
FIP10604 – Text 04 – ATOMS IN SOLIDS

So far, we have analyzed the magnetic response of atoms supposedly **isolated** from their environment except for the energy exchanges required for thermal equilibrium. Most substances that exhibit magnetic behavior are in the solid state and are crystalline (within a certain length scale). The crystal-environment effects on a particular atom involve various aspects. Some of them are listed below.

- In insulating solids, usually an atom exchanges charge (electrons) with other components, appearing in some ionization state. We then have **magnetic ions**, as we saw in the examples of paramagnetic salts mentioned in Text 03 (in that case, Cr^{3+} , Fe^{3+} and Gd^{3+}).
- Even if the ions do not interact magnetically with each other, the fact that they are **not** in a medium with spherical symmetry affects their magnetic moment (crystal-field effect), as will be discussed here.
- In most cases there is magnetic interaction between the ions, leading to collective behavior and magnetic order. In metallic solids, the important interactions are between electrons (which, by their spin, carry magnetic moment) and/or between them and magnetic ions that might also be present. For now, we still leave interactions out, and focus on how the crystal field affects atomic magnetic moments.

Crystal-field effects

Let us go back to the example of magnetic salts given in Text 03. Using Hund's rules, it is easy to check (**EXERCISE**) that the ground-state terms, with the corresponding values of the gJ product, are those listed below.

Ion	conf.	term	gJ	$M_0(\mu_B/\text{at})$
Cr^{3+}	$[\text{Ar}]3d^3$	${}^4F_{3/2}$	$3/5$	3
Fe^{3+}	$[\text{Ar}]3d^5$	${}^6S_{5/2}$	5	5
Gd^{3+}	$[\text{Xe}]4f^7$	${}^8S_{7/2}$	7	7

The last column shows **experimental** (rounded) values of the saturation magnetization M_0 expressed as the number of Bohr magnetons per atom. It is, therefore, the maximum magnetic moment of each ion in units of μ_B , which should be equal to gJ , from what we saw in Text 03. This is satisfied for Fe^{3+} and Gd^{3+} , which have $L = 0$. But for Cr^{3+} the observed magnetic moment corresponds to $2S$ instead of gJ , as if it were also from spin only, although $L \neq 0$. This is a *crystal-field* effect called **quenching of the orbital angular momentum**, and happens with most 3d ions. In the following we discuss the origin of this effect.

The Coulomb potential felt by the electrons of a given atom or ion is modified by the presence of other atoms or ions in its vicinity. The spherical symmetry of the atomic potential is thus broken, since the contribution from neighbors reflects the symmetry of their positions in space. For example, it is quite common for a transition-metal ion in an insulating compound (oxide or salt) to be at the center of an octahedron formed by six oxygen ions. If this octahedron is not distorted, the symmetry group is the **cubic group**, that is, the set of operations that leave a cube invariant.

Since the orbital degeneracy in a free-atom subshell (definite l) is due to the potential being spherically symmetric, we should doubt that this degeneracy would hold in other symmetries. Consider, for example, the atomic states nd of a transition-metal atom when the crystal has cubic symmetry. Let us see what **Group Theory** tells us (more detail can be found, for example, in V. Heine, *Group Theory in Quantum Mechanics*).

A spherically symmetric system is invariant under all operations of the rotation group in three dimensions. The generators of these operations are the angular-momentum components. The *irreducible representations* of the rotation group (with notation $D^{(l)}$) are characterized by the quantum number l , and have dimensions $(2l + 1)$. Their basis functions are the *spherical harmonics* $Y_{lm_l}(\theta, \phi)$. This means that the energy eigenvalues are degenerate for all values of $m_l = l, l - 1, \dots, -l$.

Not all rotations are symmetry operations of a cube. The cubic group consists of the *classes* $\{E, 3, 2_z, 2_d, 4_z\}$ plus the same operations associated with inversion. In this notation, E is the identity operation, $n = 2, 3, 4$ denote rotations of $2\pi/n$. The subscripts z and d specify rotation axes respectively perpendicular to the faces and parallel to a face diagonal; the 3-axes (120° rotations) lie along the body diagonals.

