

2.2. ELECTRONS

much work has been done to devise algorithms that vary linearly with N , at least for very large N (Ordejon *et al.*, 1995). First results are already available and look promising. When such schemes become generally available, it will be possible to study very large systems with relatively little computational effort. This interesting development could drastically change the accessibility of electronic structure results for large systems.

2.2.12. The linearized augmented plane wave method

The electronic structure of solids can be calculated with a variety of methods as described above (Section 2.2.11). One representative example is the (full-potential) linearized augmented plane wave (LAPW) method. The LAPW method is one among the most accurate schemes for solving the effective one-particle (the so-called Kohn–Sham) equations (2.2.10.3) and is based on DFT (Section 2.2.10) for the treatment of exchange and correlation.

The LAPW formalism is described in many references, starting with the pioneering work by Andersen (1975) and by Koelling & Arbman (1975), which led to the development and the description of the computer code *WIEN* (Blaha *et al.*, 1990; Schwarz & Blaha, 1996). An excellent book by Singh (1994) is highly recommended to the interested reader. Here only the basic ideas are summarized, while details are left to the articles and references therein.

In the LAPW method, the unit cell is partitioned into (non-overlapping) atomic spheres centred around the atomic sites (type I) and an interstitial region (II) as shown schematically in Fig. 2.2.12.1. For the construction of basis functions (and only for this purpose), the muffin-tin approximation (MTA) is used. In the MTA, the potential is assumed to be spherically symmetric within the atomic spheres but constant outside; in the former atomic-like functions and in the latter plane waves are used in order to adapt the basis set optimally to the problem. Specifically, the following basis sets are used in the two types of regions:

(1) Inside the atomic sphere t of radius R_t (region I), a linear combination of radial functions times spherical harmonics $Y_{\ell m}(\hat{r})$ is used (we omit the index t when it is clear from the context):

$$\phi_{\mathbf{k}_n} = \sum_{\ell m} [A_{\ell m} u_{\ell}(r, E_{\ell}) + B_{\ell m} \dot{u}_{\ell}(r, E_{\ell})] Y_{\ell m}(\hat{r}), \quad (2.2.12.1)$$

where \hat{r} represents the angles ϑ and φ of the polar coordinates. The radial functions $u_{\ell}(r, E)$ depend on the energy E . Within a certain energy range this energy dependence can be accounted for by using a linear combination of the solution $u_{\ell}(r, E_{\ell})$ and its energy derivative $\dot{u}_{\ell}(r, E_{\ell})$, both taken at the same energy E_{ℓ} (which is normally chosen at the centre of the band with the corresponding ℓ -like character). This is the linearization in the LAPW method. These two functions are obtained on a radial mesh inside the atomic sphere by numerical integration of the radial Schrödinger equation using the spherical part of the potential inside sphere t and choosing the solution that is regular at the origin $r = 0$. The coefficients $A_{\ell m}$ and $B_{\ell m}$ are chosen by matching conditions (see below).

(2) In the interstitial region (II), a plane-wave expansion (see the Sommerfeld model, Section 2.2.5) is used:

$$\phi_{\mathbf{k}_n} = (1/\sqrt{\Omega}) \exp(i\mathbf{k}_n \cdot \mathbf{r}), \quad (2.2.12.2)$$

where $\mathbf{k}_n = \mathbf{k} + \mathbf{K}_n$, \mathbf{K}_n are vectors of the reciprocal lattice, \mathbf{k} is the wavevector in the first Brillouin zone and Ω is the unit-cell volume [see (2.2.5.3)]. This corresponds to writing the periodic function $u_{\mathbf{k}}(\mathbf{r})$ (2.2.4.19) as a Fourier series and combining it with the Bloch function (2.2.4.18). Each plane wave (corresponding to \mathbf{k}_n) is augmented by an atomic-like function in every atomic sphere, where the coefficients $A_{\ell m}$ and $B_{\ell m}$ in (2.2.12.1) are chosen to match (in value and slope) the atomic solution with the

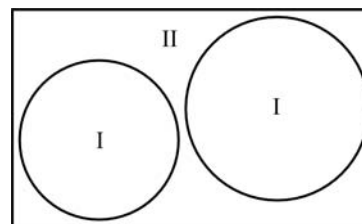


Fig. 2.2.12.1. Schematic partitioning of the unit cell into atomic spheres (I) and an interstitial region (II).

corresponding plane-wave basis function of the interstitial region.

