the energies of the states. This calculation is also shown in Appendix A. Finally, we may draw a correlation diagram which goes from the limit of strong spin-orbit interaction to the limit of strong crystal-field interaction [7]. This diagram is shown in Figure 4. Although there is no data for organoactinide or

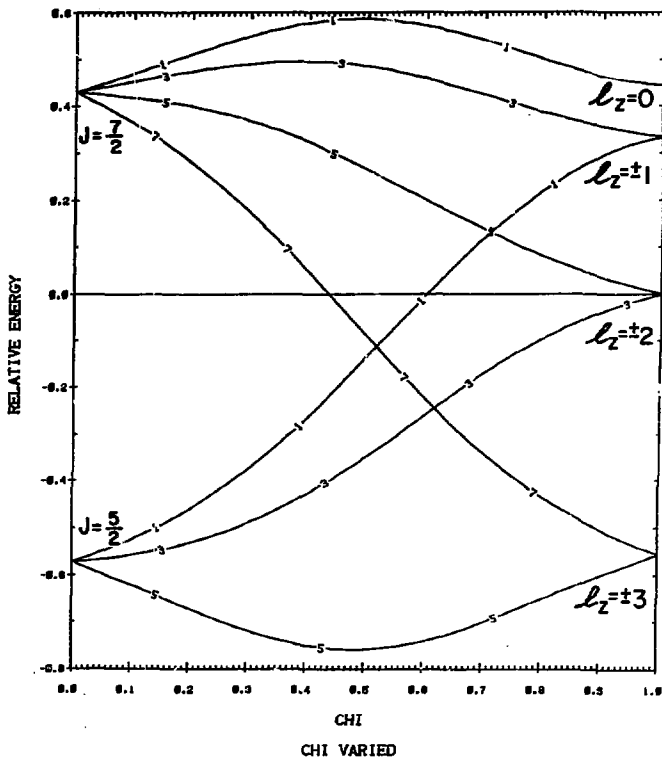


Figure 4. Energy levels of the f^1 configuration as a function of the relative strengths of the spin-orbit and crystal field interactions. For $\chi = 0$, only the spin-orbit interaction is considered; for $\chi = 1$, only the crystal field interaction is considered. The energy levels are numbered by $2 \times J_z$.

lanthanide compounds on the relative strengths of the two interactions we may extrapolate from inorganic complexes and estimate that χ is approximately .4 for the actinides and possibly .3 or .2 for the lanthanides. If covalent bonding is very important for the actinides we would expect χ to be larger.

It should be emphasized that we are evaluating exactly only the angular terms in the Hamiltonian, the radial terms are being treated as parameters. For inorganic complexes these radial terms show a smooth variation across the series for a particular type of complex. For example, Figure 5 shows the variation of the spin-orbit coupling constant for the entire Lanthanide series as determined from optical spectra of Ln^{3+} in LaCl_3 [8]. This curve is shifted slightly upward by $\sim 5\%$ for the Ln^{3+} in LaF_3 . The lanthanide series is considered to be ionic; if covalent effects are more important in the actinide series, then we would expect a much larger variation in the empirical radial parameters for the 5f series as a function of the crystal host or compound.

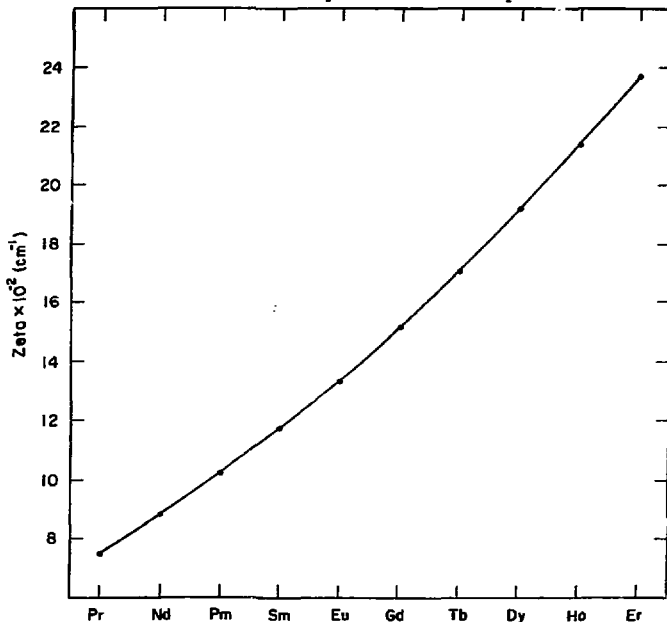


Figure 5. Variation of the empirically determined spin-orbit coupling constant for Ln^{3+} ions in LaCl_3 [8].

The Electrostatic and Spin-Orbit Hamiltonians for f^2 .

For an f^n configuration the energy levels of the electrostatic interaction

$$\mathcal{K}_1 = \frac{e^2}{r_{ij}^2}$$

are written in terms of the Slater integrals

$$F(k) = e^2 \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} \left[R_{nf}(r_1) R_{nf}(r_j) \right]^2 dr_1 dr_j \quad (13)$$

where $r_<$ is the lesser and $r_>$ is the greater of r_i and r_j . The limitations on k are obtained from the properties of Legendre polynomials and are: k must be even, and $k \leq 2l$, which for f electrons means k is restricted to $k = 0, 2, 4, 6$. For a much more detailed discussion see Condon and Shortley or Judd [2,3].

It is convenient to define a related set of parameters which avoids the occurrence of fractional coefficients for $F(k)$'s:

$$\begin{aligned} F_0 &= F^{(0)} \\ F_2 &= \frac{F^{(2)}}{225} \\ F_4 &= \frac{F^{(4)}}{1089} \\ F_6 &= \frac{25F^{(6)}}{184041} \end{aligned} \quad (14)$$

The electrostatic interaction is diagonal in the L-S representation. This is the representation usually used in calculations involving f electrons. We show in Appendix B the calculation of the electrostatic energies in this representation using the diagonal sum method.

The effect of the spin-orbit interaction, \mathcal{K}_2 , may be readily evaluated within a particular L-S multiplet. This is equivalent to assuming $\mathcal{K}_1 \gg \mathcal{K}_2$. We may write

$$\langle SLJ | \zeta(SL) | SLJ \rangle = \zeta(SL) \left\{ \frac{J(J+1) - L(L+1) - S(S+1)}{2} \right\} \quad (15)$$

From this expression it can easily be shown that the energy interval between two states of the same multiplet which differ by 1 in their J value is

$$E_{L,S,J} - E_{L,S,J-1} = J\zeta(SL) \quad (16)$$

This is called the Landé interval rule.

For the lanthanide series as mentioned previously, Russell-Saunders coupling is a reasonable approximation for the ground terms except for the ions Sm^{3+} and Eu^{3+} . In the actinide series this approximation is worse because the effects of spin-orbit coupling increase as Z increases. The relatively simple methods we have discussed earlier are inadequate to determine the energies of the configuration f^n with $n > 2$. In the early 1940's Racah [9] developed more powerful methods which have since been applied to atomic spectroscopy. We shall simply mention the results of these methods here.

Results of Tensor Operator Methods

Racah defined a new set of radial parameters (called Racah parameters) which are related to the Slater integrals by

$$\begin{aligned} E^0 &= F_0 - 10F_2 - 33F_4 - 286F_6 \\ E^1 &= (70F_2 + 231F_4 + 200F_6) \times \frac{1}{9} \\ E^2 &= (F_2 - 3F_4 + 7F_6) \times \frac{1}{9} \\ E^3 &= (5F_2 + 6F_4 - 91F_6) \times \frac{1}{3} \end{aligned} \quad (17)$$

Expressions for the angular parts of the electrostatic and spin-orbit matrix elements may be obtained in terms of fractional parentage coefficients and can be relatively easily evaluated by a digital computer. These matrix elements have been tabulated for all f^n configurations and published in book form by Nielson and Koster [10].

The spin-orbit matrix elements may be evaluated by the expression

$$\begin{aligned}
& \langle \ell^N \alpha S L J | \zeta_{n\ell} \sum (\delta_1 \cdot \ell_1) | \ell^N \alpha' S' L' J \rangle \\
& = \zeta_{n\ell} (-1)^{J+L+S'} \left\{ \begin{matrix} L & L' & 1 \\ S' & S & J \end{matrix} \right\} \times [\ell(\ell+1)(2\ell+1)]^{1/2} \\
& \times \langle \ell^N \alpha S L || v^{(11)} || \ell^N \alpha' S' L' \rangle \quad (18)
\end{aligned}$$

In this expression the part in the curly brackets $\left\{ \right\}$ is a 6-j symbol and the $\langle \alpha S L || v^{(11)} || \ell^N \alpha' S' L' \rangle$ is the $v^{(11)}$ reduced matrix element. The 6-j symbols are tabulated in the book by Rotenberg, Bivins, Metropolis, and Wooten [11] while the $v^{(11)}$ reduced matrix elements are given in Nielson and Koster for the entire f^n series. The symbol α in these matrix elements represent additional quantum numbers which are necessary to specify a particular state. Note that these formulas allow us to calculate off-diagonal elements also.

