

## 2.2. ELECTRONS

## 2.2.8. Bloch functions

We can provide a physical interpretation for a Bloch function by the following considerations. By combining the group-theoretical concepts based on the translational symmetry with the free-electron model, we can rewrite a Bloch function [see (2.2.4.18)] in the form

$$\psi_{\mathbf{k}}^j(\mathbf{r}) = |\mathbf{k}\rangle u_{\mathbf{k}}^j(\mathbf{r}), \quad (2.2.8.1)$$

where  $|\mathbf{k}\rangle$  denotes the plane wave (ignoring normalization) in Dirac's ket notation (2.2.5.3). The additional superscript  $j$  denotes the band index associated with  $E^j(\mathbf{k})$  (see Section 2.2.6.2). The two factors can be interpreted most easily for the two limiting cases, namely:

(i) For a constant potential, for which the first factor corresponds to a plane wave with momentum  $\hbar\mathbf{k}$  [see (2.2.5.5)] but the second factor becomes a constant. Note that for a realistic (non-vanishing) potential, the  $\mathbf{k}$  vector of a Bloch function is no longer the momentum and thus is often denoted as pseudomomentum.

(ii) If the atoms in a crystal are infinitely separated (*i.e.* for infinite lattice constants) the BZ collapses to a point, making the first factor a constant. In this case, the second factor must correspond to atomic orbitals and the label  $j$  denotes the atomic states  $1s, 2s, 2p$  etc. In the intermediate case,  $\mathbf{k}$  is quantized [see (2.2.4.13)] and can take  $N$  values (or  $2N$  states including spin) for  $N$  cells contained in the volume of the periodic boundary condition [see (2.2.4.21)]. Therefore, as the interatomic distance is reduced from infinity to the equilibrium separations, an atomic level  $j$  is broadened into a band  $E^j(\mathbf{k})$  with the quasi-continuous  $\mathbf{k}$  vectors and thus shows dispersion.

According to another theorem, the mean velocity of an electron in a Bloch state with wavevector  $\mathbf{k}$  and energy  $E^j(\mathbf{k})$  is given by

$$v^j(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial}{\partial \mathbf{k}} E^j(\mathbf{k}). \quad (2.2.8.2)$$

If the energy is independent of  $\mathbf{k}$ , its derivative with respect to  $\mathbf{k}$  vanishes and thus the corresponding velocity. This situation corresponds to the genuinely isolated atomic levels (with band width zero) and electrons that are tied to individual atoms. If, however, there is any nonzero overlap in the atomic wavefunctions, then  $E^j(\mathbf{k})$  will not be constant throughout the zone.

In the general case, different notations are used to characterize band states. Sometimes it is more appropriate to label an energy band by the atomic level from which it originates, especially for narrow bands. In other cases (with a large band width) the free-electron behaviour may be dominant and thus the corresponding free-electron notation is more appropriate.

## 2.2.9. Quantum-mechanical treatment

A description of the electronic structure of solids requires a quantum-mechanical (QM) treatment which can be parameterized (in semi-empirical schemes) but is often obtained from *ab initio* calculations. The latter are more demanding in terms of computational effort but they have the advantage that no experimental knowledge is needed in order to adjust parameters. The following brief summary is restricted to the commonly used types of *ab initio* methods and their main characteristics.

## 2.2.9.1. Exchange and correlation treatment

Hartree-Fock-based (HF-based) methods (for a general description see, for example, Pisani, 1996) are based on a wavefunction description (with one Slater determinant in the HF method). The single-particle HF equations (written for an atom in Rydberg atomic units) can be written in the following form, which is convenient for further discussions:

$$\left[ -\nabla^2 + V_{Ne}(\mathbf{r}) + \sum_{j=1}^N \int |\psi_j^{\text{HF}}(\mathbf{r}')|^2 \frac{2}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' - \sum_{j=1}^N \int \psi_j^{\text{HF}}(\mathbf{r}')^* \frac{1}{|\mathbf{r} - \mathbf{r}'|} P_{rr'} \psi_j^{\text{HF}}(\mathbf{r}') d\mathbf{r}' \right] \psi_i^{\text{HF}}(\mathbf{r}) = \epsilon_i^{\text{HF}} \psi_i^{\text{HF}}(\mathbf{r}), \quad (2.2.9.1)$$

with terms for the kinetic energy, the nuclear electronic potential, the classical electrostatic Coulomb potential and the exchange, a function potential which involves the permutation operator  $P_{rr'}$ , which interchanges the arguments of the subsequent product of two functions. This exchange term can not be rewritten as a potential times the function  $\psi_i^{\text{HF}}(\mathbf{r})$  but is truly non-local (*i.e.* depends on  $\mathbf{r}$  and  $\mathbf{r}'$ ). The interaction of orbital  $j$  with itself (contained in the third term) is unphysical, but this self-interaction is exactly cancelled in the fourth term. This is no longer true in the approximate DFT method discussed below. The HF method treats exchange exactly but contains – by definition – no correlation effects. The latter can be added in an approximate form in post-HF procedures such as that proposed by Colle & Salvetti (1990).

