Electronic Structure and Transition Intensities in Rare-Earth Materials

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Chapter 1

Introduction

This introduction to electronic structure calculations in rare-earth (lanthanide) and actinide materials is based on the material that was developed in the 1960s by many people, but in particular I would mention Brian Judd, Brian Wybourne, Bill Carnall, and Doug Newman, whose papers and personal interactions particularly inspired me.

While the classic books and papers of the 1960s contain almost all of the information required to make some sense of rare-earth spectra, my experience is that students struggle with many of the concepts. My approach here has been shaped by my experience of helping students to develop an appreciation of parametrized electronic structure calculations. My aim is to give a sound understanding of the basics. There are plenty of excellent books that explain the intricacies of angular momentum theory and perturbation theory, and I will not be attempting to duplicate that.

Much of the material here is based my, and Guokui Lui's, contributions to the book edited by Liu and Jacquier [1], and that is a good place to go for further information. The Crystal Field Handbook, edited by Newman and Ng [2], is another useful modern resource. For the $4f^{N-1}4d$ configurations there is a review by Gary Burdick and myself [3]. For more details on angular momentum theory, group theory, perturbation theory, and so on the books by Weissbluth [4], Lindgren and Morrison [5], and Henderson and Imbusch [6] are excellent, but the older books by Judd [7], Wybourne [8], and Hüfner [9] also contain a lot of useful information.

Chapter 2

Hamiltonians

It is important to understand that the “crystal-field” calculations that became very important in the 1960s, and will form much of the material in the current work, have a basis that goes far beyond a simple electrostatic model of the interaction of ions with a condensed-matter environment. These calculations are better described as “effective Hamiltonian” calculations.

A large literature exists on the concept of effective Hamiltonians, and the interested reader is urged to refer to that literature for clarification of the many subtleties [10, 11, 12, 13, 2]. My Appendix A of Liu and Jacquier [1] contains a summary of some the important issues that I will gloss over here.

2.1 Effective Hamiltonians and effective operators

Effective Hamiltonians and effective operators are defined within a *model space* M. For our purposes the model space will often be the $4f^N$ configuration, sometimes supplemented by the $4f^{N-1}5d$ configuration.

Consider eigenstates of the full Hamiltonian H,

$$H|a\rangle = E_a|a\rangle. \tag{2.1}$$

The aim is to define an *effective Hamiltonian* H_{eff} that gives identical *eigenvalues* for model-space eigenstates $|a_0\rangle$, i.e.

$$H_{\text{eff}}|a_0\rangle = E_a|a_0\rangle. \tag{2.2}$$

Transformations may be defined that connect the full states and the model-space states. It is possible to choose a *canonical* operator $\hat{k}$ so that

$$|a\rangle = \hat{k}|a_0\rangle \tag{2.3}$$

and

$$|a_0\rangle = \hat{k}^\dagger|a\rangle. \tag{2.4}$$

In analogy to an effective Hamiltonian an effective operator (such as the operator for a dipole moment) has the same matrix elements between the model eigenstates as the full operator has between the full eigenstates, i.e.

$$\langle b_0|A_{\text{eff}}|a_0\rangle = \langle b|A|a\rangle. \tag{2.5}$$

This implies that the effective operator may be calculated from

$$A_{\text{eff}} = \hat{k}^\dagger A\hat{k}. \tag{2.6}$$

These transformations are seldom used directly (though we will return to them in Chapter 6 when we discuss *ab-initio* calculations). The usual approach is to construct H_{eff}, $\hat{k}$, and A_{eff} using a time-independent Rayleigh-Schrödinger perturbation expansion. For further details see Appendix A of [1].

2.2 The crystal-field Hamiltonian

The effective Hamiltonian acting withing the $4f^N$ configuration is commonly written [14]:

$$\begin{aligned} H_{\text{eff}} &= E_{\text{avg}} + \sum_{k=2,4,6} F^k f_k + \zeta_f A_{\text{so}} + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7) \\ &+ \sum_{i=2,3,4,6,7,8} T^i t_i + \sum_{h=0,2,4} M^h m_h + \sum_{k=2,4,6} P^k p_k + \sum_{k=2,4,6} B^k_q C^{(K)}_q. \end{aligned} \tag{2.7}$$

E_{avg} is the energy difference between the ground-state energy and the configuration center of gravity (barycenter) and is included to allow the ground-state energy to be set to zero. The Coulomb interaction between the $4f$ electrons is parametrized by the radial electrostatic integrals, F^k, which multiply the angular part of the electrostatic interaction, f_k. The coupling of the electron spin magnetic moment and the magnetic field originating in the orbital motion of the electron is represented by the spinorbit coupling constant, ζ_f, which multiplies the angular part of the spinorbit interaction, A_{so}.

Higher-order terms in the Hamiltonian include two-electron Coulomb correlation contributions represented by parameters α, β, and γ and three-electron Coulomb correlation contributions parametrized by T_i. The M^h and P^k parametrize higher-order spin-dependent effects. These higher-order terms are important for accurate calculations, but the effects are subtle.

The terms in the Hamiltonian that represent the non-spherical part of the interaction with the crystal are modeled using the so-called crystal-field Hamiltonian. It is important to recognize that this Hamiltonian is not restricted to electrostatic effects, which form a minor part of the total crystal-field effect [15]. When the parameters are fitted to experimental energies, their values reflect all one-electron non-spherical interactions. The crystal-field Hamiltonian is expressed in Wybourne [8], notation as,

$$H_{\text{cf}} = \sum_{k,q} B^k_q C^{(k)}_q, \tag{2.8}$$

where the B^k_q parameters define the one-electron crystal-field interaction and the $C^{(k)}_q$ are spherical tensor operators for the $4f^N$ configuration. For f^N configurations, $k = 2,\ 4,\ 6$, and non-zero values of q depend upon the site symmetry of the lanthanide ion in the host lattice. The total number of crystal field parameters ranges from 27 parameters for C_1 or C_i symmetry, down to only two parameters for octahedral or cubic symmetry.

For the $4f^{N-1}5d$ configuration we must add $5d$ spin-orbit and crystal-field parameters, the direct (F) and exchange (G) Coulomb interaction between the f and d electrons, and a parameter $\Delta_E(fd)$ representing the average energy difference between the configurations. The additional terms are [3]:

$$\begin{aligned} H_d &= \Delta_E(fd) + \sum_{k=2,4} F^k(fd) f_k(fd) + \sum_{j=1,3,5} G^k(fd) g_k(fd) + \zeta_d A_{\text{so}}(d) \\ &+ \sum_{k=2,4,} B^k_q(d) C^{(k)}_q(d). \end{aligned} \tag{2.9}$$

2.3 Parameter fits

2.4 $4f^N$ configuration

The Hamiltonian parameters may be accurately fitted to the sharp transitions within the $4f^N$ configuration, e.g. see Ref. [14]. Since the crystal field is a small perturbation one can construct a “Dieke” or “Dieke-Carnall” diagram for the entire series of trivalent ions. See Fig. 2.1.

2.5 $4f^{N-1}5d$ configuration

Transitions between the $4f^N$ and $4f^{N-1}5d$ configurations are vibronically broadened, so detailed fitting is not possible, and a mixture of atomic calculations and fitting “by eye” has been used in most cases [3].

Since the $5d$ orbitals are much more extensive than the $4f$ they interact more strongly with the ligands, and the crystal-field parameters are generally about 40 times larger. Whereas for $4f^N$ the crystal-field is a small perturbation for $4f^{N-1}5d$ it is comparable with the Coulomb interaction, and dominates the spectra.

2.6 Superposition model

The superposition model, developed by Newman and co-workers in the late 60s [16, 17, 2], is an important framework for understanding both crystal-field and intensity parameters. The idea is to use the approximation that the contributions to the effective potential from different ligands is superposable (obviously for an electrostatic potential this is exact). If we had only one ligand on the Z axis at distance R_0 only crystal-field parameters with $q = 0$ would be non-zero, due to the cylindrical symmetry. We define the *intrinsic* parameters, $\bar{B}_k(R_0)$ as those $B_0^{(k)}$ parameters for a single ligand. Adding together the effects of all the ligands yields

$$B_q^k = \sum_L \bar{B}_k(R_0)(-1)^q C_{-q}^{(k)}(\theta_L, \phi_L) \left(\frac{R_0}{R_L}\right)^{t_k}. \tag{2.10}$$

Here $(-1)^q C_{-q}^{(k)}$ gives the effect of rotating the ligand from the Z axis, and has exactly the same form as an electrostatic potential. The distance-dependence term, $(R_0/R_L)^{t_k}$, would be the same as an electrostatic potential if we chose $t_k = k + 1$, but comparisons with experimental crystal-field parameters suggest that the power law is generally higher than electrostatic power laws. This is because the quantum-mechanical effects that give rise to the majority of the “crystal field” involves overlap of ligand orbitals, which fall off faster than electrostatic potentials. For detailed discussions see the papers and book by Newman and co-workers [16, 17, 2].

2.7 Hyperfine Calculations

Hyperfine interactions between the electronic and nuclear states give small splittings which often require high-resolution techniques to resolve. Here we give a very brief sketch to illustrate some points.

The traditional expansion of the magnetic interaction between electronic (J) and nuclear (I) angular momentum states may be written (e.g. Liu and Jacquier [1], Section 1.7.2) as:

$$H_{\mathrm{MD}} = A_\parallel J_z I_z + A_\perp (J_x I_x + J_y I_y), \tag{2.11}$$

where $A_\parallel$ and $A_\perp$ are referred to as “parallel” and “perpendicular” interactions. In spherical-tensor notation we can write:

$$H_{\mathrm{MD}} = A_\parallel J_0^{(1)} I_0 + A_\perp (-J_{+1}^{(1)} I_{-1}^{(1)} - J_{-1}^{(1)} I_{+1}^{(1)}). \tag{2.12}$$

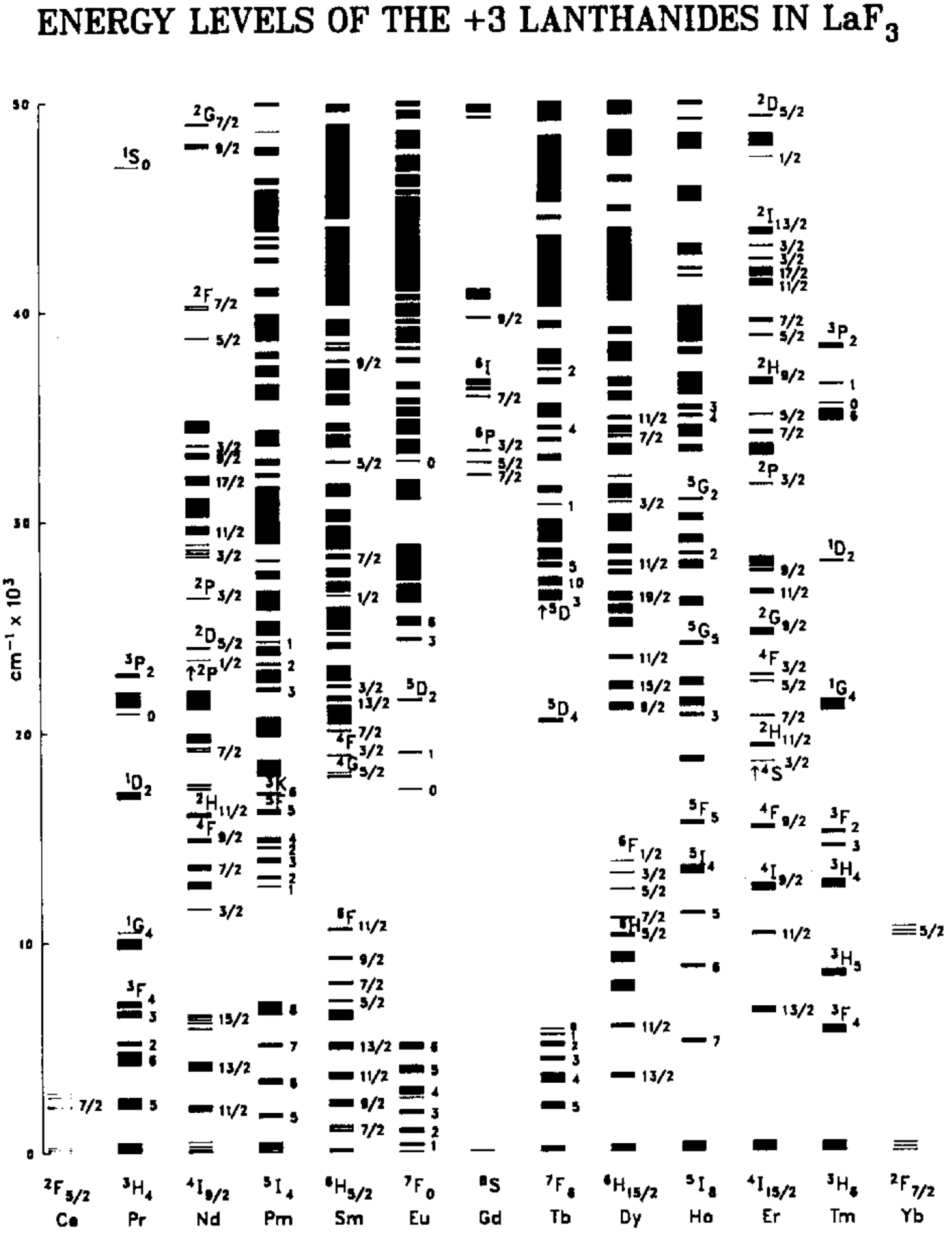

Figure 2.1: Dieke diagram for trivalent lanthanide ions in LaF_3 from [14]. The configurations range from f^1 (Ce^{3+}) to f^{13} (Yb^{3+}).

This approach gives different A parameters for each multiplet of the ion, so is not so convenient for large-scale calculations. A detailed discussion of the use of tensor-operator techniques is given by Weissbluth [4] Chapter 18. We have used this approach in Refs. [18, 19]. Starting from:

$$H_{\mathrm{MD}} = 2\beta \left[\frac{\boldsymbol{\mu} \cdot (\mathbf{L} - \mathbf{S})}{r^3} + \frac{(\boldsymbol{\mu} \cdot \mathbf{r})(\mathbf{S} \cdot \mathbf{r})}{r^5} + \frac{8\pi}{3} \delta(\mathbf{r}) \boldsymbol{\mu} \cdot \mathbf{S} \right], \tag{2.13}$$

where $\boldsymbol{\mu} = \gamma \hbar \mathbf{I}$. The last term is only relevant for s orbitals. The above references show how to express Eq. (2.13) in terms of $U^{(1)}$ and $W^{(12)1}$ tensor operators acting on the electronic states, coupled with tensor operators for the spin states.

