

## 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:

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

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.