1.2 Rare earth atoms

The starting point for the understanding of the magnetism of the rare earths is the description of the electronic states, particularly of the $4f$ electrons, in the atoms. The wavefunction $\Psi(\mathbf{r}_1\sigma_1, \mathbf{r}_2\sigma_2, \ldots, \mathbf{r}_Z\sigma_Z)$ for the electrons, which is a function of the space and spin coordinates $\mathbf{r}$ and σ of the Z electrons which constitute the electronic charge cloud (Z is the atomic number), is determined for the stationary state of energy E from the Schrödinger equation

$$\mathcal{H}\,\Psi = E\,\Psi, \tag{1.2.1}$$

where the non-relativistic Hamiltonian operator is

$$\mathcal{H} = -\frac{\hbar^2}{2m}\sum_i^Z \nabla_i^2 + \frac{1}{2}\sum_{ij}^Z \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_i^Z v_{\text{ext}}(\mathbf{r}_i) \tag{1.2.2}$$

and, in the case of an atom, the 'external' potential $v_{\text{ext}}(\mathbf{r})$ is just the Coulomb potential $-Ze^2/r_i$ due to the nuclear attraction. As is well known, the difficulties in solving this problem reside in the second term, the Coulomb interaction between the electrons. For heavy atoms, exact solutions require a prohibitive amount of computation, while any possibility of an exact solution for the electronic states in a metal is clearly out of the question. It is therefore necessary to replace the Coulomb interaction by a self-consistent field, which is most satisfactorily determined by means of the density-functional theory of Hohenberg and Kohn (1964) and Kohn and Sham (1965).

The first step is to write the Hamiltonian (1.2.2) in the symbolic form

$$\mathcal{H} = T + U + V, \tag{1.2.3}$$

incorporating the kinetic energy, the Coulomb repulsion between the electrons, and the external potential, due to the nucleus in the atom or the periodic lattice potential in the solid. Hohenberg and Kohn (1964) established two important results. Firstly, they showed that the external potential is a unique functional of the electron density $n(\mathbf{r})$, and hence that the ground-state wavefunction Φ and the energy functional

$$<\Phi\,|\,\mathcal{H}\,|\,\Phi> \,=\, <\Phi\,|\,(T+U)\,|\,\Phi> + \int v_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})d\mathbf{r} \qquad (1.2.4)$$

are unique functionals of $n(\mathbf{r})$. Secondly, they proved that the energy functional (1.2.4) attains its minimum value, the ground-state energy, for the correct ground-state density. Hence, if the universal functional $<\Phi\,|\,(T+U)\,|\,\Phi>$ were known, it would be straightforward to use this variational principle to determine the ground-state energy for any specified external potential. However, the functional is not known, and the complexity of the many-electron problem is associated with its approximate determination.

Guided by the successes of the one-electron model, Kohn and Sham (1965) considered a system of non-interacting electrons with the same density as that of the real system, satisfying the single-particle Schrödinger equation

$$\Big[-\frac{\hbar^2}{2m}\nabla^2 + v_{\mathrm{eff}}(\mathbf{r})\Big]\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}). \qquad (1.2.5)$$

The ground state Φ_S of such a system is just the antisymmetrized product, or *Slater determinant*, formed from the Z lowest-lying one-electron orbitals, so that the electron density is the sum over these orbitals:

$$n(\mathbf{r}) = \sum_i^Z |\psi_i(\mathbf{r})|^2. \qquad (1.2.6)$$

The effective potential $v_{\mathrm{eff}}(\mathbf{r})$ must therefore be determined so that $n(\mathbf{r})$ is also the ground-state density of the real system. To accomplish this, the energy functional (1.2.4) may be written in the form

$$\begin{aligned} <\Phi\,|\,\mathcal{H}\,|\,\Phi> &= <\Phi_S|\,T\,|\,\Phi_S> \\ &+ \int \Big[\frac{1}{2}\int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\mathrm{ext}}(\mathbf{r})\Big]n(\mathbf{r})d\mathbf{r} + E_{\mathrm{xc}}\{n(\mathbf{r})\}, \end{aligned} \qquad (1.2.7)$$

