

2.2. ELECTRONS

symmetry. In this case, other LM terms would vanish, so using only these terms corresponds to the application of a projection operator, *i.e.* equivalent to averaging the quantity of interest [*e.g.* $\rho(\mathbf{r})$] over the star of \mathbf{k} . Note that in another coordinate system (for the L values listed) additional M terms could appear. The group-theoretical derivation led to rules as to how the local coordinate system must be chosen. For example, the z axis is taken along the highest symmetry axis, or the x and y axes are chosen in or perpendicular to mirror planes. Since these coordinate systems are specific for each atom and may differ from the (global) crystal axes, we call them ‘local’ coordinate systems, which can be related by a transformation matrix to the global coordinate system of the crystal.

The symmetry constraints according to (2.2.13.4) are summarized by Kurki-Suonio, who has defined picking rules to choose the local coordinate system for any of the 27 non-cubic site symmetries (Table 2.2.13.1) and has listed the LM combinations, which are defined by (a linear combination of) functions $y_{\ell mp}$ [see (2.2.13.2)]. If the \pm parity appears, both the $+$ and the $-$ combination must be taken. An application of a local coordinate system to rutile TiO_2 is described in Section 2.2.16.2.

In the case of the five cubic site symmetries, which all have a threefold axis in (111), a well defined linear combination of $y_{\ell mp}$ functions (given in Table 2.2.13.2) leads to the cubic harmonics.

2.2.13.2. Interpretation for bonding

Chemical bonding is often described by considering orbitals (*e.g.* a p_z or a d_{z^2} atomic orbital) which are defined in polar coordinates, where the z axis is special, in contrast to Cartesian coordinates, where x , y and z are equivalent. Consider for example an atom coordinated by ligands (*e.g.* forming an octahedron). Then the application of group theory, ligand-field theory *etc.* requires a certain coordinate system provided one wishes to keep the standard notation of the corresponding spherical harmonics. If this octahedron is rotated or tilted with respect to the global (unit-cell) coordinate system, a local coordinate system is needed to allow an easy orbital interpretation of the interactions between the central atom and its ligands. This applies also to spectroscopy or electric field gradients.

The two types of reasons mentioned above may or may not lead to the same choice of a local coordinate system, as is illustrated for the example of rutile in Section 2.2.16.2.

2.2.14. Characterization of Bloch states

The electronic structure of a solid is specified by energy bands $E^j(\mathbf{k})$ and the corresponding wavefunctions, the Bloch functions $\psi_{\mathbf{k}}^j(\mathbf{r})$. In order to characterize energy bands there are various schemes with quite different emphasis. The most important concepts are described below and are illustrated using selected examples in the following sections.

2.2.14.1. Characterization by group theory

The energy bands are primarily characterized by the wave-vector \mathbf{k} in the first BZ that is associated with the translational symmetry according to (2.2.4.23). The star of \mathbf{k} determines an irreducible basis provided that the functions of the star are symmetrized with respect to the small representations, as discussed in Section 2.2.6. Along symmetry lines in the BZ (*e.g.* from Γ along Δ towards X in the BZ shown in Fig. 2.2.7.1), the corresponding group of the \mathbf{k} vector may show a group–subgroup relation, as for example for Γ and Δ . The corresponding irreducible representations can then be found by deduction (or by induction in the case of a group–supergroup relation). These concepts define the compatibility relations (Bouckaert *et al.*, 1930; Bradley & Cracknell, 1972), which tell us how to connect energy bands. For example, the twofold degenerate representation Γ_{12} (the e_g symmetry in a cubic system) splits into the Δ_1 and

Δ_2 manifold in the Δ direction, both of which are one-dimensional. The compatibility relations tell us how to connect bands. In addition, one can also find an orbital representation and thus knows from the group-theoretical analysis which orbitals belong to a certain energy band. This is very useful for interpretations.

2.2.14.2. Energy regions

In chemistry and physics it is quite common to separate the electronic states of an atom into those from core and valence electrons, but sometimes this distinction is not well defined, as will be discussed in connection with the so-called semi-core states. For the sake of argument, let us discuss the situation in a solid using the concepts of the LAPW method, keeping in mind that very similar considerations hold for all other band-structure schemes.

A core state is characterized by a low-lying energy (*i.e.* with a large negative energy value with respect to the Fermi energy) and a corresponding wavefunction that is completely confined inside the sphere of the respective atom. Therefore there is effectively no overlap with the wavefunctions from neighbouring atoms and, consequently, the associated band width is practically zero.

