

2.5 Calculating the Electronic Energy Levels of Rare Earth Ions

Before introducing the crystal field effects, it is necessary to calculate the energy levels of the free ion. In the case of rare earth ions, the energy levels and the spectroscopic assignments of the free ion were summarized by Dieke.¹⁴ He introduced the following Hamiltonian:

$$H = H^0 + H^1 + H^2, \quad (2.29)$$

$$H^0 = -\left(\frac{\hbar^2}{2m_e}\right) \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \frac{Ze^2}{r_i} = T_e + V_{en}, \quad (2.30)$$

where $H^1 + H^2 \equiv V_{ee} + V_{so}$, as were defined by Eqs. (2.15), (2.16a), and (2.16b); H^0 is the zero-order approximation; ∇_i is the Laplacian operator for the i th electron of mass m_e ; and H^1 is the electrostatic repulsion between the $4f$ electrons, assuming the *central field approximation*,¹⁵ whereby each electron moves *independently* in a potential field of the nucleus plus an averaged field representing all other electrons. The Hamiltonian term of the mutual electrostatic repulsion of the electrons cannot be neglected because there are many electrons in the system, so their total effect is comparable with the interaction between the nucleus and the electrons, as expressed in Eq. (2.30) by $\sum_i^N (Ze^2/r_i)$.

This approximation is justified by the following assumptions:

1. The field lacks electrostatic repulsions between the “outer” electrons, as well as spin–spin interactions;
2. The interaction between the f electrons cannot be neglected as a small perturbation to the nuclear–electron potential; and
3. The interaction potential of the i th electron with the field of the nucleus is screened by the $N-1$ other electrons that are spherically averaged.

The electrostatic repulsion between the f electrons can be treated in two limiting cases, namely, when the distance r_i from the nucleus is large or when r_i is close to the nucleus and thus is small. There is usually a balance between the repulsion and the attraction terms, and they approximately cancel each other. Suppose that there is an atomic system with N electrons that are in motion around a nucleus with a charge Z_e , such that an electron i is located at a distance r_i from the nucleus, and the other $N-1$ electrons are distributed symmetrically with an average distance r_j from the nucleus ($r_i \gg r_j$, r_{ij} is the mutual distance between the i th and j th electrons). See Fig. 2.7 for this configuration.

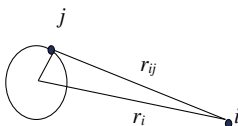


Figure 2.7 A schematic depiction of an N -electron system with $N-1$ electrons distributed symmetrically and with central field forces (modified and reprinted with permission from Condon and Shortley¹⁴).

Recall that the mutual repulsion of the electrons and the spin-orbit interaction Hamiltonian are defined by Eqs. (2.16c) and (2.16d) as

$$V_{ee} = \sum_{i>j=1}^N \frac{e^2}{r_{ij}}$$

and

$$V_{SO} = \sum_i^N \zeta(r_i) \cdot L_i \cdot S_i,$$

respectively, where the summation is over all of the electrons.

It is then assumed that $r_{ij} \approx r_i$ and that the i th electron will have a field as a result of the repulsion, attraction, and screening effects of the $N - 1$ electrons:

$$-\left(\frac{Ze^2}{r_i}\right) + \frac{(N-1)e^2}{r_i} \quad (2.31)$$

Consider a different situation, where $r_i \approx r_j$ or even $r_i \leq r_j$, and the $N - 1$ electrons are distributed spherically around the nucleus. There is a constant field and a constant potential inside the spherical shell with some radius a , and the potential energy of the i th electron located inside the shell is given by

$$-\left(\frac{Ze^2}{r_i}\right) + \frac{(N-1)e^2}{a}. \quad (2.32)$$

To summarize, the potential energy $U(r)$ is given by

$$U(r) \approx -\left(\frac{Ze^2}{r}\right) + C \quad \text{for small values of } r, \quad (2.33)$$

and

$$U(r) \approx -\left[\frac{(Z-N+1)e^2}{r}\right] \quad \text{for large values of } r. \quad (2.34)$$