Chapter 3

Energy level examples

In this Chapter we illustrate the application of the crystal-field Hamiltonian, Eqs. (2.7, 2.9). We assume that the reader is familiar with basic concepts of quantum mechanics, eigenvalues, eigenvectors, and so on.

3.1 Ce^{3+}: $4f^1 + 5d^1$

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Appendix B gives $SLJM$ matrix elements for $4f^1$ and $5d^1$. The f^1 configuration contains $^2F_{5/2}$ and $^2F_{7/2}$ multiplets and the d^1 configuration contains $^2D_{3/2}$ and $^2D_{5/2}$ multiplets. Recall that in spectroscopic notation the multiplicity superscript is $2S + 1$, so $^2F_{5/2}$ represents $S = 1/2$, $L = 3$, $J = 5/2$. The $4f^1$ configuration of Ce^{3+} is the left-most entry in Fig. 2.1.

3.1.1 Matrix elements and angular-momentum theory

Appendix A introduces the use of the Wigner-Eckart theorem to calculate matrix elements. There you will find an exercise to calculate the matrix elements of the tensor operator $C_0^{(2)}$ for the d^1 configuration from the reduced matrix elements of $C^{(2)}$ and check them against Appendix B. However, you can press on with energy-level calculations without completing that exercise.

3.1.2 Atomic (free-ion) energies

The atomic energies for Ce^{3+} (Ce IV in Atomic Spectroscopy Notation) are available at NIST (`http://physics.nist.gov`) and [20]. The energies are given in Table 3.1.

Use the matrix elements of the `ZETAFF` and `ZETADD` operators to work out the ζ_f and ζ_d parameters and the difference between the average energies of the two configurations.

Partial solution

From Section B.1 the matrix elements of the spin-orbit interaction for $^2F_{5/2}$ and $^2F_{7/2}$ are -2 and $+1.5$ respectively, so the splitting of 2253 cm^{-1} is $3.5\zeta_f$ and therefore $\zeta_f = 644$ cm^{-1}.

Table 3.1: Energies for $4f^1 + 5d^1$ configurations of gaseous Ce^{3+}.

Multiplet	Energy (cm^{-1})
$^2F_{5/2}$	0
$^2F_{7/2}$	2253
$^2D_{3/2}$	49737
$^2D_{5/2}$	52226

3.1.3 Zeeman calculation exercise

We can apply a magnetic field along the Z axis by using the matrix elements of the `MAG10` ($\mathrm{M}_0^{(1)}$) operator. For parameters in cm^{-1} a 1T field corresponds to a parameter value of 0.466860.

Calculate the splitting of the f^1 and d^1 configurations under a 1T magnetic field.

Partial solution

From Section B.2 we may obtain the matrix elements of the magnetic dipole operator $M_0^{(1)}$ (`MAG10`) appropriate for a field along Z (see Eq. A.10). (Note that the tabulated matrix elements do not include physical constants, they are just $L+2S$.) For the ${}^2F_{5/2}$ multiplet, the matrix elements for $M_J = 5/2,\ 3/2,\ 1/2,\ -1/2,\ -3/2,\ -5/2$ are respectively 2.14, 1.29, 0.43, −0.43, −1.29, −2.14. Multiplying these by 0.466860 we obtain an even splitting between each state of 0.4 cm^{-1}.

3.2 Crystal-field calculations

The crystal-field Hamiltonian was introduced in Section 2.2:

$$H_{\mathrm{CF}} = \sum B_q^k C_q^{(k)}. \tag{3.1}$$

The values of k and q are determined by symmetry.

3.2.1 Axial crystal-field exercise

1. Use the spin-orbit parameters calculated above and add a crystal-field with $B_0^4(f) = 500\mathrm{cm}^{-1}$ for the $4f^1$ configuration and $B_0^4(d) = 20000\mathrm{cm}^{-1}$ for the $5d^1$ configuration.
2. Use the spin-orbit parameters calculated above and add a crystal-field with $B_0^2(f) = 500\mathrm{cm}^{-1}$ for the $4f^1$ configuration and $B_0^2(d) = 20000\mathrm{cm}^{-1}$ for the $5d^1$ configuration.

Partial solution

The matrix elements of $C_0^{(2)}$ are diagonal in M. For the $J = 5/2$ multiplet the matrix elements are:

$$0.2286, \qquad 0.0571, \qquad -0.2857$$

for

$$M = \pm 1/2, \qquad \pm 3/2, \qquad \pm 5/2,$$

repectively. Multiplying by $B_0^2(f) = 500\mathrm{cm}^{-1}$ and setting the lowest energy to zero gives:

$$257, \qquad 171, \qquad 0\ \mathrm{cm}^{-1}.$$

Note that these axial fields do not give an even splitting of the multiplets (in contrast to a magnetic field). The $B_0^{(2)}$ parameters represent a quadrupolar potential, as opposed to the magnetic dipole.

3.2.2 Octahedral crystal-field exercise

These calculations are not really practical by hand. You will probably want to use a computer package such as Matlab, Maple, or Mathematica to calculate eigenvalues and eigenvectors.

For octahedral symmetry we can write the crystal field for the $5d^1$ configuration as

$$H_{\mathrm{CF}}(d) = B^4 \left[C_0^{(4)} + \sqrt{\frac{5}{14}} \left(C_4^{(4)} + C_{-4}^{(4)} \right) \right]. \tag{3.2}$$

(Note that you do not need the matrix elements of $C_{-4}^{(4)}$ because you can use the requirement that the Hamiltonian has to be Hermitian.)

Use this, and the spin-orbit interaction, to try to reproduce the splitting observed by van Pieterson and co-workers for Ce^{3+} in cubic sites in CaF_2 ([21], Fig. 2). Note that you can start by ignoring the spin-orbit interaction and add it later.

3.3 Hyperfine exercise

Consider the axial crystal-field exercise from above. If we consider a (fictitious) Ce nuclear spin of $I = 1/2$ (relevant to Yb) then the hyperfine matrices for the $M = \pm 5/2$ and $M = \pm 3/2$ states are diagonal. For M, I_M

$$-M, -1/2, \qquad -M, +1/2, \qquad +M, -1/2, \qquad +M, +1/2,$$

the diagonal elements have signs

$$+, \qquad -, \qquad -, \qquad +,$$

This can be understood by realising that we are dealing with matrix elements of $J_z I_z$. So for these cases the splitting is straightforward.

For $M = \pm 1/2$ the situation is a little more interesting. In this case there are off-diagonal elements arising from $J_{+1}^{(1)} I_{-1}^{(1)}$ and $J_{-1}^{(1)} I_{+1}^{(1)}$ terms in the Hamiltonian and if we write the states in the order M, I_M

$$-1/2, -1/2, \qquad -1/2, +1/2, \qquad +1/2, -1/2, \qquad +1/2, +1/2$$

we have a matrix proportional to:

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 12 & 0 \\ 0 & 12 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \tag{3.3}$$

The $\pm 1/2, \pm 1/2$ states are unmixed, with energies proportional to 1, but the $\pm 1/2, \mp 1/2$ states mix, giving energies proportional to -1 ± 6.

3.4 Superposition-model exercise

Cubic sites in CaF_2 have 8 equidistant ligands on the corners of a cube. Use the superposition model (Eq. 2.10) to show that the B^4 parameter in Eq. (3.2) should be *negative* in this case and that the B_0^2 parameters are zero.

Now consider the case of a six-fold octahedral coordination, with the ligands on the X, Y, and Z axes. Show that in this case B^4 should be *positive*.

Recall that in Cartesian form we have (Weissbluth [4] Table 1.1):

$$\begin{aligned} C_0^{(2)}(x,y,z) &= \frac{1}{r^2}\sqrt{\frac{1}{4}}(3z^2 - r^2), & (3.4)\\ C_0^{(4)}(x,y,z) &= \frac{1}{r^4}\sqrt{\frac{1}{64}}(35z^4 - 30z^2r^2 + 3r^4), & (3.5)\\ C_{\pm4}^{(4)}(x,y,z) &= \frac{1}{r^4}\sqrt{\frac{35}{128}}(x \pm iy)^4. & (3.6) \end{aligned}$$

3.5 $4f^2$ and $4f^{12}$ atomic calculations

If we are just interested in atomic calculations, or spectra of lanthanide ions in solutions or glasses then we can just work with an atomic Hamiltonian. In this exercise we do calculations for Pr^{3+} ($4f^2$) and Tm^{3+} ($4f^{12}$) to give you some feeling for these calculations.

3.5.1 Hamiltonian

For this exercise we use a simplified Hamiltonian from Section 2.2, omitting correlation effects:

$$H = F^2 f_2 + F^4 f_4 + F^6 f_6 + \zeta A_{\mathrm{so}}. \tag{3.7}$$

The Slater (F^k) parameters represent the Coulomb repulsion between the electrons and the parameter ζ represents the spin-orbit interaction. The full Hamiltonian adds corrections to these effects, but you can understand the structure using this simple Hamiltonian.

Matrix elements for the operators are provided in Appendix C. Note that for f^{12} the signs of the matrix elements of A_{so} must be changed. In this case we can think of the configuration as two positively charged f "holes", rather than two f electrons.

3.5.2 Pr^{3+}

Pr^{3+} has a $4f^2$ configuration.

1. First calculate the energies using these parameters:

$$F^2 = 68878, \qquad F^4 = 50347, \qquad F^6 = 32901. \tag{3.8}$$

2. Now use perturbation theory to add

$$\zeta = 751.7. \tag{3.9}$$

3. Now diagonalize the matrices explicitly.

Check your calculations against published energy levels, e.g. the Dieke-Carnall diagram, Fig. 2.1.

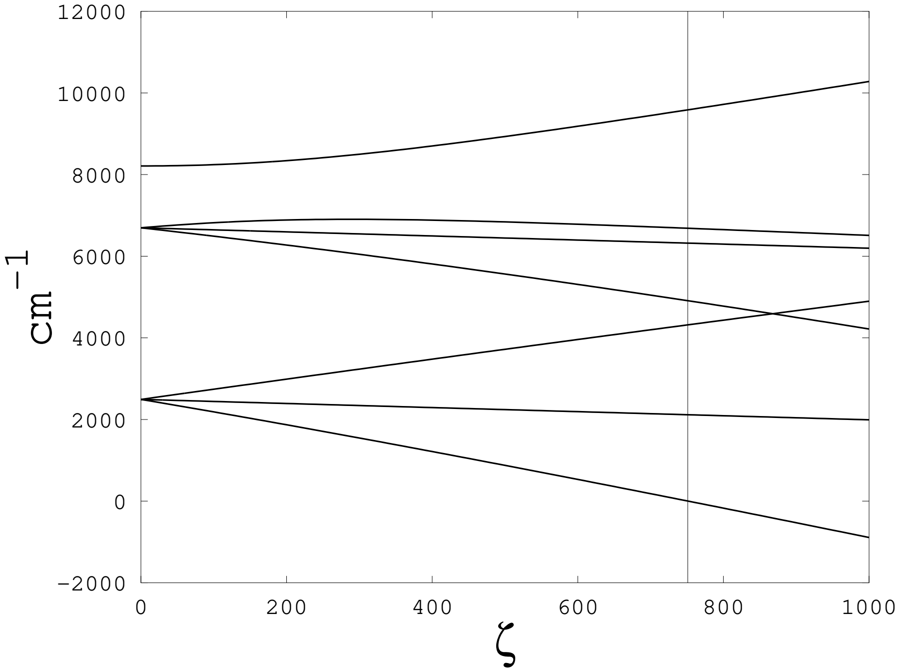

Figure 3.1: Calculation for Pr^{3+} adding the spin-orbit interaction to the Coulomb interaction. The plot shows how the lowest three terms, ${}^3H_J$, ${}^3F_J$, ${}^1G_4$, split as ζ is increased from 0 to 1000 cm^{-1}. The vertical line is at $\zeta = 751.7\mathrm{cm}^{-1}$.

Partial solution

If we ignore the spin-orbit interaction, all states with the same S and L have the same energy. The lowest three are:

$$\begin{aligned}
E({}^3H_J) &= -0.0906F^2 - 0.0328F^4 + 0.0162F^6 = -7359\ \mathrm{cm}^{-1}, && (3.10)\\
E({}^3F_J) &= -0.0239F^2 - 0.0163F^4 - 0.0209F^6 = -3155\ \mathrm{cm}^{-1}, && (3.11)\\
E({}^1G_4) &= -0.1128F^2 + 0.1031F^4 + 0.0285F^6 = -1641\ \mathrm{cm}^{-1}. && (3.12)
\end{aligned}$$

If we choose the energy of the ${}^3H_J$ multiplet to be zero we have energies 0, 4203, 5718 cm^{-1}.

This is the splitting shown on the left hand edge of Fig. 3.1, with ζ set to zero.

If we now consider only the lowest multiplet, ${}^3H_J$, and consider only the diagonal matrix elements of the spin-orbit interaction we have:

$$\begin{aligned}
E({}^3H_4) &= -3.0\zeta = -2255\ \mathrm{cm}^{-1}, && (3.13)\\
E({}^3H_5) &= -0.5\zeta = -375\ \mathrm{cm}^{-1}, && (3.14)\\
E({}^3H_6) &= +2.5\zeta = 1879\ \mathrm{cm}^{-1}. && (3.15)
\end{aligned}$$

Again, setting the energy of the ground state to zero gives energies of 0, 1879, 4134 cm^{-1}. This is not very accurate because there are off-diagonal interactions between ${}^3H_4$ and ${}^3F_J$ and ${}^1G_4$ that push down the energy ${}^3H_4$ relative to ${}^3H_5$ and ${}^3H_6$.

Figure 3.1 shows how the lowest three multiplets split as ζ is increased from 0 to 1000 cm^{-1}. The curvature of the lines is a clue to how important the off-diagonal matrix elements are.