where the first contribution is the kinetic energy of the non-interacting system, and the second is the Hartree energy of the charge cloud. The last term is the difference between the true kinetic energy and that of the non-interacting system, plus the difference between the true interaction energy of the system and the Hartree energy. This exchange-correlation energy encompasses our ignorance of this problem, and is presumably relatively small. In the *local* approximation, which is adopted to convert the density-functional theory into a practical method, this energy is written

$$E_{\rm xc}\{n(\mathbf{r})\} \approx \int \varepsilon_{\rm xc}[n(\mathbf{r})]n(\mathbf{r})d\mathbf{r}, \tag{1.2.8}$$

and the effective potential is therefore

$$v_{\rm eff}(\mathbf{r}) = \int \frac{e^2 n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{\rm ext}(\mathbf{r}) + v_{\rm xc}[n(\mathbf{r})], \tag{1.2.9}$$

where

$$v_{\rm xc}[n(\mathbf{r})] = d[n\varepsilon_{\rm xc}(n)]/dn \equiv \mu_{\rm xc}[n(\mathbf{r})] \tag{1.2.10}$$

is the local approximation to the exchange-correlation contribution to the chemical potential of the electron gas. Useful estimates of this quantity have been obtained from calculations for a homogeneous electron gas of density $n(\mathbf{r})$ by Hedin and Lundqvist (1971), von Barth and Hedin (1972), and Gunnarsson and Lundqvist (1976), and these are frequently used in calculations on both atoms and solids.

In order to determine the atomic structure, the Schrödinger equation (1.2.5) must be solved by the Hartree self-consistent procedure, in which, through a process of iteration, the potential (1.2.9) generates wavefunctions which, via (1.2.6), reproduce itself. Since this potential is spherically symmetric in atoms, the single-particle wavefunctions may be written as the product of a radial function, a spherical harmonic and a spin function

$$\psi_{nlm_lm_s}(\mathbf{r}\sigma) = i^l R_{nl}(r) Y_{lm_l}(\hat{\mathbf{r}})\chi_{m_s}, \tag{1.2.11}$$

where $\hat{\mathbf{r}}$ is a unit vector in the direction of $\mathbf{r}$, the spin quantum number m_s can take the values $\pm\frac{1}{2}$, and the phase factor i^l is included for later convenience. The radial component satisfies the equation

$$-\frac{\hbar^2}{2m}\frac{d^2[rR_{nl}(r)]}{dr^2} + \Big(v_{\rm eff}(r) + \frac{l(l+1)\hbar^2}{2mr^2} - \varepsilon\Big)[rR_{nl}(r)] = 0. \tag{1.2.12}$$

Some radial wavefunctions for rare earth atoms are shown in Fig. 1.1. The $4f$ electrons are well embedded within the atom, and shielded by the $5s$ and $5p$ states from the surroundings. The $5d$ and $6s$ electrons form the conduction bands in the metals. The incomplete screening of the increasing nuclear charge along the rare earth series causes the lanthanide contraction of the wavefunctions, which is reflected in the ionic and atomic radii in the solid state. In particular, as illustrated in Fig. 1.1, the $4f$ wavefunction contracts significantly between Ce, which has one $4f$ electron, and Tm, which has one $4f$ hole in the atom, though two in the metallic state. The angular dependences of the $4f$ wavefunctions are depicted in Fig. 1.2. The charge clouds are highly anisotropic, with pronounced multipoles whose magnitudes and signs change dramatically with m_l. As we shall see, this anisotropy is clearly manifested in the magnetic properties of the metals.

Since they are among the heavier elements, relativistic effects are of substantial importance in the rare earths. These are most straightforwardly taken into account by solving the Dirac equation in the central