Condon and Shortley¹⁴ demonstrate a functional dependence of the potential $U(r)$ on r for both small and large values of r . Here, the f electrons are termed “outer” electrons even though they lie closer to the nucleus than the $5s$ or $5p$ electrons (see Fig. 2.7). Furthermore, according to Eq. (2.29), H^1 is the electrostatic repulsion between the f electrons given by summation over all of the electron pairs, assuming a central field approximation with a spherical-symmetry electrostatic field due to the nucleus and due to other filled shells:

$$H^1 = \sum_{ij} \frac{e^2}{r_{ij}}, \quad (2.35)$$

where r_{ij} is the mutual distance between the i th and j th electrons.

2.5.1 Spin–orbit coupling

The electrostatic interaction splits the energy levels of the $4f^n$ electronic configuration into LS terms, and the appropriate wavefunctions are characterized by L , S , M_L , and M_S quantum numbers. Going back to Eq. (2.29), the term H^2 is defined as the spin–orbit interaction, and it is given by:

$$H^2 = \sum_{i=1}^n \zeta_i (l_i \cdot s_i). \quad (2.36)$$

where ζ_i is the spin–orbit interaction constant of the i th electron. This constant is proportional to the effective positive charge and to the fine structure constant. As can be seen in Table 2.4, there is a correlation between the atomic number of the rare earth ion and the value of ζ .

Once again, note that if the energy separation between different LS terms [Eq. (2.35)] is large compared with the spin–orbit coupling energy, a situation arises where there is little mixing of the LS terms and the spin coupling states. In this case, the Russell–Saunders approximation is used, and the spin–orbit coupling operator appears as $V_{LS} = \lambda \cdot L \cdot S$ (see Section 2.2). Similarly, there is a functional correlation between ζ_i , defined by Eq. (2.36), and the value of λ . Under Russell–Saunders approximation, the wavefunctions are characterized by L , S , J , and M_J quantum numbers. The spin–orbit interaction causes further splitting of each LS term into various values of J and M_J (J multiplets).

The physical origin of the spin–orbit coupling is a result of the interaction of the magnetic moment of the electron spin, $M_S = qSm_e$ (where q is the electron charge, m_e is the electron mass, and S is the electron spin), with the magnetic field that results from the motion of the electron in the electrostatic field of the nucleus, which is defined as $B = -1/c^2(v \cdot E)$. The interaction

Table 2.4 Numerical values of the spin–orbit coupling parameter for several rare earth ions (data from Dieke¹¹). The number of electrons in the $4f$ shell and the atomic number are also included.

Rare earth ion	Atomic number (Z)	Number of electrons (n)	Empirical parameter ζ (cm^{-1})
Ce ³⁺	58	1	640
Pr ³⁺	59	2	759
Nd ³⁺	60	3	885
Eu ³⁺	63	6	1320
Gd ³⁺	64	7	1470
Tb ³⁺	65	8	1705
Ho ³⁺	67	10	2163
Er ³⁺	68	11	2393
Tm ³⁺	69	12	2617
Yb ³⁺	70	13	2883

energy between the magnetic moment of the spin and the magnetic field B is given by $W = -M_S \cdot \mathbf{B}$; after some mathematics, the magnetic field is given by $B = -K \cdot \mathbf{P} \cdot \mathbf{R} = K \cdot \mathbf{L}$, and the spin-orbit interaction energy is given by

$$W_{LS} = K' \cdot \mathbf{L} \cdot \mathbf{S},$$

where K' is the spin-orbit constant defined as

$$K' = \xi(R) = \left(\frac{e^2}{m_e c^2} \right) \left(\frac{1}{R^3} \right), \quad (2.37)$$

and R is the electron-nucleus distance (which is on the order of the Bohr radius, namely, $a_0 = \hbar/m_e e^2$).