3.5.3 Tm^{3+}

Tm^{3+} has a $4f^{12}$ configuration.

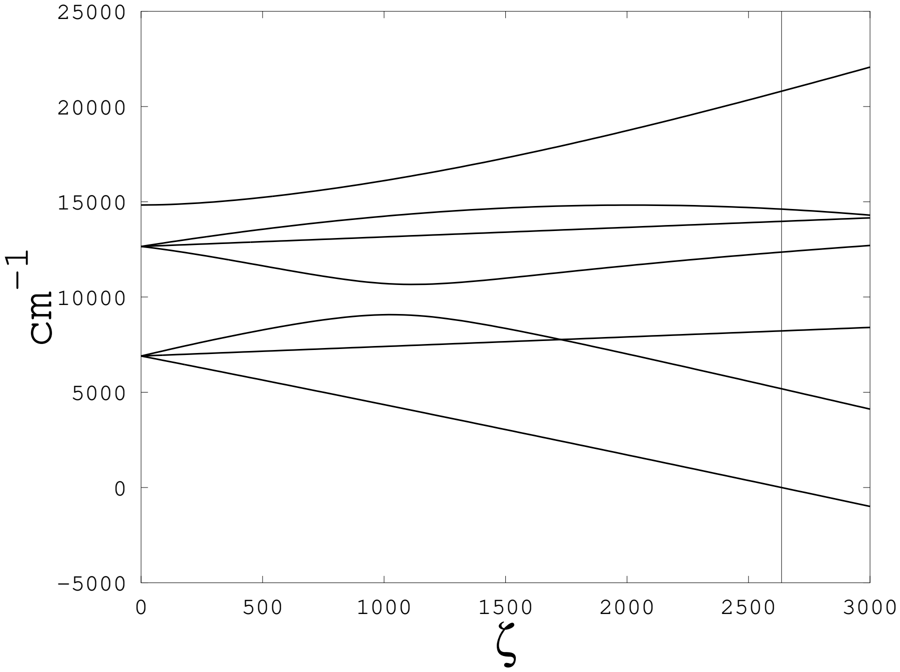

Figure 3.2: Calculation for Tm^{3+} adding the spin-orbit interaction to the Coulomb interaction. The plot shows how the lowest three terms, ${}^3H_J$, ${}^3F_J$, ${}^1G_4$, split as ζ is increased from 0 to 3000 cm^{-1}. The vertical line is at $\zeta = 2636\mathrm{cm}^{-1}$.

1. First calculate the energies using these parameters:

$$F^2 = 100134, \qquad F^4 = 69613, \qquad F^6 = 55975. \tag{3.16}$$

2. Now use perturbation theory to add

$$\zeta = 2636. \tag{3.17}$$

3. Now diagonalize the matrices explicitly.

Check your calculations against published energy levels.

Partial solution

See Figure 3.2 for a plot of the calculation. The sign of the spin-orbit interaction changes for f^{12} relative to f^2 (we can think of it as two positively-charged holes in the f-shell). This means that in this case the ground state is ${}^3H_6$. As ζ is increased from 0 to 2636 cm^{-1} the ${}^3H_4$ state "bounces" off the ${}^3F_4$, and an analysis of the states shows that the first excited multiplet is predominantly ${}^3F_4$ at $\zeta = 2636$ cm^{-1}. Though the levels do not cross, the eigenvectors "switch over".

Chapter 4

Transition Intensities

The relevant equations for oscillator strengths and Einstein coefficients are given in my Chapter 2 of Liu and Jacquier [1]. Here I reproduce parts of that Chapter, but for full details on Judd-Ofelt theory I refer the reader to there, or to the original references.

For many applications not only the energies, but also the intensities of the optical transitions, are of crucial importance. A range of optical processes are relevant to lanthanide spectroscopy, the most obvious being one-photon transitions within the $4f^N$ configuration. However, other processes are also of interest. These include two-photon transitions (two-photon absorption, Raman scattering and second-harmonic generation), circular dichroism, and transitions outside of the $4f^N$ configuration. In the latter case there is the possibility of exciting a $4f$ electron into a $5d$ orbital, or exciting a ligand electron into a $4f$ orbital, a charge-transfer transition.

The modeling of transition probabilities within the $4f^N$ configuration dates back to Judd [22] and Ofelt [23]. Early work concentrated on total intensities between J multiplets. However, transitions between crystal-field levels were examined soon after by [24], who also did the first calculations for two-photon processes [25]. Electric-dipole transitions within the $4f^N$ configuration are forbidden in the absence of an odd-parity interaction with the crystal. The original papers considered only the mixing of atomic configurations by the crystal field but subsequent work, summarized by [26], demonstrated that excitations involving ligand states (dynamic polarization and charge transfer) were also important. Significant progress in both understanding the underlying mechanisms and phenomenological modeling of the transitions has been made over the last two decades, for both one-photon [27, 28, 29] and two-photon transitions [30, 31].

In this Chapter we provide an overview of available methods for modeling one-photon transition intensities within the $4f^N$ configuration. We also discuss the calculation of transition intensities between the $4f^N$ and $4f^{N-1}5d$ configurations.

Note that the equations presented here use SI units. Many papers and books use Gaussian units, and failing to realise this can lead to considerable confusion.

4.1 Basic equations

Spectroscopic experiments measure observables such as absorption cross sections, branching ratios, and radiative lifetimes. These observables may, in principle, be calculated from squares of matrix elements of electric-dipole, magnetic-dipole, and higher-order operators. It is the purpose of this section to show how the matrix elements are related to the observable quantities. The following sections will consider the matrix elements in more detail. A more detailed discussion of the basic principles may be found in, for example, [4, 32, 6].

4.1.1 Electric and magnetic dipole operators

The electric dipole operator is

$$-eD_q^{(1)} = -erC_q^{(1)}, \tag{4.1}$$

and the magnetic dipole operator

$$M_q^{(1)} = \frac{-e\hbar}{2mc}\left(L_q^{(1)} + 2S_q^{(1)}\right). \tag{4.2}$$

In these equations $C_q^{(1)}$ is a spherical tensor operator. The other operators and physical constants have their usual meanings. We consider only electric dipole and magnetic dipole transitions in what follows. Electric quadrupole contributions to the transition intensities are also possible [33] but are usually too small to be important.

The starting point for our calculations is the line strength (or dipole strength). The electric dipole line strength for a transition between initial and final states I and F with polarization q ($q = 0, \pm1$) is defined to be

$$S_{FI,q}^{\mathrm{ED}} = \sum_i \sum_f e^2 \left|\langle Ff|D_q^{(1)}|Ii\rangle\right|^2, \tag{4.3}$$

and the magnetic dipole line strength is defined to be

$$S_{FI,q}^{\mathrm{MD}} = \sum_i \sum_f \left|\langle Ff|M_q^{(1)}|Ii\rangle\right|^2. \tag{4.4}$$

In these equations the sums are over the components of the initial and final states.

For linearly polarized light there is no interference between electric dipole and magnetic dipole moments, so the observables may be evaluated by adding the contributions from electric and magnetic dipole strengths. However, for circularly polarized light interference is possible, leading to circular dichroism (see Section 2.3.6 of Liu and Jacquier [1] and Ref. [34]).

To obtain observables such as oscillator strengths, Einstein coefficients, or lifetimes it is necessary to multiply the line strengths by appropriate constants and average over the possible initial state components by dividing by the degeneracy of the initial state, g_I. If initial states of different energy could be occupied then the appropriate Boltzmann factors must also be included.

Most of the expressions we give here are for polarized light. However, the quantity of interest is sometimes an average over all possible polarizations, and in those cases the expressions must be summed over the q components and divide by 3, as discussed in the following Section.

Observables measured in absorption are directly related to oscillator strengths. The electric dipole and magnetic dipole oscillator strengths are defined as

$$f_{FI,q}^{\mathrm{ED}} = \frac{2m\omega}{\hbar e^2}\frac{\chi_{\mathrm{L}}}{n}\frac{1}{g_I}S_{FI,q}^{\mathrm{ED}}, \tag{4.5}$$

and

$$f_{FI,q}^{\mathrm{MD}} = \frac{2m\omega}{\hbar e^2} n \frac{1}{g_I}S_{FI,q}^{\mathrm{MD}}. \tag{4.6}$$

The absorption cross section is related to the oscillator strength by:

$$\sigma_{FI,q}^{\mathrm{ED/MD}} = \frac{\pi e^2}{2\epsilon_0 mc} f_{FI,q}^{\mathrm{ED/MD}}. \tag{4.7}$$

The refractive index n appears in eqs. (4.5) and (4.6) because the electric and magnetic fields have values in the medium different from their values in free space. The bulk correction factors are supplemented by a local correction to the electric field, χ_{L}, to account for the fact that the ion is less polarizable than the bulk medium. This local electric field correction is usually taken to be

$$\chi_{\mathrm{L}} = \left(\frac{n^2+2}{3}\right)^2 . \tag{4.8}$$

This equation is only strictly correct for high-symmetry sites [6]. It is common to define a χ that is a product of our χ_{L} (4.8) and the bulk refractive index correction $1/n$ (e.g. [35]). Since the exact form of the local correction has a much more tenuous justification than the bulk correction it seems appropriate to keep them separate.

For spontaneous emission the observable quantities are related to the spontaneous emission rates, i.e. the Einstein A coefficients. The electric dipole and magnetic dipole contributions to the A coefficients for a single polarization are given by

$$A^{\mathrm{ED}}_{FI,q} = \frac{1}{4\pi\epsilon_0}\frac{4\omega^3}{\hbar c^3} n\chi_{\mathrm{L}} \frac{1}{g_I} S^{\mathrm{ED}}_{FI,q} \tag{4.9}$$

and

$$A^{\mathrm{MD}}_{FI,q} = \frac{1}{4\pi\epsilon_0}\frac{4\omega^3}{\hbar c^3} n^3 \frac{1}{g_I} S^{\mathrm{MD}}_{FI,q}. \tag{4.10}$$

The sum of the A coefficients, averaged over all polarizations, is the inverse of the radiative lifetime, i.e.

$$\frac{1}{\tau_{\mathrm{radiative}}} = \frac{1}{3}\sum_{Fq}\left(A^{\mathrm{ED}}_{FI,q} + A^{\mathrm{MD}}_{FI,q}\right) . \tag{4.11}$$

4.1.2 Polarization selection rules

Polarized light is often used to obtain detailed information about optical transitions. Equations (4.3–4.4), which are in a spherical basis ($q = 0, \pm 1$), may be used to calculate dipole strengths for the polarizations of interest.

In cases where the lanthanide ion sites are randomly oriented (as in a powder or solution) or embedded in a cubic crystal (for example, $\mathrm{CaF_2}$, $\mathrm{Cs_2NaYCl_6}$, or many garnets) and the light is unpolarized or linearly polarized the physical observables are proportional to an average over the polarization components and the isotropic dipole strength is defined as

$$\bar{S}^{\mathrm{ED}}_{FI} = \frac{1}{3}\sum_{q} S^{\mathrm{ED}}_{FI,q}. \tag{4.12}$$

For polarized light and oriented crystals the situation is more complex. General expressions may be derived by transforming from a spherical ($0, \pm 1$) basis to a Cartesian (x, y, z) basis. The electric dipole moment has odd parity, so the transformation involves the odd parity irreducible representation (irrep) 1^- of the group O_3, which contains rotation, reflection, and inversion operators. The spherical tensor operators in Eq. (4.1) transforming as 1^- may be written as combinations of x, y, and z as follows:

$$C^{(1)}_0 = z/r, \qquad C^{(1)}_{\pm 1} = \mp\frac{1}{\sqrt{2}}(x \pm iy)/r. \tag{4.13}$$

The magnetic dipole operator has even parity and therefore transforms as the irrep 1^+ of O_3. The decomposition in terms of Cartesian coordinates is

$$\begin{aligned} M^{(1)}_0 &= \frac{-e\hbar}{2mc}\left(L_z + 2S_z\right), \\ M^{(1)}_{\pm 1} &= \frac{-e\hbar}{2mc}\left(\mp(L_x \pm iL_y) \mp 2(S_x \pm iS_y)\right), \end{aligned} \tag{4.14}$$

In the following discussion we generally restrict ourselves to the case of unpolarized radiation or uniaxial crystal systems (i.e. crystals containing sites with parallel axes of at least three-fold symmetry). The traditional experimental arrangements are orthoaxial (propagation vector perpendicular to the high symmetry axis) and axial (propagation vector parallel to the axis). For very low symmetry sites (such as C_1, C_2 or C_s) the polarization properties are not completely characterized by measurements with polarization vectors along the X, Y, and Z axes, and measurements at intermediate angles would be necessary to extract maximum information [36, 37]. However, crystals that have such low symmetries generally have sites of several different orientations with respect to the bulk crystal axes and so detailed polarization measurements would not be straightforward.

We begin with the case of an orthoaxial measurement using linearly polarized light with the electric field along the Z axis (π polarization). Equation (4.13) indicates that the expression for the electric dipole line strength is given by the spherical expression (4.3) with $q = 0$, i.e.

$$S^{\mathrm{ED}}_{FI,\pi} = S^{\mathrm{ED}}_{FI,0}. \tag{4.15}$$

The magnetic field of the radiation is perpendicular to the electric field, so for π polarization it is in the x-y plane. Without loss of generality we may choose the magnetic field to be along the x axis. Then, from equation (4.14), an expression containing the square moduli of the matrix elements of the operator $\left(-M^{(1)}_1 + M^{(1)}_{-1}\right)/\sqrt{2}$ may be derived. The cross terms cancel to obtain

$$S^{\mathrm{MD}}_{FI,\pi} = \frac{1}{2}\left(S^{\mathrm{MD}}_{FI,1} + S^{\mathrm{MD}}_{FI,-1}\right). \tag{4.16}$$

For linearly polarized light with the electric field perpendicular to the z axis (σ polarization) the electric dipole strength is

$$S^{\mathrm{ED}}_{FI,\sigma} = \frac{1}{2}\left(S^{\mathrm{ED}}_{FI,1} + S^{\mathrm{ED}}_{FI,-1}\right), \tag{4.17}$$

$$S^{\mathrm{MD}}_{FI,\sigma}, = S^{\mathrm{MD}}_{FI,0}. \tag{4.18}$$

For axial spectra the polarization is irrelevant (as long as it is linear) and the dipole strengths are

$$S^{\mathrm{ED}}_{FI,\mathrm{axial}} = S^{\mathrm{ED}}_{FI,\sigma}, \tag{4.19}$$

$$S^{\mathrm{MD}}_{FI,\mathrm{axial}} = S^{\mathrm{MD}}_{FI,\pi}. \tag{4.20}$$

Circularly polarized measurements are generally performed on isotropic samples or in an axial configuration so that the dichroism of the bulk medium does not obscure the circular dichroism (CD) of the lanthanide sites. In the convention used by most chemists (where the incoming radiation is presumed to be viewed from the sample) the $q = \pm 1$ components of the dipole moment operators correspond to the absorption of left and right circular polarization [32]. Most physicists use the opposite convention [6].