The irreducible representations of this group are denoted as

$$\begin{aligned} a_{1g}, a_{2g}, e_g, t_{1g}, t_{2g} &\rightarrow \text{even with respect to inversion,} \\ a_{1u}, a_{2u}, e_u, t_{1u}, t_{2u} &\rightarrow \text{odd with respect to inversion,} \end{aligned}$$

with representations a_α , e_α and t_α being respectively one-, two-, and three-dimensional. Recalling that the parity of a spherical harmonic is $(-1)^l$, we see that irreducible representations containing the subscript g apply to l even, which includes the example that we are analyzing ($l = 2$).

The representation $D^{(2)}$, when rotations are restricted to those allowed by the cubic symmetry, is **reduced** into the representations e_g and t_{2g} . This is easily verified if we consider possible basis functions for these representations:

$$\begin{aligned} e_g &\rightarrow \{x^2 - y^2, 3z^2 - r^2\}, \\ t_{2g} &\rightarrow \{xy, xz, yz\}, \end{aligned}$$

where $r^2 = x^2 + y^2 + z^2$. These functions, in terms of their angular dependence for fixed r , can be written as linear combinations of the spherical harmonics $Y_{2m_l}(\theta, \phi)$. In particular,

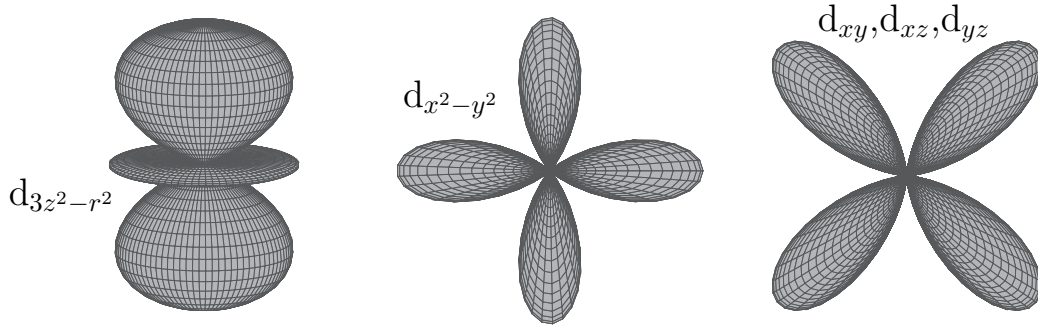


Figure 1: Graphical representation (polar form) of the d-orbitals belonging to the e_g (left, center) and t_{2g} (right) irreducible representations of the cubic symmetry group. The reference plane of the last drawing changes for each of the orbitals as indicated by their subscripts.

$3z^2 - r^2$ is proportional to Y_{20} , xz and yz are linear combinations of $Y_{2,\pm 1}$ (with equal weights), while $x^2 - y^2$ and xy are linear combinations of $Y_{2,\pm 2}$ (with equal weights).

In summary, the $D^{(2)}$ representation, relevant to d-states in an isolated atom, is **reducible** into the representations e_g and t_{2g} when the atom is in a cubic (octahedral) environment. The basis functions of these representations are appropriate linear combinations of spherical harmonics, and can be viewed as *atomic orbitals*. In this context, is common to refer to the d orbitals as $d_{3z^2-r^2}$, $d_{x^2-y^2}$, d_{xy} , etc. Figure 1 shows their graphical representations.

The above discussion shows that a crystal field of cubic symmetry partially lifts the 5-fold degeneracy of $l = 2$ states that would be observed in an isolated atom, separating states belonging to the e_g and t_{2g} representations. This effect, which also happens for other symmetries (with their respective groups), is usually called *crystal-field splitting*. Determining which states are lower or higher in energy depends on details of the potential. Since in general the magnetic ion is positively charged, its neighbors (typically oxygen ions) tend to have negative charge. Then, for an octahedral environment, electrons occupying e_g orbitals of the magnetic ion have higher energy than those in t_{2g} orbitals since they are more strongly **repelled** by neighboring oxygens.