Nielson and Koster also tabulate another useful series of reduced matrix elements, the $U(k)$ reduced matrix elements. These are written as

$$\langle f^N \alpha S L || U^{(k)} || f^N \alpha' S' L' \rangle \quad (19)$$

where $k \leq 6$ for f electrons.

In Figure 6 the energy levels of the f^2 configuration are plotted as a function of η , ξ , the relative magnitude of the electrostatic and spin-orbit interactions [12]. At the left hand side of the figure $\xi = 0$, and the energy levels represent the limit for pure Russell-Saunders coupling, while on the right hand side $\xi = 1$, which represents the energy levels in the limit of $j-j$ coupling. For the lanthanide ion Pr^{3+} ξ is ~ 1 while for U^{4+} ξ is ~ 3 . As can be seen the ordering of the energy levels are very sensitive to the relative strengths of these interactions and can change from one compound to another.

The discussion up to this point has been concerned with the free ion model. We have defined the electrostatic and spin-orbit radial parameters which can be used as variables in order to fit spectra. Ideally these parameters should be independent of the compound in which they are measured. In fact it is found that, as mentioned earlier for the spin-orbit coupling constant, the values of the Slater parameters for Ln^{3+} in LaCl_3 are slightly different than those found in LaF_3 . For example, the data for $F^{(2)}$ are plotted in Figure 7. In the actinide series these effects are more important. For the octahedral UX_6^{2-} series ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) [13] the value of $F^{(2)}$ is found to vary by 20% as X goes from

F to I. This point will be discussed later.

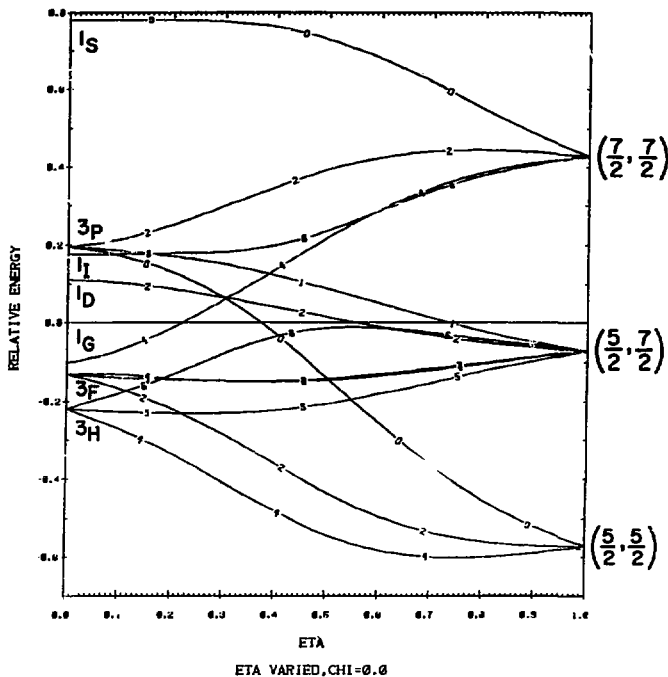


Figure 6. Energy levels of the f^2 configuration for relative values of the spin-orbit and electrostatic interactions. For $\eta = 0$, only the electrostatic interaction is considered; for $\eta = 1$, only the spin-orbit interaction is considered. The energy levels are numbered by the J values.

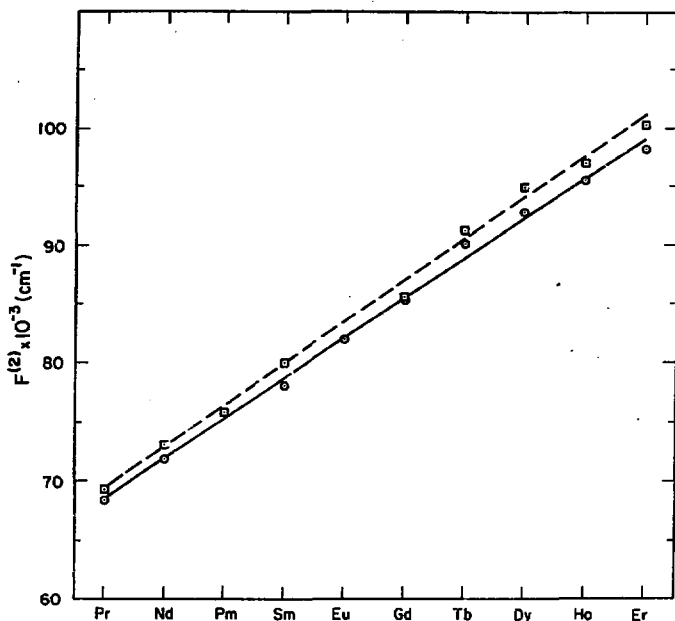


Figure 7. Variation of $F^{(2)}$ for the Ln^{3+} ions diluted in LaF_3 (dashed line) and LaCl_3 (solid line) [8].

Ligand Field Effects for the f^2 Configuration - Uranocene.*

We may apply the operator equivalent method discussed earlier for the f^2 case on the lowest term for the U^{4+} ion, $^3\text{H}_4$. In this example we will use all the terms in the ligand field Hamiltonian allowed by the symmetry of the molecules. Since uranocene has a C_8 axis there will be no off-diagonal terms allowed ($q = 0$) and

*For energy levels in the strong ligand field limit, see Appendix E.

$$\begin{aligned} \mathcal{H}_3 = & \sum_{1, k=2, 4, 6} K_k A_k^0 \langle r^k \rangle O_k^0(\Theta_1, \phi_1) \\ & - \sum_1 \left[\alpha A_2^0 \langle r^2 \rangle O_2^0(\Theta_1, \phi_1) + \beta A_4^0 \langle r^4 \rangle O_4^0(\Theta_1, \phi_1) \right. \\ & \left. + \gamma A_6^0 \langle r^6 \rangle O_6^0(\Theta_1, \phi_1) \right] \end{aligned} \quad (20)$$

We may easily write down the matrix elements for this operator by using Table 17 (Appendix B) of Abragam and Bleaney. The results are shown in Table 2.

From this matrix we can immediately write down the energy levels of ligand field levels in the J, J_z representation. The energy levels for the $J = 4$ state are:

$$\begin{aligned} E_{J_z=0} &= -20\alpha A_2^0 \langle r^2 \rangle + 1080\beta A_4^0 \langle r^4 \rangle - 25200\gamma A_6^0 \langle r^6 \rangle \\ E_{J_z=\pm 1} &= -17\alpha A_2^0 \langle r^2 \rangle + 540\beta A_4^0 \langle r^4 \rangle + 1260\gamma A_6^0 \langle r^6 \rangle \\ E_{J_z=\pm 2} &= -8\alpha A_2^0 \langle r^2 \rangle - 660\beta A_4^0 \langle r^4 \rangle + 27720\gamma A_6^0 \langle r^6 \rangle \\ E_{J_z=\pm 3} &= 7\alpha A_2^0 \langle r^2 \rangle - 1260\beta A_4^0 \langle r^4 \rangle - 21420\gamma A_6^0 \langle r^6 \rangle \\ E_{J_z=\pm 4} &= 28\alpha A_2^0 \langle r^2 \rangle + 840\beta A_4^0 \langle r^4 \rangle + 5040\gamma A_6^0 \langle r^6 \rangle \end{aligned} \quad (21)$$

Table 2

Ligand field matrix for a $J = 4$ state for a molecule with a C_8 symmetry axis. In this matrix $B_2 = \alpha A_2^0 \langle r^2 \rangle$, $B_4 = \beta 60 A_4^0 \langle r^4 \rangle$, and $B_6 = \gamma 1260 A_6^0 \langle r^6 \rangle$.