Derivations of the selection rules for optical transitions may be found in many references [8, 9, 32, 6, 37, 27]. For uniaxial crystals the operators corresponding to π and σ polarization transform as different irreps of the point group of the site. The transformation properties may be determined from appropriate tables [38, 39, 40]. For example, the transition will be electric dipole allowed if the product of the irrep of the initial state with the irrep of the dipole-moment operator, $\Gamma_I \times \Gamma^{\mathrm{ED}}_T$, contains the complex conjugate of the final-state irrep Γ^*_F. The polarization T may be σ or π in the examples considered here. Recall that the *odd-parity* irrep 1^- of O_3 is required for the case of the electric-dipole operator and the *even-parity* irrep 1^+ of O_3 for the case of the magnetic-dipole operator (equations 4.13 and 4.14). In addition, it is necessary to take into account that the electric and magnetic fields of the radiation are perpendicular. An example illustrating this is given in Section 2.3.7.2 of Ref. [1].

4.1.3 Vibronic transitions

The initial and final states that appear in the matrix elements discussed above need not be pure electronic states, but may be combinations of electronic and vibrational (vibronic) states. If the vibrational part of the wavefunction does not change during the transition then it may be ignored. However, if it does change then it is necessary to use wavefunctions that include both electronic and vibrational parts. In the following discussion we consider, for clarity, a single vibrational mode, labeled by frequency ν. The initial and final states, with vibrational quantum numbers n_i and n_f, are now written as

$$|Ii, \nu n_I\rangle, \qquad |Ff, \nu n_F\rangle. \tag{4.21}$$

There are two extreme cases of interest. The first case applies to transitions within the $4f^N$ configuration. In this case the coupling to the lattice is small and, most importantly, the coupling is almost identical for the initial and final states. In this case vibronic transitions are weak, and generally only become important for centrosymmetric systems, where purely electronic electric-dipole transitions are forbidden. Transitions where there is a change of more than one vibrational quantum number are rare. The other case applies to transitions between the $4f^N$ configuration and the $4f^{N-1}5d$ configuration or charge-transfer states. In this case the coupling to the lattice is very different for the initial and final states and transitions may involve a change of several quanta of vibration. For details the reader is referred to Section 2.2.3 of Ref. [1] and other references, such as [41, 42].

4.2 Allowed electric and magnetic dipole transitions

For magnetic-dipole transitions within the $4f^N$ configuration and electric-dipole transitions between the $4f^N$ and $4f^{N-1}5d$ configurations it is relatively easy to apply the equations given above. For transitions between the $4f^N$ and $4f^{N-1}5d$ configurations there is considerable vibronic broadening. In many cases it is adequate to represent this by a Gaussian function, though more sophisticated approaches are also possible [41, 42].

4.3 One photon transitions within the $4f^N$ configuration

Now that we have discussed the general principles, we can consider some specific cases. We begin with one-photon transitions within the $4f^N$ configuration. As in the case of crystal-field splittings, fully reliable ab-initio calculations are at present not possible for ED transitions so we rely on parametrization schemes. This makes use of the concept of effective operators and perturbation theory. Chapter 2 of Liu and Jacquier [1], and references therein, covers the details. Here I will simply give the basic equations and make some remarks.

4.3.1 General theory

Since the electric-dipole moment vanishes between pure $4f^N$ states, instead of the dipole moment operator $D_q^{(1)}$ an *effective* dipole moment operator is required. This may be derived from a perturbation expansion for a general effective operator, Eq. (2.5):

$$D_{\mathrm{eff},q} = D_q^{(1)} + D_q^{(1)} \sum_{\beta \notin \mathrm{M}} \frac{|\beta\rangle\langle\beta| V}{E_0 - E_\beta^{(0)}} + \sum_{\beta \notin \mathrm{M}} \frac{V|\beta\rangle\langle\beta|}{E_0 - E_\beta^{(0)}} D_q^{(1)} + \dots \tag{4.22}$$

In this equation the $|\beta\rangle$ are excited states on the lanthanide *or* ligand. This operator is evaluated within the $4f^N$ space. Hence the first-order term, $D_q^{(1)}$, vanishes because this odd-parity operator cannot connect states of the same parity.

As discussed in Appendix A of Liu and Jacquier [1] and Ref. [13], the denominators in the two summations in equation (4.22) are equal term by term and the effective operator is Hermitian. The time-reversal plus Hermiticity symmetry argument that restricts the one-electron phenomenological crystal field to even rank operators (see, for example, Chapter 1 of [1] and Ref. [16]) may be applied to our effective dipole-moment operator, and only even-rank operators are required to parametrize the one-electron, spin-independent, part of the effective dipole-moment operator. Since they are one-electron operators for the $4f^N$ configuration, with $l = 3$ the rank of the effective operators is restricted to be less than or equal to 6 (see Appendix A).

4.3.2 Transitions between crystal-field levels

The original papers of Judd [22] and Ofelt [23], made use of the perturbation theory expansion (4.22). An adaption of their parametrization by Reid and Richardson [43, 44] is now in common use. In the notation of Reid and Richardson the effective electric dipole moment operator is written as

$$D_{\mathrm{eff},q} = \sum_{\lambda,t,p} A_{tp}^{\lambda} U_{p+q}^{(\lambda)} (-1)^q \langle \lambda(p+q), 1-q|tp\rangle, \tag{4.23}$$

with $\lambda = 2, 4, 6$, $t = \lambda - 1$, λ, $\lambda + 1$ and p restricted by the site symmetry. From equation (4.22) it is clear that the effective dipole moment arises from coupling the dipole moment operator $D_q^{(1)}$ with the perturbation operator V. Since the perturbation is a scalar of the site symmetry the A_{tp}^{λ} are non-zero only if tp (or linear combinations of tp) transform as the identity irrep of the site symmetry group. Equation (4.23) emphasizes the coupling between the perturbation (transforming as tp), and the dipole moment operator (transforming as $1q$) to give an effective operator (transforming as $\lambda(p+q)$).

Parametrization (4.23) is amenable to analysis by the superposition model, and in the superposition approximation t must be odd. For a discussion of these issues and some ambiguities in the paramterization see Ref. [45] and Chapter 2 of [1].

4.3.3 Transitions between J multiplets

Judd [22] showed that the intensities for total J-multiplet to J-multiplet transitions may be fitted to a three parameter linear model. The standard parameters are now labeled Ω_λ, with $\lambda = 2, 4, 6$ [26, 27]. Consider transitions from an initial multiplet $|\alpha_I J_I\rangle$ to a final multiplet $|\alpha_F J_F\rangle$. If all components of the initial multiplet are assumed to be equally populated then it is possible to average over all polarizations and sum the dipole strength over the M components of the multiplets, and use the orthogonality of the $3j$ symbols to derive an expression for the isotropic dipole strength,

$$\bar{S}^{\mathrm{ED}}_{\alpha_F J_F, \alpha_I J_I} = \frac{1}{3} e^2 \sum_{\lambda} \Omega_\lambda \langle \alpha_F J_F \| \mathbf{U}^{(\lambda)} \| \alpha_I J_I \rangle^2, \tag{4.24}$$

with

$$\Omega_\lambda = \sum_{t,p} \frac{1}{2\lambda+1} \left| A_{tp}^{\lambda} \right|^2. \tag{4.25}$$

Note that the reduced matrix elements in equation (4.24) are "intermediate-coupled", i.e. the eigenvectors of the free-ion Hamiltonian have been calculated (as in Section 3.5), and the matrix elements are taken between these eigenvectors.

A similar expression applies to the magnetic dipole transitions:

$$\bar{S}^{\mathrm{MD}}_{\alpha_F J_F, \alpha_I J_I} = \frac{1}{3} \langle \alpha_F J_F \| \mathbf{M}^{(1)} \| \alpha_I J_I \rangle^2. \tag{4.26}$$

The parametrization (4.24) has the virtue of being linear in the Ω_λ parameters which makes fitting to experimental data quite straightforward. Unfortunately, in forming the sum and reducing the parametrization to just three parameters a considerable amount of information is lost, since each Ω_λ parameter is a combination of A^{λ}_{tp} parameters with $t = \lambda - 1,\ \lambda,\ \lambda + 1$ and vibronic intensity is absorbed into the Ω_λ parametrization. Thus tests of models, such as the superposition model, or detailed comparisons with *ab-initio* calculations are not possible, since the Ω_λ parameters contain many contributions and furthermore are merely magnitudes, with no *sign* information. Also, the assumption that the states of the initial multiplet are evenly populated may not be accurate in some cases. Nevertheless, the relative simplicity of the measurements and calculations have permitted extremely useful analyses of huge amounts of experimental data.

Chapter 5

Intensity Examples

Now we will use the energy levels and eigenstates that you calculated in Part I to calculate transition intensities.

The relevant equations for oscillator strengths and Einstein coefficients are given in Chapter 4.

5.1 Ce^{3+} examples

5.1.1 Atomic calculation exercise

Note that you have the matrix elements of the unit tensors $U_q^{(1)}$ coupling f^1 with d^1. You need to multiply these by the factor $\sqrt{3}$ to convert them to $C_q^{(1)}$ and you need the radial integral of r between $4f$ and $5f$, which is 4.35×10^{-11}m. Also note that our `MAG10` and `MAG11` operators only include $L + 2S$, not the physical constants making up the magnetic dipole operator (Eq. 4.2). The Tables only contain operators with $Q \geq 0$. The others can be obtained by symmetry. Since we will be squaring the matrix elements the possible changes in sign for matrix elements with all of the M quantum numbers negated do not need to be taken into account.

1. Use your previous atomic calculation to calculate the dipole strengths and oscillator strengths of transitions from the ground $4f$ state to the $5d$ states and the lifetime of the lowest $5d$ state.
2. Use your previous atomic calculation to calculate the oscillator strengths of transitions from the ground $4f$ state to highest $4f$ state and the lifetime of the highest $4f$ state.

Partial solutions

From the Tables in Appendix B, we can use Eq. (4.3) to calculate the electric dipole strength between the ground multiplet, ${}^2F_{5/2}$ and ${}^2D_{3/2}$. Since we sum over both multiplets, for each of $q = 0, \pm 1$ this is 1.5×10^{-21} $\mathrm{C^2m^2}$. The angular frequency ω may be calculated from the "energy" in cm^{-1}. We obtain an oscillator strength of 0.04 for the absorption transition and a radiative lifetime of about 10 ns. The sum of the oscillator strengths for all possible transitions is 1 [4], so these are strong transitions. The lifetime is about a factor of 3 higher [46]. This is because we use a Hartree-Fock calculation of the radial integral. Correlation effects reduce the value, as discussed in the reference.

5.1.2 Zeeman calculation exercise

Now apply a magnetic field of 1T along Z. Calculate the oscillator strengths for transitions from the lowest $4f$ state with light polarized along Z and X and the lifetime of the lowest $5d$ state.

Sketch a plot of the polarized spectra.

Table 5.1: Oscillator strengths for transitions from the ground state $^7F_0$ in Eu^{3+} in oxyfluoride glass[47].

Final state	Energy (cm^{-1})	$f \times 10^{-6}$
$^5D_0$	17270	0.01
$^5D_1$	21500	0.07*
$^5D_2$	21500	0.15
$^5D_3$	24080	0.03
$^5L_6$	25350	0.91

* This value is not tabulated. I have estimated it from Figure 12 of [47].

5.1.3 Crystal-field calculations

Now apply a crystal-field with $B(f)^{(2)}_0 = 500\text{cm}^{-1}$ for the $4f^1$ configuration and $B(d)^{(2)}_0 = 20000\text{cm}^{-1}$ for the $5d^1$ configuration. Calculate the oscillator strengths for transitions from the lowest $4f$ state with light polarized along Z and X and the lifetime of the lowest $5d$ state.

Sketch a plot of the polarized spectra.

5.1.4 Hyperfine splitting

Consider the $M = \pm 5/2$ and $M = \pm 3/2$ states considered in Section 3.3 which each split into $\pm M, \mp I_M$ and $\mp M, \pm I_M$ doublets.

Suppose the radition is linearly polarized and propagating perpendicular to the Z axis. The selection rules from the Wigner-Eckart Theorem show that transitions must involve $q = \pm 1$. For electric-dipole transitions this means that the electric vector of the radiation must be perpendicular to Z. However, whereas for magnetic-dipole transitions the *magnetic* vector must be perpendicular to Z, hence the electric vector is parallel to Z.

See Section 4.1.2 for further discussion of polarization selection rules.

5.2 Multiplet-multiplet Judd-Ofelt calculations

I have provided you with the relevant matrix elements for Eu^{3+} and Nd^{3+} in Appendix C.

5.3 Eu^{3+} in oxyfluoride glass

B. Klimesz et al. [47] have measured absorption and emission spectra of several ions in an oxyfluoride glass. We start by considering their measurements on Eu^{3+}.

1. Use the Ω_λ parametrization given in Section 3.5 of the paper to calculate the Ω_λ parameters from the absorption oscillator strengths from the ground state $^7F_0$ to the excited $^5D_0$, $^5D_1$, $^5D_2$, $^5D_3$, $^5L_6$ multiplets. These are given in Table 5.1. Assume a refractive index $n = 1.65$

2. Use the Ω_λ parameters to calculate the A coefficients for emission from $^5D_0$ and $^5D_1$ multiplets to the ^7F_J multiplets and hence calculate the radiative lifetimes. The measured lifetime of $^5D_0$ is 1.7 ms.

5.3.1 Questions

1. For some transitions your calculations give zero intensity. Why do you think this is?
2. Why is the calculated lifetime different from the measured lifetime?