The valence electrons occupy the highest states and have wavefunctions that strongly overlap with their counterparts at adjacent sites, leading to chemical bonding, large dispersion (*i.e.* a strong variation of the band energy with \mathbf{k}) and a significant band width.

The semi-core states are in between these two categories. For example, the $3s$ and $3p$ states of the $3d$ transition metals belong here. They are about 2–6 Ry (1 Ry = 13.6 eV) below the valence bands and have most of the wavefunctions inside their atomic spheres, but a small fraction (a few per cent) of the corresponding charge lies outside this sphere. This causes weak interactions with neighbouring atoms and a finite width of the corresponding energy bands.

Above the valence states are the unoccupied states, which often (*e.g.* in DFT or the HF method) require special attention.

2.2.14.3. Decomposition according to wavefunctions

For interpreting chemical bonding or the physical origin of a given Bloch state at $E^j(\mathbf{k})$, a decomposition according to its wavefunction is extremely useful but always model-dependent. The charge density $\psi_{\mathbf{k}}^j(\mathbf{r})^* \psi_{\mathbf{k}}^j(\mathbf{r})$ corresponding to the Bloch state at $E^j(\mathbf{k})$ can be normalized to one per unit cell and is (in principle) an observable, while its decomposition depends on the model used. The following considerations are useful in this context:

(1) *Site-centred orbitals.* In many band-structure methods, the Bloch functions are expressed as a linear combination of atomic orbitals (LCAO). These orbitals are centred at the various nuclei that constitute the solid. The linear-combination coefficients determine how much of a given orbital contributes to the wavefunction (Mulliken population analysis).

(2) *Spatially confined functions.* In many schemes (LMTO, LAPW, KKR; see Section 2.2.11), atomic spheres are used in which the wavefunctions are described in terms of atomic-like orbitals. See, for example, the representation (2.2.12.1) in the LAPW method (Section 2.2.12), where inside the atomic sphere the wavefunction is written as an ℓ -like radial function times spherical harmonics (termed partial waves). The latter require a local coordinate system (Section 2.2.13) which need not to be the same as the global coordinate system of the unit cell. The reasons for choosing a special local coordinate system are twofold: one is a simplification due to the use of the point-group symmetry, and the other is the interpretation, as will be illustrated below for TiO_2 in the rutile structure (see Section 2.2.16.2).

(3) *Orbital decomposition.* In all cases in which ℓ -like orbitals are used (they do not require a local coordinate system) to construct the crystalline wavefunction, an ℓ -like decomposition

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can be done. This is true for both atom-centred orbitals and spatially confined partial waves. A corresponding decomposition can be done on the basis of partial electronic charges, as discussed below. A further decomposition into the m components can only be done in a local coordinate system with respect to which the spherical harmonics are defined.

(4) *Bonding character.* As in a diatomic molecule with an orbital on atom A and another on atom B, we can form bonding and antibonding states by adding or subtracting the corresponding orbitals. The bonding interaction causes a lowering in energy with respect to the atomic state and corresponds to a constructive interference of the orbitals. For the antibonding state, the interaction raises the energy and leads to a change in sign of the wavefunction, causing a nodal plane that is perpendicular to the line connecting the nuclei. If the symmetry does not allow an interaction between two orbitals, a nonbonding state occurs. Analogous concepts can also be applied to solids.

(5) *Partial charges.* The charge corresponding to a Bloch function of state $E^j(\mathbf{k})$ – averaged over the star of \mathbf{k} – can be normalized to 1 in the unit cell. A corresponding decomposition of the charge can be done into partial electronic charges. This is illustrated first within the LAPW scheme. Using the resolution of the identity this 1 (unit charge) of each state $E^j_{\mathbf{k}}$ can be spatially decomposed into the contribution $q^{\text{out}}(E^j_{\mathbf{k}})$ from the region outside all atomic spheres (interstitial region II) and a sum over all atomic spheres (with superscript t) which contain the charges $q^t(E^j_{\mathbf{k}})$ (confined within atomic sphere t). The latter can be further decomposed into the partial ℓ -like charges $q^t_{\ell}(E^j_{\mathbf{k}})$, leading to $1 = q^{\text{out}}(E^j_{\mathbf{k}}) + \sum_t \sum_{\ell} q^t_{\ell}(E^j_{\mathbf{k}})$. In a site-centred basis a similar decomposition can be done, but without the term $q^{\text{out}}(E^j_{\mathbf{k}})$. The interpretation, however, is different, as will be discussed for Cu (see Section 2.2.16). If the site symmetry (point group) permits, another partitioning according to m can be made, e.g. into the t_{2g} and e_g manifold of the fivefold degenerate d orbitals in an octahedral ligand field. The latter scheme requires a local coordinate system in which the spherical harmonics are defined (see Section 2.2.13). In general, the proper m combinations are given by the irreducible representations corresponding to the site symmetry.