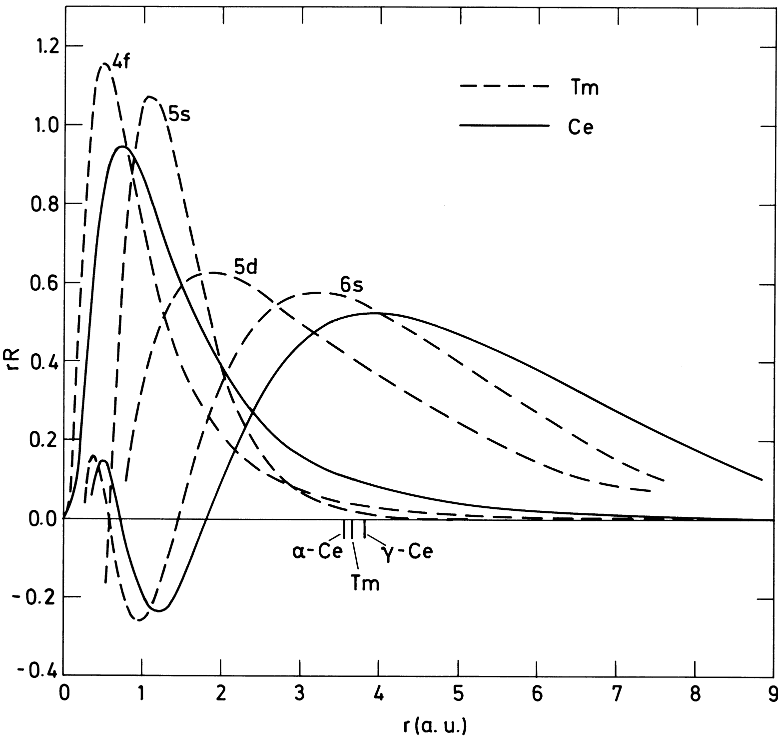

Fig. 1.1. The radial components of atomic wavefunctions for Ce, which has one $4f$ electron, and Tm, which has 13 $4f$ electrons, or one $4f$ hole. The Tm wavefunctions are contracted, relative to those of Ce, due to the incomplete shielding of the greater nuclear charge. As a consequence, the amplitude of the $4f$ wavefunction at the indicated Wigner–Seitz radius is much greater in Ce than in Tm, which has important consequences for the character of the $4f$ states in the metals.

field, rather than the Schrödinger equation, but it may be more instructive to consider them as perturbations which, to order $(p/mc)^2$, augment the one-electron potential with

$$-\frac{p^4}{8m^3c^2} - \frac{\hbar^2}{4m^2c^2}\frac{dv}{dr}\frac{\partial}{\partial r} + \frac{1}{2m^2c^2r}\frac{dv}{dr}\,\mathbf{s}\cdot\mathbf{l}. \qquad (1.2.13)$$

The first term, which is due to the increase of mass with velocity, reduces the energy of all states by an amount which decreases with l, while the second 'Darwin' term increases the energy of s states only. These effects may both be incorporated into the central field, but the last term couples together the spin and orbital motion in a way that has far-reaching consequences for the magnetic properties.

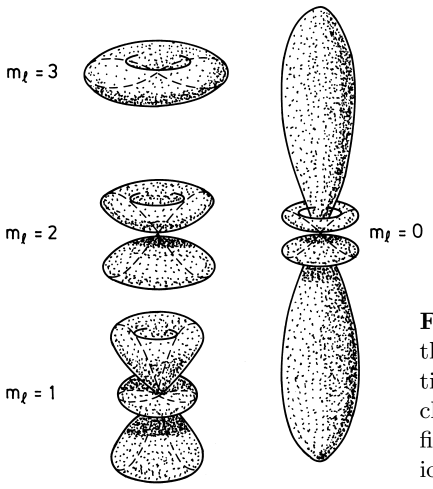

Fig. 1.2. The angular variation of the $4f$ wavefunctions. The interaction of the highly anisotropic charge clouds with the crystalline electric fields gives rise to the large single-ion anisotropies observed in the rare earth metals.

In the Russell–Saunders coupling scheme, which is an accurate procedure for the $4f$ electrons, the spins $\mathbf{s}_i$ of the individual $4f$ electrons are coupled by the exchange interaction, diagonal in the total spin $\mathbf{S}$ of the incompletely filled subshell, while the Coulomb interaction similarly combines the $\mathbf{l}_i$ into the total orbital momentum $\mathbf{L}$. In terms of the one-electron functions, the wavefunction for the subshell may be written

$$\Psi(LSM_LM_S) = \sum_{m_l m_s} C(LSM_LM_S; m_l m_s)\psi(m_l m_s), \qquad (1.2.14)$$

where the $C(LSM_LM_S; m_l m_s)$ are the *Clebsch–Gordan* or *Wigner* coefficients. It is convenient to write this expansion in a representationindependent form, in terms of the state vectors

$$|LSM_LM_S\!> \,= \sum_{m_lm_s} <\!m_lm_s|LSM_LM_S\!>|m_lm_s\!> . \qquad (1.2.15)$$

The exchange and Coulomb interactions are sufficiently large that the magnetic properties at all accessible temperatures are determined by the S and L states of lowest energy. These are found from Hund's rules; S is maximized and, subject to this maximum S value, L is also maximized. This results in the values for the trivalent ions shown in Table 1.1.

