The Magnetic Hamiltonian

Most of the magnetic properties that we shall consider arise from electrons. In this chapter we shall develop the Hamiltonian which pertains to the magnetic behavior of a system of electrons. It has been found experimentally that the electron possesses an intrinsic magnetic moment, or *spin*. The existence of such a moment is a consequence of relativistic considerations. Therefore it is essential that we look for a relativistic description of the motion of an electron. This is given by the *Dirac wave equation*. We shall limit our discussion of the Dirac equation to the origin of the spin and the form of the spin-orbit interaction (for a more thorough treatment see [6]).

2.1 The Dirac Equation

The objective in developing a relativistic quantum theory of the electron is to ensure that space coordinates and time enter the theory symmetrically. There are several ways of doing this. One way is to start with the general wave equation

$$i\hbar\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = \mathcal{H}\psi(\boldsymbol{r},t)\,. \tag{2.1}$$

Since the first derivative with respect to time enters on the left, the Hamiltonian must contain a linear space derivative, that is, the Hamiltonian must be linear in the momentum, $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla}$. Thus we assume that the Hamiltonian has the form

$$\mathcal{H} = c\boldsymbol{\alpha}\cdot\boldsymbol{p} + \beta mc^2\,, \tag{2.2}$$

where $\boldsymbol{\alpha}$ and β are arbitrary coefficients. By imposing certain requirements on the solutions of (2.1), such as that it gives the correct energy-momentum relation $E^2 = p^2c^2 + m^2c^4$ we obtain conditions on the quantities $\boldsymbol{\alpha}$ and β. These conditions may be satisfied by the 4×4 representations

$$\beta = \begin{bmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{bmatrix} \quad\text{and}\quad \boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{bmatrix}\,, \tag{2.3}$$

where the σ_i are the Pauli matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \mathbf{1} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (2.4)$$

Thus the wave function ψ must be a four-component object. Two of the components correspond to positive-energy solutions and the other two correspond to negative-energy solutions. Holes in the negative-energy spectrum correspond to positrons and require energies of the order of mc^2 for their production.

From a Lagrangian formulation we find that the effect of an external electromagnetic field described by the vector potential $\boldsymbol{A}$ and the scalar potential ϕ may be included by making the substitutions $\boldsymbol{p} \to \boldsymbol{p} - (e/c)\boldsymbol{A}$ and adding $e\phi$ to the Hamiltonian. Thus the Dirac equation becomes

$$i\hbar \frac{\partial \psi}{\partial t} = \left[c\boldsymbol{\alpha} \cdot \left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A} \right) + \beta mc^2 + e\phi \right] \psi. \quad (2.5)$$

Since the energies encountered in magnetic phenomena are much smaller than mc^2, it is convenient to decouple the positive- and negative-energy solutions. This is accomplished by a canonical transformation due to Foldy and Wouthuysen [7]. The resulting Hamiltonian associated with the positive-energy solutions has the form

$$\mathcal{H} = \left[mc^2 + \frac{1}{2m}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A} \right)^2 - \frac{p^4}{8m^3c^2} \right] + e\phi - \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot \boldsymbol{H}$$

$$- i\frac{e\hbar^2}{8m^2c^2}\boldsymbol{\sigma} \cdot \boldsymbol{\nabla} \times \boldsymbol{E} - \frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot \boldsymbol{E} \times \boldsymbol{p} - \frac{e\hbar^2}{8m^2c^2}\boldsymbol{\nabla} \cdot \boldsymbol{E}. \quad (2.6)$$

The interesting terms in this Hamiltonian are the last four. The term

$$-(e\hbar/2mc)\boldsymbol{\sigma} \cdot \boldsymbol{H}$$

corresponds to the interaction of the intrinsic spin of the electron with the external field $\boldsymbol{H}$. The next two terms are spin-orbit terms. In a stationary vector potential $\boldsymbol{\nabla} \times \boldsymbol{E} = 0$. And, if the scalar potential, $V(r)$, is spherically symmetric,

$$\boldsymbol{\sigma} \cdot \boldsymbol{E} \times \boldsymbol{p} = -\frac{1}{r}\frac{\partial V}{\partial r}\boldsymbol{\sigma} \cdot \boldsymbol{r} \times \boldsymbol{p} = -\frac{\hbar}{r}\frac{\partial V}{\partial r}\boldsymbol{\sigma} \cdot \boldsymbol{l},$$

where $\hbar\boldsymbol{l} = \boldsymbol{r} \times \boldsymbol{p}$. Thus, the spin-orbit terms reduce to

$$\frac{e\hbar^2}{4m^2c^2}\frac{1}{r}\frac{\partial V}{\partial r}\boldsymbol{\sigma} \cdot \boldsymbol{l}. \quad (2.7)$$

This is what would be expected for an electron spin interacting with the field produced by its orbital motion, except that it is reduced by a factor

of $\frac{1}{2}$ due to relativistic kinematics, also known as the Thomas precession. The last term in (2.6), the so-called *Darwin term*, represents a correction to the Coulomb interaction due to fluctuations (zitterbewegung) in the electron position arising from the presence of the negative-energy component in the wave function.

The term $p^4/8m^3c^2$ in (2.6) is very small, and along with the Darwin term, it may be neglected for our purposes. If we define the zero of energy as the rest-mass energy, the Hamiltonian which governs the magnetic behavior of an electron is

$$\mathcal{H} = \frac{1}{2m} \left(\boldsymbol{p} - \frac{e}{c} \boldsymbol{A} \right)^2 + e\phi - \frac{e\hbar}{2mc} \boldsymbol{\sigma} \cdot \boldsymbol{H} + \zeta \boldsymbol{l} \cdot \boldsymbol{\sigma} \,, \qquad (2.8)$$

where we have introduced the spin-orbit parameter

$$\zeta = \frac{e\hbar^2}{4m^2c^2} \frac{1}{r} \frac{\partial V}{\partial r} \,.$$

The wave functions associated with (2.8) have two components. These two component functions transform differently under rotations in 3-dimensional space, as we shall see below, than vectors. They are called spinors.

2.2 Sources of Fields

In developing the general Hamiltonian for a single electron we found that the interaction of an electron with its environment is described by the scalar potential ϕ and the vector potential $\boldsymbol{A}$. Both these potentials are functions of the position of the electron under consideration as well as of the coordinates and momenta of any other particles in the system, that is,

$$\phi(\boldsymbol{r}; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{p}_1, \boldsymbol{p}_2, \ldots) \quad \text{and} \quad \boldsymbol{A}(\boldsymbol{r}; \boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{p}_1, \boldsymbol{p}_2, \ldots) \,.$$

In this section we shall investigate the form these potentials take in a crystalline solid. Our objective is to catalog all the interactions that enter into the magnetic properties of solids so that we shall be free to draw on these results later.

2.2.1 Uniform External Field

The simplest potentials are those arising from uniform external fields. For an electric field $\boldsymbol{E}$, uniform over all space, the interaction $e\phi$ becomes $-e\boldsymbol{r} \cdot \boldsymbol{E}$, where $e\boldsymbol{r}$ is the electric-dipole-moment operator.

For a uniform magnetic field $\boldsymbol{H}$ the magnetic vector potential is not uniquely defined. However, it is convenient to take $\boldsymbol{A} = \frac{1}{2} \boldsymbol{H} \times \boldsymbol{r}$. In this gauge $\nabla \cdot \boldsymbol{A} = 0$. Thus $(\boldsymbol{p} - e\boldsymbol{A}/c)^2/2m$ becomes

$$\frac{p^2}{2m} - \frac{e}{2mc}(\boldsymbol{r} \times \boldsymbol{p}) \cdot \boldsymbol{H} + \frac{e^2}{8mc^2}(\boldsymbol{H} \times \boldsymbol{r})^2 \,. \tag{2.9}$$

The first term is the kinetic-energy term. The second term is a paramagnetic term. Since $\boldsymbol{r} \times \boldsymbol{p} = \hbar \boldsymbol{l}$ is related to the electron's orbital moment $\boldsymbol{\mu}_l$, by

$$\boldsymbol{\mu}_l = \frac{e}{2mc}\boldsymbol{r} \times \boldsymbol{p} = -\frac{|e|\hbar}{2mc}\boldsymbol{l} = -\mu_B\boldsymbol{l} \,, \tag{2.10}$$

where

$$\mu_B \equiv \frac{|e|\hbar}{2mc}$$

is the *Bohr magneton*, this second term may be written as $\mu_B \boldsymbol{l} \cdot \boldsymbol{H}$. The third term is a diamagnetic term. When $\boldsymbol{H}$ is in the z direction, that is, $\boldsymbol{H} = H\hat{\boldsymbol{z}}$, then this term reduces to $(e^2H^2/8mc^2)(x^2 + y^2)$. This gives, for the total Hamiltonian of an electron in a uniform magnetic field,

$$\mathcal{H} = \frac{p^2}{2m} + \mu_B(\boldsymbol{l} + \boldsymbol{\sigma}) \cdot \boldsymbol{H} + \frac{e^2H^2}{8mc^2}\cdot(x^2 + y^2) + \zeta\boldsymbol{l} \cdot \boldsymbol{\sigma} \,. \tag{2.11}$$

2.2.2 The Electric Quadrupole Field

Let us now look into the potentials the electron sees as it moves around or past a nucleus. If we assume that the electron remains outside the nuclear charge and current distributions, we may expand $|\boldsymbol{r} - \boldsymbol{r}_n|^{-1}$ in spherical harmonics, which results in a *multipole expansion*.

Let us first consider the charge distribution. If $\rho(\boldsymbol{r}_n)$ is the charge density at a point $\boldsymbol{r}_n$ inside the nucleus, the electrostatic potential becomes

$$\phi(\boldsymbol{r}) = \int d\boldsymbol{r}_n \frac{\rho(\boldsymbol{r}_n)}{|\boldsymbol{r} - \boldsymbol{r}_n|}$$

$$= 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{Y_l^m(\theta, \varphi)}{(2l+1)r^{l+1}} \int d\boldsymbol{r}_n \rho(\boldsymbol{r}_n) Y_l^{m^*}(\theta_n, \varphi_n) r_n^l \,, \tag{2.12}$$

where $Y_l^m(\theta, \varphi)$ is the sperical harmonic (see Table 2.1). Writing out the first few terms explicitly, we have

$$\phi(\boldsymbol{r}) = 4\pi \frac{Y_0^0(\theta, \varphi)}{r} \int d\boldsymbol{r}_n \rho(\boldsymbol{r}_n) Y_0^{0^*}(\theta_n, \varphi_n)$$

$$+ 4\pi \sum_{m=-1}^{1} \frac{Y_1^m(\theta, \varphi)}{3r^2} \int d\boldsymbol{r}_n \rho(\boldsymbol{r}_n) r_n Y_1^{m^*}(\theta_n, \varphi_n)$$

$$+ 4\pi \sum_{m=-2}^{2} \frac{Y_2^m(\theta, \varphi)}{5r^3} \int d\boldsymbol{r}_n \rho(\boldsymbol{r}_n) r_n^2 Y_2^{m^*}(\theta_n, \varphi_n) + \dots \,. \tag{2.13}$$

Table 2.1. Spherical Harmonics

Y_0^0	$\sqrt{(1/4\pi)}$	$\sqrt{(1/4\pi)}$
Y_1^{-1}	$\sqrt{(3/8\pi)}\sin\theta e^{-i\varphi}$	$\sqrt{(3/8\pi)}(x-iy)/r$
Y_1^0	$\sqrt{(3/4\pi)}\cos\theta$	$\sqrt{(3/4\pi)}(z/r)$
Y_1^1	$-\sqrt{(3/8\pi)}\sin\theta e^{i\varphi}$	$-\sqrt{(3/8\pi)}(x+iy)/r$
Y_2^{-2}	$\sqrt{(15/32\pi)}\sin^2\theta e^{-2i\varphi}$	$\sqrt{(15/32\pi)}[(x-iy)^2/r^2]$
Y_2^{-1}	$\sqrt{(15/8\pi)}\sin\theta\cos\theta e^{-i\varphi}$	$\sqrt{(15/8\pi)}[z(x-iy)/r^2]$
Y_2^0	$\sqrt{(5/16\pi)}(3\cos^2\theta-1)$	$\sqrt{(5/16\pi)}[(3z^2-r^2)/r^2]$
Y_2^1	$-\sqrt{(15/8\pi)}\sin\theta\cos\theta e^{i\varphi}$	$-\sqrt{(15/8\pi)}[z(x+iy)/r^2]$
Y_2^2	$\sqrt{(15/32\pi)}\sin^2\theta e^{2i\varphi}$	$\sqrt{(15/32\pi)}[(x+iy)^2/r^2]$

Since $Y_0^0(\theta,\varphi)=1/\sqrt{4\pi}$, the first term becomes

$$\frac{1}{r}\int d\boldsymbol{r}_n\rho(\boldsymbol{r}_n)=\frac{Ze}{r}\,,\tag{2.14}$$

which is just the field arising from a point charge *at the origin*. We can make use of the spherical-harmonic addition theorem

$$\frac{4\pi}{2l+1}\sum_{m=-l}^{l}Y_l^{m*}(\theta_1,\varphi_1)Y_l^m(\theta_2,\varphi_2)=P_l(\cos\theta_{12})\tag{2.15}$$

to write the second term as

$$\frac{\hat{\boldsymbol{r}}}{r^2}\cdot\int d\boldsymbol{r}_n\rho(\boldsymbol{r}_n)\boldsymbol{r}_n\,.\tag{2.16}$$

The integral is the electric-dipole-moment operator of the nucleus. If the nuclear states have definite parity, the diagonal matrix elements of this operator vanish by symmetry. The third term is the *quadrupole* term.

Since we shall eventually be interested in computing matrix elements of the quadrupole term, as well as various other similar operators, it is appropriate to digress for a moment to develop a technique known as operator equivalents, for rewriting such operators in a form which greatly facilitates the evaluation of their matrix elements. This technique is based on the transformation properties of these operators.

Operator Equivalents. Suppose we consider a rotation of our coordinate system through some angle θ about an axis defined by $\hat{\boldsymbol{n}}$. Let this rotation be defined by a linear operator R which rotates any vector $\boldsymbol{r}$ into $R\boldsymbol{r}$. If θ is regarded as infinitesimally small, then

$$Rr = r + \theta\hat{n} \times r\,. \tag{2.17}$$

Under such a rotation a **scalar** wave function $\psi(r)$ is transformed into a new wave function $\psi'(Rr)$. If the system is invariant under rotation, then

$$\psi'(Rr) = \psi(r)\,. \tag{2.18}$$

This change may be characterized by a transformation $U_R(\theta)$ defined by

$$U_R(\theta)\psi(r) = \psi'(r)\,. \tag{2.19}$$

Using (2.18) this becomes

$$U_R(\theta)\psi(r) = \psi(R^{-1}r)\,. \tag{2.20}$$

Expanding the right side,

$$U_R(\theta)\psi(r) = \psi(r - \theta\hat{n} \times r) \simeq \psi(r) - (\theta\hat{n} \times r) \cdot \boldsymbol{\nabla}\psi(r)$$

$$\simeq \psi(r) - \frac{i}{\hbar}(\theta\hat{n} \times r) \cdot p\psi(r)\,.$$

Therefore

$$U_R(\theta) \simeq 1 - i\theta\hat{n} \cdot l\,, \tag{2.21}$$

where l is the orbital angular momentum in units of $\hbar$. For this reason we refer to l as the "generator" of infinitesimal rotations. This argument may be extended to finite rotations with the result

$$U_R(\theta) = \exp(-i\theta\hat{n} \cdot l)\,. \tag{2.22}$$

Since the *spinor* wave function associated with the Dirac equation is defined with respect to a definite axis, a rotation in ordinary three-dimensional space will also transform the components of this wave function. Rotation in the complex two-dimensional space is described by 2×2 complex unitary matrices. For example, the matrix for a clockwise rotation of θ about the z-axis is [13], p. 109

$$\begin{pmatrix} \cos\dfrac{\theta}{2} - i\sin\dfrac{\theta}{2} & 0 \\ 0 & \cos\dfrac{\theta}{2} + i\sin\dfrac{\theta}{2} \end{pmatrix} = \mathbf{1}\cos\frac{\theta}{2} - i\sigma_z\sin\frac{\theta}{2}\,.$$

Since $\sigma_z^{2n} = 1$ and $\sigma_z^{2n+1} = \sigma_z$, where n is an integer, this matrix expression is equivalent to $\exp(-\frac{1}{2}i\theta\sigma_z)$ which may be generalized to

$$\exp(-i\theta\hat{n} \cdot \boldsymbol{\sigma}/2) \tag{2.23}$$

Since $\boldsymbol{\sigma}/2$ is therefore the generator for rotations in spinor space we identify it as the spin angular momentum, s. The total angular momentum then becomes

$$\boldsymbol{j} = \boldsymbol{l} + \boldsymbol{s}$$

and the transformation generalizes to

$$U_R(\theta) = \exp(-i\theta\hat{\boldsymbol{n}} \cdot \boldsymbol{j})\,. \tag{2.24}$$

The orbital part, $\boldsymbol{l}$, acts on the $\boldsymbol{r}$-dependence of the wave function while $\boldsymbol{s}$ rearranges the components of the wave function.