2.2.14.4. Localized versus itinerant electrons

Simple metals with valence electrons originating from s - and p -type orbitals form wide bands which are approximately free-electron like (with a large band width W). Such a case corresponds to itinerant electrons that are delocalized and thus cause metallic conductivity.

The other extreme case is a system with $4f$ (and some $5f$) electrons, such as the lanthanides. Although the orbital energies

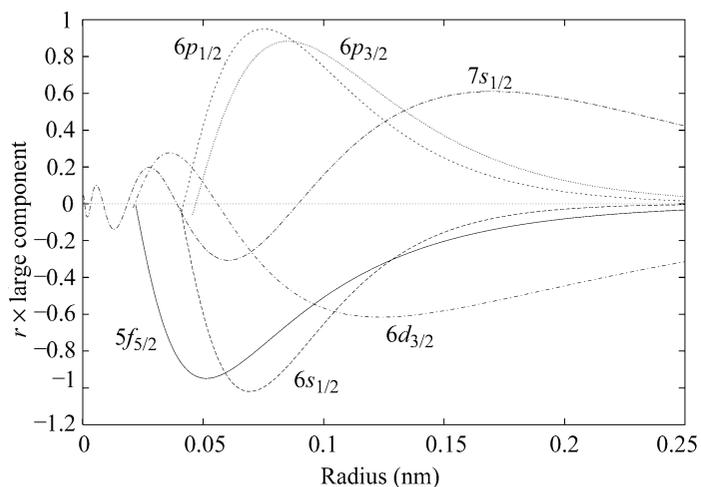


Fig. 2.2.14.1. Relativistic radial wavefunctions (large component) of the uranium atom. Shown are the outer lobes of valence and semi-core states excluding the [Xe] core, and the $4f$ and $5d$ core states.

of these electrons are in the energy range of the valence electrons, they act more like core electrons and thus are tightly bound to the corresponding atomic site. Such electrons are termed localized, since they do not hop to neighbouring sites (controlled by a hopping parameter t) and thus do not contribute to metallic conductivity. Adding another of these electrons to a given site would increase the Coulomb repulsion U . A large U (i.e. $U > t$) prevents them from hopping.

There are – as usual – borderline cases (e.g. the late $3d$ transition-metal oxides) in which a delicate balance between t and U , the energy gain by delocalizing electrons and the Coulomb repulsion, determines whether a system is metallic or insulating. This problem of metal/insulator transitions is an active field of research of solid-state physics which shall not be discussed here.

In one example, however, the dual role of f electrons is illustrated for the uranium atom using relativistic wavefunctions (with a large and a small component) characterized by the quantum numbers n , ℓ and j . Fig. 2.2.14.1 shows the outermost lobe (the large component) of the electrons beyond the [Xe] core without the $4f$ and $5d$ core-like states. One can see the $6s_{1/2}$, $6p_{1/2}$ and $6p_{3/2}$ (semi-core) electrons, and the $6d_{3/2}$ and $7s_{1/2}$ (valence) electrons.

On the one hand, the radial wavefunction of the $5f_{5/2}$ orbital has its peak closer to the nucleus than the main lobes of the semi-core states $6s_{1/2}$, $6p_{1/2}$ and $6p_{3/2}$, and thus demonstrates the *core nature* of these $5f$ electrons. On the other hand, the $5f_{5/2}$ orbital decays (with distance) much less than the semi-core states and electrons in this orbital can thus also play the role of *valence electrons*, like electrons in the $6d_{3/2}$ and $7s_{1/2}$ orbitals. This dual role of the f electrons has been discussed, for example, by Schwarz & Herzig (1979).