Partial solutions

This calculation is very simple. Since we start from states with $J = 0$, electric-dipole transitions are only allowed to states with $J' = 2, 4, 6$, via matrix elements of $U^{(2)}$, $U^{(4)}$, and $U^{(6)}$ respectively. Therefore, calculating the Ω_λ is very simple. Magnetic-dipole transitions to states with $J' = 1$ are also allowed. Transitions to $J' = 0$ and $J' = 3$ are calculated to be zero in this approximation, and are very small. They arise due to crystal-field mixing between the J-multiplets.

5.4 Nd^{3+} in various hosts

5.4.1 Nd^{3+} in YAG

The paper by W. F. Krupke [48] is a classic. Your aim is to check his calculations using the matrix elements that you have been given.

1. Use your matrix elements to verify Krupke's calculations of oscillator strengths.
2. Use your matrix elements to verify Krupke's calculations of the lifetime of the $^4\mathrm{F}_{3/2}$ state.

5.4.2 Nd^{3+} in polycrystalline $\mathrm{Y}_2\mathrm{O}_3$

D. K. Sardar et al. [49] is a recent paper on a different crystal system.

1. Use your matrix elements to verify the calculations of oscillator strengths.
2. Use your matrix elements to verify the calculations of the lifetime of the $^4\mathrm{F}_{3/2}$ state.

5.4.3 Nd^{3+} in oxyfluoride glass

The paper by Klimesz et al. [47] also has measurements for Nd^{3+}.

1. Use your matrix elements to verify Klimesz's calculations of oscillator strengths.
2. Use your matrix elements to verify Klimesz's calculations of the lifetime of the $^4\mathrm{F}_{3/2}$ state.

5.4.4 Questions

1. Which transitions have very different intensities in different host crystals? Which Judd-Ofelt parameter is most responsible for this difference?
2. Could you adjust the Judd-Ofelt parameters so that there was more radiation emitted at 1.06 μm (which is the common laser transition)?

5.5 Fitting

If you want an extra challenge you could do some fits of the Judd-Ofelt parameters for Nd^3+. This is quite easy with packages such as Matlab, or even a spreadsheet.

Chapter 6

Ab-initio Calculations

The vast majority of energy-level and transition-intensity calculations for $4f^N$ configurations of lanthanide ions make use of the parametrized "crystal-field" Hamiltonian, though there have been some *ab initio* calculations [50, 51].

For $4f^{N-1}5d$ configurations there are various calculations, the most comprehensive is for the $\mathrm{SrCl_2{:}Yb^{2+}}$ system [52, 53].

Unfortunately *ab-initio* calculations such as in Refs. [52, 53] do not give parameters that can be compared to the parametrized models. Though it is possible to fit the effective Hamiltonian parameters to calculated energy levels, as in [54], it is desirable to have a more robust method.

We have shown that that it is possible to construct an effective Hamiltonian matrix from *ab initio* calculations [55, 56, 57], and hence determine crystal-field and other parameters by a straightforward projection technique. However, that work was on systems with a single valence electron. In systems with more than one valence electron, the labelling of the states in terms of the states used in the effective Hamiltonian approach is not straightforward.

Crystal-field parameters for $5d$ states are quite well estimated by these methods, as demonstrated in Table 6.1.

Table 6.1: Crystal-field parameters for the $5d^1$ configuration of $\mathrm{Ce^{3+}}$ in $\mathrm{LiYF_4}$. Units are $\mathrm{cm^{-1}}$. From Ref. [57].

Parameter	Experiment	Theory
B^2_0	4673	4075
B^4_0	-18649	-14296
B^4_4	-23871	-25162

Appendix A

Angular Momentum

Many calculations rely on the use of angular-momentum theory and group theory. There are a number of books available that give a complete introduction to angular-momentum calculations [7, 8, 4, 5]. Here I present an abbreviated and modified version of my Appendix B of the Liu and Jacquier [1].

A.1 Angular momentum states and operators

The essential concepts of angular momentum in quantum mechanics may be derived from considering basic angular momentum operators, their eigenstates and their commutators. We begin with the general angular-momentum operators J_x, J_y, and J_z, with well-known commutation relations

$$[J_x, J_y] = iJ_z, \tag{A.1}$$

and cyclic permutations (we have set $\hbar = 1$). The operator $\mathbf{J}^2 \equiv J_x^2 + J_y^2 + J_z^2$ commutes with each of the J_x, J_y, and J_z operators and it is traditional to use the simultaneous eigenstates of $\mathbf{J}^2$ and J_z^2 as basis functions in atomic calculations. These basis states are labeled $|jm\rangle$ and have the following properties:

$$\begin{aligned} J_z|jm\rangle &= m|jm\rangle, & \text{(A.2)}\\ \mathbf{J}^2|jm\rangle &= j(j+1)|jm\rangle, & \text{(A.3)}\\ D(R)|jm\rangle &= \sum_{m'} D^{(j)}_{m'm}|jm'\rangle, & \text{(A.4)} \end{aligned}$$

where the last equation describes the behavior of the states under the rotation R, with $D(R)$ being the quantum-mechanical operator and $D^{(j)}_{m'm}$ the rotation matrix for a particular j.

A.2 Clebsh-Gordan coefficients and $3j$ symbols

The coupling of angular momenta is the key concept that we require for any serious calculation. We may be coupling spin and orbital angular momentum, or the angular momenta of two electrons. In any case, the idea is to create a linear combination of angular-momentum states that behave as an angular-momentum state, as defined by equations (A.2–A.4). This is accomplished by the Clebsh-Gordan coefficients (sometimes called coupling coefficients) defined by

$$|jm\rangle = \sum_{m_1,m_2} |j_1m_1\rangle|j_2m_2\rangle\langle j_1m_1, j_2m_2|jm\rangle. \tag{A.5}$$

It is often convenient to use the more symmetrical $3j$ symbol, defined by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3}\frac{1}{\sqrt{2j_3+1}}\langle j_1m_1, j_2m_2|j_3{-}m_3\rangle. \tag{A.6}$$

In the derivation of selection rules the properties of the $3j$ symbols play a key role. The $3j$ symbol is zero unless $m_1 + m_2 + m_3 = 0$, $|m_1| < j_1$, $|m_2| < j_2$, $|m_3| < j_3$, and j_1, j_2 and j_3 form a triangle ($|j_1 - j_2| \leq j_3 \leq j_1 + j_2$).

A.3 Tensor operators and the Wigner-Eckart theorem

Tensor operators have angular-momentum quantum numbers, just like angular-momentum states. A tensor operator $T_q^{(k)}$ may be defined by its commutation relations, such as

$$[J_z, T_q^{(k)}] = qT_q^{(k)}, \tag{A.7}$$

or by its behavior under rotations

$$D(R)T_q^{(k)}D(R)^\dagger = \sum_{q'} D_{q'q}^{(j)} T_{q'}^{(k)}. \tag{A.8}$$

The latter equation, in particular, emphasizes that the transformation properties of tensor operators and state kets are intimately related.

The matrix elements of tensor operators may be written in terms of the $3j$ symbols as

$$\langle \alpha JM | T_q^{(k)} | \alpha' J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle \alpha J || T^{(k)} || \alpha' J' \rangle. \tag{A.9}$$

The final braket on the right hand side is known as a *reduced matrix element.* The key concept of the Wigner-Eckart theorem is that the “angular dependence” on the M quantum numbers is decoupled from the “physical” dependence of the reduced matrix element.

The properties of the $3j$ symbols discussed in the previous section give important selection rules on these matrix elements. For example, one-electron operators within the $4f^N$ configuration must have $k \leq 6$.

Exercise

The reduced matrix element for the $C^{(2)}$ operator in the ${}^2D_{3/2}$ multiplet of d^1 is $\langle {}^2D_{3/2} || C^{(2)} || {}^2D_{3/2} \rangle = -0.89443$. Use Eq. A.9 to calculate the matrix elements of $C_0^{(2)}$ and check them against the tables in Section B.2.

Note that you can calculate 3j symbols easily online using Wolfram Alpha:
`http://www.wolframalpha.com`. Search for: “3j symbol”:
`http://www.wolframalpha.com/input/?i=3j+symbol`.

A.4 More complex situations

The calculations discussed in this involve complicated angular momentum couplings of the $4f^N$ configuration, based on techniques pioneered by Racah over 50 years ago and discussed in detail in various books [7, 8, 4, 5]. We do not reproduce here all the equations involving the $3j$, $6j$ and $9j$ symbols, but emphasize that in principle the tools (and computer programs) exist to carry out such calculations. Thus we are free to concentrate on the physical meaning of the results.

A.5 Spherical Tensors

The crystal-field parametrization in the Wybourne convention uses the spherical tensor operators $C_q^{(k)}$, rather than spherical harmonics or unit tensor operators used in some of the tables I have presented. However, the matrix elements are simply related by equations given in the above references.

The spherical tensor operators differ from spherical harmonics by only a factor of $\sqrt{4\pi/(2k+1)}$. The lowest-rank spherical tensor operators may be written in Cartesian form as [4]:

$$\begin{aligned}
C_0^{(0)} &= 1 \\
C_0^{(1)} &= z/r \\
C_{\pm 1}^{(1)} &= \mp\sqrt{\frac{1}{2}}(x \pm iy)/r \\
C_0^{(2)} &= \sqrt{\frac{1}{4}}(3z^2 - r^2)/r^2 \\
C_{\pm 1}^{(2)} &= \mp\sqrt{\frac{3}{2}}z(x \pm iy)/r^2 \\
C_{\pm 2}^{(2)} &= \sqrt{\frac{3}{8}}(x \pm iy)^2/r^2. \qquad \text{(A.10)}
\end{aligned}$$

These expressions are often useful for working out selection rules and symmetry operations.

Appendix B

f^1 and d^1 Matrix Elements

Note that in this Appendix we leave out the /2 for all labels, so, for example `[2F 7 7>` means $|^2F\frac{7}{2}\frac{7}{2}\rangle$

B.1 Free-ion operators

Note: we often list the *parameter* rather than the *operator*, unless there is a possibility of confusion.

There are four multiplets

```
1 [2F  5>
2 [2F  7>
3 [2D  3>
4 [2D  5>
```

E_{avg}. Any value of $M \leq J$ is allowed.

```
<2F  5 M][2F 5 M>= 1
```

$\Delta(fd)$. Any value of $M \leq J$ is allowed.

```
<2F  7 M][2F 7 M>=  1
```

$\zeta(f)$. Any value of $M \leq J$ is allowed.

```
<2F  5 M][2F 5 M>= -2.000000     <2F  7 M][2F 7 M>=  1.500000
```

$\zeta(d)$. Any value of $M \leq J$ is allowed.

```
<2D 3 M][2D 3 M>= -1.500000     <2D 5 M][(2D 5 M>=  1.000000
```

B.2 Crystal-field and magnetic dipole

```
 24 SLJM LABELS

    SLJMLABEL

  1 [2F 7  7>
  2 [2F 5  5>
  3 [2F 7  5>
  4 [2D 5  5>
  5 [2F 5  3>
  6 [2F 7  3>
  7 [2D 3  3>
  8 [2D 5  3>
  9 [2F 5  1>
 10 [2F 7  1>
 11 [2D 3  1>
 12 [2D 5  1>
 13 [2F 5 -1>
 14 [2F 7 -1>
 15 [2D 3 -1>
 16 [2D 5 -1>
 17 [2F 5 -3>
 18 [2F 7 -3>
 19 [2D 3 -3>
 20 [2D 5 -3>
 21 [2F 5 -5>
 22 [2F 7 -5>
 23 [2D 5 -5>
 24 [2F 7 -7>
```

f^1 matrix elements

Note that only the upper diagonal of the matrices are given and only operators with $Q \geq 0$ are listed. The lower diagonal may be obtained from Hermiticity requirements and the M labels are ordered so that the $Q < 0$ operators do not have any non-zero matrix elements in the upper diagonal.

```
C20FF    S= 0   L= 2   K= 2   Q= 0

<2F 7  7][2F 7  7>= -0.33333331   <2F 5  5][2F 5  5>= -0.28571426   <2F 5  5][2F 7  5>=  0.11664236
<2F 7  5][2F 7  5>= -0.04761904   <2F 5  3][2F 5  3>=  0.05714285   <2F 5  3][2F 7  3>=  0.09035078
<2F 7  3][2F 7  3>=  0.14285713   <2F 5  1][2F 5  1>=  0.22857141   <2F 5  1][2F 7  1>=  0.03299144
<2F 7  1][2F 7  1>=  0.23809522   <2F 5 -1][2F 5 -1>=  0.22857141   <2F 5 -1][2F 7 -1>= -0.03299144
<2F 7 -1][2F 7 -1>=  0.23809522   <2F 5 -3][2F 5 -3>=  0.05714285   <2F 5 -3][2F 7 -3>= -0.09035078
<2F 7 -3][2F 7 -3>=  0.14285713   <2F 5 -5][2F 5 -5>= -0.28571426   <2F 5 -5][2F 7 -5>= -0.11664236
<2F 7 -5][2F 7 -5>= -0.04761904   <2F 7 -7][2F 7 -7>= -0.33333331
```

```
C40FF   S= 0   L= 4   K= 4     Q= 0

<2F 7  7][2F 7  7>=  0.09090892   <2F 5  5][2F 5  5>=  0.04761896   <2F 5  5][2F 7  5>= -0.10603831
<2F 7  5][2F 7  5>= -0.16883085   <2F 5  3][2F 5  3>= -0.14285687   <2F 5  3][2F 7  3>=  0.10951590
<2F 7  3][2F 7  3>= -0.03896096   <2F 5  1][2F 5  1>=  0.09523791   <2F 5  1][2F 7  1>=  0.07498041
<2F 7  1][2F 7  1>=  0.11688289   <2F 5 -1][2F 5 -1>=  0.09523791   <2F 5 -1][2F 7 -1>= -0.07498041
<2F 7 -1][2F 7 -1>=  0.11688289   <2F 5 -3][2F 5 -3>= -0.14285687   <2F 5 -3][2F 7 -3>= -0.10951590
<2F 7 -3][2F 7 -3>= -0.03896096   <2F 5 -5][2F 5 -5>=  0.04761896   <2F 5 -5][2F 7 -5>=  0.10603831
<2F 7 -5][2F 7 -5>= -0.16883085   <2F 7 -7][2F 7 -7>=  0.09090892
```

```
 C44FF    S= 0   L= 4   K= 4       Q= 4

<2F 7  7][2F 5 -1>=  0.14845364   <2F 7  7][2F 7 -1>=  0.12856462   <2F 5  5][2F 5 -3>=  0.17817382
<2F 5  5][2F 7 -3>= -0.10244274   <2F 7  5][2F 5 -3>=  0.15870362   <2F 7  5][2F 7 -3>=  0.18819934
<2F 5  3][2F 5 -5>=  0.17817382   <2F 5  3][2F 7 -5>= -0.15870362   <2F 7  3][2F 5 -5>=  0.10244274
<2F 7  3][2F 7 -5>=  0.18819934   <2F 5  1][2F 7 -7>= -0.14845364   <2F 7  1][2F 7 -7>=  0.12856462
```

```
C60FF       S= 0   L= 6   K= 6     Q= 0

<2F 7  7][2F 7  7>= -0.01165500   <2F 5  5][2F 7  5>=  0.02854881   <2F 7  5][2F 7  5>=  0.05827502
<2F 5  3][2F 7  3>= -0.11056908   <2F 7  3][2F 7  3>= -0.10489504   <2F 5  1][2F 7  1>=  0.20187060
<2F 7  1][2F 7  1>=  0.05827502   <2F 5 -1][2F 7 -1>= -0.20187060   <2F 7 -1][2F 7 -1>=  0.05827502
<2F 5 -3][2F 7 -3>=  0.11056908   <2F 7 -3][2F 7 -3>= -0.10489504   <2F 5 -5][2F 7 -5>= -0.02854881
<2F 7 -5][2F 7 -5>=  0.05827502   <2F 7 -7][2F 7 -7>= -0.01165500

C64FF     S= 0   L= 6   K= 6    Q= 4

<2F 7  7][2F 5 -1>= -0.12767418   <2F 7  7][2F 7 -1>= -0.11056908   <2F 5  5][2F 7 -3>=  0.18501746
<2F 7  5][2F 5 -3>=  0.23885652   <2F 7  5][2F 7 -3>=  0.07553306   <2F 5  3][2F 7 -5>= -0.23885652
<2F 7  3][2F 5 -5>= -0.18501746   <2F 7  3][2F 7 -5>=  0.07553306   <2F 5  1][2F 7 -7>=  0.12767418
<2F 7  1][2F 7 -7>= -0.11056908
```