For many-electron systems, such as atoms or ions, the total angular momentum is the vector sum of the angular momenta of the individual electrons,

$$\boldsymbol{L} = \sum_i \boldsymbol{l}_i\,, \quad \boldsymbol{S} = \sum_i \boldsymbol{s}_i \tag{2.25}$$

and $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$.

Let $|JM\rangle$ be an eigenfunction of $\boldsymbol{J}^2$ and J_z. (Since $\boldsymbol{J}^2$ commutes with J_z one can form a complete set of common eigenfunctions of $\boldsymbol{J}^2$ and J_z.) Then

$$U_R(\theta)|JM\rangle = \exp(-i\theta\hat{\boldsymbol{n}} \cdot \boldsymbol{J})|JM\rangle\,. \tag{2.26}$$

Inserting the identity in the form

$$\sum_{M'} |JM'\rangle\langle JM'| = 1$$

on the right gives

$$U_R(\theta)|JM\rangle = \sum_{M'} \langle JM'| \exp(-i\theta\hat{\boldsymbol{n}} \cdot \boldsymbol{J})|JM\rangle|JM'\rangle = \sum_{M'} D^j_{MM'}(\alpha\beta\gamma)|JM'\rangle\,. \tag{2.27}$$

Thus the rotation operator transforms the function $|JM\rangle$ into a linear combination of the states $|JM'\rangle$ whose coefficients are the matrix elements of the rotation operator itself, $D^J_{MM'}(\alpha\beta\gamma)$, where α, β, and γ are the Euler angles that specify the rotation.

Under the rotation U_R an *operator* O is transformed into $U_R O U_R^{-1}$. If the operator O consists of $2J+1$ functions T_{JM} $(M = -J, -J+1, \ldots, J)$, and *if* it transforms according to

$$U_R T_{JM} U_R^{-1} = \sum_{M'} D^J_{MM'}(\alpha\beta\gamma) T_{JM'}\,, \tag{2.28}$$

then it is called an *irreducible tensor operator* of rank J. This may seem a rather restrictive definition. However, it turns out that many operators encountered in physical situations are, in fact, tensor operators. For example, a vector is a tensor of rank 1; moments of inertia and quadrupole moments are tensors of rank 2. An example of an operator which may not be a tensor is the density operator discussed earlier.

Tensors have their own algebra, including various theorems. One of the most useful of these for our purposes is the *Wigner–Eckart theorem*. This states

that the matrix element of a tensor operator may be factored into a part which involves the projection quantum numbers and is independent of the tensor itself, and a part not involving the projection quantum numbers, called the *reduced matrix element*. The first part is, in fact, just the *Clebsch–Gordan coefficient* encountered in the coupling of angular momenta. Thus we have

$$\langle J'M'|T_{J''M''}|JM\rangle = C(JJ''J'; MM''M')\langle J'\|T_{J''}\|J\rangle, \tag{2.29}$$

where $C(JJ''J'; MM''M')$ is the Clebsch-Gordan coefficient and $\langle J'\|T_{J''}\|J\rangle$ is the reduced matrix element. Notice that if T' is also a tensor operator of the same rank as T, then the matrix elements of T are proportional to those of T'. This result has immense practical application to our magnetic Hamiltonian.

Let us return now to the quadrupole terms in $\phi(\boldsymbol{r})$. Writing the nuclear charge density as

$$\rho(\boldsymbol{r}_n) = e\sum_i \delta(\boldsymbol{r}_n - \boldsymbol{r}_i), \tag{2.30}$$

where $\boldsymbol{r}_i$ is the coordinate of a proton, the quadrapole moment Q_2^M becomes

$$Q_2^M = \sqrt{\frac{4\pi}{5}}\sum_i er_i^2 Y_2^M(\theta_i, \varphi_i). \tag{2.31}$$

Since the quadrupole moment operators Q_2^M are proportional to the spherical harmonics, they are tensor operators of rank 2. We can also form a tensor of rank 2 from the components of the total nuclear angular momentum $\boldsymbol{I}$. Thus if

$$T_2^{+1} = Q_2^{+1} = \frac{\sqrt{6}}{4}\sum_i z_i(x_i + iy_i), \tag{2.32}$$

this suggests that we form

$$(T')_2^{+1} = \frac{\sqrt{6}}{4}(I_z I^+ + I^+ I_z). \tag{2.33}$$

Notice that (2.33) is written in the symmetrized form. The reason for this is that the coordinates entering (2.32) commute with each other, whereas the angular momenta do not. Therefore, in order to preserve this symmetry, we must symmetrize the operator equivalent. By the Wigner–Eckart theorem, the matrix elements of these two operators must be proportional. Thus

$$\langle IM'|Q_2^{+1}|IM\rangle = \alpha\langle IM'|\frac{\sqrt{6}}{4}(I_z I^+ + I^+ I_z)|IM\rangle, \tag{2.34}$$

or,

$$\langle IM'|Q_2^{+1}|IM\rangle = \alpha\frac{\sqrt{6}}{4}(2M+1)\sqrt{(I-M)(I+M+1)}\delta_{M',M+1}. \tag{2.35}$$

It is customary to define the particular matrix element $\langle II|Q_2^0|II\rangle$ as eQ. The proportionality constant α then becomes $eQ/I(2I-1)$.

As long as we remain within a manifold in which I is a good quantum number, we may also equate the operators themselves. Thus

$$Q_2^{+1} = \frac{eQ}{I(2I-1)} \frac{\sqrt{6}}{4} (I_z I^+ + I^+ I_z) \tag{2.36}$$

with similar expressions for the other operators. The corresponding term in the quadrupole potential is therefore

$$-\sqrt{\frac{4\pi}{5}} \frac{Y_2^{-1}}{r^3} \frac{eQ}{I(2I-1)} \frac{\sqrt{6}}{4} (I_z I^+ + I^+ I_z) \, . \tag{2.37}$$

It is obvious that we could now write the *electron* part in terms of the total orbital angular momentum of the electron state [8,9]. Thus,

$$e\phi(\boldsymbol{r}) = -\frac{Ze^2}{r} + e^2 Q\xi[3(\boldsymbol{l}\cdot\boldsymbol{I})^2 + 3/2(\boldsymbol{l}\cdot\boldsymbol{I}) - l(l+1)I(I+1)] \, ,$$

where ξ is a constant that is proportional to the reduced matrix element of the electronic angular momentum. Notice that an s-state electron is not affected by the quadrupole field of the nucleus. The quadrupole field is, in general, small compared with other fields acting on the electron. From the point of view of the nucleus, however, this interaction is very important. If the electron is in a nondegenerate state characterized by the orbital quantum numbers l, m_l, and the coordinates are chosen to lie along the principal axes of the tensor $l_\mu l_\nu$, then the nuclear Hamiltonian becomes

$$\mathcal{H}_Q = \frac{e^2 qQ}{4I(2I-1)} \left[3I_z^2 - I(I-1) + \frac{1}{2}\eta(I_+^2 + I_-^2)\right] \, , \tag{2.38}$$

where

$$q = \xi\langle l_z^2\rangle \quad \text{and} \quad \eta = \frac{(\langle l_x^2\rangle - \langle l_y^2\rangle)}{\langle l_z^2\rangle} \, .$$

The same expression also characterizes the interaction with a more general surrounding charge distribution. In this case q is proportional to the electric field gradient produced by this charge distribution.

2.2.3 The Magnetic Dipole (Hyperfine) Field

The vector potential arising from the nuclear currents may also be expanded to yield

$$\boldsymbol{A}(\boldsymbol{r}) = \int d\boldsymbol{r}_n \frac{\rho(\boldsymbol{r}_n)\boldsymbol{v}(\boldsymbol{r}_n)}{c\,|\boldsymbol{r} - \boldsymbol{r}_n|}$$

$$= \frac{1}{cr} \int d\boldsymbol{r}_n \rho(\boldsymbol{r}_n)\boldsymbol{v}(\boldsymbol{r}_n) + \frac{1}{2cr^3} \int d\boldsymbol{r}_n \rho(\boldsymbol{r}_n)$$

$$\times \{(\boldsymbol{r} \cdot \boldsymbol{r}_n)\boldsymbol{v}(\boldsymbol{r}_n) + [\boldsymbol{r} \cdot \boldsymbol{v}(\boldsymbol{r}_n)]\boldsymbol{r}_n\}$$

$$- \frac{\boldsymbol{r}}{r^3} \times \frac{1}{2c} \int d\boldsymbol{r}_n \rho(\boldsymbol{r}_n)[\boldsymbol{r}_n \times \boldsymbol{v}(\boldsymbol{r}_n)] + \dots . \qquad (2.39)$$

If the current distribution is stationary with respect to the angular-momentum axis, then the first two terms vanish, leaving only the third. The integral in this term is the nuclear magnetic dipole moment $\boldsymbol{\mu}_I$, which is related to the nuclear angular momentum by

$$\boldsymbol{\mu}_I = g_N \mu_N \boldsymbol{I} = \gamma_N \hbar \boldsymbol{I} \,,$$

where μ_N is the nuclear magneton, γ_N is the nuclear gyromagnetic ratio, and g_N is the nuclear g value.

Notice that the nuclear angular momentum $\boldsymbol{I}$ is in units of $\hbar$. Thus

$$\boldsymbol{A}(\boldsymbol{r}) = \boldsymbol{\mu}_I \times \frac{\boldsymbol{r}}{r^3} \,. \qquad (2.40)$$

Substituting this into the expression

$$\frac{1}{2m}\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right)^2 - \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot \boldsymbol{\nabla} \times \boldsymbol{A} \qquad (2.41)$$

and recognizing that $\boldsymbol{\nabla} \cdot \boldsymbol{A}(\boldsymbol{r}) = 0$, we obtain

$$\frac{\boldsymbol{p}^2}{2m} - \frac{e}{mc}\frac{(\boldsymbol{\mu}_I \times \boldsymbol{r}) \cdot \boldsymbol{p}}{r^3} + \frac{e\hbar}{2mc}\boldsymbol{\sigma} \cdot \left[\frac{\boldsymbol{\mu}_I}{r^3} - 3\frac{(\boldsymbol{r} \cdot \boldsymbol{\mu}_I)\boldsymbol{r}}{r^5}\right] . \qquad (2.42)$$

Interchanging the dot and cross products in the second term gives the *orbital hyperfine interaction*

$$2\mu_B \frac{\boldsymbol{\mu}_I \cdot \boldsymbol{\ell}}{r^3} \,. \qquad (2.43)$$

The last term in (2.42) containing the square brackets is the *dipolar hyperfine interaction*.

If the electron is in an s state, then the matrix elements of the orbital hyperfine interaction will clearly vanish. Similarly, the matrix elements of the dipolar hyperfine interaction also vanish for an s-state electron. However, there is an additional interaction for s-state electrons that is not included in expansion (2.39), since it is valid only for charge distributions which vanish at the nucleus. To obtain this additional interaction we consider the matrix element of the hyperfine interaction for an electron orbital state $\psi(\boldsymbol{r})$:

$$-\frac{e\hbar}{2mc}\int_{\text{all space}} d\boldsymbol{r}\psi^*(\boldsymbol{r})\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}\times\boldsymbol{A}(\boldsymbol{r})\psi(\boldsymbol{r})$$

$$=-\frac{e\hbar}{2mc}\int_{r<R} d\boldsymbol{r}\psi^*(\boldsymbol{r})\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}\times\boldsymbol{A}(\boldsymbol{r})\psi(\boldsymbol{r})$$

$$-\frac{e\hbar}{2mc}\int_{r>R} d\boldsymbol{r}\psi^*(\boldsymbol{r})\boldsymbol{\sigma}\cdot\boldsymbol{\nabla}\times\boldsymbol{A}(\boldsymbol{r})\psi(\boldsymbol{r})\,. \qquad (2.44)$$

The radius R defines a sphere which encloses the nucleus. Outside this sphere $\boldsymbol{A}(\boldsymbol{r})$ has the form $(\boldsymbol{\mu}_I\times\boldsymbol{r})/r^3$. The second term in (2.44) gives the dipolar hyperfine interaction derived previously. The first term is the additional interaction, which may be rewritten as

$$-\frac{e\hbar}{2mc}\int_{r<R} d\boldsymbol{r}\,\boldsymbol{\nabla}\cdot(\boldsymbol{A}\times\boldsymbol{\sigma})|\psi(\boldsymbol{r})|^2 = -\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\int d\boldsymbol{S}\times\boldsymbol{A}|\psi(\boldsymbol{r})|^2\,. \qquad (2.45)$$

Because the sphere of integration has been chosen to lie outside the nucleus, $\boldsymbol{A}(\boldsymbol{r})$ has the form $(\boldsymbol{\mu}_I\times\boldsymbol{r})/R^3$. Since $\psi(\boldsymbol{r})$ is essentially constant over this surface and is equal to $\psi(0)$, the interaction becomes

$$-\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\int\frac{\boldsymbol{r}\times(\boldsymbol{\mu}_I\times\boldsymbol{r})}{R^2}d\Omega|\psi(0)|^2 = -\frac{8\pi}{3}\frac{e\hbar}{2mc}\boldsymbol{\sigma}\cdot\boldsymbol{\mu}_I|\psi(0)|^2$$

$$=\frac{16\pi}{3}g_N\mu_B\mu_N\boldsymbol{I}\cdot\boldsymbol{\sigma}|\psi(0)|^2\,. \,(2.46)$$

This is the *contact hyperfine interaction*, often written as the operator

$$(8\pi/3)g_N\mu_B\mu_N\boldsymbol{I}\cdot\boldsymbol{\sigma}\delta(\boldsymbol{r})\,.$$

Combining these results gives us the total hyperfine interaction,

$$\mathcal{H}_{\text{hyper}} = 2g_N\mu_B\mu_N\frac{\boldsymbol{l}\cdot\boldsymbol{I}}{r^3} - g_N\mu_B\mu_N\boldsymbol{\sigma}\cdot\left[\frac{\boldsymbol{I}}{r^3}-3\frac{(\boldsymbol{r}\cdot\boldsymbol{I})\boldsymbol{r}}{r^5}\right]$$

$$+\frac{8\pi}{3}g_N\mu_B\mu_N\boldsymbol{\sigma}\cdot\boldsymbol{I}\delta(\boldsymbol{r})\,. \qquad (2.47)$$

The Hamiltonian (2.11) plus the interactions (2.38), (2.47) determine the behavior of a single electron in the presence of a nucleus.

2.2.4 Other Electrons on the Same Ion

Let us now consider the effect of other electrons. One of the most important sources of the electric field felt by an ionic electron is the Coulomb field arising from the other electrons on the same ion,

$$\phi(\boldsymbol{r}) = \sum_i\frac{e}{|\boldsymbol{r}-\boldsymbol{r}_i|}\,. \qquad (2.48)$$

In ionic materials this interaction leads to the term levels (the determination of these many-electron states in terms of their Coulomb integrals is discussed in [10]). In itinerant-electron materials it is often assumed that the electrons experience a Coulomb repulsion only if they both happen to be in the same ionic cell. We shall consider the corresponding Hamiltonian for this situation later.

2.2.5 Crystalline Electric Fields

The Coulomb interactions between each electron and all the charges external to the ion are described by the electrostatic potential $V(\boldsymbol{r})$. In the case of iron-group ions the magnetic electrons (the $3d$ electrons) are outermost and hence are strongly affected by such a potential. In the case of rare-earth ions the magnetic $4f$ electrons are shielded by the $5s^2 5p^6$ shells and are less affected.

Since the charge distribution associated with neighboring ions may overlap that of the electron in question, the full treatment of this problem is very complex. The external charge distributions of these neighboring ions are called *ligands*, and their effects are computed by means of *ligand field theory* [11]. However, for our purposes, it will be sufficient to treat the neighboring ions as point charges; the problem may then be handled by *crystal field theory*. The advantage of using point charges is that $V(\boldsymbol{r})$ satisfies Laplace's equation and may be expanded in spherical harmonics as

$$V(r,\theta,\varphi) = \sum_{L'}\sum_{M'} A_{L'}^{M'} r^{L'} Y_{L'}^{M'}(\theta,\varphi). \tag{2.49}$$

The number of terms that need be considered is greatly reduced, for the following reasons. Suppose we consider an iron-group ion in a crystal field. Then we shall eventually be interested in matrix elements of the form $\int \chi^* V \psi d\tau$, where χ and ψ are d-electron wave functions. Since the density $\chi^*\psi$, when expanded in spherical harmonics will not contain terms with $L' > 4$, the integrals with $L' > 4$ will vanish by orthogonality of the spherical harmonics. Similarly, the integral vanishes for all terms in V which have L' odd. The term for $L' = 0$ is usually dropped because it is an additive constant. If we are considering several $3d$ electrons within a term, then $L'_{\max}$ is determined by the L value of this term (for example, $L' \leq 6$ for an F-state ion, i.e., $L' \leq 2L$).