2.2.14.5. Spin polarization

In a non-fully-relativistic treatment, spin remains a good quantum number. Associated with the spin is a spin magnetic moment. If atoms have net magnetic moments they can couple in various orders in a solid. The simplest cases are the collinear spin alignments as found in ferromagnetic (FM) or antiferromagnetic (AF) systems with parallel (FM) and antiparallel (AF) moments on neighbouring sites. Ferrimagnets have opposite spin alignments but differ in the magnitude of their moments on neighbouring sites, leading to a finite net magnetization. These cases are characterized by the electronic structure of spin-up and spin-down electrons. More complicated spin structures (e.g. canted spins, spin spirals, spin glasses) often require a special treatment beyond simple spin-polarized calculations. In favourable cases, however, as in spin spirals, it is possible to formulate a generalized Bloch theorem and treat such systems by band theory (Sandratskii, 1990).

In a fully relativistic formalism, an additional orbital moment may occur. Note that the orientation of the total magnetic moment (spin and orbital moment) with respect to the crystal axis is only defined in a relativistic treatment including spin-orbit interactions. In a spin-polarized calculation without spin-orbit coupling this is not the case and only the relative orientation (majority-spin and minority-spin) is known. The magnetic structures may lead to a lowering of symmetry, a topic beyond this book.

2.2.14.6. The density of states (DOS)

The density of states (DOS) is the number of one-electron states (in the HF method or DFT) per unit energy interval and per unit cell volume. It is better to start with the integral quantity $I(\varepsilon)$, the number of states below a certain energy ε ,

$$I(\varepsilon) = \frac{2}{V_{\text{BZ}}} \sum_j \int_{\text{BZ}} \vartheta(\varepsilon - \varepsilon_{\mathbf{k}}^j) d\mathbf{k}, \quad (2.2.14.1)$$

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where V_{BZ} is the volume of the BZ, the factor 2 accounts for the occupation with spin-up and spin-down electrons (in a non-spin-polarized case), and $\vartheta(\varepsilon - \varepsilon_{\mathbf{k}}^i)$ is the step function, the value of which is 1 if $\varepsilon_{\mathbf{k}}^i$ is less than ε and 0 otherwise. The sum over \mathbf{k} points has been replaced by an integral over the BZ, since the \mathbf{k} points are uniformly distributed. Both expressions, sum and integral, are used in different derivations or applications. The Fermi energy is defined by imposing that $I(E_F) = N$, the number of (valence) electrons per unit cell.

The total DOS is defined as the energy derivative of $I(\varepsilon)$ as

$$n(\varepsilon) = \frac{dI(\varepsilon)}{d\varepsilon}, \quad (2.2.14.2)$$

with the normalization

$$N = \int_{-\infty}^{E_F} n(\varepsilon) d\varepsilon, \quad (2.2.14.3)$$

where the integral is taken from $-\infty$ if all core states are included or from the bottom of the valence bands, often taken to be at zero. This defines the Fermi energy (note that the energy range must be consistent with N). In a bulk material, the origin of the energy scale is arbitrary and thus only relative energies are important. In a realistic case with a surface (*i.e.* a vacuum) one can take the potential at infinity as the energy zero, but this situation is not discussed here.

The total DOS $n(\varepsilon)$ can be decomposed into a partial (or projected) DOS by using information from the wavefunctions as described above in Section 2.2.14.3. If the charge corresponding to the wavefunction of an energy state is partitioned into contributions from the atoms, a site-projected DOS can be defined as $n^t(\varepsilon)$, where the superscript t labels the atom t . These quantities can be further decomposed into ℓ -like contributions within each atom to give $n_\ell^t(\varepsilon)$. As discussed above for the partial charges, a further partitioning of the ℓ -like terms according to the site symmetry (point group) can be done (in certain cases) by taking the proper m combinations, *e.g.* the t_{2g} and e_g manifold of the fivefold degenerate d orbitals in an octahedral ligand field. The latter scheme requires a local coordinate system in which the spherical harmonics are defined (see Section 2.2.13). In this context all considerations as discussed above for the partial charges apply again. Note in particular the difference between site-centred and spatially decomposed wavefunctions, which affects the partition of the DOS into its wavefunction-dependent contributions. For example, in atomic sphere representations as in LAPW we have the decomposition

$$n(\varepsilon) = n^{\text{out}}(\varepsilon) + \sum_t \sum_\ell n_\ell^t(\varepsilon). \quad (2.2.14.4)$$

In the case of spin-polarized calculations, one can also define a spin-projected DOS for spin-up and spin-down electrons.