The solutions to the Kohn–Sham equations are expanded in this combined basis set of LAPWs,

$$\psi_{\mathbf{k}} = \sum_n c_n \phi_{\mathbf{k}_n}, \quad (2.2.12.3)$$

where the coefficients c_n are determined by the Rayleigh–Ritz variational principle. The convergence of this basis set is controlled by the number of PWs, *i.e.* by the magnitude of the largest \mathbf{K} vector in equation (2.2.12.3).

In order to improve upon the linearization (*i.e.* to increase the flexibility of the basis) and to make possible a consistent treatment of semi-core and valence states in one energy window (to ensure orthogonality), additional (k_n -independent) basis functions can be added. They are called ‘local orbitals’ (Singh, 1994) and consist of a linear combination of two radial functions at two different energies (*e.g.* at the 3s and 4s energy) and one energy derivative (at one of these energies):

$$\phi_{\ell m}^{\text{LO}} = [A_{\ell m} u_{\ell}(r, E_{1,\ell}) + B_{\ell m} \dot{u}_{\ell}(r, E_{1,\ell}) + C_{\ell m} u_{\ell}(r, E_{2,\ell})] Y_{\ell m}(\hat{r}). \quad (2.2.12.4)$$

The coefficients $A_{\ell m}$, $B_{\ell m}$ and $C_{\ell m}$ are determined by the requirements that ϕ^{LO} should be normalized and has zero value and slope at the sphere boundary.

In its general form, the LAPW method expands the potential in the following form:

$$V(r) = \begin{cases} \sum_{LM} V_{LM}(r) K_{LM}(\hat{r}) & \text{inside sphere} \\ \sum_K V_K \exp(iK r) & \text{outside sphere} \end{cases} \quad (2.2.12.5)$$

where K_{LM} are the crystal harmonics compatible with the point-group symmetry of the corresponding atom represented in a local coordinate system (see Section 2.2.13). An analogous expression holds for the charge density. Thus no shape approximations are made, a procedure frequently called the ‘full-potential LAPW’ (FLAPW) method.

The muffin-tin approximation (MTA) used in early band calculations corresponds to retaining only the $L = 0$ and $M = 0$ component in the first expression of (2.2.12.5) and only the $K = 0$ component in the second. This (much older) procedure corresponds to taking the spherical average inside the spheres and the volume average in the interstitial region. The MTA was frequently used in the 1970s and works reasonable well in highly coordinated (metallic) systems such as face-centred-cubic (f.c.c.) metals. For covalently bonded solids, open or layered structures, however, the MTA is a poor approximation and leads to serious discrepancies with experiment. In all these cases a full-potential treatment is essential.

The choice of sphere radii is not very critical in full-potential calculations, in contrast to the MTA, where this choice may affect the results significantly. Furthermore, different radii would be found when one uses one of the two plausible criteria, namely based on the potential (maximum between two adjacent atoms) or the charge density (minimum between two adjacent atoms).