The potential energy of a charge q' at (r,θ,φ), in a potential due to charges q at a distance d from the origin and arranged in a *cubic coordination*, is

$$V_c(r,\theta,\varphi) = D'_4 \left\{ Y_4^0(\theta,\varphi) + \sqrt{\frac{5}{14}} \left[Y_4^4(\theta,\varphi) + Y_4^{-4}(\theta,\varphi) \right] \right\}$$

$$+ D'_6 \left\{ Y_6^0(\theta,\varphi) - \sqrt{\frac{7}{2}} \left[Y_6^4(\theta,\varphi) + Y_6^{-4}(\theta,\varphi) \right] \right\}, \tag{2.50}$$

where, for example, $D'_4 = +\frac{7}{3}\sqrt{\pi}q'r^4/d^5$ for sixfold coordination. The coefficients in such expansions have been tabulated by Hutchings [12]. The potential may also be expressed in terms of cartesian coordinates (see Table 2.1). Thus the above potential may be written as

$$V_c(x, y, z) = C_4\left[(x^4 + y^4 + z^4) - \frac{3}{5}r^4\right] + C_6\left[(x^6 + y^6 + z^6)\right.$$

$$\left. + \frac{15}{4}(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - \frac{15}{14}r^6\right], \qquad (2.51)$$

where $C_4 = +\frac{35}{4}qq'/d^5$ for sixfold coordination.

We are now faced with the problem of calculating the matrix elements of this potential. This is easily accomplished by the operator-equivalent method, which makes use of the fact that the matrix elements of operators involving x, y, and z within a given L or J manifold are proportional to those of L_x, L_y, and L_z or J_x, J_y, and J_z. As pointed out earlier, the fact that the angular-momentum operators do not commute necessitates some care in constructing the operator equivalents. Fortunately there are tables for these (a good source is [12]). For example, within a manifold where L is constant the sum of the potential energies of all the electrons contributing to L is

$$\sum\left(x^4 + y^4 + z^4 - \frac{3}{5}r^4\right)$$

$$\Rightarrow \frac{\beta\overline{r^4}}{8}\left[35L_z^4 - 30L(L+1)L_z^2 + 25L_z^2 - 6L(L+1) + 3L^2(L+1)^2\right]$$

$$+ \frac{\beta\overline{r^4}}{8}\left[(L^+)^4 + (L^-)^4\right] \equiv \frac{\beta\overline{r^4}}{20}O_4^0 + \frac{\beta\overline{r^4}}{4}O_4^4 = B_4^0O_4^0 + B_4^4O_4^4, \quad (2.52)$$

where $\overline{r^4}$ is the average value of the fourth power of the electron radius. The operators O_n^m appear frequently in the literature. The ground state β is a constant which depends on the term; for a ^2D or a ^5D term $\beta = \frac{2}{63}$.

Consider a single $3d$ electron. This has the term ^2D, which is fivefold orbitally degenerate, with states $^2D(L_z, S_z)$. The matrix elements of V_c are [12]

$$\begin{array}{ccccc} ^2D(2) & ^2D(1) & ^2D(0) & ^2D(-1) & ^2D(-2) \end{array}$$

$$\frac{\beta\overline{r^4}}{20}\begin{bmatrix} 12 & 0 & 0 & 0 & 60 \\ 0 & -48 & 0 & 0 & 0 \\ 0 & 0 & 72 & 0 & 0 \\ 0 & 0 & 0 & -48 & 0 \\ 60 & 0 & 0 & 0 & 12 \end{bmatrix}. \qquad (2.53)$$

The eigenvalues and eigenvectors are easily found to be

$$
\begin{array}{cc}
\textit{Energy} & \textit{Eigenfunctions} \\
\end{array}
$$

$$
\frac{12}{5}\beta\overline{r^4}
\begin{cases}
{}^2D(1,S_z) \\
{}^2D(-1,S_z) \\
\dfrac{1}{\sqrt{2}}[{}^2D(2,S_z) - {}^2D(-2,S_z)]
\end{cases}
$$

$$
-\frac{18}{5}\beta\overline{r^4}
\begin{cases}
{}^2D(0,S_z) \\
\dfrac{1}{\sqrt{2}}[{}^2D(2,S_z) + {}^2D(-2,S_z)].
\end{cases}
$$

The quantity 6β is often written as Δ. Therefore we find that the ${}^2D$ term is split into two states separated by $C_4 r^4 \Delta$. Notice that C_4 can be positive or negative, depending on the coordination. This is illustrated in Fig. 2.1.

The nature of such splittings obviously depends on the symmetry of the crystal field. For this reason group theory is a powerful tool in determining the degeneracies associated with various symmetries. Group theory as applied to crystal wave functions is discussed fully elsewhere [13], Chap. 4, but it is worth our while to digress again briefly to introduce some of the group-theory terminology and notation which will enter our discussions from time to time.

Symmetry Representations. The symmetry of a system is generally specified by those operations which leave its physical appearance unchanged. For example, the symmetry operations which leave an equilateral triangle unchanged are listed in Table 2.2. A collection of symmetry operations that satisfies certain conditions is called a *group*. In order to take advantage of the powerful
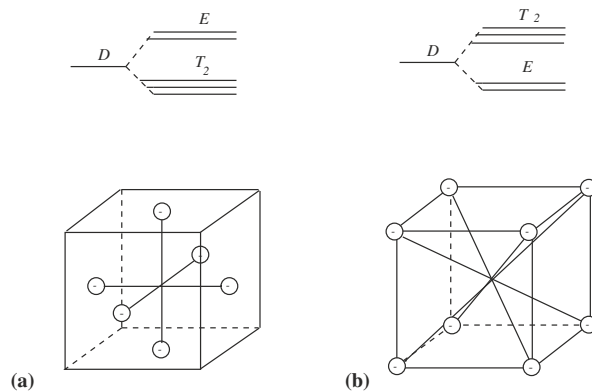

Fig. 2.1. Splitting of a D state in a cubic crystal field for (**a**) sixfold coordination and (**b**) eightfold coordination

Table 2.2. Symmetry operations associated with an equilateral triangle

E = identity

C_2^A = rotation of π around the A-axis

C_2^B = rotation of π around the B-axis

C_2^C = rotation of π around the C-axis

C_3^z = rotation of $2\pi/3$ around the z-axis

$(C_3^z)^2$ = rotation of $4\pi/3$ around the z-axis
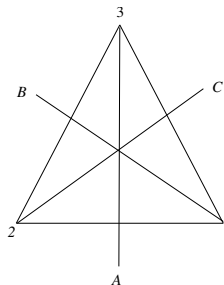
theorems associated with group theory we always work with those symmetry operations which do, in fact, constitute a group. These operations may be specifically represented by matrices which describe how a *coordinate point* transforms under the particular symmetry operation. Thus, if $\boldsymbol{r}$ represents a rotation and $\boldsymbol{t}$ represents a translation, the most general coordinate transformation is $\boldsymbol{x}' = \boldsymbol{r}\boldsymbol{x} + \boldsymbol{t}$. Such a collection of operations is called a *space group*. The rotational part, obtained by setting $\boldsymbol{t} = 0$, itself forms a group, called the *point group*. When we are dealing with noninteracting ions, the point group is sufficient to characterize the properties of the system. However, for interacting systems the full space group must be employed. Fortunately, since the point groups in a crystal must be compatible with translational symmetry, there are only 32 such groups [13], p. 55. Our equilateral triangle is characterized by the point group labeled D_3 in the so-called Schöflies notation, or 32 in the "international" notation.

Now, let us consider a *function* whose form depends on the arrangement of the system. For example, suppose that three protons are located at the vertices of an equilateral triangle. The energy of an electron in such an environment depends on the positions of the protons, but this energy is unchanged under any permutation of the protons. Notice that there are 3!, or six, such permutations. These are just the result of the six symmetry operations which leave the triangle invariant. If a figure is defined by some arrangement of identitical particles, the operations which leave it invariant also leave the interaction energy between these two particles and other particles invariant. Thus it is convenient to introduce a new group, isomorphic to the coordinate-transformations group, in which the group elements are operators which operate on *functions* rather than on *coordinates*. These operators are defined by

$$P_R f(\boldsymbol{x}) \equiv f(\boldsymbol{r}^{-1}\boldsymbol{x}) \, . \tag{2.54}$$

The particular function with which we shall be concerned is the energy in its operator form, the Hamiltonian $\mathcal{H}$. Those symmetry operations which leave the Hamiltonian invariant comprise the "group of the Schrödinger equation".

If P_R leaves $\mathcal{H}$ invariant, then it must commute with $\mathcal{H}$. Therefore

$$P_R \mathcal{H} \psi_n = \mathcal{H} P_R \psi_n = E_n P_R \psi_n \,. \tag{2.55}$$

Thus any function $P_R \psi_n$ obtained by operating on an eigenfunction ψ_n with a symmetry operator of the group of the Schrödinger equation will also be an eigenfunction having the same energy. Suppose that the state n is l_n-fold degnerate. Then the function $P_R \psi_n$ must be a linear combination of l_n orthonormal eigenfunctions, which we shall denote $\psi_\mu^{(n)} (\mu = 1, \dots, l_n)$. Therefore

$$P_R \psi_\mu^{(n)} = \sum_{\nu=1}^{l} \boldsymbol{\Gamma}^{(n)}(\boldsymbol{r})_{\mu\nu} \psi_\nu^{(n)} \,. \tag{2.56}$$

The transformation coefficients constitute a set of matrices which form an *irreducible representation* of the group of the Schrödinger equation. Furthermore, we see that the nth representation is associated with the nth eigenstate, and the *dimensionality of the representation is equal to the degeneracy* of this eigenstate. This representation is irreducible, since there is always an operator in the group that will transform each function into any other function. If this were not true, we could construct smaller sets of states which would, in general, have different eigenvalues, contradicting our original hypothesis.

Because of the relation (2.56), we speak of the $\psi^{(n)}$ as "transforming according to $\Gamma^{(n)}$". For this reason energy eigenstates are labeled by their irreducible representations. Also, since the representations are generated from the eigenfunctions, we say that the l_n degenerate eigenfunctions $\psi_\mu^{(n)}$ form a *basis* for an l_n-dimensional representation $\Gamma^{(n)}$ of the group of the Schrödinger equation.

The number and nature of the irreducible representations associated with the various symmetry groups have all been tabulated in what is known as a *character table*. The character $\chi_n(\boldsymbol{r})$ associated with the operation $\boldsymbol{r}$ belonging to the nth irreducible representation is merely the trace of the matrix of that representation, that is,

$$\chi_n(\boldsymbol{r}) = \sum_\mu \Gamma^{(n)}(\boldsymbol{r})_{\mu\mu} \,. \tag{2.57}$$

One of the powerful features of group theory is that it enables us to determine the irreducible representations and all their characters without ever having to know specifically the basis functions. The character table for the equilateral-triangle symmetry group D_3 is given in Table 2.3. To see what this character table implies, let us suppose that we have a single electron, bound, say, to some ionic core giving rise to certain eigenstates. Since this system has complete rotational symmetry, these states are labeled by the familiar s, p, d, etc. Let us surround the system by three protons located at the vertices of an equilateral triangle. The symmetry of this system is D_3. The character table for D_3 tells us that the eigenfunctions of the electron are now labeled by the irreducible

Table 2.3. Character table for the point group D_3

Symmetry Group	Operations		
D_3	E	$2C_3$	$3C_3'$
Irreducible representations	Characters		
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

representations A_1, A_2, or E. The character associated with the identity operation, E, tells us the degeneracy of the various representations. For example, A_1 and A_2 are nondegenerate states, and E is doubly degenerate.

Exactly how the original states decompose into the new types of states depends on the original states themselves and on the symmetry group characterizing the environment. Fortunately, such decompositions have been tabulated for a great number of situations. For example, in Fig. 2.1 we saw that a D state, when exposed to a cubic crystal field, splits into a doublet labeled by E and a triplet labeled by T_2. Group theory, however, does not tell us the ordering of the states or their relative separations. Such specific information can be obtained only by doing a calculation, as we did at the beginning of this section.

Quenching. At this point it is convenient to introduce a general property of angular momentum. This might be stated as a theorem:

> *The matrix element of the orbital angular momentum between non-degenerate states has an arbitrary phase. In particular, it may be pure real or pure imaginary.*

To prove this let us consider the time-reversal operator T acting on a state ψ [13], p. 141. If we neglect the spin, then $T\psi = \psi^*$. Furthermore, if the Hamiltonian of the system is Hermitian, then ψ^* has the same eigenvalue as ψ, but if ψ is nondegenerate, then ψ and ψ^* must be linearly dependent. That is, $\psi^* = c\psi$, where c is a coefficient of proportionality. Operating on this relation with T gives $\psi = |c|^2\psi$ which requires that $|c|^2 = 1$ or $c = e^{i\varphi}$, where φ is a real quantity.

Now consider the matrix element $\langle n|\boldsymbol{L}|m\rangle$. Inserting the identity operator $T^{-1}T$, we may write this as $\langle n|T^{-1}T\boldsymbol{L}T^{-1}T|m\rangle$. Under time reversal the angular momentum changes sign, $T\boldsymbol{L}T^{-1} = -\boldsymbol{L}$. Also, since T satisfies $\langle n|T^{-1}|m\rangle = \langle Tn|m\rangle^*$, we obtain

$$\langle n|\boldsymbol{L}|m\rangle = -\exp[i(\varphi_n - \varphi_m)]\langle n|\boldsymbol{L}|m\rangle^*.$$

Since the phases are arbitrary we could, for example, choose $\varphi_n - \varphi_m = 0$, in which case this matrix element would be the negative of its complex conjugate,

which would make it pure imaginary. If $\varphi_n - \varphi_m = \pi/2$, then it would be pure real.

This theorem has an important corollary:

The expectation value of $\boldsymbol{L}$ for any nondegenerate state is 0.

In the theorem, if $|m\rangle = |n\rangle$, then $\langle n|\boldsymbol{L}|n\rangle$ must be pure imaginary. But $\langle n|\boldsymbol{L}|n\rangle$ is a physical observable. Therefore it must be 0.

Thus if the crystal field has sufficiently low symmetry to remove all the orbital degeneracy, then, to lowest order, the orbital angular momentum is 0, and we say that the crystal field has completely *quenched* it. For this reason the static susceptibility of iron-group salts is found experimentally to arise predominantly from the spin.

2.2.6 Dipole–Dipole Interaction

The magnetic neighbors surrounding a given ion will contribute to the vector potential a term similar to that which we found for the electron-nucleus magnetic coupling, (2.42). If the ions have moments $\boldsymbol{\mu}_i$, the dipole-dipole interaction has the form

$$\mathcal{H}_{\mathrm{dip}} = \sum_{\substack{i,j\neq j \\ i}} \frac{1}{r_{ij}^3} \left[\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - 3(\boldsymbol{\mu}_i \cdot \hat{\boldsymbol{r}}_{ij})(\boldsymbol{\mu}_j \cdot \hat{\boldsymbol{r}}_{ij}) \right] . \tag{2.58}$$

It is convenient to separate this into various terms, the meaning of which will become evident later. Assuming the moments arise from spin, $\boldsymbol{\mu}_i = g\mu_B \boldsymbol{S}_i$, and (2.58) becomes

$$\begin{aligned}
\mathcal{H}_{\mathrm{dip}} = g^2 \mu_B^2 \sum_{i>j} \Bigg\{ &-\frac{3\cos^2\theta_{ij}-1}{r_{ij}^3} S_i^z S_j^z \\
&+\frac{3\cos^2\theta_{ij}-1}{4r_{ij}^3}(S_i^+ S_j^- + S_i^- S_j^+) \\
&-\frac{3}{2}\frac{\sin\theta_{ij}\cos\theta_{ij}\exp(-i\varphi_{ij})}{r_{ij}^3}(S_i^z S_j^+ + S_i^+ S_j^z) \\
&-\frac{3}{2}\frac{\sin\theta_{ij}\cos\theta_{ij}\exp(-i\varphi_{ij})}{r_{ij}^3}(S_i^z S_j^- + S_i^- S_j^z) \\
&-\frac{3}{2}\frac{\sin^2\theta_{ij}}{r_{ij}^3}[\exp(-2i\varphi_{ij})S_i^+ S_j^+ + \exp(2i\varphi_{ij})S_i^- S_j^-] \Bigg\} , \quad (2.59)
\end{aligned}$$

where θ_{ij} and φ_{ij} are the angles that $\boldsymbol{r}_{ij}$ makes with the fixed coordinate system.

2.2.7 Direct Exchange

The exchange energy is the contribution to the interaction energy of a system of electrons which arises from the use of antisymmetrized wave functions, as opposed to single products of one-electron wave functions. Under certain conditions the same effect may be achieved with single-product wave functions if an exchange-interaction term is added to the Hamiltonian. This effect was discovered simultaneously and independently by Dirac and Heisenberg in 1926. Since then a great deal of work has been done on this subject, particularly in developing the appropriate Hamiltonian [14]. In this section we shall discuss the origin of exchange and indicate the approximations under which it may be represented by an effective interaction Hamiltonian.