In many solids, the oxygen octahedra are either slightly “stretched” or “shortened” along one of the principal axes (which we may choose as the z direction). This characterizes a *tetragonal* distortion of a cube, which causes new splittings: it lifts the double degeneracy of the e_g orbitals, and separates the xy from the xz and yz orbitals in the t_{2g} basis. So, these representations are no longer irreducible, and are split into lower-dimension ones.

For most transition-metal ions in oxide compounds, these orbitals are filled according to Hund’s rules, yielding a *high spin* configuration. However, if the crystal-field splitting is large in comparison to the residual Coulomb interaction, the lower-energy states will be filled with electrons of both spin orientations before starting the occupation of the higher-energy ones, which leads to a *low-spin configuration*.

Quenching of the orbital angular momentum

Since a crystal field implies reduction of rotation symmetry, it often happens that it yields a **non-degenerate** ground state (not counting spin degeneracy). Through a purely mathematical argument, we can conclude that in such a case any component of \mathbf{L} has zero expectation value. The argument applies to a time-reversal-invariant system, for which the complex conjugate of an energy eigenfunction $\psi(\mathbf{r})$ is also an eigenfunction corresponding to the same eigenvalue. If the eigenvalue is non-degenerate, we conclude that $\psi(\mathbf{r})$ is **real** (except for an arbitrary global phase factor). Then, since any component of \mathbf{L} in coordinate representation involves a factor i , its expectation value, if not null, would be purely imaginary, which is impossible for an observable. Therefore, $\langle \psi | L_\alpha | \psi \rangle = 0$.

It is less obvious if there is degeneracy, but it is easy to verify (**EXERCISE**) that any component of the angular momentum of an electron has zero average value in the basis functions of the e_g or t_{2g} representations. For more than one electron, although the analysis becomes more complex, the argument can still be applied at least at the Hartree level, so that in most cases the (total) **orbital** angular momentum averages to zero.

A zero $\langle \mathbf{L} \rangle$ implies that the orbital angular momentum does not contribute (explicitly) to the magnetic moment. This is the previously mentioned *quenching* of angular momentum. However, second order orbital effects may exist, as discussed below.

Second-order orbital effects

We will focus on situations where **there is quenching** of \mathbf{L} .

In the absence of a magnetic field and neglecting spin-orbit interaction, the ground state is degenerate in M_S , belonging to a subspace whose basis vectors may be denoted as

$$|\Gamma\gamma; SM_S\rangle = |\Gamma\gamma\rangle |SM_S\rangle, \quad (1)$$

where S is the total spin determined by Hund's rules, Γ identifies the irreducible representation to which the ground state belongs, and γ refers to a specific basis function (orbital) in the Γ representation.

We now include the Zeeman and spin-orbit terms,

$$\mathcal{H}_Z = \mu_B \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S}), \quad \mathcal{H}_{so} = \xi \mathbf{L} \cdot \mathbf{S}, \quad (2)$$

as perturbations. A simple projection of these terms on the **orbital** ground-state involves the average

$$\langle \Gamma\gamma | \mathcal{H}_Z + \mathcal{H}_{so} | \Gamma\gamma \rangle = 2\mu_B \mathbf{H} \cdot \mathbf{S}, \quad (3)$$

thus eliminating the orbital part, which reproduces what we obtained for an **isolated** atom with the replacement $gJ \rightarrow 2S$. Note that we still have a single atom (in the sense that we are not considering magnetic interactions), but not isolated because it is subjected to the crystal field.

Since the “orbital ground state” that we are using does not take into account spin-orbit interaction or the presence of magnetic field, to get a better estimate of the Hamiltonian projected on this state we must take into account $\mathcal{H}_Z + \mathcal{H}_{so}$ in second order of perturbation theory. We then build the **effective** Hamiltonian

$$\mathcal{H}_{\text{eff}} = 2\mu_B \mathbf{H} \cdot \mathbf{S} - \sum_{\Gamma', \gamma'} \frac{|\langle \Gamma' \gamma' | \mu_B \mathbf{H} \cdot \mathbf{L} + \xi \mathbf{L} \cdot \mathbf{S} | \Gamma \gamma \rangle|^2}{E_{\Gamma' \gamma'} - E_{\Gamma \gamma}}, \quad (4)$$