J_z	± 0	± 1	± 2	± 3	± 4
0	$-20B_2 + 18B_4 - 20B_6$	0	0	0	0
± 1	0	$-17B_2 + 9B_4 + B_6$	0	0	0
± 2	0	0	$-8B_2 - 11B_4 + 22B_6$	0	0
± 3	0	0	0	$7B_2 - 7B_4 - 17B_6$	0
± 4	0	0	0	0	$28B_2 + 14B_4 + 4B_6$

Now let us assume as was done earlier, that the second order term is the most important, i.e., $\alpha A_2^0(r^2) \gg \beta A_4^0(r^4)$ or $\gamma A_6^0(r^6)$. Then if αA_2^0 is positive the $J_z = \pm 4$ ligand field state is lowest in energy.

It is interesting at this point to determine the energy levels of the f^2 configuration as a function of the strength of the crystal field. Figures 8a and 8b show the energy levels of this configuration drawn for two values of η , the ratio of the spin-orbit interaction to the electrostatic interaction as defined earlier.

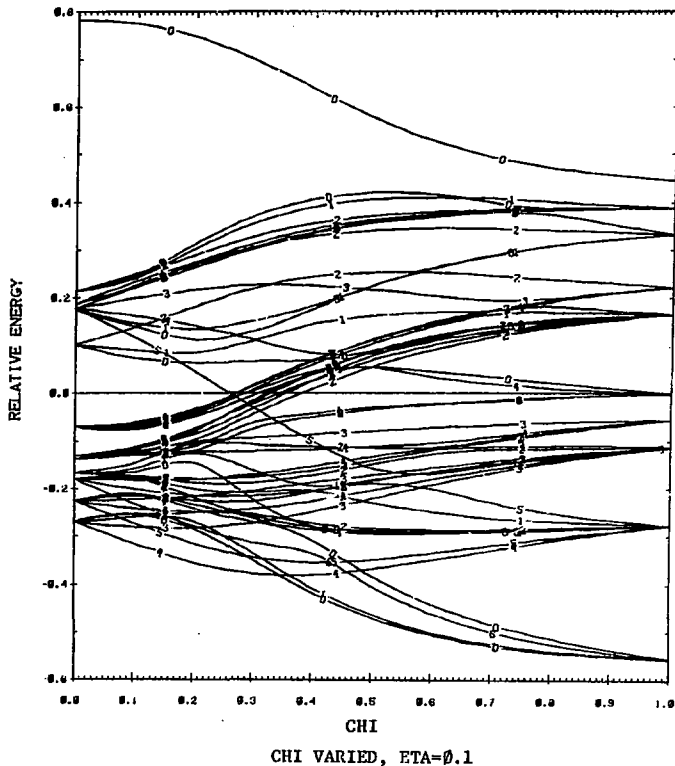


Figure 8a

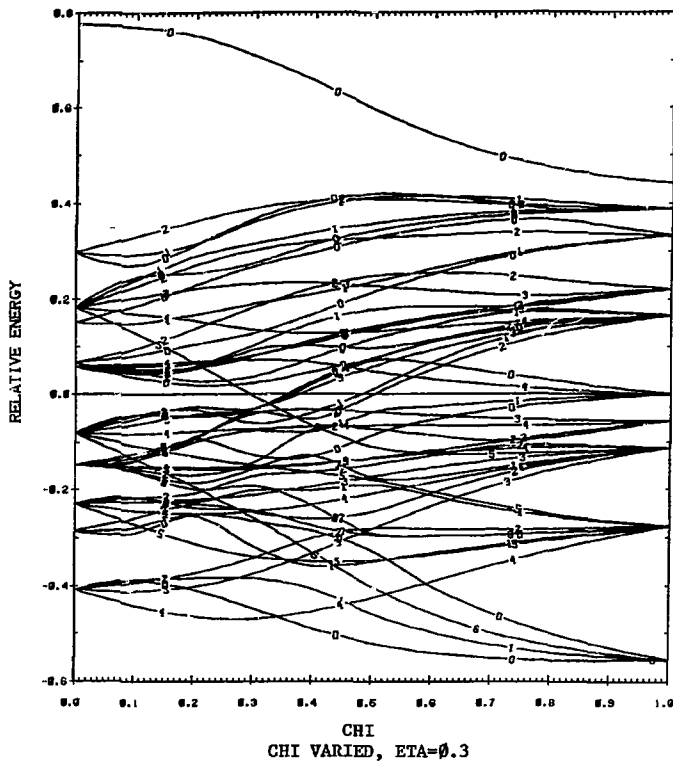


Figure 8b
 Figures 8a and 8b. Energy levels of the f^2 configuration for a fixed ratio (η) of the electrostatic and spin-orbit interactions as a function of the strength of the crystal field. For $\chi = 0$, only the fixed ratio of the electrostatic and spin-orbit interactions is considered; for $\chi = 1$, only the crystal field interaction is considered. a) $\eta = .1$, χ varies from 0 to 1; b) $\eta = .3$, χ varies from 0 to 1. The energy levels are numbered by the J_z values.

At the right hand side of the figures, $\chi = 1$, the energy levels are drawn considering only the crystal field interaction. At the left hand side of the figures, $\chi = 0$, the energy levels are drawn for the particular value of η and no crystal field interaction as obtained from Figure 6. The values of $\eta = .1$ and $.3$ are reasonable estimates for the lanthanide and actinide series respectively. The value of χ , the ratio of the crystal field interaction to the electrostatic and spin-orbit interaction is probably about $.2-.3$ for the two series. These graphs represent Tanabe-Sugano diagrams for the f^2 configuration [14].

The magnetic susceptibility of uranocene has been measured from 4.2°K to room temperature [15-18]. On the basis of the above much over-simplified model we may calculate the magnetic susceptibility of this compound. We assume only the ground crystal field state contributes to the susceptibility and second order effects can be neglected.

The magnetic susceptibility χ is defined for our purposes as

$$\chi = \frac{N \sum \left(\frac{W_1^2}{kT} - 2W_2 \right) e^{-W_0/kT}}{\sum e^{-W_0/kT}} \quad (22)$$

where N is Avogadro's number and the summation is over all energy levels. We assume the energy level E may be expanded in a power series of H , the magnetic field, as

$$E = W_0 + W_1 H + W_2 H^2 + \dots \quad (23)$$

Since we are neglecting second order effects $W_2 = 0$.

To evaluate W_1 for our example we need to calculate the matrix element

$$\begin{aligned} \langle LSJ_z | L + 2S | LSJ_z' \rangle &= g_J \langle J_z | J | J_z' \rangle \\ &= g_J \langle J_z | J_x + J_y + J_z | J_z' \rangle \end{aligned} \quad (24)$$

If $J_z = J_z'$ then

$$\langle J_z | J_z | J_z \rangle = J_z \quad (25)$$

If $J_z \neq J_z'$ this component is zero.

$$J_x + iJ_y = J_+$$

$$J_x - iJ_y = J_-$$

and

$$\langle JJ_z | J_{\pm} | JJ_z \pm 1 \rangle = \left[(J(J+1) - J_z(J_z \pm 1)) \right]^{1/2} \quad (26)$$

If $\Delta J_z > 1$ the off-diagonal matrix elements are zero.

In our simplified model with $\alpha A_2^0 > 0$ we have found the degenerate $J_z = \pm 4$ state is lowest. In a magnetic field of magnitude H parallel to the symmetry axis z the energies of the two levels are

$$E_{J_z=+4} = g_J \beta H \langle J_z=4 | J_z | J_z=4 \rangle = 4g_J \beta H$$

$$E_{J_z=-4} = g_J \beta H \langle J_z=-4 | J_z | J_z=-4 \rangle = -4g_J \beta H \quad (27)$$

Since $\Delta J_z > 1$ for the off-diagonal components the susceptibility is zero in the perpendicular direction. Then

$$\chi_{\perp} = \frac{(16g_J^2 \beta^2) \times 2}{2kT} = \frac{16g_J^2 \beta^2}{kT}$$

$$\chi_{\parallel} = 0$$

$$\begin{aligned} \chi_{\text{Ave}} &= \frac{1}{3} (\chi_{\perp} + 2\chi_{\parallel}) \\ &= \frac{1}{3} \frac{(16g_J^2 \beta^2)}{kT} \end{aligned} \quad (28)$$

$g_J = \frac{4}{5}$ for U^{4+} and then

$$\chi_{\text{Ave}} = \frac{\mu_{\text{eff}}^2}{3kT}$$

$$\mu_{\text{eff}} = 3.2\beta$$

The experimental value for the magnetic susceptibility for uranocene in the low temperature range ($4.2^\circ\text{K} < T < \sim 80^\circ\text{K}$) is $\mu_{\text{eff}} = 2.4\beta$. In the original calculation [15] the orbital reduction factor k was introduced by replacing the Zeeman operator $L + 2S$ with

$kl + 2S$. The deviation of the value of the orbital reduction factor from unity is a measure of the covalency of the molecule. The experimental value of the magnetic susceptibility was fit with $k = .8$.