Let us begin by considering two electrons interacting with each other and a fixed positive point charge Ze. Let us assume that we know the eigenfunctions of the one-electron Hamiltonian $\mathcal{H}_0(\boldsymbol{r}, \boldsymbol{\sigma})$. For the time being let us assume that this does not include the spin-orbit interaction. Then $\mathcal{H}_0(\boldsymbol{r}, \boldsymbol{\sigma}) = \mathcal{H}_0(\boldsymbol{r})$ and we may write the eigenfunctions as products of an orbital function $\varphi_n(\boldsymbol{r})$ and a spinor $\eta_\mu(\boldsymbol{\sigma})$. We shall consider the modifications introduced by the spin-orbit interaction later.

The two-electron Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0(\boldsymbol{r}_1) + \mathcal{H}_0(\boldsymbol{r}_2) + \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|}. \tag{2.60}$$

Let us assume that the electron-electron interaction is, on average, smaller than $\mathcal{H}_0$, so that it may be treated by perturbation theory. We must now determine what functions to use as the basis for computing the matrix elements of the electron-electron interaction. The fact that the Hamiltonian *without* the electron-electron interaction is separable suggests that we try product wave functions. Thus, if electron 1 is in an orbital state n with spin up and electron 2 is in an orbital state m, also with spin up, we might try $\varphi_n(\boldsymbol{r}_1)\,\alpha(\boldsymbol{\sigma}_1)\,\varphi_m(\boldsymbol{r}_2)\,\alpha(\boldsymbol{\sigma}_2)$, where α is the spin-up spinor. However, the Pauli exclusion principle requires that the wave functions be antisymmetric with respect to particle interchanges. This condition may be satisfied by writing the wave function as a normalized *Slater determinant*. If the single-electron wave functions are orthogonal, the appropriate determinantal wave function is

$$\frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_n(\boldsymbol{r}_1)\alpha(\boldsymbol{\sigma}_1) & \varphi_n(\boldsymbol{r}_2)\alpha(\boldsymbol{\sigma}_2) \\ \varphi_m(\boldsymbol{r}_1)\alpha(\boldsymbol{\sigma}_1) & \varphi_m(\boldsymbol{r}_2)\alpha(\boldsymbol{\sigma}_2) \end{vmatrix}. \tag{2.61}$$

Since there are an infinite number of orbital states, we could construct an infinite number of such Slater determinants. The general wave function would be a linear combination of such determinants. However, if the electron-electron interaction is small, we may neglect this admixture of other orbital states. In particular, let us assume that electron 1 has a low-lying nondegenerate

orbital state φ_a with energy E_a and electron 2 has a similar low-lying non-degenerate orbital state φ_b with energy E_b. If both spin functions are up, the determinantal wave function becomes

$$\psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(\boldsymbol{r}_1)\alpha(\boldsymbol{\sigma}_1) & \varphi_a(\boldsymbol{r}_2)\alpha(\boldsymbol{\sigma}_2) \\ \varphi_b(\boldsymbol{r}_1)\alpha(\boldsymbol{\sigma}_1) & \varphi_b(\boldsymbol{r}_2)\alpha(\boldsymbol{\sigma}_2) \end{vmatrix}. \tag{2.62}$$

If the spin function associated with orbital a is down, then

$$\psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(\boldsymbol{r}_1)\beta(\boldsymbol{\sigma}_1) & \varphi_a(\boldsymbol{r}_2)\beta(\boldsymbol{\sigma}_2) \\ \varphi_b(\boldsymbol{r}_1)\alpha(\boldsymbol{\sigma}_1) & \varphi_b(\boldsymbol{r}_2)\alpha(\boldsymbol{\sigma}_2) \end{vmatrix}. \tag{2.63}$$

There are two additional possible spin configurations which lead to wave functions ψ_3 and ψ_4. These four functions form a complete orthonormal set and therefore constitute an appropriate bais with which to evaluate the matrix elements of $\mathcal{H}$. The result is

$$H = \begin{bmatrix} E_a + E_b + K_{ab} - J_{ab} & 0 & 0 & 0 \\ 0 & E_a + E_b + K_{ab} & -J_{ab} & 0 \\ 0 & -J_{ab} & E_a + E_b + K_{ab} & 0 \\ 0 & 0 & 0 & E_a + E_b + K_{ab} - J_{ab} \end{bmatrix}, \tag{2.64}$$

where

$$K_{ab} = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \frac{e^2}{r_{12}} |\varphi_a(\boldsymbol{r}_1)|^2 |\varphi_b(\boldsymbol{r}_2)|^2 \tag{2.65}$$

and

$$J_{ab} = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \varphi_a^*(\boldsymbol{r}_1)\varphi_b^*(\boldsymbol{r}_2) \frac{e^2}{r_{12}} \varphi_b(\boldsymbol{r}_1)\varphi_a(\boldsymbol{r}_2). \tag{2.66}$$

Diagonalizing this matrix gives a singlet with energy

$$E_s = E_a + E_b + K_{ab} + J_{ab} \tag{2.67}$$

and a triplet with energy

$$E_t = E_a + E_b + K_{ab} - J_{ab}. \tag{2.68}$$

Since J_{ab} is the self-energy of the charge distribution $e\varphi_a^*(\boldsymbol{r})\varphi_b(\boldsymbol{r})$, it is positive definite. Therefore the triplet always has a lower energy than the singlet. This is the origin of *Hund's rule*, which says that the ground state of an atom has *maximum multiplicity*.

Dirac noticed that the eigenvalues (2.67), (2.68) could be obtained with a basis consisting only of products of spin functions if an *exchange interaction* were added to the Hamiltonian. To obtain the form of this effective interaction

term we notice that just as any 2×2 matrix may be expressed as a linear combination of Pauli matrices plus the unit matrix, any 4×4 matrix may be written as a quadratic function of *direct* products of Pauli matrices [13], p. 320. For example, if

$$\sigma_{1x} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \text{and} \quad \sigma_{2x} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \tag{2.69}$$

then

$$\sigma_{1x} \otimes \sigma_{2x} = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}. \tag{2.70}$$

We are particularly interested in that quadratic form which gives three equal eigenvalues. Such a form is

$$\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \tag{2.71}$$

Therefore the Hamiltonian which will produce in a *spinor basis* the same eigenvalues as (2.52) evaluated in a fully *antisymmetrized basis* is

$$\overline{\mathcal{H}} = \frac{1}{4}(E_s + E_t) - \frac{1}{4}(E_s - E_t)\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2 = \text{const.} - \frac{1}{4}J\boldsymbol{\sigma}_1 \cdot \boldsymbol{\sigma}_2. \tag{2.72}$$

Thus the exchange interaction, which is a purely electrostatic effect, may be expressed as a spin-spin interaction. The exchange parameter J is $E_s - E_t$. If J is *positive*, we say that the interaction is *ferromagnetic*.

In obtaining the exchange interaction (2.72) we have made two important assumptions. The first was that we could restrict ourselves to a certain subset of nondegenerate orbital states. There is no real justification for this, as the Coulomb interaction does, in fact, couple different orbital states. We shall see this more clearly in our discussion of exchange in the N-electron system. The second assumption was that the orbital functions were orthogonal. When we are dealing with wave functions that have a common origin, as in an atom, this is usually the case. However, as soon as we begin talking about electrons centered at different sites the problem becomes very complex.

The hydrogen molecule is perhaps the simplest example of such a two-center problem. This was first considered by Heitler and London in 1927 [15]. In the limit of infinite separation we shall assume we have two neutral hydrogen atoms. The Hamiltonian for a single hydrogen atom located at $\boldsymbol{r}_a$ is

$$\mathcal{H}_\infty(\boldsymbol{r}) = -\frac{\hbar^2 \nabla^2}{2m} - \frac{e^2}{|\boldsymbol{r} - \boldsymbol{r}_a|}. \tag{2.73}$$

The corresponding orbital eigenfunctions are $\varphi(\boldsymbol{r} - \boldsymbol{r}_a) \equiv a(r)$. The Hamiltonian for the two-proton system is

$$\mathcal{H} = -\frac{\hbar^2 \nabla_1^2}{2m} - \frac{\hbar^2 \nabla_2^2}{2m} - \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_a|} - \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_b|} - \frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{r}_a|} - \frac{e^2}{|\boldsymbol{r}_2 - \boldsymbol{r}_b|}$$
$$+ \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} + \frac{e^2}{|\boldsymbol{r}_a - \boldsymbol{r}_b|} . \tag{2.74}$$

Heitler and London assumed basis functions of the form (2.61) but rather than taking eigenfunctions of noninteracting electrons in the field of *two* nuclei, they took the eigenfunctions of isolated free atoms. Thus, if both electrons are "up",

$$\psi_1 = \frac{1}{\sqrt{2 - 2\ell^2}} \begin{vmatrix} a(1)\alpha(1) & a(2)\alpha(2) \\ b(1)\alpha(1) & b(2)\alpha(2) \end{vmatrix} , \tag{2.75}$$

where $\ell = \int d\boldsymbol{r}\, a^*(r)b(r)$ is the overlap integral. If one spin is "up" and the other "down" there are two Slater determinants

$$\phi_1 = \begin{vmatrix} a(1)\alpha(1) & a(2)\alpha(2) \\ b(1)\beta(1) & b(2)\beta(2) \end{vmatrix} \tag{2.76}$$

and

$$\phi_2 = \begin{vmatrix} a(1)\beta(1) & a(2)\beta(2) \\ b(1)\alpha(1) & b(2)\alpha(2) \end{vmatrix} . \tag{2.77}$$

Due to the overlap, these are not orthogonal, i.e.,

$$\langle \phi_1 | \phi_2 \rangle = -2\ell^2 . \tag{2.78}$$

An orthogonalized pair of basis functions is

$$\psi_2 = \frac{1}{2\sqrt{1 - \ell^2}}(\phi_1 + \phi_2) \tag{2.79}$$

$$\psi_3 = \frac{1}{2\sqrt{1 - \ell^2}}(\phi_1 - \phi_2) . \tag{2.80}$$

The fourth basis function is identical to (2.75) with β in place of α. In this basis the Hamiltonian matrix is, in fact, diagonal:

$$H = \begin{pmatrix} E_t & 0 & 0 & 0 \\ 0 & E_t & 0 & 0 \\ 0 & 0 & E_s & 0 \\ 0 & 0 & 0 & E_t \end{pmatrix} , \tag{2.81}$$

where

$$E_t = E_a^0 + E_b^0 + \frac{e^2}{|\boldsymbol{r}_a - \boldsymbol{r}_b|} - \frac{K - \Delta_a - \Delta_b - 2\ell\Delta_{ab} - J}{1 - \ell^2} \,, \qquad (2.82)$$

$$E_s = E_a^0 + E_b^0 + \frac{e^2}{|\boldsymbol{r}_a - \boldsymbol{r}_b|} + \frac{K - \Delta_a - \Delta_b - 2\ell\Delta_{ab} + J}{1 + \ell^2} \,. \qquad (2.83)$$

Here Δ_a and Δ_b represent shifts in the distant-atom eigenvalues, E_a^0 and E_b^0, respectively, due to the other core. Δ_{ab} is the interaction of the "overlap charge density", $a(r)b(r)$, with a core, and

$$K = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 |a(r_1)|^2 |b(r_2)|^2 \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \qquad (2.84)$$

and

$$J = \iint d\boldsymbol{r}_1 d\boldsymbol{r}_2 \, a^*(r_1) b^*(r_2) \frac{e^2}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} b(r_1) a(r_2) \,. \qquad (2.85)$$

The difference between the singlet and the triplet is

$$E_s - E_t = -2\frac{(K - \Delta_a - \Delta_b - 2\ell\Delta_{ab})\ell^2 - J}{1 - \ell^4} \,. \qquad (2.86)$$

Notice that this may be positive or negative, depending upon the relative sizes of the various parameters. Thus, it is not obvious whether the ground state will be ferromagnetic or antiferromagnetic. Actual evaluation shows that for realistic separations the singlet lies lowest. As the nuclei are brought together, and ℓ increases, the denominators in E_t and E_s cause E_t to increase and E_s to decrease. Eventually, internuclear repulsion also causes E_s to increase:
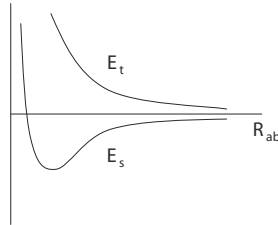
Equation (2.86) can be evaluated exactly for the case of hydrogenic wave functions. It is found that for very large separations the triplet has lower energy. This cannot be, for, as Herring pointed out, the lowest eigenvalue of a semibounded Sturm–Liouville differential operator, such as (2.74), must be free of nodes. This means it must always be a singlet. This would be a good description of the chemical bond, but would not explain magnetism. The problem arises from the oversimplified nature of the Heitler–London states. The exchange coupling measures the rate at which two identifiable electrons

exchange places by tunneling through the barrier separating them. In the Heitler–London approximation this tunneling is uncorrelated. In reality, however, the two electrons will tend to avoid one another. This reduces the amplitude of the wave function for configurations with both electrons close to the internuclear line. Fortunately, however, (2.85) is a reasonably good approximation for separations generally encountered.

In considering more than two electrons we find that difficulties arise from the nonorthogonality of the wave functions we have been using thus far. When the Heitler–London method is applied to a very large system the nonorthogonality integrals enter the secular equation with high powers and lead to an apparent divergence. This "nonorthogonality catastrophy" is a purely mathematical difficulty [14], and Herring has reviewed various treatments that show that even for large systems the energies and eigenstates are given by the exchange interaction with exchange constants having the same values as for a two-site system.

One approach to the problem of exchange among many sites is to give up our well-defined but nonorthogonal functions and work with functions which are orthogonal. An example of such a set of orthogonal functions are *Wannier functions*. The Wannier function $\phi_{n\lambda}(\mathbf{r} - \mathbf{r}_a)$ resembles the nth atomic orbital with spin λ near the αth lattice site, but it falls off throughout the crystal in such a way that it is orthogonal to similar functions centered at other sites. Since the exchange interaction is essentially a quantum-statistical effect the technique of second quantization discussed in Chap. 1 is very convenient for obtaining the exchange Hamiltonian.

Let us consider N electrons reasonably localized on N lattice sites. The Hamiltonian for such a system is

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} - \sum_{i,a} \frac{Ze^2}{|\mathbf{r}_i - \mathbf{r}_a|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \,. \tag{2.87}$$

In Chap. 1 we found that the prescription for second quantizing such a Hamiltonian entailed introducing a field operator which could be expanded in terms of a complete set of single-particle wave functions. In this case the appropriate set of functions are the Wannier functions. Thus the field operator (1.122) becomes

$$\psi(\mathbf{r}) = \sum_{\alpha,n,\lambda} \phi_{n\lambda}(\mathbf{r} - \mathbf{r}_\alpha) a_{n\lambda}(\mathbf{r}_\alpha) \,, \tag{2.88}$$

where $a_{n\lambda}(\mathbf{r}_\alpha)$ annihilates an electron in orbital state n and spin state λ at the lattice site α. The interaction part of the Hamiltonian (2.87) becomes

$$\frac{1}{2} \sum_{\substack{\alpha_1,\alpha_2,\alpha_3,\alpha_4 \\ n_1,n_2,n_3,n_4 \\ \lambda_1,\lambda_2}} \langle \alpha_1 n_1; \alpha_2 n_2 \,|V|\, \alpha_3 n_3; \alpha_4 n_4 \rangle$$

$$\times a_{n_1\lambda_1}^\dagger(\mathbf{r}_{\alpha_1}) a_{n_2\lambda_2}^\dagger(\mathbf{r}_{\alpha_2}) a_{n_4\lambda_2}(\mathbf{r}_{\alpha_4}) a_{n_3\lambda_1}(\mathbf{r}_{\alpha_3}) \,. \tag{2.89}$$

Since the Wannier states are localized to within a unit cell, the main contributions to (2.89) arise from those terms in which $\alpha_3 = \alpha_1$ and $\alpha_4 = \alpha_2$ or $\alpha_3 = \alpha_2$ and $\alpha_4 = \alpha_1$. The remaining terms involve various orbital excitations induced by the Coulomb interaction. These lead to *off-diagonal exchange*. Just as in the two-electron case, we shall restrict each electron to a definite orbital state. That is, we shall keep only those terms in which $n_3 = n_1$ and $n_4 = n_2$ or $n_3 = n_2$ and $n_4 = n_1$. If, for simplicity, we also neglect orbital-transfer terms, in which two electrons interchange orbital states, then (2.89) reduces to

$$\frac{1}{2}\sum_{\substack{\alpha,\alpha' \\ n,n' \\ \lambda,\lambda'}} \left[\langle \alpha, n;\, \alpha', n'|V|\alpha, n;\, \alpha', n'\rangle a_{n\lambda}^\dagger(\boldsymbol{r}_\alpha)a_{n'\lambda'}^\dagger(\boldsymbol{r}_{\alpha'})a_{n'\lambda'}(\boldsymbol{r}_{\alpha'})a_{n\lambda}(R_\alpha) \right.$$

$$\left. + \langle \alpha, n;\, \alpha', n'|V|\alpha', n';\, \alpha, n\rangle a_{n\lambda}^\dagger(\boldsymbol{r}_\alpha)a_{n'\lambda'}^\dagger(\boldsymbol{r}_{\alpha'})a_{n,\lambda'}(\boldsymbol{r}_\alpha)a_{n'\lambda}(\boldsymbol{r}_{\alpha'}) \right]. \tag{2.90}$$