Density functional theory (DFT) is an alternative approach in which both effects, exchange and correlation, are treated in a combined scheme but both approximately. Several forms of DFT functionals are available now that have reached high accuracy, so many structural problems can be solved adequately. Further details will be given in Section 2.2.10.

## 2.2.9.2. The choice of basis sets and wavefunctions

Most calculations of the electronic structure in solids (Pisani, 1996; Singh, 1994; Altmann, 1994) use a linear combination of basis functions in one form or another but differ in the basis sets. Some use a linear combination of atomic orbitals (LCAO) where the AOs are given as Gaussian- or Slater-type orbitals (GTOs or STO); others use plane-wave (PW) basis sets with or without augmentations; and still others make use of muffin-tin orbitals (MTOs) as in LMTO (linear combination of MTOs; Skriver, 1984) or ASW (augmented spherical wave; Williams *et al.*, 1979). In the former cases, the basis functions are given in analytic form, but in the latter the radial wavefunctions are obtained numerically by integrating the radial Schrödinger equation (Singh, 1994) (see Section 2.2.11).

Closely related to the choice of basis sets is the explicit form of the wavefunctions, which can be well represented by them, whether they are nodeless pseudo-wavefunctions or all-electron wavefunctions including the complete radial nodal structure and a proper description close to the nucleus.

## 2.2.9.3. The form of the potential

In the muffin-tin or the atomic sphere approximation (MTA or ASA), each atom in the crystal is surrounded by an atomic sphere in which the potential is assumed to be spherically symmetric [see (2.2.12.5) and the discussion thereof]. While these schemes work reasonably well in highly coordinated, closely packed systems (such as face-centred-cubic metals), they become very approximate in all non-isotropic cases (*e.g.* layered compounds, semiconductors, open structures or molecular crystals). Schemes that make no shape approximation in the form of the potential are termed full-potential schemes (Singh, 1994; Blaha *et al.*, 1990; Schwarz & Blaha, 1996).

With a proper choice of pseudo-potential one can focus on the valence electrons, which are relevant for chemical bonding, and replace the inner part of their wavefunctions by a nodeless pseudo-function that can be expanded in PWs with good convergence.

## 2. SYMMETRY ASPECTS OF EXCITATIONS

### 2.2.9.4. Relativistic effects

If a solid contains only light elements, non-relativistic calculations are well justified, but as soon as heavier elements are present in the system of interest relativistic effects can no longer be neglected. In the medium range of atomic numbers (up to about 54), so-called scalar relativistic schemes are often used (Koelling & Harmon, 1977), which describe the main contraction or expansion of various orbitals (due to the Darwin  $s$ -shift or the mass-velocity term) but omit spin-orbit splitting. Unfortunately, the spin-orbit term couples spin-up and spin-down wavefunctions. If one has  $n$  basis functions without spin-orbit coupling, then including spin-orbit coupling in the Hamiltonian would lead to a  $2n \times 2n$  matrix equation, which requires about eight times as much computer time to solve it (due to the  $n^3$  scaling). Since the spin-orbit effect is generally small (at least for the valence states), one can simplify the procedure by diagonalizing the Hamiltonian including spin-orbit coupling in the space of the low-lying bands as obtained in a scalar relativistic step. This version is called second variational method (see *e.g.* Singh, 1994). For very heavy elements it may be necessary to solve Dirac's equation, which has all these terms (Darwin  $s$ -shift, mass-velocity and spin-orbit) included. Additional aspects are illustrated in Section 2.2.14 in connection with the uranium atom.

### 2.2.10. Density functional theory

The most widely used scheme for calculating the electronic structure of solids is based on density functional theory (DFT). It is described in many excellent books, for example that by Dreizler & Gross (1990), which contains many useful definitions, explanations and references. Hohenberg & Kohn (1964) have shown that for determining the ground-state properties of a system all one needs to know is the electron density  $\rho(\mathbf{r})$ . This is a tremendous simplification considering the complicated wavefunction of a crystal with (in principle infinitely) many electrons. This means that the total energy of a system (a solid in the present case) is a functional of the density  $E[\rho(r)]$ , which is independent of the external potential provided by all nuclei. At first it was just proved that such a functional exists, but in order to make this fundamental theorem of practical use Kohn & Sham (1965) introduced orbitals and suggested the following procedure.

In the universal approach of DFT to the quantum-mechanical many-body problem, the interacting system is mapped in a unique manner onto an effective non-interacting system of quasi-electrons with the same total density. Therefore the electron density plays the key role in this formalism. The non-interacting particles of this auxiliary system move in an effective local one-particle potential, which consists of a mean-field (Hartree) part and an exchange-correlation part that, in principle, incorporates all correlation effects exactly. However, the functional form of this potential is not known and thus one needs to make approximations.