where $E_{\Gamma \gamma}$ is the energy of the unperturbed state $|\Gamma \gamma\rangle$. Defining

$$\Lambda_{\mu\nu} \equiv \sum_{\Gamma', \gamma'} \frac{\langle \Gamma \gamma | L_\mu | \Gamma' \gamma' \rangle \langle \Gamma' \gamma' | L_\nu | \Gamma \gamma \rangle}{E_{\Gamma' \gamma'} - E_{\Gamma \gamma}} \quad (5)$$

and

$$g_{\mu\nu} \equiv 2(\delta_{\mu\nu} - \xi \Lambda_{\mu\nu}), \quad (6)$$

we have

$$\mathcal{H}_{\text{eff}} = \sum_{\mu\nu} \left(\mu_B g_{\mu\nu} H_\mu S_\nu - \xi^2 \Lambda_{\mu\nu} S_\mu S_\nu - \mu_B^2 \Lambda_{\mu\nu} H_\mu H_\nu \right). \quad (7)$$

\mathcal{H}_{eff} falls in the category of the so-called *spin Hamiltonians* (here, for a single atom), since only spin operators remain. However, orbital effects are present in three features of this new Hamiltonian: (1) the g factor became a **tensor**; (2) there is a quadratic spin term, with different coefficients for different components, that is, an anisotropy in spin space which is known as *crystal-field anisotropy*; (3) the last term shows an **induced** magnetic moment **in the direction of the field**, which characterizes the *Van Vleck paramagnetism* ($\chi > 0$ and independent of temperature).

In the (quite common) case of **axial symmetry**, choosing z as the symmetry axis, the only non-zero components of the tensor $\mathbf{\Lambda}$ are

$$\Lambda_{zz} \equiv \Lambda_{\parallel}, \quad \Lambda_{xx} = \Lambda_{yy} \equiv \Lambda_{\perp}. \quad (8)$$

The tensor \mathbf{g} is also diagonal, with components g_{\parallel} and g_{\perp} . Leaving aside the Van Vleck term and additive constants, the effective single-atom Hamiltonian can be written as

$$\mathcal{H}_{\text{eff}} = g_{\parallel} \mu_B H_z S_z + g_{\perp} \mu_B (H_x S_x + H_y S_y) - D S_z^2, \quad (9)$$

where $D \equiv \xi^2(\Lambda_{\parallel} - \Lambda_{\perp})$. Note that the z axis is an *easy axis* if $D > 0$, and a *hard axis* (or the xy plane is an *easy plane*) for $D < 0$, since the energy is minimized if the eigenvalue of S_z^2 is large in the first case and small in the second.

Equation (7), or the particular case described by Eq. (9), still refers to a single localized magnetic moment. However, it is associated only to spin, with its behavior modified by the combined effects of orbital angular momentum and crystal field via spin-orbit interaction. The paramagnetic susceptibility can still be evaluated as in Text 03, but it will no longer be

a scalar in the general case. Nevertheless, it should be noticed that even when quenching of the orbital angular momentum occurs, the symmetry may be sufficiently high to yield an isotropic spin Hamiltonian, as, for instance, in the case of a cubic crystal field. Then we have exactly the same situation analyzed in Text 03, except that the magnetic moment is exclusively due to the atomic spin.

Rare earth ions

Crystal-field effects on rare-earth ions (incomplete 4f shell) are much weaker than on transition-metal ions. This is mainly due to the narrow spatial extent of 4f orbitals in comparison to the occupied 6s orbitals, which implies that the 6s electrons screen the effect of neighboring atoms on the 4f ones. In consequence, the relative importance of crystal field and spin-orbit interaction is reversed between transition-metal and rare-earth ions. For the latter one must first use Hund's rules to determine the total angular momentum \mathbf{J} of the atom (no *quenching*) as if in spherical symmetry. Then, as a secondary effect, a crystal field of axial symmetry splits the levels into doublets with $\pm M_J$. In addition, the g -factor is not a scalar, presenting a noticeable anisotropy. However, crystal-field effects on rare-earth ions are weak, being relevant only at very low temperatures.