The first term is called the *direct term* and the second is the *exchange term*. Using the fermion anticommutation relation

$$\left\{ a_{n\lambda}^\dagger(\boldsymbol{r}_\alpha), a_{n'\lambda'}(\boldsymbol{r}_{\alpha'}) \right\} = \delta_{\alpha\alpha'}\delta_{nn'}\delta_{\lambda\lambda'}, \tag{2.91}$$

we may write the exchange term as

$$-\frac{1}{2}\sum_{\substack{\alpha,\alpha' \\ n,n' \\ \lambda,\lambda'}} J_{nn'}(\boldsymbol{r}_\alpha, \boldsymbol{r}_{\alpha'})a_{n\lambda}^\dagger(\boldsymbol{r}_\alpha)a_{n\lambda'}(\boldsymbol{r}_\alpha)a_{n'\lambda'}^\dagger(\boldsymbol{r}_{\alpha'})a_{n'\lambda}(\boldsymbol{r}_{\alpha'}). \tag{2.92}$$

When the spin sum is expanded, we obtain four terms. These may be written in a particularly revealing way by noting the following. First of all, if we allow only one electron to occupy each orbital, then

$$N_{n\uparrow}(\boldsymbol{r}_\alpha) + N_{n\downarrow}(\boldsymbol{r}_\alpha) = 1, \tag{2.93}$$

where $N_{n\lambda}(\boldsymbol{r}_\alpha) = a_{n\lambda}^\dagger(\boldsymbol{r}_\alpha)a_{n\lambda}(\boldsymbol{r}_\alpha)$ is the number operator associated with the nth orbital with spin λ at the site α. We also have

$$N_{n\uparrow}(\boldsymbol{r}_\alpha) - N_{n\downarrow}(\boldsymbol{r}_\alpha) = \sigma_z(\boldsymbol{r}_\alpha). \tag{2.94}$$

Combining these two relations gives

$$N_{n\uparrow}(\boldsymbol{r}_\alpha)N_{n'\uparrow}(\boldsymbol{r}_{\alpha'}) + N_{n'\downarrow}(\boldsymbol{r}_\alpha)N_{n'\downarrow}(\boldsymbol{r}_{\alpha'}) = \frac{1}{2}\sigma_z(\boldsymbol{r}_\alpha)\sigma_z(\boldsymbol{r}_{\alpha'}) + \frac{1}{2}. \tag{2.95}$$

We also note that

$$a_{n\uparrow}^\dagger(\boldsymbol{r}_\alpha)a_{n\downarrow}(\boldsymbol{r}_\alpha) = \frac{1}{2}\sigma^+(\boldsymbol{r}_\alpha) \tag{2.96}$$

and

$$a_{n\downarrow}^{\dagger}(\boldsymbol{r}_\alpha)a_{n\uparrow}(\boldsymbol{r}_\alpha) = \frac{1}{2}\sigma^-(\boldsymbol{r}_\alpha)\,. \tag{2.97}$$

With these results the exchange interaction (2.92) becomes

$$\sum_{\substack{\alpha\alpha' \\ nn'}} J_{nn'}(\boldsymbol{r}_\alpha,\,\boldsymbol{r}_{\alpha'})\left[\frac{1}{4} + \frac{1}{4}\boldsymbol{\sigma}(\boldsymbol{r}_\alpha)\cdot\boldsymbol{\sigma}(\boldsymbol{r}_{\alpha'})\right]\,. \tag{2.98}$$

This is the many-electron generalization of our earlier result for two electrons. Since the wave functions used in $J_{nn'}$ are orthogonal, this exchange is always ferromagnetic. In the next section on superexchange we shall see that when we allow for the fact that an electron can hop onto a neighboring site giving it a double occupancy, the result is an exchange of the form (2.98) but with an antiferromagnetic coupling.

In most practical situations we do not have just N electrons each localized on one of N lattice sites, but rather Nh electrons, where h is the number of unpaired electrons on each ion. If these h electrons all have the same exchange integrals with all the other electrons, then the interaction may be expressed in terms of the total ionic spin,

$$\mathcal{H}_{\mathrm{ex}} = -\sum_{\substack{\alpha,\alpha' \\ n,n'}} J_{nn'}(\boldsymbol{r}_\alpha,\,\boldsymbol{r}_{\alpha'})\left[\frac{1}{4} + \boldsymbol{S}(\boldsymbol{r}_\alpha)\cdot\boldsymbol{S}(\boldsymbol{r}_{\alpha'})\right]\,. \tag{2.99}$$

As Van Vleck has pointed out, this form is also valid if the unfilled shells of each ion are half full and the atom is in its state of maximum multiplicity [16]. Such a situation is always true for S-state ions but may also arise as a result of quenching by crystal fields. We shall consider an example of this in our discussion on effective exchange. Equation (2.99), usually referred to as the *Heisenberg exchange* interaction, often forms the starting point for discussions of ferromagnetism or antiferromagnetism in insulators. The fact that it is valid only under certain conditions does not seem to deter its application. In fact, it works surprisingly well, as we shall see in later chapters.

2.2.8 Superexchange

The exchange constant in (2.99) involves essentially an eigenfunction of the whole crystal. Needless to say, such a function is difficult to obtain. Let us therefore consider an approach which has proven useful in discussing exhange in insulators. The transition-metal flourides MnF_2, FeF_2, and CoF_2 are all observed to be antiferromagnets at low temperatures, with crystal structure and spin configuration indicated in Fig. 2.2. This exchange is difficult
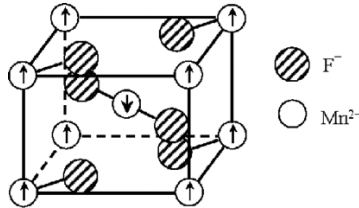
Fig. 2.2. Spin configuration of the transition-metal flourides
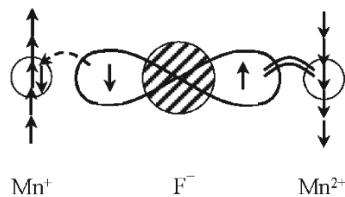

Mn^+ F^- Mn^{2+}

**Fig. 2.3.** Schematic representations of one of the intermediate states in super-exchange

to understand in terms of direct exchange between the cations because of the intervening flourine anions. A similar situation arises in the case of magnetic oxides. In 1934 Kramers proposed the explanation that the cation wave functions were being strongly admixed with the flourine wave functions, enabling the cations to couple indirectly with each other. Kramers applied perturbation theory to obtain the effective exchange resulting from this mechanism. Let us consider two Mn^{2+} ions and an intervening F^- ion. Because of the overlap of their wave functions, one of the p electrons from the F^- hops over to one of the Mn^{2+} ions. The remaining unpaired p electron on the F then enters into a direct exchange with the other Mn^{2+} ion. This excited state is illustrated in Fig. 2.3 for the case in which the exchange between the unpaired p electron and the Mn^{2+} is antiferromagnetic. By using such excited states in a perturbation calculation of the total energy of the system we obtain an effective exchange between the Mn^{2+} ions. The sign of this exchange depends on the nature of the orbitals involved. However, a number of general features that have evolved through the work of Goodenough [17] and Kanamori [18] enable us to qualitatively predict the nature of the superexchange. Two such features are that the electron transfer can take place only if the cation and anion orbitals are nonorthogonal, and that if the cation-anion orbitals are orthogonal, the direct exchange referred to above is positive (ferromagnetic); otherwise it is negative (antiferromagnetic).

As an example of the application of these rules, let us consider the antiferromagnet $CaMnO_3$. In this material the manganese occurs in the tetravelent state Mn^{4+}, which means that we have three d electrons. The crystal field at

the Mn^{4+} sites is cubic. The d electrons are strongly affected by this crystal field. In fact, the approximation is often made that the crystal field is stronger than the intraionic Coulomb interaction, so that the latter may be neglected. Then each electron may be considered separately. The effect of a cubic field on the fivefold orbitally degenerate d state of a single electron is to split this state into a threefold degenerate state labeled t_{2g} and a twofold degenerate state labeled e_g. This splitting with the associated wave functions is shown in Fig. 2.4. There is, in fact, some intraionic Coulomb interaction, which leads to a *Hund's rule* coupling of the spins. Therefore, since the t_{2g} state lies lowest for the particular coordination in $CaMnO_3$, the three electrons will each go into one of the t_{2g} orbitals with their spins up.

The superexchange in this case involves the p electrons of the O^{2-}. The p orbitals are illustrated in Fig. 2.5. Examination of the wave functions in Fig. 2.4, shows that the p_z orbital is orthogonal to all the cation orbitals except $d_{x^2-y^2}$. Therefore, if a p_z electron hops over to a Mn^{4+}, it must go into this e_g orbital. Since Hund's rule requires that the total spin be a maximum, it is the up spin from the p_z orbital that transfers if the spins of the Mn^{4+} to which it is going are up. The remaining p_z down spin, since it is orthogonal to e_g orbitals, couples ferromagnetially to the other Mn^{4+}. As a result, we find that the p_z orbital has produced a net antiferromagnetic coupling between the cations themselves. It turns out that the contributions from the p_x orbitals are much smaller.

The Goodenough–Kanamori rules predict that $180°$ superexchange between electronic configurations $d^3 - d^5$ bridged via an oxygen is ferromagnetic.
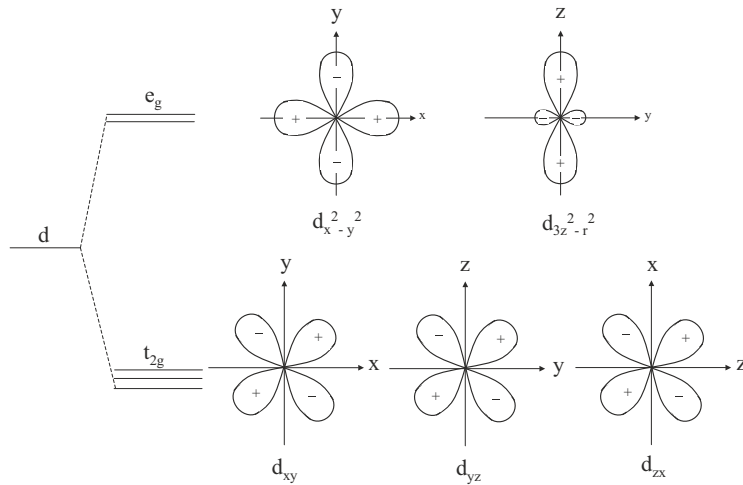
Fig. 2.4. Representations of the eigenvalues and eigenfunctions of a d electron in a cubic crystal field
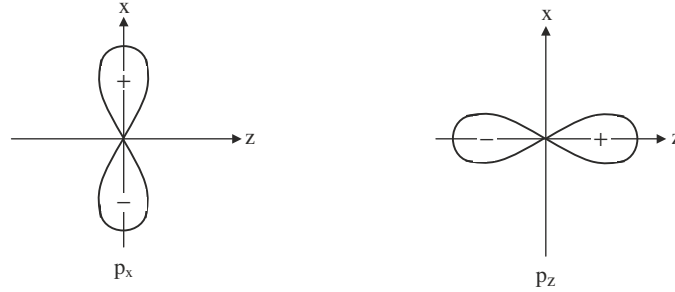
**Fig. 2.5.** Representations of the p orbitals

An example is Fe^{3+} and Cr^{3+} introduced alternately on the B sites of the perovskites, ABO_3. Attempts to synthesize a ferromagnet with $LaCr_{0.5} Fe_{0.5} O_3$ originally failed because the material phase separates into the antiferromagnets $LaCrO_3$ and $LaFeO_3$. However, with new thin film fabrication techniques, such as laser molecular beam epitaxy, it is possible to deposit alternating monolayers of $LaCrO_3$ and $LaFeO_3$. The resulting superlatttice is indeed a ferromagnet with a Curie temperature of 375 K [19].

Anderson [20] reformulated Kramer's theory in an attempt to avoid the high order perturbation expansion, and his results suggest that antiferromagnetism may be more common than Kramer's theory implies. Anderson worked in a basis of ligand wave functions which are a covalent admixture of cation and anion functions. In Anderson's theory magnetism is the result of the interplay between two effects–the hopping of electrons between ligand complexes, characterized by a hopping matrix element $t_{\alpha\alpha'}$, and an average Coulomb interaction U between electrons on the same complex. In the limit where the hopping may be treated as a perturbation, Anderson found that the super-exchange interaction has the same spin dependence as (2.99) but with a coefficient $-t_{\alpha\alpha'}^2/U$.

In recent years chemists have recast superexchange in terms of molecular orbitals. Hay et al. [21] for example, have shown that the exchange interaction between two spin $\frac{1}{2}$ ions can be expressed as

$$J = J_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{K_{aa} - K_{bb}} . \qquad (2.100)$$

The exchange J_{ab} involves orthogonalized molecular orbitals and is therefore inherently ferromagnetic. The energies ϵ_1 and ϵ_2 are the bonding and anti-bonding energies associated with the molecular orbitals on the two metal ions. The K's are defined in terms of molecular orbitals analogous to (2.84). Since $K_{aa} > K_{bb}$ the nature of the exchange depends upon the magnitude of $\epsilon_1 - \epsilon_2$. This quantity turns out to be a sensitive function of the metal-ligand-metal angle. Willett [22] and his co-workers have exploited this fact to synthesize a
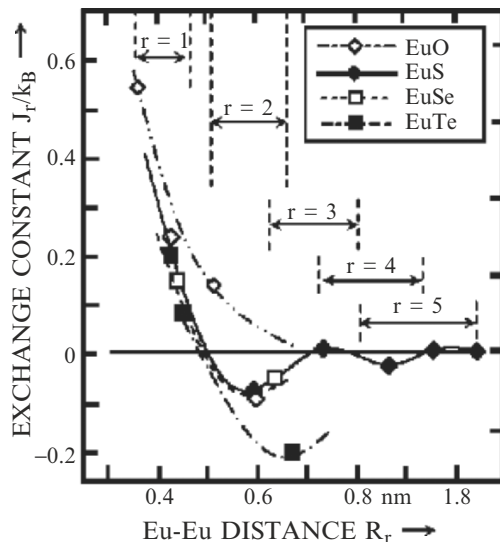
Fig. 2.6. Exchange interactions between Eu-Eu pairs in Eu monochalcogenides versus the pair separation R_τ. The horizontal arrows indicate the range of R_τ values from the oxides to the tellurides. Open symbols indicate results deduced assuming only second-nearest-neighbor coupling [23]. Units are degrees K

variety of pseudo-one-dimensional magnetic systems based on copper dimeric species.

In semiconductors the anion energies form bands. As a result the superexchange can extend to distant neighbors as illustrated in Fig. 2.6. These results were deduced from the measured spin-wave dispersion relations just as atomic force constants are deduced from phonon dispersion relations. We shall discuss spin-waves in Chap. 8.

2.2.9 Molecular Magnets

Ordinarily we do not associate magnetism with organic or molecular-based materials. Recently, however, chemists have synthesized materials with interesting magnetic properties. One approach has been to synthesize organic molecules with large numbers of unpaired spins that are in a high-spin state. Examples include a hexacarbene with $S = 6$ and a nonocarbene with $S = 9$. Incorporating these molecules into solids is still a challenge.