The mutual interaction between the magnetic moment of the spin and the magnetic field is regarded as a small perturbation to the energy levels that result from a purely Coulombic interaction. Consider the simple case of a one-electron system. Because the spin-orbit interaction couples both the spin and the orbital motions of the electron, the appropriate angular momenta m_l and m_s are not independent and thus are not “good” quantum numbers. The total angular momentum j ($j = l + s$) and its z component represent an atomic system similar to Eqs. (2.3) and (2.4), with total-angular-momentum quantum numbers in the range of $|l - s| \leq j \leq |l + s|$ and in steps of $j + 1$. The same is true for J , L , and S , so that $[J_z, H_{so}] = [L_z + S_z, H_{so}] = 0$, and $[J_z, H_{so}] = 0$, as well.

For atoms with a low atomic number, the effect of H^2 is low, and thus $H^2 < H^1$. For atoms with a high atomic number, the effect of spin-orbit coupling is *greater* than the Coulombic interaction between the outer electrons [see Eqs. (2.35) and (2.36) for more details]. In this case, there is a coupling of the spin and orbital angular momenta on single electrons to form individual j values, which are further coupled via Coulombic interaction between the electrons; this is the case with jj coupling. For the case of $H^2 < H^1$, namely, when the spin-orbit interaction is smaller than the Coulombic interaction, it was shown by Tinkham¹⁶ that the matrix elements of the spin-orbit operator, i.e., $H_{so} = \lambda \cdot \mathbf{L} \cdot \mathbf{S} = \lambda/2(\mathbf{J}^2 - \mathbf{L}^2 - \mathbf{S}^2)$, and the eigenvalues are $\lambda/2[(J(J+1) - L(L+1) - S(S+1))] = \lambda J$, similar to Eqs. (2.10a) and (2.10b). The spin-orbit splitting is also shown to be proportional to the larger values of J when the two adjacent J levels are considered.

2.6 Energy Levels of Rare Earth Ions

Because the degeneracy of the f levels is removed by the interactions expressed by the H^1 and H^2 Hamiltonians, as well as by the lattice crystal field, there are ~ 3400 levels and wavefunctions to be computed with one configuration. To simplify the situation, it was first assumed that the dominant interaction is between states within one configuration only, and the interactions between

states of different configurations are ignored. This assumption is partially justified because the $4f^n$ configuration is shielded from the $5p$ and $5s$ configurations; however, it was found that the overlap integral between the $4f$ and $5p$ configurations is quite large, as can be seen in Fig. 2.2. The general perturbation matrix $\mathbf{S} = S(H^1, H^2, \dots, H^k)$ represents a general combination of perturbation matrices H^k . With the assumption of Russell–Saunders coupling, the energy levels of rare earth ions are characterized by L , S , and J , and each level is $(2L + 1)(S + 1)$ -fold degenerate.

As an example, the Yb^{3+} ion ($4f^{13}$) has a unique electronic structure due to its large Coulombic interaction, as well as a large spin–orbit interaction constant ζ . Because of these larger interactions, the first excited state of Yb^{3+} (namely, ${}^4F_{5/2}$) is $\sim 10,000 \text{ cm}^{-1}$ above the ground state ${}^4F_{7/2}$. The main assumption of the energy-level calculations in the central field approximation is that the wavefunction of a many-electron system is a sum of a single electron wavefunction.¹⁷ As a consequence of this assumption, the matrix representation of an N electron system is reduced to the sums of the components of individual electrons, and can be calculated using the Coulomb integral or exchange integral. The energies of the wavefunctions are calculated using a set of Slater integrals, denoted by F^k , such that

$$F^k = \int_0^\infty \int_0^\infty \frac{r_{<}^k}{r_{>}^{k+1}} R_i^2(n^a l^a) R_j^2(n^b l^b) dr_i dr_j, \quad (2.38)$$