d^1 matrix elements

```
 C20DD     S= 0   L= 2   K= 2   Q= 0

<2D 5  5][2D 5  5>= -0.28571438   <2D 3  3][2D 3  3>= -0.20000007   <2D 3  3][2D 5  3>=  0.17142863
<2D 5  3][2D 5  3>=  0.05714288   <2D 3  1][2D 3  1>=  0.20000007   <2D 3  1][2D 5  1>=  0.06998544
<2D 5  1][2D 5  1>=  0.22857150   <2D 3 -1][2D 3 -1>=  0.20000007   <2D 3 -1][2D 5 -1>= -0.06998544
<2D 5 -1][2D 5 -1>=  0.22857150   <2D 3 -3][2D 3 -3>= -0.20000007   <2D 3 -3][2D 5 -3>= -0.17142863
<2D 5 -3][2D 5 -3>=  0.05714288   <2D 5 -5][2D 5 -5>= -0.28571438

C40DD    S= 0   L= 4   K= 4    Q= 0

<2D 5  5][2D 5  5>=  0.04761906   <2D 3  3][2D 5  3>= -0.09523813   <2D 5  3][2D 5  3>= -0.14285719
<2D 3  1][2D 5  1>=  0.23328481   <2D 5  1][2D 5  1>=  0.09523813   <2D 3 -1][2D 5 -1>= -0.23328481
<2D 5 -1][2D 5 -1>=  0.09523813   <2D 3 -3][2D 5 -3>=  0.09523813   <2D 5 -3][2D 5 -3>= -0.14285719
<2D 5 -5][2D 5 -5>=  0.04761906

C44DD    S= 0   L= 4   K= 4    Q= 4

<2D 5  5][2D 3 -3>=  0.35634844   <2D 5  5][2D 5 -3>=  0.17817422   <2D 3  3][2D 5 -5>= -0.35634844
<2D 5  3][2D 5 -5>=  0.17817422
```

Magnetic dipole matrix elements

Note that these are matrix elements of $L_q + 2S_q$, and must be multiplied by the constants in Eq. (4.2) to obtain matrix elements of $M_q^{(1)}$.

```
MAG10   S= 0   L= 0   K= 1     Q= 0


<2F 7  7][2F 7  7>=  4.00116000   <2F 5  5][2F 5  5>=  2.14202857   <2F 5  5][2F 7  5>=  0.35073894
<2F 7  5][2F 7  5>=  2.85797143   <2D 5  5][2D 5  5>=  3.00116000   <2F 5  3][2F 5  3>=  1.28521714
<2F 5  3][2F 7  3>=  0.45280202   <2F 7  3][2F 7  3>=  1.71478286   <2D 3  3][2D 3  3>=  1.19930400
<2D 3  3][2D 5  3>=  0.40092800   <2D 5  3][2D 5  3>=  1.80069600   <2F 5  1][2F 5  1>=  0.42840571
<2F 5  1][2F 7  1>=  0.49601976   <2F 7  1][2F 7  1>=  0.57159429   <2D 3  1][2D 3  1>=  0.39976800
```

```
<2D 3  1][2D 5  1>=  0.49103451   <2D 5  1][2D 5  1>=  0.60023200   <2F 5 -1][2F 5 -1>= -0.42840571
<2F 5 -1][2F 7 -1>=  0.49601976   <2F 7 -1][2F 7 -1>= -0.57159429   <2D 3 -1][2D 3 -1>= -0.39976800
<2D 3 -1][2D 5 -1>=  0.49103451   <2D 5 -1][2D 5 -1>= -0.60023200   <2F 5 -3][2F 5 -3>= -1.28521714
<2F 5 -3][2F 7 -3>=  0.45280202   <2F 7 -3][2F 7 -3>= -1.71478286   <2D 3 -3][2D 3 -3>= -1.19930400
<2D 3 -3][2D 5 -3>=  0.40092800   <2D 5 -3][2D 5 -3>= -1.80069600   <2F 5 -5][2F 5 -5>= -2.14202857
<2F 5 -5][2F 7 -5>=  0.35073894   <2F 7 -5][2F 7 -5>= -2.85797143   <2D 5 -5][2D 5 -5>= -3.00116000
<2F 7 -7][2F 7 -7>= -4.00116000
```

```
 MAG11   S= 0   L= 0   K= 1    Q= 1

<2F 7  7][2F 5  5>=  0.65617247   <2F 7  7][2F 7  5>= -2.13870998   <2F 5  5][2F 5  3>= -1.35473782
<2F 5  5][2F 7  3>= -0.14318857   <2F 7  5][2F 5  3>=  0.55456695   <2F 7  5][2F 7  3>= -2.80022868
<2D 5  5][2D 3  3>=  0.63392283   <2D 5  5][2D 5  3>= -1.89810024   <2F 5  3][2F 5  1>= -1.71362286
<2F 5  3][2F 7  1>= -0.24800988   <2F 7  3][2F 5  1>=  0.45280202   <2F 7  3][2F 7  1>= -3.13075084
<2D 3  3][2D 3  1>= -0.97922762   <2D 3  3][2D 5  1>= -0.20046400   <2D 5  3][2D 3  1>=  0.49103451
<2D 5  3][2D 5  1>= -2.40092800   <2F 5  1][2F 5 -1>= -1.81757151   <2F 5  1][2F 7 -1>= -0.35073894
<2F 7  1][2F 5 -1>=  0.35073894   <2F 7  1][2F 7 -1>= -3.23342556   <2D 3  1][2D 3 -1>= -1.13071465
<2D 3  1][2D 5 -1>= -0.34721383   <2D 5  1][2D 3 -1>=  0.34721383   <2D 5  1][2D 5 -1>= -2.54656870
<2F 5 -1][2F 5 -3>= -1.71362286   <2F 5 -1][2F 7 -3>= -0.45280202   <2F 7 -1][2F 5 -3>=  0.24800988
<2F 7 -1][2F 7 -3>= -3.13075084   <2D 3 -1][2D 3 -3>= -0.97922762   <2D 3 -1][2D 5 -3>= -0.49103451
<2D 5 -1][2D 3 -3>=  0.20046400   <2D 5 -1][2D 5 -3>= -2.40092800   <2F 5 -3][2F 5 -5>= -1.35473782
<2F 5 -3][2F 7 -5>= -0.55456695   <2F 7 -3][2F 5 -5>=  0.14318857   <2F 7 -3][2F 7 -5>= -2.80022868
<2D 3 -3][2D 5 -5>= -0.63392283   <2D 5 -3][2D 5 -5>= -1.89810024   <2F 5 -5][2F 7 -7>= -0.65617247
<2F 7 -5][2F 7 -7>= -2.13870998
```

Electric dipole matrix elements

These $U_q^{(1)}$ matrix elements must be multiplied by $\sqrt{3}$ to obtain $C_q^{(1)}$ matrix elements.

```
UFD10  S= 0   L= 1   K= 1     Q= 0

<2F 5  5][2D 5  5>=  0.08247861   <2F 7  5][2D 5  5>=  0.20203051   <2F 5  3][2D 3  3>=  0.23094011
<2F 5  3][2D 5  3>=  0.04948717   <2F 7  3][2D 5  3>=  0.26082027   <2F 5  1][2D 3  1>=  0.28284271
<2F 5  1][2D 5  1>=  0.01649572   <2F 7  1][2D 5  1>=  0.28571429   <2F 5 -1][2D 3 -1>=  0.28284271
<2F 5 -1][2D 5 -1>= -0.01649572   <2F 7 -1][2D 5 -1>=  0.28571429   <2F 5 -3][2D 3 -3>=  0.23094011
<2F 5 -3][2D 5 -3>= -0.04948717   <2F 7 -3][2D 5 -3>=  0.26082027   <2F 5 -5][2D 5 -5>= -0.08247861
<2F 7 -5][2D 5 -5>=  0.20203051
```

```
UFD11   S= 0   L= 1   K= 1     Q= 1


<2F 7  7][2D 5  5>=  0.37796447   <2F 5  5][2D 3  3>=  0.36514837   <2F 5  5][2D 5  3>= -0.05216405
<2F 7  5][2D 5  3>=  0.31943828   <2D 5  5][2F 5  3>= -0.05216405   <2D 5  5][2F 7  3>= -0.08247861
<2F 5  3][2D 3  1>=  0.28284271   <2F 5  3][2D 5  1>= -0.06598289   <2F 7  3][2D 5  1>=  0.26082027
<2D 3  3][2F 5  1>= -0.11547005   <2D 5  3][2F 5  1>= -0.06598289   <2D 5  3][2F 7  1>= -0.14285714
<2F 5  1][2D 3 -1>=  0.20000000   <2F 5  1][2D 5 -1>= -0.06998542   <2F 7  1][2D 5 -1>=  0.20203051
<2D 3  1][2F 5 -1>= -0.20000000   <2D 5  1][2F 5 -1>= -0.06998542   <2D 5  1][2F 7 -1>= -0.20203051
<2F 5 -1][2D 3 -3>=  0.11547005   <2F 5 -1][2D 5 -3>= -0.06598289   <2F 7 -1][2D 5 -3>=  0.14285714
<2D 3 -1][2F 5 -3>= -0.28284271   <2D 5 -1][2F 5 -3>= -0.06598289   <2D 5 -1][2F 7 -3>= -0.26082027
<2F 5 -3][2D 5 -5>= -0.05216405   <2F 7 -3][2D 5 -5>=  0.08247861   <2D 3 -3][2F 5 -5>= -0.36514837
<2D 5 -3][2F 5 -5>= -0.05216405   <2D 5 -3][2F 7 -5>= -0.31943828   <2D 5 -5][2F 7 -7>= -0.37796447
```

Appendix C

f^2 free-ion matrix elements

Note that for f^{12} the sign of the ζ matrix elements must be changed. Since these operators have total angular-momentum quantum numbers $Q = 0$ the matrices are diagonal in, and independent of, M_J.

For f^2 there are 13 multiplets:

```
  1  [3P  0>
  2  [3P  1>
  3  [3P  2>
  4  [3F  2>
  5  [3F  3>
  6  [3F  4>
  7  [3H  4>
  8  [3H  5>
  9  [3H  6>
 10  [1S  0>
 11  [1D  2>
 12  [1G  4>
 13  [1I  6>

   F2           13 MES
<3P  0][3P  0>= 2.20513000e-01  <3P  1][3P  1>= 2.20513000e-01  <3P  2][3P  2>= 2.20513000e-01
<3F  2][3F  2>=-2.39320000e-02  <3F  3][3F  3>=-2.39320000e-02  <3F  4][3F  4>=-2.39320000e-02
<3H  4][3H  4>=-9.05980000e-02  <3H  5][3H  5>=-9.05980000e-02  <3H  6][3H  6>=-9.05980000e-02
<1S  0][1S  0>= 2.87179000e-01  <1D  2][1D  2>= 1.04957000e-01  <1G  4][1G  4>=-1.12821000e-01
<1I  6][1I  6>= 1.31624000e-01

   F4           13 MES
<3P  0][3P  0>= 4.42890000e-02  <3P  1][3P  1>= 4.42890000e-02  <3P  2][3P  2>= 4.42890000e-02
<3F  2][3F  2>=-1.63170000e-02  <3F  3][3F  3>=-1.63170000e-02  <3F  4][3F  4>=-1.63170000e-02
<3H  4][3H  4>=-3.28460000e-02  <3H  5][3H  5>=-3.28460000e-02  <3H  6][3H  6>=-3.28460000e-02
<1S  0][1S  0>= 1.95804000e-01  <1D  2][1D  2>=-7.69230000e-02  <1G  4][1G  4>= 1.03059000e-01
<1I  6][1I  6>= 2.22500000e-02

   F6           13 MES
<3P  0][3P  0>=-1.56894000e-01  <3P  1][3P  1>=-1.56894000e-01  <3P  2][3P  2>=-1.56894000e-01
<3F  2][3F  2>=-2.09190000e-02  <3F  3][3F  3>=-2.09190000e-02  <3F  4][3F  4>=-2.09190000e-02
<3H  4][3H  4>= 1.61650000e-02  <3H  5][3H  5>= 1.61650000e-02  <3H  6][3H  6>= 1.61650000e-02
<1S  0][1S  0>= 2.51031000e-01  <1D  2][1D  2>= 1.15056000e-01  <1G  4][1G  4>= 2.85260000e-02
<1I  6][1I  6>= 1.80670000e-02

     ZETA         15 MES
<3P  0][3P  0>=-1.00000050e+00  <3P  0][1S  0>=-3.46410337e+00  <3P  1][3P  1>=-5.00000252e-01
<3P  2][3P  2>= 5.00000252e-01  <3P  2][1D  2>= 2.12131926e+00  <3F  2][3F  2>=-2.00000021e+00
<3F  2][1D  2>=-2.44948893e+00  <3F  3][3F  3>=-5.00000052e-01  <3F  4][3F  4>= 1.50000015e+00
<3F  4][1G  4>= 1.91485369e+00  <3H  4][3H  4>=-3.00000027e+00  <3H  4][1G  4>=-1.82574126e+00
<3H  5][3H  5>=-5.00000045e-01  <3H  6][3H  6>= 2.50000022e+00  <3H  6][1I  6>= 1.22474493e+00
```

Appendix D

Intensity Matrix Elements

Note that for the magnetic dipole case we give reduced matrix elements of $L + 2S$, and must be multiplied by the constants in Eq. (4.2) to obtain reduce matrix elements of $M^{(1)}$.