A more successful approach has been the synthesis of organometallic solids comprised of linear chains of alternating metallocenium donors and cyanocarbon acceptors. One such system is $[\text{FeCp}_2^*]^+ [\text{TCNE}]^-$ based on decamethyferrocene ($\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$) and tetracyanoethylene, shown in Fig. 2.7.
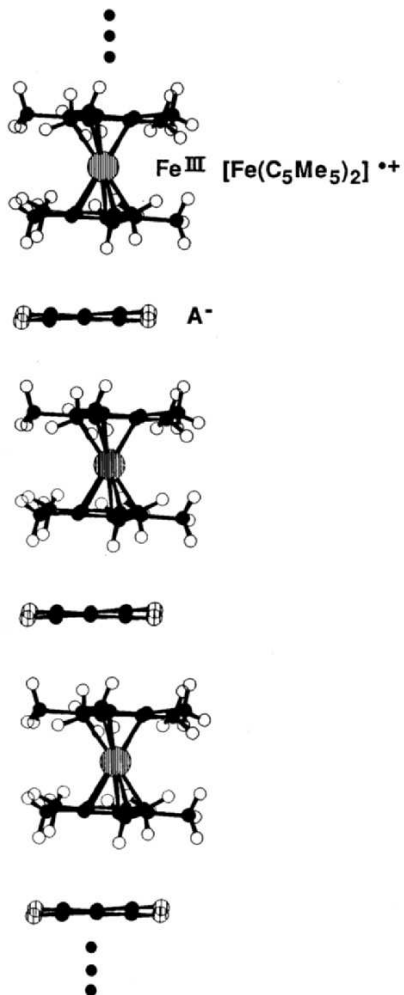
Fig. 2.7. Alternating donor/acceptor linear chain structure observed for $[FeCp_2^*]^+[TCNE]^-$. Open circles $= H$, solid circles $= C$, small hatched circles $= N$, and larged hatched circles $= Fe$ [J. Miller]

There are many variations in which the iron is replaced by other transition metals ions and the radical anion is replaced by other radical anions such as TCNQ (tetracyano-p-quinodimethanide) or DDQ (dichloro-5,6-dicyanobenzoquinone). As their long names suggest, the magnetic species are widely separated which means that the magnetization, or magnetic moment per unit volume is small. The magnetization of $[FeCp_2^*]^+$ $[TCNE]^-$

is $47\,\mathrm{emu/cm^3}$ which is to be compared with that of iron of $1715\,\mathrm{emu/cm^3}$. The large separation between cations is also responsible for relatively weak exchange interactions as reflected in low ordering temperatures. The Curie temperature of our example Fig. 2.7 is $4.8\,\mathrm{K}$. It may be surprising that these materials show any coupling, considering that the transition metal ion sits in the center of a relatively large molecule. The point is, however, that the wavefunctions of these molecules are molecular orbitals with charge density and spin density that extends throughout the molecule. These molecular orbitals have been calculated for the similar, but simpler, molecule, ferrocene, $Fe(C_5H_5)_2$, usually written $Fe(Cp)_2$. The structure consists of two planar C_5H_5 rings with the iron sandwiched in between. There are low-lying bonding states associated with the C_5 rings. The states involving the Fe^{III} are:
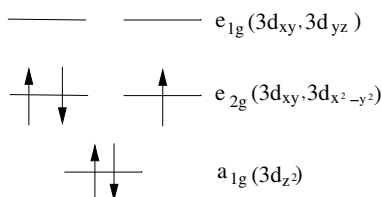

Fe^{III} has the low spin d^5 configuration. These five electrons fill the orbitals as shown, giving a molecular spin of $1/2$. The $TCNE^-$ also has one unpaired electron.

There is some overlap of the cation and anion orbitals that gives rise to an exchange interaction. McConnell [24] was the first to point out that such ionic crystals could have ferromagnetic exchange. The mechanism McConnell proposed is based on the virtual charge transfer. Suppose, for example, the anion $(A = acceptor)$ and cation $(D = donor)$ spins are ferromagnetically aligned:
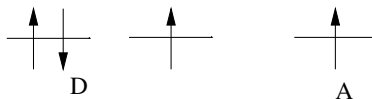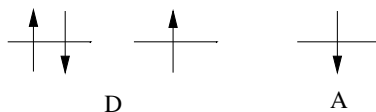

Then the charge transfer $D^+A^- \rightarrow D^{+2}A^{-2}$ leads to an intermediate state, in which there are two electrons in orthogonal orbitals with parallel spin on the cation:
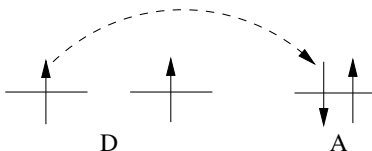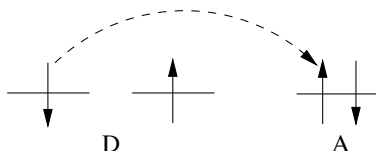

Had we started with an antiferromagnetic alignment:

then the intermediate state would have antiparallel spins on the cation:

The parallel configuration has the lower energy (Hund's rule). Therefore the charge transfer favors the ferromagnetic state.

The unpaired electron on the anion could also transfer back to the cation (i.e., $D^+ A \to D^\circ A^\circ$). This favors antiferromagnetic coupling. Consistant with the observed data the exchange is governed more by the $D \to A$ transfer. There are also various interchain exchange interactions that could influence the nature of the 3-dimensional ordering. However, it appears that the ordering in these salts is governed by the intrachain exchange.

Much of the recent work on these molecular magnets has been done by Miller and Epstein [25] who have also discovered a polymeric magnet involving vanadium with a Curie temperature about $400\,\mathrm{K}$.

2.2.10 Double Exchange

In Anderson's formulation of superexchange, the electron hopping is a virtual process. If, however, we actually have carriers in the magnetic material, then the hopping matrix element $t_{\alpha\alpha'}$ enters directly into the band energy in a tight-binding approximation. If we assume that the intra-atomic exchange is so strong that the spin of a carrier is parallel to the local ionic spin then the band energy is dependent upon the ionic spin configuration. This correlation between the magnetism and the conductivity was first addressed by Zener [26] and subsequently in more detail by Anderson and Hasegawa [27]. To determine how the magnetic order affects a conduction electron, we recall our discussion of how the spinor part of the electron wavefunction transforms under rotations. Let us consider the following geometry:
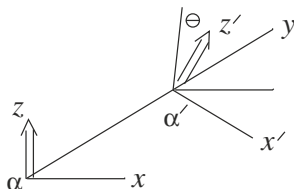
The ionic spin is assumed to be rotated by an angle θ about the y-axis. If the spinor at site α is $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, then at site α', it is given by the matrix for a rotation about the y-axis,

$$\begin{pmatrix} \cos\frac{\theta}{2} & \sin\frac{\theta}{2} \\ -\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} \cos\frac{\theta}{2} \\ -\sin\frac{\theta}{2} \end{pmatrix} .$$

Since we assume electron hopping can only occur if the electron hops into the $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ state, the orbital transfer integral $b_{\alpha\alpha'}$ is multiplied by $\cos\frac{\theta}{2}$. Thus,

$$t_{\alpha\alpha'} = b_{\alpha\alpha'} \cos\frac{\theta}{2} . \tag{2.101}$$

If the ionic spins have an exchange, J, then the tipping between α and α' gives an exchange energy proportional to $J\cos\theta$. DeGennes has shown [28] that minimizing the kinetic energy associated with the hopping and the exchange energy can lead to a canted spin structure. Distortion of the spin lattice around the hopping electron results in a magnetic polaron. This is discussed in Sect. 10.4.

2.2.11 Exchange on a Surface

Recent developments in nanotechnology enable one to experimentally study the exchange interaction between individual atoms. Figure 2.8 shows the tip on a scanning tunneling microscope which is used to position Mn atoms next to one another (0.36 nm apart) on an insulating surface. The tip can also be
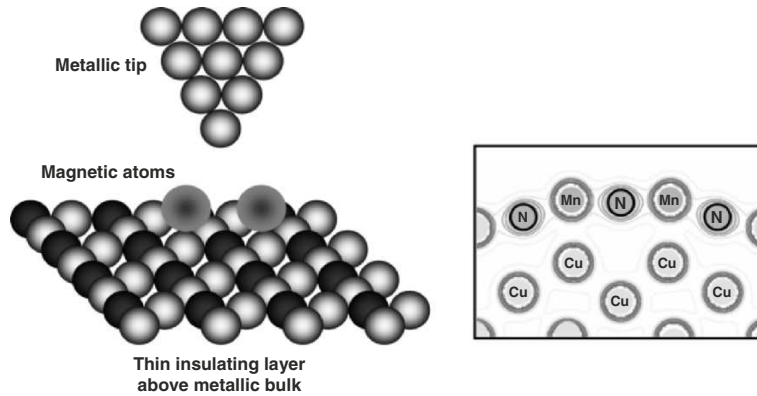
Fig. 2.8. CuN surface showing how a scanning tunneling microscope can be used to position two manganese atoms next to one another (C.F. Hirjibehedin)

used to measure the conductance of these artificially created Mn clusters. The inelastic electron tunneling spectra for a dimer shows structure that has been indentified as an excitation between an antiparallel ground state involving two spin 5/2 moments and a parallel excited state ref [29]. The voltage at which this structure occurs enables a determination of the exchange interaction between the two Mn moments. This has the values $2.7\,\text{meV}$ or $6.4\,\text{meV}$ at $0.6\,\text{K}$ depending upon where the dimer sits on the CuN surface. The insert in Fig. 2.8 shows the cross-section of the charge density as calculated from a "first-principles" calculation. The Mn $3d$ electrons couple to this surrounding charge density through an "s-d" exchange interaction, $J_{sd}\,\mathbf{S.s}$. This provides an effective exchange between the two Mn moments of the order of J_{sd}^2/E_g, where E_g is the bandgap of the CuN. Since J_{sd} is of order $0.1\,\text{eV}$ and E_g is several eV the Mn-Mn exchange is of order of several meV as observed.

2.3 The Spin Hamiltonian

The Hamiltonian developed in the preceding section is completely general, and a knowledge of its eigenvalues would accurately describe the magnetic properties of any material. Unfortunately, because of the large number of particles involved, such a knowledge is beyond us at this time. Therefore we try to project out of the Hamiltonian those terms which adequately describe the situation and yet are amenable to calculation. Experimentalists in particular often propose "phenomenological" Hamiltonians to explain certain observations, leaving to theoreticians the job of establishing the legitimacy of such forms. In the remainder of this chapter we shall indicate the origin of such phenomenological Hamiltonians.

2.3.1 Transition-Metal Ions

The first row of transition-metal ions and their electronic configurations are listed in Table 2.4. The important feature about transition-metal ions is that the magnetic, or unpaired, electrons lie in the outermost shell of the ion. Therefore they are easily influenced by any external field produced by neighboring ligands. That is, the crystal field is likely to be one of the largest terms in the Hamiltonian. Thus we might expect that the contributions to the Hamiltonian, in order of descending strength, are

$$\mathcal{H} = \mathcal{H}_{\text{intraatomic Coulomb}} + \mathcal{H}_{\text{crystal field}} + \mathcal{H}_{\text{spin}-\text{orbit}} + \mathcal{H}_{\text{Zeeman}} . \qquad (2.102)$$

Of course, depending on the situation, we may have to consider additional terms, such as the hyperfine interaction. However, let us consider the eigenstates of the Hamiltonian (2.102). First of all, the intraatomic Coulomb interaction leads to spectroscopic energy levels, the lowest of which is determined by Hund's rules. This ground state is indicated in the last column of Table 2.4.

For most magnetic properties it is sufficient to consider only the lowest term. This is because term energies are of the order of tens of thousands of wave numbers, whereas magnetic energies are at most tens of wave numbers.

The behavior of a given term in the crystal field may be calculated by the technique developed in the last section. Cubic symmetry is the predominant symmetry encountered in most crystals, and Fig. 2.9 indicates how group theory predicts splitting of the various terms of Table 2.4 in such a case. The eigenfunctions of $\mathcal{H}_{\text{intra}} + \mathcal{H}_{\text{cryst}}$ will be denoted as $|\Gamma, \gamma; S, M_S\rangle$, where Γ is the irreducible representation of the point-group symmetry.

Consider, for example, the $3d^3$ configuration. From Hund's rules, the ground state is

$$|L, M_L; S, M_S\rangle = \left|3, M_L; \frac{3}{2}, M_S\right\rangle, \qquad (2.103)$$

which is $(2L + 1)(2S + 1) = 28$-fold degenerate. In the presence of a cubic crystal field this state splits as shown in Fig. 2.9. Thus the ground state would be denoted as $|A_2, \gamma; \frac{3}{2}, M_S\rangle$.

The g Tensor. Now consider the spin-orbit and Zeeman terms. Since we are considering matrix elements only within a given LS term, the matrix elements of
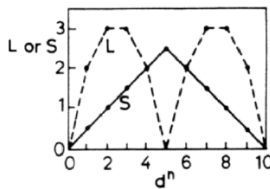
$$\sum_i \xi(\boldsymbol{r}_i)\boldsymbol{l}_i \cdot \boldsymbol{s}_i$$

are proportional to those of $\boldsymbol{L} \cdot \boldsymbol{S}$, by the Wigner–Eckhart theorem. Thus the *spin-orbit Hamiltonian* may be written

$$\mathcal{H}_{\text{sp-orb}} = \lambda \boldsymbol{L} \cdot \boldsymbol{S}, \qquad (2.104)$$

Table 2.4. Configuration of the iron-group ions

Ti^{3+}, V^{4+}	$3d^1$	^2D	
V^{3+}	$3d^2$	^3F	
Cr^{3+}, V^{2+}	$3d^3$	^4F	
Mn^{3+}, Cr^{2+}	$3d^4$	^5D	
Fe^{3+}, Mn^{2+}	$3d^5$	^6S	
Fe^{2+}	$3d^6$	^5D	
Co^{2+}	$3d^7n$	^5D	
Co^{2+}	$3d^7n$	^5D	
Co^{2+}	$3d^7n$	^4F	
Ni^{2+}	$3d^8$	^3F	
Cu^{2+}	$3d^9$	^2D	

where λ is the spin-orbit parameter. Similarly, the *Zeeman Hamiltonian* is

$$\mathcal{H}_Z = \mu_B(\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{H}. \tag{2.105}$$

We now transform $\mathcal{H}_{\text{sp-orb}} + \mathcal{H}_Z$ into the so-called *spin Hamiltonian* by a method proposed by Pryce, in which we project out the orbital dependence. Since neither $\mathcal{H}_{\text{intra}}$ nor $\mathcal{H}_{\text{cryst}}$ has mixed orbital and spin states, our eigenfunctions are products of the form $|\Gamma, \gamma\rangle|S, M_S\rangle$. Let us evaluate the expectation value of $\mathcal{H}_{\text{sp-orb}} + \mathcal{H}_Z$ for an *orbitally nondegenerate* ground state $|\Gamma, \gamma\rangle$. To second order in perturbation theory,
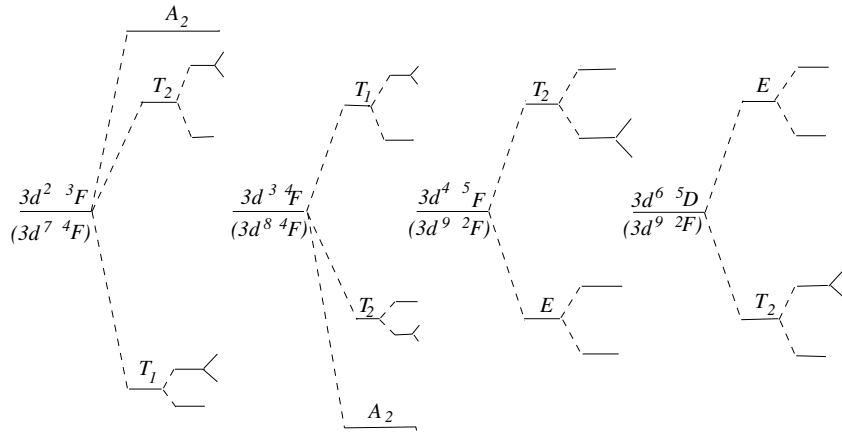
$$\mathcal{H}_{\text{eff}} = \langle \Gamma, \gamma | \mathcal{H}_{\text{sp-orb}} + \mathcal{H}_Z | \Gamma, \gamma \rangle$$

$$= 2\mu_B \boldsymbol{H} \cdot \boldsymbol{S} - \sum_{\Gamma',\gamma'} \frac{|\langle \Gamma', \gamma' | \mu_B \boldsymbol{H} \cdot \boldsymbol{L} + \lambda \boldsymbol{L} \cdot \boldsymbol{S} | \Gamma, \gamma \rangle|^2}{E_{\Gamma',\gamma'} - E_{\Gamma,\gamma}}. \tag{2.106}$$

Expanding the square gives

$$\mathcal{H}_{\text{eff}} = 2\mu \boldsymbol{H} \cdot \boldsymbol{S} - 2\mu_B \lambda \sum_{\mu,\nu} \Lambda_{\mu\nu} S_\mu H_\nu - \lambda^2 \sum_{\mu,\nu} \Lambda_{\mu\nu} S_\mu S_\nu - \mu_B^2 \sum_{\mu,\nu} H_\mu H_\nu, \tag{2.107}$$

where

$$\Lambda_{\mu\nu} = \sum_{\Gamma'\gamma'} \frac{\langle \Gamma, \gamma | L_\mu | \Gamma', \gamma' \rangle \langle \Gamma', \gamma' | L_\nu | \Gamma, \gamma \rangle}{E_{\Gamma',\gamma'} - E_{\Gamma,\gamma}}. \tag{2.108}$$

Fig. 2.9. Crystal-field splittings of the iron-group ion ground states. The first set of splittings are the result of a cubic crystal field. Subsequent splittings are due to an additional tetragonal distortion

This may be written as

$$\mathcal{H}_{\text{eff}} = \sum_{\mu,\nu} (\mu_B g_{\mu\nu} H_\mu S_\nu - \lambda^2 \Lambda_{\mu\nu} S_\mu S_\nu - \mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu), \qquad (2.109)$$

where $g_{\mu\nu}$ is the g tensor

$$g_{\mu\nu} = 2(\delta_{\mu\nu} - \lambda \Lambda_{\mu\nu}). \qquad (2.110)$$

The fact that $g_{\mu\mu}$ differs from 2 tells us that owing to the spin-orbit interaction, the magnetization is now no longer spin only. That is, a small amount of orbital angular momentum has been admixed back into the ground state.