2. SYMMETRY ASPECTS OF EXCITATIONS

Table 2.2.13.1. Picking rules for the local coordinate axes and the corresponding LM combinations (ℓmp) of non-cubic groups taken from Kurki-Suonio (1977)

Symmetry	Coordinate axes	ℓ, m, p of $y_{\ell mp}$	Crystal system
1 $\bar{1}$	Any Any	All (ℓ, m, \pm) ($2\ell, m, \pm$)	Triclinic
2 m $2/m$	$2 \parallel z$ $m \perp z$ $2 \parallel z, m \perp z$	($\ell, 2m, \pm$) ($\ell, \ell - 2m, \pm$) ($2\ell, 2m, \pm$)	Monoclinic
222 $mm2$ mmm	$2 \parallel z, 2 \parallel y$ ($2 \parallel x$) $2 \parallel z, m \perp y$ ($2 \perp x$) $2 \perp z, m \perp y, 2 \perp x$	($2\ell, 2m, +$), ($2\ell + 1, 2m, -$) ($\ell, 2m, +$) ($2\ell, 2m, +$)	Orthorhombic
4 $\bar{4}$ $4/m$ 422 $4mm$ $\bar{4}2m$ $4mmm$	$4 \parallel z$ $-4 \parallel z$ $4 \parallel z, m \perp z$ $4 \parallel z, 2 \parallel y$ ($2 \parallel x$) $4 \parallel z, m \perp y$ ($2 \perp x$) $-4 \parallel z, 2 \parallel x$ ($m = xy \rightarrow yx$) $4 \parallel z, m \perp z, m \perp x$	($\ell, 4m, \pm$) ($2\ell, 4m, \pm$), ($2\ell + 1, 4m + 2, \pm$) ($2\ell, 4m, \pm$) ($2\ell, 4m, +$), ($2\ell + 1, 4m, -$) ($\ell, 4m, +$) ($2\ell, 4m, +$), ($2\ell + 1, 4m + 2, -$) ($2\ell, 4m, +$)	Tetragonal
3 $\bar{3}$ 32 $3m$ $\bar{3}m$	$3 \parallel z$ $-3 \parallel z$ $3 \parallel z, 2 \parallel y$ $3 \parallel z, m \perp y$ $-3 \parallel z, m \perp y$	($\ell, 3m, \pm$) ($2\ell, 3m, \pm$) ($2\ell, 3m, +$), ($2\ell + 1, 3m, -$) ($\ell, 3m, +$) ($2\ell, 3m, +$)	Rhombohedral
6 $\bar{6}$ $6/m$ 622 $6mm$ $62m$ $6mmm$	$6 \parallel z$ $-6 \parallel z$ $6 \parallel z, m \perp z$ $6 \parallel z, 2 \parallel y$ ($2 \parallel x$) $6 \parallel z, m \parallel y$ ($m \perp x$) $-6 \parallel z, m \perp y$ ($2 \parallel x$) $6 \parallel z, m \perp z, m \perp y$ ($m \perp x$)	($\ell, 6m, \pm$) ($2\ell, 6m, +$), ($2\ell + 1, 6m + 3, \pm$) ($2\ell, 6m, \pm$) ($2\ell, 6m, +$), ($2\ell + 1, 6m, -$) ($\ell, 6m, +$) ($2\ell, 6m, +$), ($2\ell + 1, 6m + 3, +$) ($2\ell, 6m, +$)	Hexagonal

Therefore in the MTA one must make a compromise, whereas in full-potential calculations this problem practically disappears.

2.2.13. The local coordinate system

The partition of a crystal into atoms (or molecules) is ambiguous and thus the atomic contribution cannot be defined uniquely. However, whatever the definition, it must follow the relevant site symmetry for each atom. There are at least two reasons why one would want to use a *local coordinate system* at each atomic site: the concept of crystal harmonics and the interpretation of bonding features.