2.2.15. Electric field gradient tensor

2.2.15.1. Introduction

The study of hyperfine interactions is a powerful way to characterize different atomic sites in a given sample. There are many experimental techniques, such as Mössbauer spectroscopy, nuclear magnetic and nuclear quadrupole resonance (NMR and NQR), perturbed angular correlations (PAC) measurements *etc.*, which access hyperfine parameters in fundamentally different ways. Hyperfine parameters describe the interaction of a nucleus with the electric and magnetic fields created by the chemical environment of the corresponding atom. Hence the resulting level splitting of the nucleus is determined by the product of a nuclear and an extra-nuclear quantity. In the case of quadrupole interactions, the nuclear quantity is the nuclear quadrupole moment (Q) that interacts with the electric field gradient (EFG)

produced by the charges outside the nucleus. For a review see, for example, Kaufmann & Vianden (1979).

The EFG tensor is defined by the second derivative of the electrostatic potential V with respect to the Cartesian coordinates x_i , $i = 1, 2, 3$, taken at the nuclear site n ,

$$\Phi_{ij} = \left. \frac{\partial^2 V}{\partial x_i \partial x_j} \right|_n - \frac{1}{3} \delta_{ij} \nabla^2 \left. V \right|_n, \quad (2.2.15.1)$$

where the second term is included to make it a traceless tensor. This is more appropriate, since there is no interaction of a nuclear quadrupole and a potential caused by s electrons. From a theoretical point of view it is more convenient to use the spherical tensor notation because electrostatic potentials (the negative of the potential energy of the electron) and the charge densities are usually given as expansions in terms of spherical harmonics. In this way one automatically deals with traceless tensors (for further details see Herzig, 1985).

The analysis of experimental results faces two obstacles: (i) The nuclear quadrupole moments (Pyykkö, 1992) are often known only with a large uncertainty, as this is still an active research field of nuclear physics. (ii) EFGs depend very sensitively on the anisotropy of the charge density close to the nucleus, and thus pose a severe challenge to electronic structure methods, since an accuracy of the density in the per cent range is required.

In the absence of a better tool, a simple point-charge model was used in combination with so-called Sternheimer (anti-) shielding factors in order to interpret the experimental results. However, these early model calculations depended on empirical parameters, were not very reliable and often showed large deviations from experimental values.

In their pioneering work, Blaha *et al.* (1985) showed that the LAPW method was able to calculate EFGs in solids accurately without empirical parameters. Since then, this method has been applied to a large variety of systems (Schwarz & Blaha, 1992) from insulators (Blaha *et al.*, 1985), metals (Blaha *et al.*, 1988) and superconductors (Schwarz *et al.*, 1990) to minerals (Winkler *et al.*, 1996).

Several other electronic structure methods have been applied to the calculation of EFGs in solids, for example the LMTO method for periodic (Methfessel & Frota-Pessoa, 1990) or non-periodic (Petrilli & Frota-Pessoa, 1990) systems, the KKR method (Akai *et al.*, 1990), the DVM (discrete variational method; Ellis *et al.*, 1983), the PAW method (Petrilli *et al.*, 1998) and others (Meyer *et al.*, 1995). These methods achieve different degrees of accuracy and are more or less suitable for different classes of systems.

As pointed out above, measured EFGs have an intrinsic uncertainty related to the accuracy with which the nuclear quadrupole moment is known. On the other hand, the quadrupole moment can be obtained by comparing experimental hyperfine splittings with very accurate electronic structure calculations. This has recently been done by Dufek *et al.* (1995a) to determine the quadrupole moment of ^{57}Fe . Hence the calculation of accurate EFGs is to date an active and challenging research field.

2.2.15.2. EFG conversion formulas

The nuclear quadrupole interaction (NQI) represents the interaction of Q (the nuclear quadrupole moment) with the electric field gradient (EFG) created by the charges surrounding the nucleus, as described above. Here we briefly summarize the main ideas (following Petrilli *et al.*, 1998) and provide conversions between experimental NQI splittings and electric field gradients.

Let us consider a nucleus in a state with nuclear spin quantum number $I > 1/2$ with the corresponding nuclear quadrupole moment $Q_{i,j} = (1/e) \int d^3r \rho_n(r) r_i r_j$, where $\rho_n(r)$ is the nuclear