This same type of calculation was performed for the higher Z compounds, neptunocene and plutonocene. For $\text{Pu}(\text{COT})_2$ the ground term is a 5I_4 . Since $J = 4$ for this term the crystal field Hamiltonian is of exactly the same form as shown earlier for $\text{U}(\text{COT})_2$ except the value of α , β , and γ are different. If we assume again $B_2^0 \gg B_0^0$ and B_4^0 , then the only difference between the f^2 and f^4 ion will be the value of α . (We have also assumed $A_2^0 \langle r^2 \rangle$ does not change much in the two compounds.) From Table 20 (Appendix B) in Abragam and Bleaney we find

$$\begin{aligned} \langle f^{23}_{H_4} || \alpha || f^{23}_{H_4} \rangle &= \frac{-2^2 \times 13}{3^2 \times 5^2 \times 11} \\ \langle f^{45}_{I_4} || \alpha || f^{45}_{I_4} \rangle &= \frac{2 \times 7}{3 \times 5 \times 11^2} \end{aligned} \quad (29)$$

Since the signs of these factors are different, if the $J_z = \pm 4$ state is lowest for $\text{U}(\text{COT})_2$ then the $J_z = 0$ state must be lowest for $\text{Pu}(\text{COT})_2$. The experimental magnetic susceptibility data for $\text{Pu}(\text{COT})_2$ show this compound is diamagnetic which is consistent with the above calculations.

Another approach to evaluating the energy levels of uranocene-type molecules is the effective crystal field model. In this model, first suggested for actinide COT complexes by Hayes and Edelstein [19], the ligand field splittings were calculated for an f^1 system. Hayes and Edelstein used the Wolfsberg-Helmholz approximation to determine the one electron orbitals derived from the metal f orbitals. This calculation showed the filled ring orbitals were quite a bit lower in energy than the metal orbitals. The level scheme for the metal orbitals is shown in Figure 9. These splittings were used to evaluate the crystal field parameters ($A_k^q \langle r^k \rangle$) given for the f^1 case in axial symmetry in Appendix C. The crystal field parameters evaluated in this fashion were then used with the values of the electrostatic and spin-orbit parameters derived for U^{4+} in UCl_4 and the energy splittings and magnetic moment of the ground crystal field state were obtained.

The results of these calculations should be treated with caution. Even in well-characterized systems of f -transition ions it appears the empirical fitting of radial parameters to optical and magnetic data is open to some question. As mentioned previously, in the octahedral UX_6^{2-} series ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) the value of $F(2)$ varied by $\sim 20\%$ as X changed from F to I [13]. These systems

$$\begin{array}{l}
 l_2 \\
 \pm 2 \text{ ————— } 3313 \text{ cm}^{-1} = 0B_2^0 - \frac{56}{33} B_4^0 + \frac{160}{11 \times 13} B_6^0 \\
 0 \text{ ————— } 2511 \text{ cm}^{-1} = \frac{8}{15} B_2^0 + \frac{16}{11} B_4^0 + \frac{1600}{33 \times 13} B_6^0 \\
 \\
 \pm 1 \text{ ————— } 166 \text{ cm}^{-1} = \frac{2}{5} B_2^0 + \frac{8}{33} B_4^0 - \frac{400}{11 \times 13} B_6^0 \\
 \pm 3 \text{ ————— } 0 \text{ cm}^{-1} = -\frac{2}{3} B_2^0 + \frac{8}{11} B_4^0 - \frac{80}{33 \times 13} B_6^0
 \end{array}$$

Figure 9. Results of the Wolfsberg-Helmholz calculation [19] for the metal-like orbitals of uranocene. $B_k^0 = A_k^0(r^k)$.

were characterized by fitting the electrostatic, spin-orbit, and crystal field parameters to optical data. It was suggested that the value of the Slater parameter $F^{(2)}$ is affected by the type of ligand in the complex and may have adsorbed some of the effects of the ligand field. This appeared to be true to a lesser extent for the spin-orbit coupling constant. If the value of $F^{(2)}$ and ζ were affected by the ligands, then the values found for the ligand field parameters would also not be the "correct" value.

General Method for Calculating Crystal Field Matrix Elements for f^n Configuration.

The operator equivalent method is useful for determining crystal field splittings for the lowest J state of a lanthanide or actinide ion since the necessary α , β , γ 's are tabulated. However, if we include higher lying J states, the effects of intermediate coupling and the mixing of various J states by the relatively strong crystal field are important, especially for actinide ions. Then it is much simpler to calculate the necessary matrix elements by the tensor operator technique. Unfortunately, the definition used for the crystal field parameters B_q^k 's in the tensor operator method is different than that of the operator equivalent method. Note also that we are now using B_q^k for the parameters where k is the superscript and q the subscript; this is the opposite to the earlier B_k^q 's which are defined differently. Table 3, taken from Kassman [20], shows the relationship between the tensor operator notation B_q^k and the operator equivalent

Table 3

Relationship of the tensor operator parameters B_q^k to the operator equivalent parameters A_k^q (from Kassman).

$B_0^2 = 2A_2^0 \langle r^2 \rangle$	$B_0^6 = 16A_6^0 \langle r^6 \rangle$
$B_2^2 = (1/3)(6)^{1/2} A_2^2 \langle r^2 \rangle$	$B_2^6 = (16/105)(105)^{1/2} A_6^2 \langle r^6 \rangle$
$B_0^4 = 8A_4^0 \langle r^4 \rangle$	$B_3^6 = -(8/105)(105)^{1/2} A_6^3 \langle r^6 \rangle$
$B_2^4 = (2/5)(10)^{1/2} A_4^2 \langle r^4 \rangle$	$B_4^6 = (8/21)(14)^{1/2} A_6^4 \langle r^6 \rangle$
$B_3^4 = -(2/35)(35)^{1/2} A_4^3 \langle r^4 \rangle$	$B_6^6 = (16/231)(231)^{1/2} A_6^6 \langle r^6 \rangle$
$B_4^4 = (4/35)(70)^{1/2} A_4^4 \langle r^4 \rangle$	

notation $A_k^q \langle r^k \rangle$. (Note that Table 6.1 of Wybourne [4] contains a number of errors. The phase factor in Equation 6-5 of Wybourne is also incorrect.)

A general formula for crystal field matrix elements is given in Appendix D along with an example of its application.

Electron Paramagnetic Resonance

We have previously discussed the Zeeman operator \mathcal{H}_4 which was written as

$$\mathcal{H}_4 = \beta H \cdot (L + 2S)$$

which for an isolated J level, which we will consider here, may be rewritten

$$\mathcal{H}_4 = g_J (H \cdot J) = g_J \beta (H_z J_z + H_x J_x + H_y J_y)$$

where g_J is the free ion g value for a particular J level, and β is the Bohr magneton, and H the magnetic field. Now EPR experiments are usually described in terms of a phenomenological Hamiltonian called a spin-Hamiltonian [6]

$$\mathcal{H} = \beta H \cdot g \cdot S' = (g_x H_x S'_x + g_y H_y S'_y + g_z H_z S'_z) \quad (30)$$

We see by comparison of the two Hamiltonians that if the wavefunction of the ground crystal field state is known we can calculate the g values which will be found in the EPR spectrum, i.e.,

$$\begin{aligned} g_{\parallel} &= 2g_J \langle SLJJ_z | J_z | SLJJ_z \rangle \\ g_x &= 2g_J \langle SLJJ_z | J_x | SLJJ_z \pm 1 \rangle \\ g_y &= 2g_J \langle SLJJ_z | J_y | SLJJ_z \pm 1 \rangle \end{aligned} \quad (31)$$

If $g_x = g_y$, then the g value in the xy plane is called g_{\perp} . If $\Delta J_z \neq 0, \pm 1$ the matrix elements will be zero and no EPR spectrum will be observed. In the f transition series, the orbital angular momentum is not quenched as in the d transition series and the measured g values may vary from 0 to 18. The magnitude of the g value is a very sensitive test of the crystal field wavefunction.

In the above Hamiltonian we have not included the hyperfine interaction term. This term is written as

$$H_{\text{hf}} = AI \cdot J \quad (32)$$

for an isolated J state is proportional to free ion g_J value and the free hyperfine coupling constant value a_J :

$$\frac{A}{g} = \frac{a_J}{g_J} = \frac{A_{\parallel}}{g_{\parallel}} = \frac{A_{\perp}}{g_{\perp}} \quad (33)$$

If these proportionalities do not hold, it is an indication that crystal field mixing of different J states is important.