The g value of the free electron is not precisely 2. There are quantum electrodynamic corrections which lead to the value $g = 2.002319$.

As an example of how this value is changed in a solid let us consider the semiconductor silicon. In the ideal crystalline state each silicon atom has four valence electrons which form bonds with four neighboring silicon atoms. If this ideal crystal is irradiated, with high-energy electrons, for example, defects are introduced. One of these is the divacancy illustrated in Fig. 2.10a. The removal of the two atoms A and B leaves six broken bonds, or unpaired electrons. Those electrons associated with atoms 2 and 3 and those associated with 5 and 6 reconstruct bonds as indicated in the figure. The remaining two electrons from atoms 1 and 4 then form an "extended" bond across the vacancy. If one of these latter two electrons is removed by some means, leaving the defect with a net positive charge, the remaining electron is found to have the g value [30]
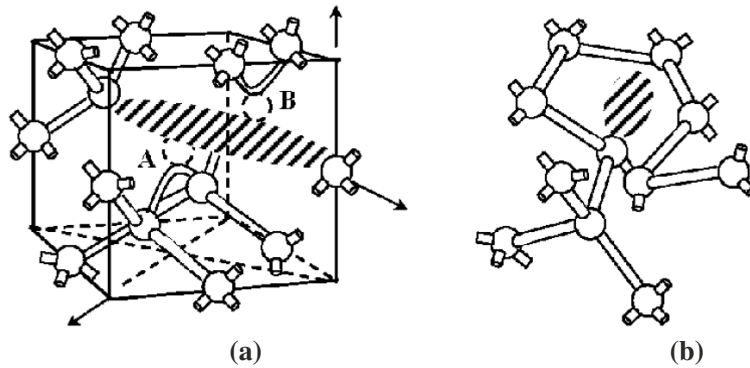
Fig. 2.10. Defects in (**a**) crystalline and (**b**) amorphous silicon having nearly free electron g values

$$g_1 = 2.0004\,,$$
$$g_2 = 2.0020\,,$$
$$g_3 = 2.0041\,.$$

If the silicon is prepared as an *amorphous* film, by the decomposition of silane gas, for example, then the atomic disorder sometimes leaves a silicon atom with only three other silicon neighbors as illustrated schematically in Fig. 2.10b. The fourth unpaired electron is referred to as a "dangling" bond. This electron is found to have the average g value [31]

$$g = 2.0055\,.$$

Although these g values differ by less than 1% these differences are easily measured, as we shall discuss in Chap. 5, and provide an extremely important characterization of the electronic center.

Anisotropy. The second term in (2.109) represents the fine-structure or single-ion *anisotropy*. Notice that $\wedge_{\mu\nu}$ reflects the symmetry of the crystal. The spin Hamiltonian must also display this symmetry; for example, in a cubic crystal $\wedge_{xx} = \wedge_{yy} = \wedge_{zz}$. Thus the anisotropy term reduces to a constant. For axial symmetry $\wedge_{xx} = \wedge_{yy} = \wedge_{\perp}$ and $\wedge_{zz} = \wedge_{||}$. Thus, if we neglect the last term, the effective axial Hamiltonian is

$$\mathcal{H}_{\text{eff}} = g_{||}\mu_B H_z S_z + g_{\perp}\mu_B(H_x S_x + H_y S_y) + D[S_z^2 - \frac{1}{3}S(S+1)]$$

$$+\frac{1}{3}S(S+1)\left(2\wedge_{\perp} + \varLambda_{||}\right)\lambda^2\,, \tag{2.111}$$

where $D = \lambda^2(\wedge_{||} - \wedge_{\perp})$. A Hamiltonian of this form based on the symmetry of the crystal is usually taken as the starting point in describing paramagnetic systems involving transition-metal ions. Thus such ions in crystals are characterized by their g, D, etc., parameters.

   An important experimental fact is that these crystal-field parameters do not change appreciably for concentrated versions of the same salt. Hence, we shall find these paramagnetic states useful when we discuss ferromagnetism. For example, we can see from the discussion above that the anisotropy constants depend on the energy levels, which in turn depend on the positions of the neighboring ions. Thus, if these ions move because of the presence, say, of phonons, then we have a coupling between this motion and the spins.

   The last term in the Hamiltonian (2.109) will survive the two field derivatives leading to the static susceptibility, resulting in the so-called *Van Vleck susceptibility*, which is temperature independent.

   As an example of the application of the spin Hamiltonian, let us consider a spin $\frac{3}{2}$ in an axially symmetric system with an external field applied along the c axis. If we assume that the crystal field is of sufficiently low symmetry
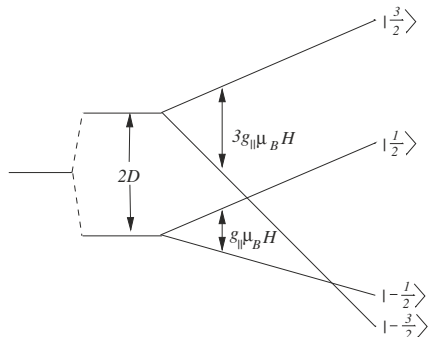
Fig. 2.11. Representation of the effect of the spin-orbit and Zeeman interactions on an orbital singlet with spin $\frac{3}{2}$

to remove any orbital degeneracy of the ground state, then (2.111) applies. Dropping the constant part, we have

$$\mathcal{H}_{\text{eff}} = g_{||}\mu_B H S_z + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] . \tag{2.112}$$

The matrix of $\mathcal{H}_{\text{eff}}$ in the basis $|\frac{3}{2}, M_S\rangle$ is

$$\mathcal{H}_{\text{eff}} = \begin{array}{c} \\ \langle -\frac{3}{2}| \\ \langle -\frac{1}{2}| \\ \langle \frac{1}{2}| \\ \langle \frac{3}{2}| \end{array} \begin{array}{cccc} |-\frac{3}{2}\rangle & |-\frac{1}{2}\rangle & |\frac{1}{2}\rangle & |\frac{3}{2}\rangle \\ \left[\begin{array}{cccc} D - \frac{3}{2}g_{||}\mu_B H & 0 & 0 & 0 \\ 0 & -D - \frac{1}{2}g_{||}\mu_B H & 0 & 0 \\ 0 & 0 & -D + \frac{1}{2}g_{||}\mu_B H & 0 \\ 0 & 0 & 0 & D + \frac{3}{2}g_{||}\mu_B H \end{array}\right] . \end{array}$$

$$\tag{2.113}$$

The eigenvalues are shown in Fig. 2.11. We see that there is a zero-field splitting of $2D$.

Effective Exchange. In our discussion of exchange in the last section we neglected spin-orbit effects as well as off-diagonal exchange effects. We found above that the spin-orbit interaction leads to important contributions to the spin Hamiltonian. It can also modify the form of the exchange interaction. To illustrate these effects, let us consider the exchange between a Mn^{2+} impurity and a neighboring Co^{2+} ion in $CoCl_2 \cdot 2H_2O$ [32]. Co^{2+} has seven d electrons which correspond to three *holes* in the d shell. These holes behave just as electrons would. Therefore we find that the intraatomic Coulomb interaction leads to a ^4F ground state with a spin of $\frac{3}{2}$. The crystal field in $CoCl_2 \cdot 2H_2O$ is predominantly cubic, with a small tetragonal distortion. The cubic part splits the ^4F into three states, the lowest being $^4T_1$, which has a threefold

orbital degeneracy. As mentioned above, crystal-field effects on the transition-metal ions are rather large. Therefore, in so far as we are concerned only with magnetic properties, we may restrict our considerations to this $^4T_1$ ground state.

We now investigate how the tetragonal crystal-field component and the spin-orbit interaction affect this level. Any threefold orbitally degenerate state behaves as though it had an *effective* quantum number $L = 1$. We saw earlier that if we restrict ourselves to a manifold of states in which, say, L is a good quantum number, then we may express the crystal-field Hamiltonian in powers of L_x, L_y, and L_z. The same argument applies even if L is only a good *effective* quantum number. Thus the effect of a tetragonal crystal field upon our $^4T_1$ ground state may be described by the Hamiltonian

$$\mathcal{H}_{\text{tetra}} = -\delta \left(L_z^2 - \frac{3}{2} \right) , \qquad (2.114)$$

where δ is a phenomenological crystal-field parameter and $L = 1$. The spin-orbit interaction may also be expressed in terms of the effective orbital angular momentum,

$$\mathcal{H}_{\text{sp−orb}} = \lambda' \boldsymbol{L} \cdot \boldsymbol{S}_{\text{Co}} , \qquad (2.115)$$

where λ' is an effective spin-orbit parameter. The operators L^+ and L^- are the raising and lowering operators for the components of the $^4T_1$, just as the corresponding real operators would connect the components of a real P state. This technique of writing Hamiltonians in terms of effective-angular-momentum operators is an extremely useful tool for understanding the qualitative features of the electromagnetic absorption spectra of magnetic systems.

The basis functions for our $^4T_1$ state have the form $|M_L, M_S\rangle$, where $M_L = -1, 0$, or $+1$, and $M_S = \pm\frac{1}{2}$ or $\pm\frac{3}{2}$. The effect of $\mathcal{H}_{\text{tetra}} + \mathcal{H}_{\text{sp−orb}}$ is to split the $^4T_1$ into six doublets. Again, for magnetic considerations, we consider the lowest of these. The eigenfunctions have the form

$$\psi^\pm = a \left| \mp 1, \pm\frac{3}{2} \right\rangle + b \left| 0, \pm\frac{1}{2} \right\rangle + c \left| \pm 1, \mp\frac{1}{2} \right\rangle , \qquad (2.116)$$

where a, b, and c are certain mixing coefficients which may, in general, be complex. We now inquire how the exchange with the neighboring Mn^{2+} affects this doublet. Since it is a doublet, the exchange should be expressible as an effective spin of $\frac{1}{2}$ interacting with the Mn^{2+} spin. The purpose of this example is to show that when the exchange is in fact expressed in terms of an effective spin of $\frac{1}{2}$, it does not have the simple isotropic form we have so far been using.

The first thing we must do is establish an expression for the exchange which we know to be correct. Recall the the $^4T_1$ state has a threefold orbital degeneracy, and that the three d holes can be treated just as electrons. Therefore we have a situation in which there is only one state of maximum multiplicity, which means that the total spin is a good quantum number. Also, since

the ground state of Mn^{2+} is an S state, the total spin of this ion is a good quantum number. Therefore the exchange interaction may be written as

$$\mathcal{H}_{ex} = - \sum_{M_L M'_L} J(M_L, M'_L) \boldsymbol{S}_{Mn} \cdot \boldsymbol{S}_{Co} .$$ (2.117)

Notice that we are explicitly including the possibility of off-diagonal exchange. Thus, in terms of actual electron interchange, the exchange integral $J(M_L, M'_L)$ would characterize the interchange in which an electron from a Co^{2+} in the state M_L jumps over to the Mn^{2+}, while an electron from the Mn^{2+} jumps back to the Co^{2+} and in so doing changes it to the M'_L state. These off-diagonal exchange integrals may be complex. As long as the orbital states so connected lie within the $^4T_1$ manifold, the scalar spin product may be used even to describe this off-diagonal exchange.

We now wish to know what form this exchange takes when expressed in terms of the effective spin $\frac{1}{2}$ of the Co^{2+} ground state. The most general interaction has the form

$$\mathcal{H}_{eff} = -\boldsymbol{S}_{eff} \cdot \mathcal{J} \cdot \boldsymbol{S}_{Mn} ,$$ (2.118)

where $\mathcal{J}$ is an exchange dyadic. If we evaluate the matrix elements of (2.117) in the basis $|\psi^{\pm}, M_S\rangle$, where M_S is the Mn^{2+} spin quantum number ($S = \frac{5}{2}$), and compare them with the matrix elements of (2.118) evaluated in the basis $|\pm \frac{1}{2}, M_S\rangle$, we find that *all* the elements of $\mathcal{J}_{\mu\nu}$ are nonzero. For example,

$$\mathcal{J}_{xy} = -2c^2 \text{Im}\{J(1,-1)\} .$$ (2.119)

The general matrix $\mathcal{J}_{\mu\nu}$ may be separated into a symmetric and an antisymmetric part. The *antisymmetric exchange* may be written as

$$\boldsymbol{D} \cdot \boldsymbol{S}_{eff} \times \boldsymbol{S}_{Mn} ,$$ (2.120)

where the vector coupling coefficient $\boldsymbol{D}$ is related to $\mathcal{J}_{\mu\nu}$. This exchange is also referred to as the Dzialoshinski–Moriya exchange [33]. If the elements of the symmetric exchange are different, we speak of this as *anisotropic exchange*. There are two limiting forms that are popularly used: the Ising model

$$\mathcal{H}_{Ising} = -2J \sum_{i,\delta} S_i^z S_{i+\delta}^z ,$$

and the XY model

$$\mathcal{H}_{XY} = -2J \sum_{i,\delta} (S_i^x, S_{i+\delta}^x + S_i^y S_{i+\delta}^y) .$$

Here δ refers to a nearest neighbor. Thus we see that when the exchange interaction is expressed in terms of the effective spin of the ground state, it may have a very general form owing to the presence of orbital effects.

Table 2.5. Configurations of the rare-earth ions

Ce^{3+}	$4f^1 5s^2 p^6$	$^2F_{5/2}$
Pr^{3+}	$4f^2 5s^2 p^6$	$^3H_4$
Nd^{3+}	$4f^3 5s^2 p^6$	$^4I_{9/2}$
Pm^{3+}	$4f^4 5s^2 p^6$	$^6I_4$
Sm^{3+}	$4f^5 5s^2 p^6$	$^6H_{5/2}$
Eu^{3+}	$4f^6 5s^2 p^6$	$^7F_0$
Gd^{3+}	$4f^7 5s^2 p^6$	$^8S_{7/2}$
Tb^{3+}	$4f^8 5s^2 p^6$	$^7F_6$
Dy^{3+}	$4f^9 5s^2 p^6$	$^6H_{15/2}$
Ho^{3+}	$4f^{10} 5s^2 p^6$	$^5I_8$
Er^{3+}	$4f^{11} 5s^2 p^6$	$^4I_{15/2}$
Tm^{3+}	$4f^{12} 5s^2 p^6$	$^3H_6$
Yb^{3+}	$4f^{13} 5s^2 p^6$	$^2F_{7/2}$

2.3.2 Rare-Earth Ions

The electronic configurations of the rare-earth ions are listed in Table 2.5. For these ions we see that the unpaired electrons lie inside the $5s^2 p^6$ shells. Consequently they are not very strongly affected by crystal fields, and we might expect the Hamiltonian to consist of the following terms, in order of descending strength:

$$\mathcal{H} = \mathcal{H}_{\text{intraatomic Coulomb}} + \mathcal{H}_{\text{spin-orbit}} + \mathcal{H}_{\text{crystal field}} + \mathcal{H}_{\text{Zeeman}} . \qquad (2.121)$$

The intraatomic Coulomb interaction produces states characterized by L, M_L, S, and M_S. When the spin-orbit interaction is added, only the total angular momentum $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ is conserved. Therefore the states have the form $|J, M_J; L, S\rangle$.

Let us consider, for the moment, the effect of the Zeeman term in the absence of any crystal field,

$$\mathcal{H}_Z = \mu_B (\boldsymbol{L} + 2\boldsymbol{S}) \cdot \boldsymbol{H} . \qquad (2.122)$$

Since the states are characterized by the eigenvalues of $\boldsymbol{J}$, we rewrite this as

$$\mathcal{H}_{\text{Zeeman}} = g_J \mu_B \boldsymbol{J} \cdot \boldsymbol{H} , \qquad (2.123)$$

where g_J is the *Landé g value*, defined by $g_J \boldsymbol{J} = \boldsymbol{L} + 2\boldsymbol{S}$. This has the value

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \, . \tag{2.124}$$

Thus the state $|J, M_J\rangle$ is split into $2J + 1$ equally spaced states with the separation $g_J \mu_B H$. For Ce^{3+}, for example, $g_J = \frac{6}{7}$.

In the presence of a crystal field the splitting of the state $|J, M_J\rangle$ is easily determined by expressing the crystal field in operator equivalents of $\boldsymbol{J}$. Thus for a crystal field of D_2 symmetry we have

$$\mathcal{H}_{\text{cryst}} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4$$
$$+ B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6 \, . \tag{2.125}$$

where the operators 0_n^m were defined in (2.52).