Magnetic systems (with collinear spin alignments) require a generalization, namely a different treatment for spin-up and spin-down electrons. In this generalized form the key quantities are the spin densities  $\rho_\sigma(r)$ , in terms of which the total energy  $E_{\text{tot}}$  is

$$E_{\text{tot}}(\rho_\uparrow, \rho_\downarrow) = T_s(\rho_\uparrow, \rho_\downarrow) + E_{ee}(\rho_\uparrow, \rho_\downarrow) + E_{Ne}(\rho_\uparrow, \rho_\downarrow) + E_{xc}(\rho_\uparrow, \rho_\downarrow) + E_{NN}, \quad (2.2.10.1)$$

with the electronic contributions, labelled conventionally as, respectively, the kinetic energy (of the non-interacting particles), the electron-electron repulsion, the nuclear-electron attraction and the exchange-correlation energies. The last term  $E_{NN}$  is the repulsive Coulomb energy of the fixed nuclei. This expression is still exact but has the advantage that all terms but one can be calculated very accurately and are the dominating (large) quan-

ties. The exception is the exchange-correlation energy  $E_{xc}$ , which is defined by (2.2.10.1) but must be approximated. The first important methods for this were the local density approximation (LDA) or its spin-polarized generalization, the local spin density approximation (LSDA). The latter comprises two assumptions:

(i) That  $E_{xc}$  can be written in terms of a local exchange-correlation energy density  $\varepsilon_{xc}$  times the total (spin-up plus spin-down) electron density as

$$E_{xc} = \int \varepsilon_{xc}(\rho_\uparrow, \rho_\downarrow) * [\rho_\uparrow + \rho_\downarrow] dr. \quad (2.2.10.2)$$

(ii) The particular form chosen for  $\varepsilon_{xc}$ . For a homogeneous electron gas  $\varepsilon_{xc}$  is known from quantum Monte Carlo simulations, *e.g.* by Ceperley & Alder (1984). The LDA can be described in the following way. At each point  $\mathbf{r}$  in space we know the electron density  $\rho(\mathbf{r})$ . If we locally replace the system by a homogeneous electron gas of the same density, then we know its exchange-correlation energy. By integrating over all space we can calculate  $E_{xc}$ .

The most effective way known to minimize  $E_{\text{tot}}$  by means of the variational principle is to introduce (spin) orbitals  $\chi_{jk}^\sigma$  constrained to construct the spin densities [see (2.2.10.7) below]. According to Kohn and Sham (KS), the variation of  $E_{\text{tot}}$  gives the following effective one-particle Schrödinger equations, the so-called Kohn-Sham equations (Kohn & Sham, 1965) (written for an atom in Rydberg atomic units with the obvious generalization to solids):

$$[-\nabla^2 + V_{Ne} + V_{ee} + V_{xc}^\sigma] \chi_{jk}^\sigma(r) = \epsilon_{jk}^\sigma(r) \chi_{jk}^\sigma(r), \quad (2.2.10.3)$$

with the external potential (the attractive interaction of the electrons by the nucleus) given by

$$V_{Ne}(r) = \frac{2Z}{r}, \quad (2.2.10.4)$$

the Coulomb potential (the electrostatic interaction between the electrons) given by

$$V_{ee}(\mathbf{r}) = V_C(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.2.10.5)$$

and the exchange-correlation potential (due to quantum mechanics) given by the functional derivative

$$V_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho}. \quad (2.2.10.6)$$

In the KS scheme, the (spin) electron densities are obtained by summing over all occupied states, *i.e.* by filling the KS orbitals (with increasing energy) according to the *Aufbau* principle.

$$\rho_\sigma(r) = \sum_{j,k} \rho_{jk}^\sigma |\chi_{jk}^\sigma(r)|^2. \quad (2.2.10.7)$$

Here  $\rho_{jk}^\sigma$  are occupation numbers such that  $0 \leq \rho_{jk}^\sigma \leq 1/w_k$ , where  $w_k$  is the symmetry-required weight of point  $\mathbf{k}$ . These KS equations (2.2.10.3) must be solved self-consistently in an iterative process, since finding the KS orbitals requires the knowledge of the potentials, which themselves depend on the (spin) density and thus on the orbitals again. Note the similarity to (and difference from) the Hartree-Fock equation (2.2.9.1). This version of the DFT leads to a (spin) density that is close to the exact density provided that the DFT functional is sufficiently accurate.

In early applications, the local density approximation (LDA) was frequently used and several forms of functionals exist in the literature, for example by Hedin & Lundqvist (1971), von Barth & Hedin (1972), Gunnarsson & Lundqvist (1976), Vosko *et al.* (1980) or accurate fits of the Monte Carlo simulations of Ceperley & Alder (1984). The LDA has some shortcomings, mostly due to the tendency of overbinding, which causes, for example, too-small lattice constants. Recent progress has been