D.1 Eu^{3+} matrix elements for Judd-Ofelt Intensity Calculations

We give only the lowest 12 free-ion energy levels. Note that in states like `5D1 0` or `5D3 0` the labels `1` and `3` distinguish states with the same S and L. The reduced matrix elements below are calculated between the free-ion eigenvectors.

```
PARAMETERS

    F2          =   83125.0000
    F4          =   59268.0000
    F6          =   42560.0000
    ALPHA       =      20.1600
    BETA        =    -566.0000
    GAMMA       =    1500.0000
    T2          =     300.0000
    T3          =      40.0000
    T4          =      60.0000
    T6          =    -300.0000
    T7          =     370.0000
    T8          =     320.0000
    ZETA        =    1338.0000
    M0          =       2.1000
    P2          =     360.0000

ENERGIES and EIGENVECTORS

       Largest two components              Energy
   1  -0.97 [7F  0>  + 0.19 [5D1 0>      0.000000
   2  -0.97 [7F  1>  + 0.17 [5D1 1>    382.280778
   3  -0.98 [7F  2>  + 0.14 [5D1 2>   1051.745175
   4   0.99 [7F  3>  - 0.10 [5D1 3>   1913.683906
   5  -0.99 [7F  4>  - 0.08 [5F2 4>   2898.069679
   6  -0.99 [7F  5>  - 0.09 [5G1 5>   3956.481323
   7   0.98 [7F  6>  + 0.13 [5G1 6>   5055.294405
   8  -0.68 [5D3 0>  + 0.54 [5D1 0>  17303.939101
   9   0.71 [5D3 1>  - 0.57 [5D1 1>  19062.381439
  10  -0.74 [5D3 2>  + 0.59 [5D1 2>  21552.658483
  11  -0.74 [5D3 3>  + 0.60 [5D1 3>  24465.310601
  12   0.94 [5L  6>  + 0.17 [3K5 6>  25289.533334
```

```
Detailed Eigenvevctors.

  1      0.00   -0.9663( 93%)  1 [7F  0>   0.1880(  4%) 12 [5D1 0>  -0.1678(  3%) 22 [5D3 0>

  2    382.28   -0.9729( 95%)  2 [7F  1>   0.1704(  3%) 13 [5D1 1>  -0.1485(  2%) 23 [5D3 1>

  3   1051.75   -0.9809( 96%)  3 [7F  2>   0.1409(  2%) 14 [5D1 2>  -0.1170(  1%) 24 [5D3 2>

  4   1913.68    0.9867( 97%)  4 [7F  3>  -0.1040(  1%) 15 [5D1 3>

  5   2898.07   -0.9890( 98%)  5 [7F  4>

  6   3956.48   -0.9873( 97%)  6 [7F  5>

  7   5055.29    0.9814( 96%)  7 [7F  6>   0.1264(  2%) 41 [5G1 6>  -0.1232(  2%) 51 [5G3 6>

  8  17303.94    0.2434(  6%)  1 [7F  0>   0.5444( 30%) 12 [5D1 0>   0.1810(  3%) 17 [5D2 0>
                -0.6772( 46%) 22 [5D3 0>   0.1741(  3%) 82 [3P1 0>  -0.2221(  5%) 88 [3P3 0>
                -0.2513(  6%) 97 [3P6 0>

  9  19062.38   -0.2148(  5%)  2 [7F  1>  -0.5699( 32%) 13 [5D1 1>  -0.1934(  4%) 18 [5D2 1>
                 0.7140( 51%) 23 [5D3 1>  -0.1274(  2%) 83 [3P1 1>   0.1611(  3%) 89 [3P3 1>
                 0.1834(  3%) 98 [3P6 1>

 10  21552.66    0.1667(  3%)  3 [7F  2>   0.5890( 35%) 14 [5D1 2>   0.1943(  4%) 19 [5D2 2>
                -0.7384( 55%) 24 [5D3 2>  -0.1045(  1%) 99 [3P6 2>

 11  24465.31    0.1116(  1%)  4 [7F  3>   0.5979( 36%) 15 [5D1 3>   0.1772(  3%) 20 [5D2 3>
                 -0.7433( 55%) 25 [5D3 3>  0.1363(  2%) 34 [5F2 3>

 12  25289.53   -0.1092(  1%) 73 [5K  6>   0.9358( 88%) 77 [5L  6>   0.1476(  2%)208 [3K1 6>
                 0.1388(  2%)211 [3K2 6>   0.1747(  3%)220 [3K5 6>


REDUCED MATRIX ELEMENTS

  U2

  (7F  0][7F  2)= -0.37071251     (7F  0][5D3 2)=  0.02863683     (7F  1][7F  1)=  0.39247451
  (7F  1][7F  2)= -0.22763455     (7F  1][7F  3)=  0.45744059     (7F  1][5D3 1)=  0.05139697
  (7F  1][5D3 2)=  0.01209694     (7F  1][5D3 3)=  0.02100905     (7F  2][7F  2)=  0.31624714
  (7F  2][7F  3)=  0.43165963     (7F  2][7F  4)= -0.47188391     (7F  2][5D3 0)=  0.05734750
  (7F  2][5D3 1)=  0.02800057     (7F  2][5D3 2)= -0.04296343     (7F  2][5D3 3)=  0.01495244
  (7F  3][7F  3)=  0.16619088     (7F  3][7F  4)=  0.62292816     (7F  3][7F  5)=  0.41895169
  (7F  3][5D3 1)=  0.06234619     (7F  3][5D3 2)=  0.04891052     (7F  3][5D3 3)=  0.03328467
  (7F  4][7F  4)= -0.10845512     (7F  4][7F  5)= -0.75402011     (7F  4][7F  6)=  0.29274168
  (7F  4][5D3 2)=  0.04542062     (7F  4][5D3 3)= -0.06292137     (7F  4][5L  6)=  0.00209655
  (7F  5][7F  5)= -0.52537734     (7F  5][7F  6)=  0.73568597     (7F  5][5D3 3)=  0.01199047
  (7F  5][5L  6)=  0.00051674     (7F  6][7F  6)= -1.09663378     (7F  6][5L  6)= -0.01494471
  (5D3 0][5D3 2)= -0.11855803     (5D3 1][5D3 1)=  0.11449795     (5D3 1][5D3 2)=  0.11009838
  (5D3 1][5D3 3)=  0.13407535     (5D3 2][5D3 2)=  0.03344036     (5D3 2][5D3 3)= -0.18573543
  (5D3 3][5D3 3)= -0.12237537     (5L  6][5L  6)=  0.07283253

  U4

  (7F  0][7F  4)= -0.37441512     (7F  1][7F  3)= -0.35801908     (7F  1][7F  4)= -0.41730018
  (7F  1][7F  5)= -0.34535052     (7F  1][5D3 3)= -0.03501958     (7F  2][7F  2)= -0.34926575
  (7F  2][7F  3)= -0.46089269     (7F  2][7F  4)= -0.07907540     (7F  2][7F  5)= -0.56157621
  (7F  2][7F  6)=  0.21857838     (7F  2][5D3 2)=  0.03894144     (7F  2][5D3 3)= -0.04483753
  (7F  2][5L  6)= -0.00165383     (7F  3][7F  3)=  0.16126061     (7F  3][7F  4)= -0.36775763
```

```
(7F  3][7F  5)=  0.50270946     (7F  3][7F  6)= -0.48069214     (7F  3][5D3 1)= -0.04382844
(7F  3][5D3 2)= -0.05145212     (7F  3][5D3 3)=  0.02252201     (7F  3][5L  6)=  0.00159663
(7F  4][7F  4)=  0.53305535     (7F  4][7F  5)= -0.11324434     (7F  4][7F  6)=  0.71735681
(7F  4][5D3 0)=  0.04863370     (7F  4][5D3 1)=  0.05312134     (7F  4][5D3 2)=  0.01983420
(7F  4][5D3 3)=  0.01621312     (7F  4][5L  6)=  0.01610288     (7F  5][7F  5)=  0.45432571
(7F  5][7F  6)=  0.80328987     (7F  5][5D3 1)= -0.02686983     (7F  5][5D3 2)= -0.04010542
(7F  5][5D3 3)=  0.03706854     (7F  5][5L  6)= -0.00137712     (7F  6][7F  6)= -0.62777005
(7F  6][5D3 2)= -0.00183953     (7F  6][5D3 3)=  0.00505868     (7F  6][5L  6)= -0.01084512
(5D3 1][5D3 3)=  0.08046925     (5D3 2][5D3 2)=  0.08633918     (5D3 2][5D3 3)= -0.11735793
(5D3 2][5L  6)= -0.06481513     (5D3 3][5D3 3)= -0.05128556     (5D3 3][5L  6)=  0.00800706
(5L  6][5L  6)=  0.96783203

 U6

(7F  0][7F  6)=  0.38087135     (7F  0][5L  6)= -0.12481988     (7F  1][7F  5)=  0.23337971
(7F  1][7F  6)=  0.61436055     (7F  1][5L  6)=  0.09627774     (7F  2][7F  4)= -0.18141599
(7F  2][7F  5)=  0.45700642     (7F  2][7F  6)=  0.68522063     (7F  2][5L  6)= -0.00458318
(7F  3][7F  3)=  0.16766906     (7F  3][7F  4)=  0.39847104     (7F  3][7F  5)= -0.61924624
(7F  3][7F  6)= -0.64292354     (7F  3][5D3 3)= -0.00885480     (7F  3][5L  6)=  0.03679338
(7F  4][7F  4)= -0.59382265     (7F  4][7F  5)=  0.66407974     (7F  4][7F  6)=  0.51865701
(7F  4][5D3 2)= -0.00186583     (7F  4][5D3 3)=  0.00855545     (7F  4][5L  6)=  0.06845869
(7F  5][7F  5)=  0.56780014     (7F  5][7F  6)=  0.34829042     (7F  5][5D3 1)=  0.00479840
(7F  5][5D3 2)=  0.00250659     (7F  5][5D3 3)=  0.00257834     (7F  5][5L  6)= -0.02818820
(7F  6][7F  6)= -0.17154948     (7F  6][5D3 0)= -0.01593991     (7F  6][5D3 1)= -0.01853482
(7F  6][5D3 2)= -0.01004934     (7F  6][5D3 3)=  0.00323950     (7F  6][5L  6)= -0.01382675
(5D3 0][5L  6)= -0.48716326     (5D3 1][5L  6)= -0.38629569     (5D3 2][5L  6)= -0.39672798
(5D3 3][5D3 3)=  0.05812686     (5D3 3][5L  6)=  0.13018251     (5L  6][5L  6)=  0.41796013

MAGMOM

(7F  0][7F  1)= -3.40676841     (7F  0][5D3 1)= -0.14558928     (7F  1][7F  1)=  3.67316019
(7F  1][7F  2)= -4.67927145     (7F  1][5D3 0)= -0.33272544     (7F  1][5D3 1)= -0.00804884
(7F  1][5D3 2)=  0.09869999     (7F  2][7F  2)=  8.20971048     (7F  2][7F  3)=  5.42146193
(7F  2][5D3 1)=  0.48401251     (7F  2][5D3 2)=  0.01508383     (7F  2][5D3 3)=  0.04660906
(7F  3][7F  3)= 13.73009882     (7F  3][7F  4)=  5.70215162     (7F  3][5D3 2)=  0.53143780
(7F  3][5D3 3)= -0.01278092     (7F  4][7F  4)= 20.08678887     (7F  4][7F  5)= -5.44718494
(7F  4][5D3 3)= -0.47922304     (7F  5][7F  5)= 27.17889146     (7F  5][7F  6)=  4.39517396
(7F  5][5L  6)=  0.04084936     (7F  6][7F  6)= 34.92962427     (7F  6][5L  6)=  0.11243984
(5D3 0][5D3 1)=  2.36623040     (5D3 1][5D3 1)=  3.65964067     (5D3 1][5D3 2)=  3.19187227
(5D3 2][5D3 2)=  8.16871057     (5D3 2][5D3 3)= -3.45458814     (5D3 3][5D3 3)= 13.62628255
(5L  6][5L  6)= 17.38045477
```