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Appendix A

To evaluate the spin-orbit coupling in this basis set we need the following matrix elements

$$\zeta \ell \cdot s = \zeta \left[\frac{1}{2} (\ell_+ s_- + \ell_- s_+) + \ell_z s_z \right]$$

$$\begin{aligned} \langle \ell \ell_z s s_z | \ell_+ s_- | \ell', \ell_z - 1, s, s_z + 1 \rangle \\ = \left[(\ell + \ell_z) (\ell - \ell_z + 1) (s - s_z) (s + s_z + 1) \right]^{1/2} \end{aligned}$$

$$\begin{aligned} \langle \ell \ell_z s s_z | \ell_- s_+ | \ell, \ell_z + 1, s, s_z - 1 \rangle \\ = \left[(\ell - \ell_z) (\ell + \ell_z + 1) (s + s_z) (s - s_z + 1) \right]^{1/2} \end{aligned}$$

$$\langle \ell \ell_z s s_z | \ell_z s_z | \ell \ell_z s s_z \rangle = \ell_z s_z$$

Now for $\ell = 3$, $s = \frac{1}{2}$

$$\begin{aligned} \langle 3, \ell_z, \frac{1}{2}, s_z | \ell_+ s_- | 3, \ell_z - 1, \frac{1}{2}, s_z + 1 \rangle \\ = \left[(3 + \ell_z) (4 - \ell_z) \left(\frac{1}{2} - s_z\right) \left(\frac{3}{2} + s_z\right) \right]^{1/2} \end{aligned}$$

$$\begin{aligned} \langle 3, \ell_z, \frac{1}{2}, s_z | \ell_- s_+ | 3, \ell_z + 1, s, s_z - 1 \rangle \\ = \left[(3 - \ell_z) (4 + s_z) \left(\frac{1}{2} + s_z\right) \left(\frac{3}{2} - s_z\right) \right]^{1/2} \end{aligned}$$

$$\begin{aligned} \langle 3, \frac{1}{2} | \ell_+ s_- + \ell_- s_+ | 2, -\frac{1}{2} \rangle &= \langle 3, \frac{1}{2} | \ell_+ s_- | 2, -\frac{1}{2} \rangle^* \\ &+ \langle 3, \frac{1}{2} | \ell_- s_+ | 2, -\frac{1}{2} \rangle = 0 + 0 \end{aligned}$$

*We have changed the notation here and are using only the $\ell_z s_z$ values since ℓ and s are fixed at 3 and $\frac{1}{2}$ respectively, i.e., $\langle \ell_z, s_z | \ell_z, s_z \rangle$.

$$\begin{aligned}
\langle 2, +\frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | 3, -\frac{1}{2} \rangle &= \left[(3-2)(4+2) \left(\frac{1}{2} + \frac{1}{2}\right) \left(\frac{3}{2} - \frac{1}{2}\right) \right]^{1/2} = (6)^{1/2} \\
\langle 2, +\frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | 1, -\frac{1}{2} \rangle &= 0 \\
\langle 3, -\frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | 2, \frac{1}{2} \rangle &= \left[(6)(1) \left(\frac{1}{2} - (-\frac{1}{2})\right) \left(\frac{3}{2} + -\frac{1}{2}\right) \right]^{1/2} = (6)^{1/2} \\
\langle 1, -\frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | 0, \frac{1}{2} \rangle &= \left[(4)(3) \left(\frac{1}{2} - -\frac{1}{2}\right) (1) \right]^{1/2} = 2(3)^{1/2} \\
\langle 0, \frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | 1, -\frac{1}{2} \rangle &= 2(3)^{1/2} \\
\langle -1, -\frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | -2, \frac{1}{2} \rangle &= \left[(3-1)(4-(-1))(1)(1) \right]^{1/2} = (10)^{1/2} \\
\langle -2, \frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | -1, -\frac{1}{2} \rangle &= \left[(3-(-2))(4+(-2))(1)(1) \right]^{1/2} = (10)^{1/2} \\
\langle -3, -\frac{1}{2} | \ell_{+}\delta_{-} + \ell_{-}\delta_{+} | -2, \frac{1}{2} \rangle &= 0
\end{aligned}$$

Using these results (and those of Eq. (12)) we may write down the matrices of the spin-orbit interaction in the ℓ_z, s_z representation as follows:

$$\ell_z, s_z \begin{array}{c} 3, -\frac{1}{2} \quad 2, +\frac{1}{2} \\ \hline 3, -\frac{1}{2} \quad -\frac{3}{2}\zeta + \epsilon_3 \quad \frac{1}{2}(6)^{\frac{1}{2}}\zeta \\ 2, +\frac{1}{2} \quad \frac{1}{2}(6)^{\frac{1}{2}}\zeta \quad +\zeta + \epsilon_2 \end{array}$$

$$\begin{array}{c} 1, -\frac{1}{2} \\ 0, \frac{1}{2} \end{array} \begin{array}{c} 1, -\frac{1}{2} \quad 0, \frac{1}{2} \\ \hline -\frac{1}{2}\zeta + \epsilon_1 \quad (3)^{\frac{1}{2}}\zeta \\ (3)^{\frac{1}{2}}\zeta \quad +\epsilon_0 \end{array}$$

$$\begin{array}{c} -1, -\frac{1}{2} \\ -2, \frac{1}{2} \end{array} \begin{array}{c} -1, -\frac{1}{2} \quad -2, \frac{1}{2} \\ \hline \zeta/2 + \epsilon_1 \quad \frac{1}{2}(10)^{\frac{1}{2}}\zeta \\ \frac{1}{2}(10)^{\frac{1}{2}}\zeta \quad -\zeta + \epsilon_2 \end{array}$$

$$\begin{array}{c} -3, -\frac{1}{2} \\ -3, -\frac{1}{2} \end{array} \begin{array}{c} -3, -\frac{1}{2} \\ \hline \frac{3}{2}\zeta + \epsilon_3 \end{array}$$

Similarly,

$$\langle 3, \frac{1}{2} | \ell_{+} s_{-} + \ell_{-} s_{+} | 2, -\frac{1}{2} \rangle = 0$$

$$\langle 2, -\frac{1}{2} | \ell_{+} s_{-} + \ell_{-} s_{+} | 1, \frac{1}{2} \rangle = [(3+2)(4-2)(1)(1)]^{1/2} = (10)^{1/2}$$

$$\langle 1, \frac{1}{2} | \ell_{+} s_{-} + \ell_{-} s_{+} | 2, -\frac{1}{2} \rangle = [(2)(5)(1)(1)]^{1/2} = (10)^{1/2}$$

$$\langle 1, \frac{1}{2} | \ell_{+} s_{-} + \ell_{-} s_{+} | 0, -\frac{1}{2} \rangle = 0$$

$$\langle 0, -\frac{1}{2} | \ell_{+} s_{-} + \ell_{-} s_{+} | -1, \frac{1}{2} \rangle = [(3)(4)(1)(1)]^{1/2} = 2(3)^{1/2}$$

$$\langle -1, \frac{1}{2} | \ell_{+} s_{-} + \ell_{-} s_{+} | -2, -\frac{1}{2} \rangle = 0$$

$$\langle -2, -\frac{1}{2} | \ell_{+} \ell_{-} + \ell_{-} \ell_{+} | -3, \frac{1}{2} \rangle = [(1)(6)^{1/2}(1)(1)]^{1/2} = (6)^{1/2}$$

and the spin-orbit matrices are:

$$\begin{array}{c}
 \begin{array}{c} 3, \frac{1}{2} \\ \hline 3, \frac{1}{2} \end{array} \begin{array}{c} \frac{3}{2} \zeta + \epsilon_3 \end{array} \\
 \\
 \begin{array}{c} 2, -\frac{1}{2} \\ \hline 2, -\frac{1}{2} \end{array} \begin{array}{cc} 2, -\frac{1}{2} & 1, \frac{1}{2} \\ -\zeta + \epsilon_2 & \frac{1}{2}(10)^{1/2} \zeta \end{array} \\
 \\
 \begin{array}{c} 1, \frac{1}{2} \\ \hline 1, \frac{1}{2} \end{array} \begin{array}{cc} \frac{1}{2}(10)^{1/2} \zeta & \frac{1}{2} \zeta + \epsilon_1 \end{array} \\
 \\
 \begin{array}{c} 0, -\frac{1}{2} \\ \hline 0, -\frac{1}{2} \end{array} \begin{array}{cc} 0, -\frac{1}{2} & -1, \frac{1}{2} \\ +\epsilon_0 & (3)^{1/2} \zeta \end{array} \\
 \\
 \begin{array}{c} -1, \frac{1}{2} \\ \hline -1, \frac{1}{2} \end{array} \begin{array}{cc} (3)^{1/2} \zeta & -\frac{1}{2} \zeta + \epsilon_1 \end{array} \\
 \\
 \begin{array}{c} -2, -\frac{1}{2} \\ \hline -2, -\frac{1}{2} \end{array} \begin{array}{cc} -2, -\frac{1}{2} & -3, \frac{1}{2} \\ +\zeta + \epsilon_2 & \frac{1}{2}(6)^{1/2} \zeta \end{array} \\
 \\
 \begin{array}{c} -3, \frac{1}{2} \\ \hline -3, \frac{1}{2} \end{array} \begin{array}{cc} \frac{1}{2}(6)^{1/2} \zeta & -\frac{3}{2} \zeta + \epsilon_3 \end{array}
 \end{array}$$