The matrix of $\mathcal{H}_{\text{cryst}}$ in the basis $|J, M_J; L, S\rangle$ is easily constructed from tables in [12]. The result for Ce^{3+} is

$$
\begin{array}{ccccccc}
& \left|\tfrac{5}{2}\right\rangle & \left|\tfrac{1}{2}\right\rangle & \left|-\tfrac{3}{2}\right\rangle & \left|-\tfrac{5}{2}\right\rangle & \left|-\tfrac{1}{2}\right\rangle & \left|\tfrac{3}{2}\right\rangle
\end{array}
$$

$$
\begin{array}{c}
\left\langle\tfrac{5}{2}\right| \\
\left\langle\tfrac{1}{2}\right| \\
\left\langle-\tfrac{3}{2}\right| \\
\left\langle-\tfrac{5}{2}\right| \\
\left\langle-\tfrac{1}{2}\right| \\
\left\langle\tfrac{3}{2}\right|
\end{array}
\left[
\begin{array}{c|c}
B & 0 \\
\hline
0 & B
\end{array}
\right] \tag{2.126}
$$

where

$$
B \equiv
\begin{bmatrix}
10B_2^0 + 60_4^B & \sqrt{10}B_2^2 + 9\sqrt{10}B_4^2 & 12\sqrt{5}B_4^4 \\
\sqrt{10}B_2^2 + 9\sqrt{10}B_4^2 & -8B_2^0 + 120B_4^0 & 3\sqrt{2}B_2^2 - 15\sqrt{2}B_4^2 \\
12\sqrt{5}B_4^4 & 3\sqrt{2}B_2^2 - 15\sqrt{2}B_4^2 & -2B_2^0 - 180B_4^0
\end{bmatrix} \, .
$$

This gives three doublets which have the form

$$\psi_n^+ = a_n \left|\frac{5}{2}\right\rangle + b_n \left|\frac{1}{2}\right\rangle + c_n \left|-\frac{3}{2}\right\rangle , \tag{2.127a}$$

$$\psi_n^- = a_n \left|-\frac{5}{2}\right\rangle + b_n \left|-\frac{1}{2}\right\rangle + c_n \left|\frac{3}{2}\right\rangle . \tag{2.127b}$$

In terms of the states $|m_l m_z\rangle$, these may be written as

$$\psi_n^+ = \varphi_1 \alpha + \varphi_2 \beta \,, \tag{2.128a}$$

$$\psi_n^- = \varphi_2^* \alpha - \varphi_1^* \beta \,, \tag{2.128b}$$

where $\varphi_1^* = \varphi_1$ and $\varphi_2^* = -\varphi_2$. Under the time-reversal operator $T = iK\sigma_y$, where K is the conjugation operator, these states are related by

$$T\psi_n^+ = \psi_n^- \,, \tag{2.129a}$$

$$T\psi_n^- = -\psi_n^+ \,. \tag{2.129b}$$

Such a pair of states is said to form a *Kramers doublet*. The states (2.116) also formed a Kramers doublet.

Let us now consider the behavior of the lowest Kramers doublet in an external magnetic field. The Hamiltonian is

$$\mathcal{H}_Z = \mu_B(\boldsymbol{l} + 2\boldsymbol{s}) \cdot \boldsymbol{H} \,. \tag{2.130}$$

Since we are within a manifold where J is a good quantum number, this may be written as

$$\mathcal{H}_Z = g_J \mu_B J_z H \,. \tag{2.131}$$

The Zeeman matrix for the lowest doublet is

$$\begin{bmatrix} g_J \mu_B H \left(\frac{5}{2}a_1^2 + \frac{1}{2}b_1^2 - \frac{3}{2}c_1^2 \right) & 0 \\ 0 & -g_J \mu_B H \left(\frac{5}{2}a_1^2 + \frac{1}{2}b_1^2 - \frac{3}{2}c_1^2 \right) \end{bmatrix} \,. \tag{2.132}$$

Therefore the doublet splits linearly in the field. An effective g value is often introduced by defining the splitting of two levels in a field as $g_{\text{eff}} \mu_B H$. In this case the effective g value would be

$$g_{\text{eff}} = g_J \left(5a_1^2 + b_1^2 - 3c_1^2 \right) \,. \tag{2.133}$$

Notice that the g value depends directly on the coefficients in the wave function (2.127). For this reason measurements of the g value provide a sensitive test of the ground-state wave function.

2.3.3 Semiconductors

It is interesting to carry out the calculation for the g value of an electron moving in the periodic potential, $V(\boldsymbol{r})$, of a crystal lattice. The Hamiltonian is

$$\mathcal{H} = \mathcal{H}_{\text{kinetic}} + \mathcal{H}_{\text{crystal}} + \mathcal{H}_{\text{spin-orbit}} + \mathcal{H}_{\text{Zeeman}} \,. \tag{2.134}$$

The eigenfunctions of an electron moving in a periodic potential have the Bloch form $u_{nk}(\boldsymbol{r})\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$ which give rise to energy bands characterized by band indices n and wave vector $\boldsymbol{k}$. In the absence of the Zeeman term the function $u_{nk}(\boldsymbol{r})$ satisfies

$$\left[\frac{1}{2m}(\boldsymbol{p}+\hbar\boldsymbol{k})^2 + V(\boldsymbol{r}) + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\nabla V(\boldsymbol{r})\cdot(\boldsymbol{p}+\hbar\boldsymbol{k})\right]u_{nk}(\boldsymbol{r}) = \epsilon_{nk}u_{nk}(\boldsymbol{r})\,.$$

(2.135)

In the case of the "three-five" semiconductors, which are composed of elements from the third and fifth columns of the period table (e.g., GaAs, InSb) the valence band is p-like while the conduction band is s-like. The band structure in the vicinity of $\boldsymbol{k}=0$ is illustrated in Fig. 2.12. The labels Γ_6, etc., indicate the irreducible representations according to which the wave functions at $\boldsymbol{k}=0$ transform. The first feature to note is that the spin-orbit interaction has split the threefold degeneracy of the p-like valence band. Secondly, the curvatures of these bands are different. This curvature is a measure of the effective mass of the electron. We may obtain an estimate of this mass by treating the term $(\hbar/m)\boldsymbol{k}\cdot\boldsymbol{p}$ in (2.135) as a perturbation.

Calculating the second-order correction to the energy of the conduction band leads to the effective mass tensor [34a],

$$\left(\frac{m}{m^*}\right)_{\mu\nu} = \delta_{\mu\nu} + \frac{2}{m}\sum_{\Gamma}\frac{\langle\Gamma_6|p_\mu|\Gamma\rangle\langle\Gamma|p_\nu|\Gamma_6\rangle}{\epsilon_{\Gamma_6}-\epsilon_\Gamma}\,.$$
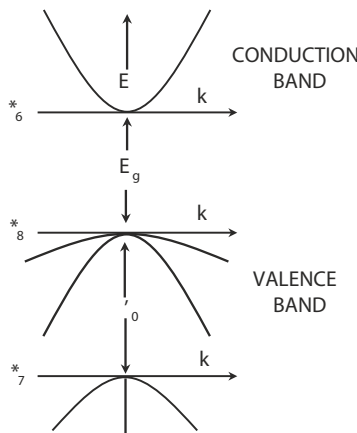
(2.136)

Fig. 2.12. Energy bands near $\boldsymbol{k}=0$ for zinc-blende crystals

The valence band wave functions are linear combinations of the usual x, y, and z components of the p state. Since the III–V compounds have the cubic zinc-blende structure, if we restrict our consideration only to the bands shown in Fig. 2.12 then there is only one parameter,

$$\frac{2}{m} \langle \Gamma, \mu | p_\mu | s \rangle |^2 \equiv P^2 \,,$$

and the effective mass becomes

$$\frac{m}{m^*} = 1 + \frac{P^2}{3} \frac{3E_g + 2\Delta}{E_g(E_g + \Delta)} \,. \tag{2.137}$$

Let us now consider the orbital moment associated with an electron at the bottom of the conduction band,

$$\langle \Gamma_6 | L_z | \Gamma_6 \rangle = \sum_\Gamma \left[\langle \Gamma_6 | x | \Gamma \rangle \langle \Gamma | p_y | \Gamma_6 \rangle - \langle \Gamma_6 | y | \Gamma \rangle \langle \Gamma | p_x | \Gamma_6 \rangle \right] \,. \tag{2.138}$$

This may be rewritten by noting that

$$[x, \mathcal{H}] = \frac{i}{m} p_x + \frac{i\hbar}{4m^2 c^2} (\boldsymbol{\sigma} \times \nabla V)_x \,. \tag{2.139}$$

Neglecting the spin-orbit contribution, which can be shown to be small, the matrix elements of (2.139) satisfy

$$\langle \Gamma | x | \Gamma_6 \rangle = \frac{1}{m} \frac{\langle \Gamma | p_x | \Gamma_6 \rangle}{\epsilon_{\Gamma_6} - \epsilon_\Gamma} \,. \tag{2.140}$$

This enables us to convert the orbital angular-momentum matrix element into a form similar to the effective mass. In particular, eliminating the linear-momentum matrix element between these two expressions leads to the relation [34b]

$$g^* = \frac{\mu^*}{\mu_B} = 1 + \langle \Gamma_6 | L_z | \Gamma_6 \rangle = 2 \left[1 - \frac{\Delta}{3E_g + 2\Delta} \left(\frac{m}{m^*} - 1 \right) \right] \,. \tag{2.141}$$

In general, one must include additional bands, in which case the relationship between the effective g value and the effective mass is not as simple. Nevertheless, when the effective mass is very small the g value can become quite large. In InSb, for example, $m^*/m = -0.014$ and $g^* = -51.4$. Herring [35] has shown that the angular momentum (2.138) may be spatially decomposed into intraatomic and interatomic contributions. The large g values were shown to be associated with the latter, corresponding to interatomic circulating currents.

In this chapter we have seen the origins of various terms in the Hamiltonian that may influence the magnetic response of a system. In the remaining chapters we shall investigate how these terms manifest themselves when the system is excited with a space-and/or time-varying magnetic field.

Problems

2.1. While the discussion in Sect. 2.2.2 dealt mainly with the effect of the nuclear charge on the electron, the electron also affects the nucleus. Co^{57}, for example, is radio-active with a half-life of 270 days. It captures an electron to form Fe^{57} which decays by γ-radiation to an excited state with $I = 3/2$ which quickly $(1.4 \times 10^{-7}\,\text{s})$ decays to the ground state with $I = 1/2$.

Ordinarily when the nucleus emits a γ-ray it recoils. However in 1958, R.L. Mossbauer discovered that nuclei embedded in solids can emit and absorb γ-rays without transferring recoil energy to the lattice. The basic experimental arrangement for measuring the γ-ray energy consists of a moving source, an absorber, and a detector placed beyond the absorber. The transmitted intensity is plotted as a function of velocity. The $14.4\,\text{KeV}$ γ-ray has a natural linewidth of $5 \times 10^{-9}\,\text{eV}$ which corresponds to a Doppler velocity of $1\,\text{mm/s}$.

(a) In Sect. 2.2.2 we also assumed that there was no electron charge at the nucleus. But, in fact, s-electrons do have nonzero amplitude, $\psi(0)$, at the origin. Assuming the electron has a constant charge density, $e|\psi(0)|^2$, and interacts with the nuclear charge through a Coulomb potential Ze/r, out to a radius r_A for the excited state and r_B for the ground state, calculate the shift in the γ-ray energy due to this electronic charge density.

(b) If the emitter and the absorber have the same electronic structure their shifts will be the same. Therefore to observe this shift, called the isomer shift, the electronic charge density at the emitter nucleus, $e|\psi_e(0)|^2$ must be different from that at the absorber nucleus, $e|\psi_a(0)|^2$. Calculate the observed isomer shift, δ, in terms of these wavefunctions.

(c) Suppose the electronic charge distribution produces an electric field gradient at the Fe^{57} nucleus. Using (2.38), sketch the effect of this gradient on the energy levels in Fig. 2.13. Assuming dipole transition selection rules, i.e., $\Delta m_I = \pm 1$, sketch the Mossbauer spectrum.

(d) In order to simplify the Mossbauer spectrum, either the source or absorber should have an unsplit line. Co^{57} diffused into stainless steel is such a case. Figure 2.14 shows the absorption of Fe^{57} in Fe_2O_3 of γ-rays emitted from a stainless steel source. What is the effective magnetic field at the nucleus? Discuss the origin of this field in the context of (2.38).

2.2. As an example of the usefulness of character tables consider an atomic electron surrounded by an environment that has cubic symmetry. In particular, suppose it has sixfold coordination as shown in Fig. 2.1a. The symmetry elements which take this environment into itself are the identity (E), eight rotations by $2\pi/3$ about the cube body diagonals (C3), three rotations by π about the cube axis(C2), six rotations by $\pi/2$ about these same axes (C4) and six rotations by π about axes through the origin parallel to face diagonals (C2). These operations constitute a group, generally labelled O. The number of elements of the group, denoted by h, is 24 in this case. Notice that
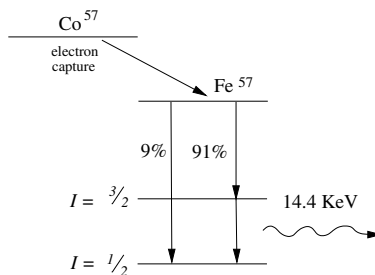
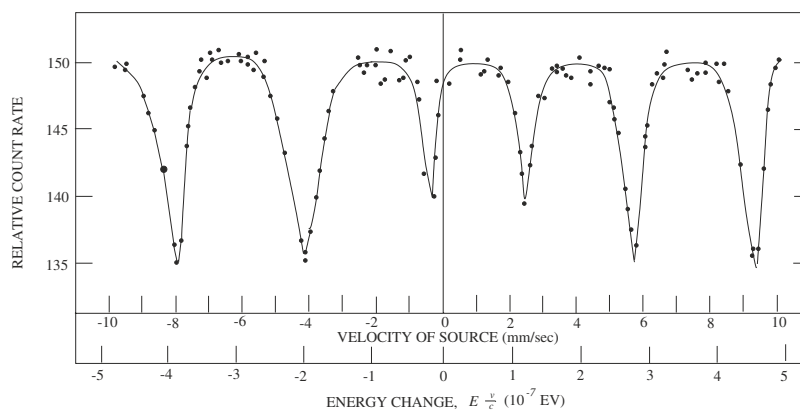**Fig. 2.13.** Decay scheme of Co^{57} and Fe^{57}

Fig. 2.14. The absorption of Fe^{57} bound in Fe_2O_3 of the 14.4 keV gamma ray emitted in the decay of Fe^{57} bound in stainless steel as a function of relative source-absorber velocity

the elements group themselves into classes, G_k, with N_k elements. It can be shown that the number of irreducible representations is equal to the number of classes. Thus the character table will always be "square". The character table for this group is Table 2.6. An electron simply in a Coulomb potential has complete spherical symmetry. The set of rotations in three-dimensional space forms an infinite group. The eigenfunctions are spherical harmonics which transform into each other under rotation,

$$ U_R(\alpha)Y_l^m = \sum \Gamma^{(l)}(\alpha)_{mm'}Y_\lambda^{m'} , $$

where $\Gamma^l(\alpha)_{mm'} = e^{im\alpha}\delta_{m,m'}$. Therefore the character is

$$ \chi^l(\alpha) = \frac{\sin(l+1/2)\alpha}{\sin(\alpha/2)} . $$

Notice that the character associated with the identity operation, E, i.e., $\alpha = 0$, is

$$\chi^{(l)}(0) = \lim_{\alpha \to 0} \frac{\sin(l + 1/2)\alpha}{\sin(\alpha/2)} = 2l + 1 \,.$$

In the presence of the lower cubic symmetry this $(2l + 1)$-dimensional representation is reducible to the irreducible representations of the O group. The decomposition of the reducible character is given by

$$\chi(R) = \sum_i a_i \chi^{(l)}(R) \,,$$

where $\chi^l(R)$ is the character of the ith representation for the group element R. The coefficient a_i is:

$$a_i = (1/h) \sum_k N_K \chi^{(i)}(G_K)^* \chi(G_K) \,.$$

Suppose, for example, we have an s-state$(1 = 0)$ electron in a cubic environment. Then the character $\chi^{(l)}(R) = 1$ for each of the five classes, and the representation is simply A_1:

$$\frac{s}{\text{free space}} \quad \frac{A_1}{\text{cubic environment}} \,.$$

Calculate how the $2l + 1$ degeneracies of p, d, and f electrons are split in a cubic environment. Which have the potential for complete quenching?

2.3. Consider the sixfold coordination shown in Fig. 2.1a. If we elongate the neighbors in the z-direction, this corresponds to a tetragonal distortion and adds a term to the potential (2.50) proportional to Y_2^0. In cartesian coordinates this becomes

$$C_2(3z^2 - r^2) \,, \quad C_2 = qq' \left[\frac{1}{a_1^3} - \frac{1}{a_2^3} \right]$$

for the sixfold tetragonal coordination we are considering. The corresponding operator equivalent is

Table 2.6. Character table for the point group O

	E	$8C_3$	$3C_2 = 3C_4^2$	$6C_2$	$6C_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1