Table 1.1. Properties of the tripositive rare earth ions.

$4f^n$	Ion^{+++}	L	S	J	g	$(g-1)^2J(J+1)$	$\Delta(K)$
0	La	0	0	0	—		
1	Ce	3	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{6}{7}$	0.18	3150
2	Pr	5	1	4	$\frac{4}{5}$	0.80	3100
3	Nd	6	$\frac{3}{2}$	$\frac{9}{2}$	$\frac{8}{11}$	1.84	2750
4	Pm	6	2	4	$\frac{3}{5}$	3.20	2300
5	Sm	5	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{2}{7}$	4.46	1450
6	Eu	3	3	0	—		500
7	Gd	0	$\frac{7}{2}$	$\frac{7}{2}$	2	15.75	
8	Tb	3	3	6	$\frac{3}{2}$	10.50	2900
9	Dy	5	$\frac{5}{2}$	$\frac{15}{2}$	$\frac{4}{3}$	7.08	4750
10	Ho	6	2	8	$\frac{5}{4}$	4.50	7500
11	Er	6	$\frac{3}{2}$	$\frac{15}{2}$	$\frac{6}{5}$	2.55	9350
12	Tm	5	1	6	$\frac{7}{6}$	1.17	11950[a]
13	Yb	3	$\frac{1}{2}$	$\frac{7}{2}$	$\frac{8}{7}$	0.32	14800
14	Lu	0	0	0	—		

[a] The lowest excited state in Tm is $^3F_4$ at 8490K.

It is a consequence of the *Wigner–Eckart theorem* that the spin–orbit term in (1.2.13) can be written

$$\mathcal{H}_{\rm so} = \pm\zeta(LS)\,\mathbf{S}\cdot\mathbf{L}, \qquad (1.2.16)$$

where

$$\zeta(LS) = \frac{\pi}{m^2c^2S}\int rR_{4f}^2(r)\frac{dv}{dr}dr, \qquad (1.2.17)$$

and the + and − signs refer respectively to a less or more than half-filled subshell. The spin and orbital angular momenta are thus combined into the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. These states may be written

$$|JM_JLS\!> \,= \sum_{M_LM_S} \,<\! LSM_LM_S|JM_JLS\!> |LSM_LM_S\!> . \qquad (1.2.18)$$

Because of the sign of (1.2.16), the value of J in the ground state is $L \mp S$, according as the subshell is less or more than half-full. Roughly speaking, $\mathbf{L}$ is always parallel to $\mathbf{J}$, but $\mathbf{S}$ is antiparallel in the first half of the series and parallel in the second half. The energy separation to the first excited multiplet may be determined from the matrix elements of (1.2.16), and is given by

$$\Delta = \zeta(LS)\begin{cases} (J+1) \\ J \end{cases} \qquad (1.2.19)$$

again depending on whether the subshell is respectively less or more than half-filled. The values of J in the ground state and of Δ, obtained from spectroscopic measurements on rare earth salts (Dieke 1968), are given in Table 1.1.

The magnetization of an assembly of N rare earth atoms or ions is given by the derivative of the free energy with respect to magnetic field:

$$M = -\frac{1}{V}\frac{\partial F}{\partial H} \qquad (1.2.20)$$

or, recalling that

$$F = -\frac{N}{\beta}\ln\sum_n e^{-\beta E_n(H)}, \qquad (1.2.21)$$

where $E_n(H)$ are the atomic energy levels in the field, and $\beta = 1/k_BT$,

$$M = \frac{N}{V}\sum_n -\frac{\partial E_n}{\partial H}e^{-\beta E_n} \Big/ \sum_n e^{-\beta E_n}. \qquad (1.2.22)$$