Let us now consider another basis set, the LSJ_Z quantum numbers. For f^1 $L = 3$, $S = 1/2$, $J = 5/2$ or $7/2$, that is ${}^2F_{5/2}$ or ${}^2F_{7/2}$. We may find the magnitude of the spin-orbit splitting from the equation for the diagonal elements

$$\begin{aligned}
 E_{so}(J = \frac{7}{2}) &= \zeta/2 [J(J+1) - L(L+1) - S(S+1)] \\
 &= \zeta/2 [\frac{7}{2}(\frac{9}{2}) - 3(4) - \frac{1}{2}(\frac{3}{2})] \\
 &= \zeta/2 [\frac{63}{4} - \frac{48}{4} - \frac{3}{4}] = \frac{3}{2} \zeta
 \end{aligned}$$

$$E_{so}(J=\frac{5}{2}) = \zeta/2[\frac{5}{2} \times \frac{7}{2} - \frac{48}{4} - \frac{3}{4}] = -2\zeta$$

We now follow the procedures for operator equivalents as we did previously. This time we are interested in the $J = 5/2$ and $J = 7/2$ states. From Table 17 of Abragam and Bleaney we can find the operator equivalent factors for the $J = 5/2$ and the $J = 7/2$ states. The energy matrices obtained including spin-orbit coupling are

$$J = \frac{5}{2}$$

J_z	$\pm\frac{1}{2}$	$\pm\frac{3}{2}$	$\pm\frac{5}{2}$
$\pm\frac{1}{2}$	$-2\zeta - 8\alpha A_2^0(r^2)$		0
$\pm\frac{3}{2}$	0	$-2\zeta - 2\alpha A_2^0(r^2)$	0
$\pm\frac{5}{2}$	0		$-2\zeta - 10\alpha A_2^0(r^2)$

$$J = \frac{7}{2}$$

J_z	$\pm\frac{1}{2}$	$\pm\frac{3}{2}$	$\pm\frac{5}{2}$	$\pm\frac{7}{2}$
$\pm\frac{1}{2}$	$\frac{3}{2}\zeta - 15\alpha A_2^0(r^2)$	0	0	0
$\pm\frac{3}{2}$	0	$\frac{3}{2}\zeta - 9\alpha A_2^0(r^2)$	0	0
$\pm\frac{5}{2}$	0	0	$\frac{3}{2}\zeta + 3\alpha A_2^0(r^2)$	0
$\pm\frac{7}{2}$	0	0	0	$\frac{3}{2}\zeta + 21\alpha A_2^0(r^2)$

The values for the second order operator equivalent factors may be obtained from Table 20 (Appendix B) of Abragam and Pryce. The factors are

$$\alpha = \langle f^1 2F_{5/2} | \alpha | f^1 2F_{5/2} \rangle = \frac{-2}{5 \times 7}$$

$$\langle f^1 2F_{5/2} | \alpha | f^1 2F_{7/2} \rangle = \frac{2^2}{3 \times 5 \times 7}$$

$$\alpha' = \langle f^{13} 2_{F_{7/2}} | \alpha | f^{13} 2_{F_{7/2}} \rangle = - \langle f^{13} 2_{F_{7/2}} | \alpha | f^{13} 2_{F_{7/2}} \rangle = \frac{-2}{3^2 \times 7}$$

Now the operator O_2^0 will mix states of different J but the same J_z value, i.e., matrix elements of the type

$$\langle J = \frac{5}{2}, J_z | O_2^0 | J = \frac{7}{2}, J_z \rangle \neq 0$$

so that 2×2 matrices need to be diagonalized in order to solve the problem exactly. We can check the energy of the $J_z = \pm 7/2$ state and compare it to that of the l_z state of $3, 1/2$ and $3, -1/2$ calculated previously.

$$\begin{aligned} E_{J=\frac{7}{2}, J_z=\frac{7}{2}} &= \frac{3}{2}\zeta + 21\alpha' A_2^0 \langle r^2 \rangle \\ &= \frac{3}{2}\zeta + 21 \times \frac{-2}{3 \times 3 \times 7} A_2^0 \langle r^2 \rangle \\ &= \frac{3}{2}\zeta - \frac{2}{3} A_2^0 \langle r^2 \rangle \\ E_{l=3, l_z=3} &= \frac{3}{2}\zeta + \epsilon_3 = \frac{3}{2}\zeta - \frac{2}{3} A_2^0 \langle r^2 \rangle \end{aligned}$$

Thus, as must be true, the energies do not depend on the basis functions chosen to do the calculations.

Appendix B

We start out the calculation of the electrostatic energies by constructing a table of the complete sets of electrons which belong to the configuration using all allowed l_z and s_z values consistent with the Pauli principle. The resulting table classified by the L_z and S_z values is shown (Table 4). We have given only a little more than half the table since the negative L_z values may be obtained by interchanging the signs of the l_z values for the positive L_z values. From this table we can determine which L-S states are allowed. The largest value of the orbital angular momentum is $L = 6$ and the spins are paired. This term must come from an 1I state which also must have singlet $L_z = 6, 5, 4, 3, \dots, 0, \dots, -5, -6$ substates. There is an $S_z = 1, L_z = 5$ state which must come from a 3H term and must have triplet and singlets $L_z = 5, 4, 3, \dots, -3, -4, -5$ substrates. By this type of elimination we arrive at the following terms allowed for an f^2 configuration

$$^1I, ^3H, ^1G, ^3F, ^1D, ^3P, ^1S$$

Now we can calculate the electrostatic energy of the various terms by use of the diagonal sum rule. This rule states that the sum of the roots of the secular equation is equal to the sum of the diagonal matrix elements. All levels of a particular term have the same energy. There are no matrix elements connecting states with different L_z or S_z values, thus the secular equation for the configuration factors into a series of secular equations. Thus writing $E(^1I)$ for the energy of this state and (3^+3^-) for its diagonal matrix element we find

Table 4

l^2	$s_z = 1$	$s_z = 0$	$s_z = -1$
$l_z = 6$		(3^+3^-)	
$l_z = 5$	(3^+2^+)	(3^+2^-)	(3^-2^+)
$l_z = 4$	(3^+1^+)	(3^+1^-)	(3^-1^+)
$l_z = 3$	(3^+0^+)	(3^+0^-)	(3^-0^+)
$l_z = 2$	(3^+-1^+)	(3^+-1^-)	(3^-1^+)
$l_z = 1$	(3^+-2^+)	(3^+-2^-)	(3^-2^+)
$l_z = 0$	(3^+-3^+)	(3^+-3^-)	(3^-3^+)

$$\begin{aligned}
L_z \\
6 \quad E(^1I) &= (3^+3^-) \\
5 \quad E(^3H) &= (3^+2^+) \\
4 \quad E(^3H)+E(^1I)+E(^1G) &= (3^+1^-)+(3^-1^+)+(2^+2^-) \\
3 \quad E(^3F)+E(^3H) &= (3^+0^+)+(2^+1^+) \\
2 \quad E(^3F)+E(^3H)+E(^1I)+E(^1G)+E(^1D) &= (3^+-1^-)+(2^+0^-)+(1^+1^-) \\
&\quad + (3^-1^+)+(2^-0^+) \\
1 \quad E(^3F)+E(^3H)+E(^3P) &= (3^+-2^+)+(1^+0^+)+(2^+-1^+) \\
0 \quad E(^3F)+E(^3H)+E(^1I)+E(^1G)+E(^1D)+E(^3P)+E(^1S) &= \\
&\quad (3^+-3^-)+(2^+-2^-)+(1^+-1^-)+(0^+0^-)+(3^-3^+)+(2^-2^+)+(1^-1^+)
\end{aligned}$$