D.2 Nd^{3+} matrix elements for Judd-Ofelt Intensity Calculations

```
PARAMETERS

    F2          =   73018.0000
    F4          =   52789.0000
    F6          =   35757.0000
    ALPHA       =      21.3400
    BETA        =    -593.0000
    GAMMA       =    1445.0000
    T2          =     298.0000
    T3          =      35.0000
    T4          =      59.0000
    T6          =    -285.0000
    T7          =     332.0000
    T8          =     305.0000
    ZETA        =    1445.0000
    mtot        =       2.1100
    ptot        =     192.0000

ENERGIES and EIGENVECTORS

      Largest two components             Energy

   1   0.97 [4I  9>  -0.24 [2H2 9>      0.000000
   2   0.99 [4I 11>  -0.14 [2H211>   3272.674553
   3   0.99 [4I 13>  +0.11 [2K 13>   6548.640764
   4   0.98 [4I 15>  +0.19 [2K 15>   9779.003745
   5  -0.92 [4F  3>  -0.33 [2D1 3>  11863.234849
   6  -0.68 [2H2 9>  -0.39 [2G1 9>  13331.798851
   7   0.97 [4F  5>  +0.21 [2D1 5>  13882.230985
   8   0.92 [4S  3>  +0.33 [2P  3>  15200.347199
   9  -0.90 [4F  7>  +0.32 [2G1 7>  15334.200388
  10  -0.84 [4F  9>  -0.47 [2H2 9>  17569.193242
  11  -0.98 [4G  5>  -0.13 [2F1 5>  17899.535989
  12   0.87 [2H211>  -0.34 [4G 11>  18809.151390
  13  -0.75 [4G  7>  +0.42 [2G1 7>  18848.102157
  14   0.98 [2K 13>  -0.14 [2I 13>  21331.940870
  15  -0.64 [4G  7>  -0.56 [2G1 7>  21582.209639
  16  -0.93 [4G  9>  -0.24 [2H2 9>  22295.296713
  17  -0.63 [2D1 3>  +0.57 [2P  3>  22794.175641
  18  -0.91 [2K 15>  +0.36 [2L 15>  24343.357892
  19   0.91 [2P  1>  +0.42 [4D  1>  25106.505993
  20   0.91 [4G 11>  -0.34 [2H111>  25213.591269
  21   0.64 [2G1 9>  -0.50 [2G2 9>  25486.111160
  22   0.96 [2D1 5>  -0.21 [4F  5>  26603.798712
  23  -0.83 [4D  5>  -0.50 [2D2 5>  29344.012631
  24  -0.82 [4D  3>  -0.48 [2D2 3>  29510.028523
  25  -0.67 [2P  3>  -0.61 [2D1 3>  30385.361864
  26  -0.87 [2I 11>  +0.43 [2H111>  31062.261555
  27   0.91 [4D  1>  -0.42 [2P  1>  31085.684716
  28   0.93 [2L 15>  +0.36 [2K 15>  32885.366746
  29   0.98 [4D  7>  -0.14 [2F1 7>  33276.460943
  30  -0.99 [2I 13>  -0.15 [2K 13>  33652.338588
  31   1.00 [2L 17>
  32   0.93 [2H1 9>  +0.30 [2H2 9>  35316.998825
  33   0.81 [2D2 3>  -0.46 [4D  3>  36751.658485
  34   0.57 [2D2 5>  -0.53 [4D  5>  37255.167135
  35  -0.77 [2H111>  -0.48 [2I 11>  38089.076298
  36  -0.64 [2D2 5>  -0.55 [2F2 5>  42222.296738
```

```
 37  -0.81 [2F2 7>  -0.53 [2F1 7>  43427.271596
 38   0.76 [2G2 9>  +0.63 [2G1 9>  50182.198760
 39   0.76 [2G2 7>  +0.62 [2G1 7>  51451.755655
 40  -0.83 [2F1 7>  +0.54 [2F2 7>  69117.483326
 41  -0.76 [2F1 5>  +0.65 [2F2 5>  70870.697921


ABSORPTION REDUCED MATRIX ELEMENTS

 U2

  (4I  9][4I  9)=  0.32494132     (4I  9][4I 11)=  0.14055614     (4I  9][4I 13)= -0.01271987
  (4I  9][2H2 9)= -0.14739649     (4I  9][4F  5)=  0.08144839     (4I  9][4F  7)=  0.07957520
  (4I  9][4F  9)= -0.03598507     (4I  9][4G  5)=  0.94465508     (4I  9][2H211)= -0.00157000
  (4I  9][4G  7)=  0.31235590     (4I  9][2K 13)= -0.12496043     (4I  9][4G  7)=  0.16613188
  (4I  9][4G  9)=  0.06304772     (4I  9][4G 11)=  0.01227618     (4I  9][2G1 9)= -0.01380033
  (4I  9][2D1 5)=  0.00133768     (4I  9][4D  5)= -0.01712736     (4I  9][2I 11)= -0.10103650
  (4I  9][4D  7)= -0.00314892     (4I  9][2I 13)= -0.01627045     (4I  9][2H1 9)= -0.01438257
  (4I  9][2D2 5)=  0.04738682     (4I  9][2H111)= -0.01609441     (4I  9][2D2 5)=  0.05312992
  (4I  9][2F2 7)=  0.00633475     (4I  9][2G2 9)= -0.01057476     (4I  9][2G2 7)= -0.02940199
  (4I  9][2F1 7)=  0.00080215     (4I  9][2F1 5)=  0.03699171

U4

  (4I  9][4I  9)= -0.39229723     (4I  9][4I 11)= -0.32649858     (4I  9][4I 13)= -0.11089575
  (4I  9][4I 15)=  0.01712573     (4I  9][4F  3)=  0.43991908     (4I  9][2H2 9)=  0.14292795
  (4I  9][4F  5)= -0.52128675     (4I  9][4S  3)= -0.11417064     (4I  9][4F  7)=  0.15032713
  (4I  9][4F  9)=  0.11590434     (4I  9][4G  5)= -0.63662140     (4I  9][2H211)= -0.08189507
  (4I  9][4G  7)= -0.50736048     (4I  9][2K 13)=  0.01621819     (4I  9][4G  7)= -0.29263908
  (4I  9][4G  9)= -0.26210931     (4I  9][2D1 3)= -0.22199864     (4I  9][2K 15)= -0.15470831
  (4I  9][2P  1)= -0.30268161     (4I  9][4G 11)=  0.08789250     (4I  9][2G1 9)=  0.08643993
  (4I  9][2D1 5)= -0.00749412     (4I  9][4D  5)=  0.24571360     (4I  9][4D  3)=  0.41143010
  (4I  9][2P  3)=  0.08349762     (4I  9][2I 11)= -0.17627634     (4I  9][4D  1)= -0.44504027
  (4I  9][2L 15)= -0.20847029     (4I  9][4D  7)= -0.05206852     (4I  9][2I 13)= -0.04690906
  (4I  9][2L 17)= -0.04169336     (4I  9][2H1 9)= -0.13196678     (4I  9][2D2 3)=  0.10775541
  (4I  9][2D2 5)=  0.00594569     (4I  9][2H111)= -0.00048046     (4I  9][2D2 5)= -0.07209596
  (4I  9][2F2 7)= -0.01896505     (4I  9][2G2 9)=  0.05989819     (4I  9][2G2 7)=  0.06599428
  (4I  9][2F1 7)= -0.01272021     (4I  9][2F1 5)= -0.04600170

U6

  (4I  9][4I  9)=  0.77966259     (4I  9][4I 11)=  1.06563601     (4I  9][4I 13)=  0.67730323
  (4I  9][4I 15)=  0.23081188     (4I  9][4F  3)=  0.19643390     (4I  9][2H2 9)= -0.45822622
  (4I  9][4F  5)= -0.61412103     (4I  9][4S  3)= -0.49937513     (4I  9][4F  7)=  0.66985221
  (4I  9][4F  9)=  0.17526152     (4I  9][4G  5)=  0.21236961     (4I  9][2H211)=  0.12916498
  (4I  9][4G  7)=  0.15077405     (4I  9][2K 13)=  0.25731276     (4I  9][4G  7)=  0.20089116
  (4I  9][4G  9)=  0.19228124     (4I  9][2D1 3)=  0.03989835     (4I  9][2K 15)= -0.19335244
  (4I  9][4G 11)= -0.07862573     (4I  9][2G1 9)= -0.07010567     (4I  9][2D1 5)=  0.07161452
  (4I  9][4D  5)= -0.15754148     (4I  9][4D  3)= -0.12438241     (4I  9][2P  3)= -0.04160467
  (4I  9][2I 11)=  0.07752943     (4I  9][2L 15)= -0.12527037     (4I  9][4D  7)=  0.08266067
  (4I  9][2I 13)=  0.05720248     (4I  9][2L 17)= -0.04132087     (4I  9][2H1 9)= -0.01461260
  (4I  9][2D2 3)= -0.03337136     (4I  9][2D2 5)= -0.07034590     (4I  9][2H111)=  0.02294124
  (4I  9][2D2 5)=  0.00263835     (4I  9][2F2 7)= -0.03992842     (4I  9][2G2 9)=  0.00854112
  (4I  9][2G2 7)=  0.02685884     (4I  9][2F1 7)=  0.03349875     (4I  9][2F1 5)=  0.02221969

 MAGNETIC DIPOLE

  (4I  9][4I  9)= 11.63640321     (4I  9][4I 11)= -4.26902156     (4I  9][2H2 9)=  0.73839556
  (4I  9][4F  7)= -0.07458429     (4I  9][4F  9)=  0.23310301     (4I  9][2H211)= -0.01580553
  (4I  9][4G  7)= -0.10396820     (4I  9][4G  7)=  0.01782362     (4I  9][4G  9)=  0.05098437
  (4I  9][4G 11)= -0.01859535     (4I  9][2G1 9)=  0.04811206     (4I  9][2I 11)=  0.09425488
```

```
  (4I  9][4D  7)=  0.00010256     (4I  9][2H1 9)= -0.01393033     (4I  9][2H111)=  0.02327034
  (4I  9][2F2 7)= -0.00029402     (4I  9][2G2 9)=  0.00158122     (4I  9][2G2 7)=  0.00226563
  (4I  9][2F1 7)=  0.00015761


MATRIX ELEMENTS RELEVANT FOR EMISSION FROM 4F3/2

 U2

  (4I  9][4I  9)=  0.32494132     (4I  9][4I 11)=  0.14055614     (4I  9][4I 13)= -0.01271987
  (4I  9][2H2 9)= -0.14739649     (4I  9][4F  5)=  0.08144839     (4I 11][4I 11)=  0.35738714
  (4I 11][4I 13)=  0.15980954     (4I 11][4I 15)= -0.01105464     (4I 11][2H2 9)= -0.07546721
  (4I 13][4I 13)=  0.41896391     (4I 13][4I 15)=  0.13705867     (4I 13][2H2 9)= -0.27044156
  (4I 15][4I 15)=  0.50517890     (4F  3][4F  3)= -0.22202961     (4F  3][4F  5)=  0.32477080
  (4F  3][4S  3)=  0.03155666     (2H2 9][2H2 9)= -0.35784693     (2H2 9][4F  5)=  0.12479459
  (4F  5][4F  5)= -0.16978398     (4F  5][4S  3)=  0.00736828     (4S  3][4S  3)= -0.06282867

U4

  (4I  9][4I  9)= -0.39229723     (4I  9][4I 11)= -0.32649858     (4I  9][4I 13)= -0.11089575
  (4I  9][4I 15)=  0.01712573     (4I  9][4F  3)=  0.43991908     (4I  9][2H2 9)=  0.14292795
  (4I  9][4F  5)= -0.52128675     (4I  9][4S  3)= -0.11417064     (4I 11][4I 11)= -0.33162509
  (4I 11][4I 13)= -0.37313977     (4I 11][4I 15)= -0.09388593     (4I 11][4F  3)= -0.37833636
  (4I 11][2H2 9)= -0.00048895     (4I 11][4F  5)= -0.38389185     (4I 11][4S  3)=  0.01175536
  (4I 13][4I 13)= -0.41584664     (4I 13][4I 15)= -0.35046537     (4I 13][2H2 9)= -0.03322274
  (4I 13][4F  5)=  0.40623054     (4I 15][4I 15)= -0.61209792     (4I 15][2H2 9)= -0.53677883
  (4F  3][2H2 9)=  0.15654490     (4F  3][4F  5)=  0.21427554     (2H2 9][2H2 9)=  0.05948131
  (2H2 9][4F  5)= -0.21445256     (2H2 9][4S  3)= -0.05242216     (4F  5][4F  5)=  0.11052035
  (4F  5][4S  3)=  0.05706933

 U6

  (4I  9][4I  9)=  0.77966259     (4I  9][4I 11)=  1.06563601     (4I  9][4I 13)=  0.67730323
  (4I  9][4I 15)=  0.23081188     (4I  9][4F  3)=  0.19643390     (4I  9][2H2 9)= -0.45822622
  (4I  9][4F  5)= -0.61412103     (4I  9][4S  3)= -0.49937513     (4I 11][4I 11)=  0.25264740
  (4I 11][4I 13)=  1.10043431     (4I 11][4I 15)=  0.65461987     (4I 11][4F  3)= -0.64391265
  (4I 11][2H2 9)= -0.11309569     (4I 11][4F  5)=  0.16718465     (4I 11][4S  3)= -0.38019056
  (4I 13][4I 13)=  0.47531127     (4I 13][4I 15)=  1.18712520     (4I 13][4F  3)=  0.41515198
  (4I 13][2H2 9)= -0.32653768     (4I 13][4F  5)=  0.62720534     (4I 13][4S  3)= -0.59235423
  (4I 15][4I 15)=  1.35840553     (4I 15][4F  3)= -0.20821748     (4I 15][2H2 9)= -0.26533241
  (4I 15][4F  5)= -0.49221327     (4I 15][4S  3)= -0.54741833     (4F  3][2H2 9)=  0.16793658
  (2H2 9][2H2 9)= -0.53646442     (2H2 9][4F  5)= -0.03515456     (2H2 9][4S  3)= -0.01856062

 MAGNETIC DIPOLE

  (4I  9][4I  9)= 11.63640321     (4I  9][4I 11)= -4.26902156     (4I  9][2H2 9)=  0.73839556
  (4I 11][4I 11)= 20.04328674     (4I 11][4I 13)= -4.96326611     (4I 11][2H2 9)= -0.71754325
  (4I 13][4I 13)= 28.89067778     (4I 13][4I 15)= -4.33735834     (4I 15][4I 15)= 38.17860756
  (4F  3][4F  3)=  1.84686548     (4F  3][4F  5)=  2.90318467     (4F  3][4S  3)=  0.74863970
  (2H2 9][2H2 9)= 15.92148461     (4F  5][4F  5)=  7.49261870     (4F  5][4S  3)=  0.48739149
  (4S  3][4S  3)=  7.26092843
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