Neglecting the small diamagnetic susceptibility, the magnetic contribution to the Hamiltonian is given by the Zeeman term

$$\mathcal{H}_Z = -\mu_B(\mathbf{L} + g_0\mathbf{S})\cdot\mathbf{H}, \qquad (1.2.23)$$

where μ_B is the Bohr magneton. Because of the negative charge on the electron, the angular momentum and the magnetic moment are *antiparallel*. This gives rise to certain difficulties, which are frequently ignored in the literature. We shall circumvent them by taking $\mathbf{L}$, $\mathbf{S}$, and $\mathbf{J}$ as signifying the *negative* of the corresponding angular-momentum vector. We shall furthermore from now on take the gyromagnetic ratio g_0 as 2. Second-order perturbation theory then gives the magnetic contribution to the energy:

$$\delta E_n(H) = -\mu_B \mathbf{H}\cdot\!<\!n|\,\mathbf{L}+2\mathbf{S}\,|n\!> + \sum_{m\neq n} \frac{|\!<\!n|\,\mu_B\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})|m\!>\!|^2}{E_n - E_m}. \tag{1.2.24}$$

Problems of degeneracy are taken care of by using the $|JM_JLS\!>$ basis, whose degeneracy is completely lifted by the field. In this basis, and within a particular JLS-multiplet, the Wigner–Eckart theorem implies that the matrix elements of $(\mathbf{L}+2\mathbf{S})$ are proportional to those of $\mathbf{J}$, so that

$$<\!JLSM_J|\,\mathbf{L}+2\mathbf{S}\,|JLSM_J'\!> = g(JLS)<\!JLSM_J|\,\mathbf{J}\,|JLSM_J'\!>, \tag{1.2.25}$$

and the proportionality constant, *the Landé factor*, is

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \tag{1.2.26}$$

Within this multiplet, we may write eqn (1.2.25) in the shorthand form $\mathbf{L}+2\mathbf{S} = g\mathbf{J}$, and consider the effective moment on the atom to be

$$\boldsymbol{\mu} = g\mu_B\mathbf{J}. \tag{1.2.27}$$

With the same proviso, we may similarly write

$$\mathbf{L} = (2-g)\mathbf{J}, \tag{1.2.28}$$

and

$$\mathbf{S} = (g-1)\mathbf{J}. \tag{1.2.29}$$

If J is non-zero, the first-order term in (1.2.24), combined with (1.2.22) gives a magnetization for the ground-state multiplet:

$$M(H,T) = \frac{N}{V} g\mu_B J B_J(\beta g\mu_B J H), \tag{1.2.30}$$

where the *Brillouin function* is

$$B_J(x) = \frac{2J+1}{2J}\coth\frac{2J+1}{2J}x - \frac{1}{2J}\coth\frac{1}{2J}x. \tag{1.2.31}$$

If $g\mu_B JH$ is small compared with k_BT, the susceptibility is constant and given by *Curie's law*:

$$\chi = \frac{M}{H} = \frac{g^2\mu_B^2 J(J+1)}{3k_BT}\frac{N}{V} \equiv \frac{C}{T}, \tag{1.2.32}$$

where C is the *Curie constant.* The second-order non-diagonal term in (1.2.24) gives a paramagnetic contribution to χ which is independent of temperature, provided that the thermal population of the excited states is negligible. This *Van Vleck paramagnetism* is very small in the heavy rare earths, but in the first half of the series it is given by

$$\chi_V = \frac{2\mu_B^2(L+1)S}{3(J+1)\Delta}\frac{N}{V}, \tag{1.2.33}$$

which may be significant, since

$$\frac{\chi_V}{\chi} = \frac{2(L+1)S}{g^2J(J+1)^2}\frac{k_BT}{\Delta} = \frac{\alpha k_BT}{\Delta}, \tag{1.2.34}$$

where, from Table 1.1, α takes the modest value of 0.19 for Pr, but is 12 for Sm. Since Δ is only 1450 K, the Van Vleck paramagnetism in Sm is significant even at rather low temperatures. In trivalent Eu, $J = 0$ in the ground state and the paramagnetic susceptibility is due entirely to the mixing of the excited states into the ground state by the field, and to the thermal excitation of these states. However, Eu metal is divalent and the ${}^8S_{7/2}$ ionic susceptibility follows Curie's law very closely. The Van Vleck paramagnetism arising from the mixing of states of different J will not play a significant role in our later discussion, but the analogous phenomenon of the mixing of states of different M_J, split by the crystalline electric field in the metal, will be of central importance.