In order to use this method we need to define two types of integrals: the direct integral

$$(ab|q|ab) = J(a,b) = \sum_{k=0}^{\infty} a^k (l^a l_z^a, l^b l_z^b) F^k (n^a l^a, n^b l^b)$$

and the exchange integral

$$(ab|q|ba) = K(a,b) = \delta(s_z^a, s_z^b) \sum_{k=0}^{\infty} b^k (l^a l_z^a, l^b l_z^b) G^k (n^a l^a, n^b l^b)$$

$$\text{and } E(A) = \sum_{a>b=1}^N [J(a,b) - K(a,b)]$$

where $q = \frac{e^2}{r_{12}}$ and the coefficients $a^k (l^a l_z^a, l^b l_z^b)$ and $b^k (l^a l_z^a, l^b l_z^b)$ are tabulated in Condon and Shortley (Table 2⁶, page 180 and Table 1⁶, page 178) for s, p, d, and f electrons. For equivalent electrons as we are dealing with here $F^k(n^a l^a, n^a l^a) = G^k(n^a l^a, n^b l^b)$. Note also that because of the δ function for s_z^a, s_z^b the exchange integral is zero for singlet states.

$$E(^1I) = F_0 + 25F_2 + 9F_4 + F_6$$

$$\begin{aligned}
E(^3H) &= F_0 + 0F_2 - 21F_4 - 6F_6 - 25F_2 - 30F_4 - 7F_6 \\
&= F_0 - 25F_2 - 51F_4 - 13F_6
\end{aligned}$$

$$E(^1G) = (3^+1^-) + (3^-1^+) + (2^+2^-) - E(^3H) - E(^1I)$$

$$= F_0 - 15F_2 + 3F_4 + 15F_6$$

$$F_0 - 15F_2 + 3F_4 + 15F_6$$

$$F_0 + 0F_2 + 49F_4 + 36F_6$$

$$-F_0 + 25F_2 + 51F_4 + 13F_6$$

$$-F_0 - 25F_2 - 9F_4 - F_6$$

$$= F_0 - 30F_2 + 97F_4 + 78F_6$$

$$E(^3F) = (3^+0^+) + (2^+1^+) - E(^3H)$$

$$= F_0 - 20F_2 + 18F_4 - 20F_6$$

$$+ 0F_2 - 63F_4 - 84F_6$$

$$+ F_0 + 0F_2 - 7F_4 - 90F_6$$

$$- 15F_2 - 32F_4 - 105F_6$$

$$- F_0 + 25F_2 + 51F_4 + 13F_6$$

$$= F_0 - 10F_2 - 33F_4 - 286F_6$$

and so on.

Appendix C

The energy levels for $\ell = 3$ with the complete crystal field Hamiltonian of Equation 20 are (using Table 17, Appendix B of Abragam and Bleaney) and the notation $A_k^0 \langle r^k \rangle = B_k^0$

$$E_{\ell_z=0} = -12\alpha B_2^0 + 360\beta B_4^0 - 3600\gamma B_6^0$$

$$E_{\ell_z=\pm 1} = -9\alpha B_2^0 + 60\beta B_4^0 + 2700\gamma B_6^0$$

$$E_{\ell_z=\pm 2} = 0\alpha B_2^0 - 420\beta B_4^0 + 1080\gamma B_6^0$$

$$E_{\ell_z=\pm 3} = 15\alpha B_2^0 + 180\beta B_4^0 + 180\gamma B_6^0$$

Now from Table 18, Appendix B

for $\ell = 3$

$$\langle 3||\alpha||3 \rangle = \frac{-2}{45}$$

$$\langle 3||\beta||3 \rangle = \frac{2}{11 \times 45}$$

$$\langle 3||\gamma||3 \rangle = \frac{-4}{11 \times 13 \times 27}$$

Then we obtain

$$E_{\ell_z=0} = +\frac{8}{15} A_2^0 \langle r^2 \rangle + \frac{16}{11} A_4^0 \langle r^4 \rangle + \frac{1600}{3 \times 11 \times 13} A_6^0 \langle r^6 \rangle$$

$$E_{\ell_z=\pm 1} = \frac{2}{5} A_2^0 \langle r^2 \rangle + \frac{8}{33} A_4^0 \langle r^4 \rangle - \frac{400}{11 \times 13} A_6^0 \langle r^6 \rangle$$

$$E_{\ell_z=\pm 2} = 0 - \frac{56}{33} A_4^0 \langle r^4 \rangle + \frac{160}{11 \times 13} A_6^0 \langle r^6 \rangle$$

$$E_{\ell_z=\pm 3} = -\frac{2}{3} A_2^0 \langle r^2 \rangle + \frac{8}{11} A_4^0 \langle r^4 \rangle - \frac{80}{3 \times 11 \times 13} A_6^0 \langle r^6 \rangle$$

Appendix D

A general equation for crystal field matrix elements may be obtained in terms of tensor operators as follows:

$$\begin{aligned} & \langle f^n \alpha SLJ_z | \mathcal{H}_3 | f^n \alpha' SL' J' J'_z \rangle \\ & = \sum B_q^k \langle f^n \alpha SLJ_z | U_q^{(k)} | f^n \alpha' SL' J' J'_z \rangle \langle f | C^{(k)} | f \rangle \end{aligned}$$

Now for f electrons

$$\begin{aligned} \langle f | C^{(k)} | f \rangle & = \langle 3 | C^{(k)} | 3 \rangle = (-1)^3 [(7)(7)]^{1/2} \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \\ \langle f^n \alpha SLJ_z | U_q^{(k)} | f^n \alpha' SL' J' J'_z \rangle \\ & = (-1)^{J-J_z} \begin{pmatrix} J & k & J' \\ -J_z & q & J'_z \end{pmatrix} \langle f^n \alpha SLJ || U^{(k)} || f^n \alpha' SL' J' \rangle \end{aligned}$$

and

$$\begin{aligned} & \langle f^n \alpha SLJ || U^{(k)} || f^n \alpha' SL' J' \rangle \\ & = (-1)^{S+L'+J+k} [(2J+1)(2J'+1)]^{1/2} \left\{ \begin{matrix} J & J' & k \\ L' & L & S \end{matrix} \right\} \langle f^n \alpha SL || U^{(k)} || f^n \alpha' S' L' \rangle \end{aligned}$$

We may gather all the terms together and write for f electrons

$$\begin{aligned} & \langle f^n \alpha SLJ_z | V | f^n \alpha' SL' J' J'_z \rangle \\ & = \sum B_q^{(k)} (-1)^{3-J_z+S+L'+2J+k} (7) \begin{pmatrix} 3 & k & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} J & k & J' \\ -J_z & q & J'_z \end{pmatrix} \left\{ \begin{matrix} J & J' & k \\ L' & L & S \end{matrix} \right\} \\ & \times [(2J+1)(2J'+1)]^{1/2} \langle f^n \alpha SL || U^{(k)} || f^n \alpha' SL \rangle \end{aligned}$$

In the above equation the $\begin{pmatrix} \\ \end{pmatrix}$ are 3-j symbols, $\left\{ \begin{matrix} & & \\ & & \end{matrix} \right\}$ is a 6-j symbol, and $\langle || U^{(k)} || \rangle$ is a reduced matrix element which is tabulated for all f^n configurations by Nielson and Koster. Note that $S = S'$, if this is not true, the matrix element is zero. The above general equation for crystal field matrix elements may be readily evaluated

by computer techniques.