2.2.13.1. Crystal harmonics

All spatial observables of the bound atom (*e.g.* the potential or the charge density) must have the crystal symmetry, *i.e.* the point-group symmetry around an atom. Therefore they must be representable as an expansion in terms of site-symmetrized spherical harmonics. Any point-symmetry operation transforms a spherical harmonic into another of the same ℓ . We start with the usual complex spherical harmonics,

$$Y_{\ell m}(\vartheta, \varphi) = N_{\ell m} P_{\ell}^m(\cos \vartheta) \exp(im\varphi), \quad (2.2.13.1)$$

which satisfy Laplacian's differential equation. The $P_{\ell}^m(\cos \vartheta)$ are the associated Legendre polynomials and the normalization $N_{\ell m}$ is according to the convention of Condon & Shortley (1953). For the φ -dependent part one can use the real and imaginary part and thus use $\cos(m\varphi)$ and $\sin(m\varphi)$ instead of the $\exp(im\varphi)$ functions,

Table 2.2.13.2. LM combinations of cubic groups as linear combinations of $y_{\ell mp}$'s (given in parentheses)

The linear-combination coefficients can be found in Kurki-Suonio (1977).

Symmetry	LM combinations
23	(0 0), (3 2-), (4 0, 4 4+), (6 0, 6 4+), (6 2+, 6 6+)
$m\bar{3}$	(0 0), (4 0, 4 4+), (6 0, 6 4+) (6 2+, 6 6+)
432	(0 0), (4 0, 4 4+), (6 0, 6 4+)
$\bar{4}3m$	(0 0), (3 2-), (4 0, 4 4+), (6 0, 6 4+),
$m\bar{3}m$	(0 0), (4 0, 4 4+), (6 0, 6 4+)

but we must introduce a parity p to distinguish the functions with the same $|m|$. For convenience we take real spherical harmonics, since physical observables are real. The even and odd polynomials are given by the combination of the complex spherical harmonics with the parity p either + or - by

$$y_{\ell mp} = \begin{cases} y_{\ell m+} = (1/\sqrt{2})(Y_{\ell m} + Y_{\ell \bar{m}}) & + \text{ parity} \\ y_{\ell m-} = -(i/\sqrt{2})(Y_{\ell m} - Y_{\ell \bar{m}}) & - \text{ parity} \end{cases}, m = 2n$$

$$y_{\ell mp} = \begin{cases} y_{\ell m+} = -(1/\sqrt{2})(Y_{\ell m} - Y_{\ell \bar{m}}) & + \text{ parity} \\ y_{\ell m-} = (i/\sqrt{2})(Y_{\ell m} + Y_{\ell \bar{m}}) & - \text{ parity} \end{cases}, m = 2n + 1. \quad (2.2.13.2)$$

The expansion of - for example - the charge density $\rho(\mathbf{r})$ around an atomic site can be written using the LAPW method [see the analogous equation (2.2.12.5) for the potential] in the form

$$\rho(\mathbf{r}) = \sum_{LM} \rho_{LM}(\mathbf{r}) K_{LM}(\hat{\mathbf{r}}) \text{ inside an atomic sphere,} \quad (2.2.13.3)$$

where we use capital letters LM for the indices (i) to distinguish this expansion from that of the wavefunctions in which complex spherical harmonics are used [see (2.2.12.1)] and (ii) to include the parity p in the index M (which represents the combined index mp). With these conventions, K_{LM} can be written as a linear combination of real spherical harmonics $y_{\ell mp}$ which are symmetry-adapted to the site symmetry,

$$K_{LM}(\hat{\mathbf{r}}) = \begin{cases} y_{\ell mp} & \text{non-cubic} \\ \sum_j c_{Lj} y_{\ell j p} & \text{cubic} \end{cases} \quad (2.2.13.4)$$

i.e. they are either $y_{\ell mp}$ [(2.2.13.2)] in the non-cubic cases (Table 2.2.13.1) or are well defined combinations of $y_{\ell mp}$'s in the five cubic cases (Table 2.2.13.2), where the coefficients c_{Lj} depend on the normalization of the spherical harmonics and can be found in Kurki-Suonio (1977).

According to Kurki-Suonio, the number of (non-vanishing) LM terms [*e.g.* in (2.2.13.3)] is minimized by choosing for each atom a local Cartesian coordinate system adapted to its site