in which $R(nl)$ is the radial eigenfunction of the relevant configuration, a and b are a set of quantum numbers that specify the central field of both i and j electron pairs, and k is an integer that was introduced via a series of Legendre polynomials (which are used to describe the electrostatic potential). Legendre polynomials are given by the expression $P_k(\cos \theta)$, where θ is the angle between r_i and r_j , with the values of k ranging from 0 to ∞ . The square of the radial eigenfunction $R^2(nl)$ is the probability of finding an electron in the radius dr_i and dr_j . The symbols $r_{<}$ and $r_{>}$ are lesser and greater than r_i and r_j , respectively. The Slater integral F^k appears in the Coulomb integral $J(a, b)$ that is used to calculate the Coulombic interaction:

$$J(a, b) = \langle a, b | e^2 r_{ij}^{-1} | a, b \rangle; \quad (2.39)$$

more specifically, it can be expressed as

$$J(a, b) = \sum_{k=0}^{\infty} a^k (l^a m_l^a, l^b m_l^b) F^k (n^a l^a, n^b l^b). \quad (2.40)$$

For f – f transitions within rare earth ions, the Slater integral is written as

$$F_k = F^k / D_k, \quad (2.41)$$

where the values of D_k are $= 1, 225, 1089, 7361.34$ for $k = 0, 2, 4, 6$.

The parameter F^0 is a common additive constant to all levels, and therefore it does not have any effect on the electronic structure of the atomic system. The energy levels of rare earth ions can be expressed by three parameters,^{17,18} namely, F_2 , F_4 , and F_6 , such that

$$\begin{aligned} F_2 &= F^2/225, \\ F_4 &= F^4/1089, \\ F_6 &= F^6/7361.64. \end{aligned} \quad (2.42)$$

These integrals can be expressed in terms of Racah parameters E^k ($k = 0, 1, 2, 3, \dots$), which are linear combinations of the Slater integrals. For example,

$$\begin{aligned} E^0 &= F^0 - \left(\frac{2F^2}{45}\right) - \left(\frac{F^4}{33}\right) - \left(\frac{50F^6}{1286}\right), \\ E^1 &= \frac{14F^2}{405} + \frac{7F^4}{297} + \frac{350F^6}{11583}, \\ E^2 &= \left(\frac{F^2}{2025}\right) - \left(\frac{F^4}{3267}\right) + 175\frac{F^6}{1656369}, \\ E^3 &= \frac{F^2}{135} + \left(\frac{2F^4}{1089}\right) - \left(\frac{175F^6}{42471}\right). \end{aligned} \quad (2.43)$$

Assuming that the wavefunctions under the central field approximation are known, then the Slater integrals F^k or F_k can be calculated. Dieke noted that by using further approximations such as the central Coulombic field for f^n configuration and the hydrogen-like radial wavefunctions, F_k can be expressed in terms of a *single* parameter F_2 and the effective nuclear charge Z :

$$\begin{aligned} F_4 &= 0.145F_2, \\ F_6 &= 0.0164F_2, \\ F_2 &= 12.4(Z - 34) \text{ (for rare earth, triply ionized ions)}. \end{aligned} \quad (2.44)$$

A useful parameter to measure the effects of spin-orbit coupling, the relative energy splitting and the relative energetic positions of the J multiplets is defined as $\chi = \zeta/F_k$. It is assumed that the F_2 parameter characterizes the Coulombic interaction strength of the system, and ζ characterizes the spin-orbit interaction. Figure 2.8 presents the relative energy positions of various multiplets as a function χ . The vertical dashed lines in this figure indicate the case of Nd^{3+} ($\chi = 2.7$) and Er^{3+} ($\chi = 5.7$). It is clear that for $\zeta = 0$ (no spin-orbit coupling), there is no splitting of the LS terms, as can be expected.

Possible errors in calculating the energy levels of the f^n configuration using the described procedure are discussed in Chapter 6 of Dieke.¹⁴ A summary and more information on the spectroscopic properties of rare-earth-doped solids can be found in Refs. [1, 7, 13, 14, and 17].