

2. SYMMETRY ASPECTS OF EXCITATIONS

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

Symmetry	Coordinate axes	$\ell, m, p$ of $y_{\ell mp}$	Crystal system
1 $\bar{1}$	Any Any	All ( $\ell, m, \pm$ ) ( $2\ell, m, \pm$ )	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 $6mm$ $\bar{6}2m$ $6mmm$	$6 \parallel z$ $-6 \parallel z$ $6 \parallel z, m \perp z$ $6 \parallel z, 2 \parallel y$ ( $2 \parallel x$ ) $6 \parallel z, m \parallel y$ ( $m \perp x$ ) $-6 \parallel z, m \perp y$ ( $2 \parallel x$ ) $6 \parallel z, m \perp z, m \perp y$ ( $m \perp x$ )	( $\ell, 6m, \pm$ ) ( $2\ell, 6m, +$ ), ( $2\ell + 1, 6m + 3, \pm$ ) ( $2\ell, 6m, \pm$ ) ( $2\ell, 6m, +$ ), ( $2\ell + 1, 6m, -$ ) ( $\ell, 6m, +$ ) ( $2\ell, 6m, +$ ), ( $2\ell + 1, 6m + 3, +$ ) ( $2\ell, 6m, +$ )	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  $\ell$ . 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  $\varphi$ -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

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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  $\text{TiO}_2$  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  $\Gamma$  along  $\Delta$  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  $\Gamma$  and  $\Delta$ . 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  $\Gamma_{12}$  (the  $e_g$  symmetry in a cubic system) splits into the  $\Delta_1$  and

$\Delta_2$  manifold in the  $\Delta$  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  $\ell$ -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  $\text{TiO}_2$  in the rutile structure (see Section 2.2.16.2).

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