To illustrate these calculations, we will evaluate the $B_0^{(6)}$ matrix element for the $J = 4, J_z = 4$ state of the 3H_4 term of f^2 .

$$\begin{aligned} & \langle f^n \alpha S L J J_z | \mathcal{H}_3 | f^n \alpha' S L' J' J'_z \rangle \\ &= B_0^{(6)} \langle f^2 {}^3H_{44} | U_0^{(6)} | f^2 {}^3H_{44} \rangle (3! C^{(6)}_{13}) \\ &= B_0^{(6)} (-1)^{3-4+1+5+8+6} \times (7) \begin{pmatrix} 3 & 6 & 3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 4 & 6 & 4 \\ -4 & 0 & 4 \end{pmatrix} \begin{Bmatrix} 4 & 4 & 6 \\ 5 & 5 & 1 \end{Bmatrix} \\ & \times (2 \times 4 + 1) \langle f^2 {}^3H_{44} | U^{(6)} | f^2 {}^3H_4 \rangle \end{aligned}$$

Now from Rotenberg, Bivens, et al.

$$\begin{aligned} \begin{pmatrix} 3 & 6 & 3 \\ 0 & 0 & 0 \end{pmatrix} &= \begin{pmatrix} 6 & 3 & 3 \\ 0 & 0 & 0 \end{pmatrix} = \left(\frac{2^2 \times 5^2}{3 \times 7 \times 11 \times 13} \right)^{1/2} \\ \begin{pmatrix} 4 & 6 & 4 \\ -4 & 0 & 4 \end{pmatrix} &= \begin{pmatrix} 6 & 4 & 4 \\ 0 & 4 & -4 \end{pmatrix} = \begin{pmatrix} 6 & 4 & 4 \\ 0 & -4 & 4 \end{pmatrix} = \left(\frac{2^2}{3^2 \times 5 \times 11 \times 13} \right)^{1/2} \\ \begin{Bmatrix} 4 & 4 & 6 \\ 5 & 5 & 1 \end{Bmatrix} &= \begin{Bmatrix} 6 & 4 & 4 \\ 1 & 5 & 5 \end{Bmatrix} = \begin{Bmatrix} 6 & 5 & 5 \\ 1 & 4 & 4 \end{Bmatrix} = \left(\frac{2^2 \times 17}{3^3 \times 5^2 \times 11^2} \right)^{1/2} \end{aligned}$$

From Nielson and Koster

$$\langle f^2 {}^3H_{44} | U^{(6)} | f^2 {}^3H_4 \rangle = - \left(\frac{5 \times 17}{3^2 \times 7} \right)^{1/2}$$

Substituting we obtain

$$\begin{aligned} & \langle f^2 {}^3H_{44} | U_0^{(6)} | f^2 {}^3H_{44} \rangle \\ &= B_0^{(6)} (-1)^{19} \times 7 \times \left(\frac{2^2 \times 5^2}{3 \times 7 \times 11 \times 13} \right)^{1/2} \times \left(\frac{2^2}{3^2 \times 5 \times 11 \times 13} \right)^{1/2} \\ & \times \left(\frac{2^4 \times 17}{3^3 \times 5^2 \times 11^2} \right)^{1/2} \times 9 \times (-1) \times \left(\frac{5 \times 17}{3^2 \times 7} \right)^{1/2} \end{aligned}$$

$$= B_6^0 \left(\frac{2^8 \times 17^2}{3^4 \times 11^4 \times 13^2} \right)^{1/2}$$

$$= B_6^0 \left(\frac{2^4 \times 17}{3^2 \times 11^2 \times 13} \right)$$

We can check this matrix element by comparing it with the value calculated by the operator equivalent method.

Now from Table 3 in operator equivalent notation this matrix element is

$$\langle f^2 \ ^3H_{44} | v_0^6 | f^2 \ ^3H_{44} \rangle = 4 \times 1260 \times \gamma A_6^0 \langle r^6 \rangle$$

Now from Table 20, Appendix B, Abragam and Bleaney

$$\langle \ ^3H_4 | \gamma | \ ^3H_4 \rangle = \frac{2^4 \times 17}{3^4 \times 5 \times 7 \times 11^2 \times 13}$$

so

$$4 \times 1260 \times \frac{2^4 \times 17}{3^4 \times 5 \times 7 \times 11^2 \times 13} A_6^0 \langle r^6 \rangle = B_0^6 \left(\frac{2^4 \times 17}{3^2 \times 11^2 \times 13} \right)$$

$$16 A_6^0 \langle r^6 \rangle = B_0^6$$

This value agrees with the entry in Table 3.

Appendix E

We have shown in Fig. 4 that the energy levels for an f^1 system in a strong axial ligand field ($\chi = 1$ and considering only a B_0^2 crystal field term in the Hamiltonian) are:

$$l_z = 0 \quad \text{or } a_2, \quad E = .444 \quad ;$$

$$l_z = \pm 1 \quad \text{or } e_1, \quad E = .333 \quad ;$$

$$l_z = \pm 2 \quad \text{or } e_2, \quad E = .000 \quad ;$$

$$l_z = \pm 3 \quad \text{or } e_3, \quad E = -.556 \quad ;$$

Now let us consider the case of two f electrons in the strong crystal or ligand field limit.

There are 10 different ways we may combine the above set of orbitals by pairs:

$$a_2 a_2 \quad e_1 e_1 \quad e_2 e_2 \quad e_3 e_3$$

$$a_2 e_1 \quad e_1 e_2 \quad e_2 e_3$$

$$a_2 e_2 \quad e_1 e_3$$

$$a_2 e_3$$

The crystal field operator is a one electron operator so if we consider the two orthogonal orbitals ϕ_1 and ϕ_2 we may write

$$\begin{aligned} \langle \phi_1 \phi_2 | V_c | \phi_1 \phi_2 \rangle &= \langle \phi_1 \phi_2 | V_1 + V_2 | \phi_1 \phi_2 \rangle = \langle \phi_1 | V_1 | \phi_1 \rangle \\ &+ \langle \phi_2 | V_2 | \phi_2 \rangle \end{aligned}$$

For example, the energy of two electrons in the $a_2 e_1$ orbital is written as

$$\langle a_2 e_1 | V_c | a_2 e_1 \rangle = \langle a_2 | V_1 | a_2 \rangle + \langle e_1 | V_2 | e_1 \rangle .$$

Now as noted previously $\langle a_2 | V_1 | a_2 \rangle = .444$,

$$\langle e_1 | V_2 | e_1 \rangle = .333 \text{ ,}$$

$$\text{so } \langle a_2 e_1 | V_c | a_2 e_1 \rangle = .444 + .333 = .777.$$

In order to obtain the normalization used in Fig. 8 the above energy .777 must be divided by 2. The following energies are obtained:

Orbital	Normalized energy
$a_2 a_2$.444
$e_1 a_2$.389
$e_1 e_1$.333
$e_2 a_2$.222
$e_2 e_1$.167
$e_2 e_2$.000
$e_3 a_2$	-.056
$e_3 e_1$	-.111
$e_3 e_2$	-.278
$e_3 e_3$	-.556

We may determine the degeneracies of each of the two electron orbitals from a probability argument. An electron may be placed in an a_2 orbital with spin up or down, that is, in two different ways. An electron may be placed in an e_1 orbital in four different ways. If the second e_1 orbital is equivalent to the first orbital there are limitations in the number of ways an electron may be placed in the second orbital due to the Pauli principle. For example, let us consider the $e_1 e_2$ orbitals. We may place the first electron in one of four ways in the first e_2 orbital, one of three ways in the second e_2 orbital so there are 4×3 or 12 ways of placing the electrons in this orbital pair. However, we must divide this number by two because the

electrons are indistinguishable and we are counting only distinct pairs; that is there are $4 \times 3/2$ or 6 different ways of putting two electrons in the e_2e_2 orbital pair. The degeneracies of the orbitals are:

Orbital	Degeneracy
a_2a_2	$2 \times 1/2 = 1$
e_1a_2	$4 \times 2 = 8$
e_2a_2	$4 \times 2 = 8$
e_3a_2	$4 \times 2 = 8$
e_1e_1	$4 \times 3/2 = 6$
e_2e_1	$4 \times 4 = 16$
e_3e_1	$4 \times 4 = 16$
e_2e_2	$4 \times 3/2 = 6$
e_2e_3	$4 \times 4 = 16$
e_3e_3	$4 \times 3/2 = 6$
<hr/>	
	TOTAL = 91

We can easily calculate for the purpose of comparison the degeneracies in the LSJ coupling scheme (Fig. 3), which will turn out to be the same as in the strong ligand field case. For each J level, there is a $(2J+1)$ degeneracy.

Level	Degeneracy
3H_4	$2 \times 4 + 1 = 9$
3H_5	$2 \times 5 + 1 = 11$
3H_6	$2 \times 6 + 1 = 13$
3F_2	$2 \times 2 + 1 = 5$

Level	Degeneracy
3F_3	$2 \times 3 + 1 = 7$
3F_4	$2 \times 4 + 1 = 9$
1G_4	$2 \times 4 + 1 = 9$
1D_2	$2 \times 2 + 1 = 5$
3P_0	$2 \times 0 + 1 = 1$
3P_1	$2 \times 1 + 1 = 3$
3P_2	$2 \times 2 + 1 = 5$
1S_0	$2 \times 0 + 1 = 1$
<hr/>	
	TOTAL = 91