while if $d > 1$ the corresponding first-order perturbed eigenvalues are th
eigenvalues of the $d \times d$ matrix $\mathbf{A}$ whose elements are given by

$$A_{lj} = \epsilon_0 \delta_{lj} + (\phi_l^p, H' \phi_j^p), \qquad (6.19$$

$j, l = 1, 2, \ldots, d$. In both cases there is a first-order effect only if $\Gamma_0^p \otimes \Gamma$
contains Γ_0^p (that is, when $n_{pq}^p \neq 0$) When this is so the Wigner-Eckar
Theorem shows that

$$(\phi_l^p, H' \phi_j^p) = \sum_{\alpha=1}^{n_{pq}^{\Gamma}} \begin{pmatrix} p & q & p, & \alpha \\ j & k & l & \end{pmatrix}^* (p|H'|p)_\alpha, \qquad (6.20$$

so that the matrix elements depend on the Clebsch-Gordan coefficients and
n_{pq}^p reduced matrix elements

For a further analysis of the case $d > 1$, see, for example, Chapter
Section 3, of Cornwell (1984).

Chapter 7

Crystallographic Space Groups

1 The Bravais lattices

An infinite three-dimensional lattice may be defined in terms of three linearly independent real "basic lattice vectors" $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ The set of all lattice vectors of the lattice is then given by

$$\mathbf{t_n} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3,$$

where $\mathbf{n} = (n_1, n_2, n_3)$, and n_1, n_2 and n_3 are integers that take all possible values, positive, negative and zero. Points in $\mathbb{R}^3$ having lattice vectors as their position vectors are called "lattice points" and a pure translation through a lattice vector $\mathbf{t_n}$, $\{\mathbf{1}|\mathbf{t_n}\}$, is called a "primitive" translation

Suppose that in a crystalline solid there are S nuclei per lattice point, and that the equilibrium positions of the nuclei associated with the lattice point $\mathbf{n} = \mathbf{0}$ have position vectors $\boldsymbol{\tau}_1, \boldsymbol{\tau}_2, \ldots, \boldsymbol{\tau}_S$. Then the equilibrium positions of the whole set of nuclei are given by

$$\mathbf{r}_{\mathbf{n}\gamma}^e = \mathbf{t_n} + \boldsymbol{\tau}_\gamma, \qquad (7.1)$$

where $\gamma = 1, 2, \ldots, S$ and $\mathbf{t_n}$ is any lattice vector In the special case when $\mathbf{n} = \mathbf{0}$, $\boldsymbol{\tau}_1$ may be taken to be $\mathbf{0}$ and the index γ may be omitted, so that $\mathbf{r}_{\mathbf{n}}^e = \mathbf{t_n}$

The set of all primitive translations of a lattice form a group which will be denoted by $\mathcal{T}^\infty$. $\mathcal{T}^\infty$ is Abelian but of infinite order In Section 2 the Born cyclic boundary conditions will be introduced They have the effect of replacing this infinite group by a similar group of large but finite order, so that all the theorems on finite groups of the previous chapters apply

The "maximal point group" $\mathcal{G}_0^{max}$ of a crystal lattice may be defined as the set of all pure rotations $\{\mathbf{R}(T)|\mathbf{0}\}$ such that, for every lattice vector $\mathbf{t_n}$,

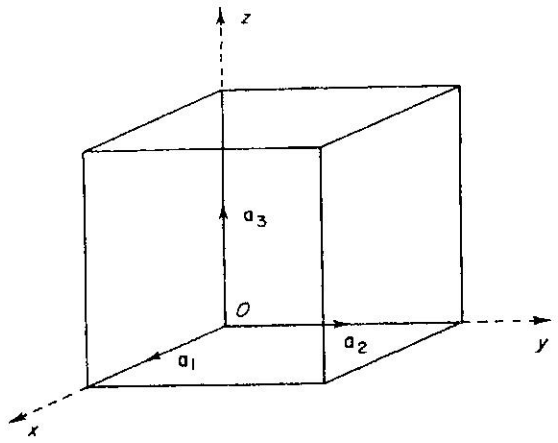

Figure 7 1 Basic lattice vectors of the simple cubic lattice, Γ_c.

the quantity $\mathbf{R}(T)\mathbf{t_n}$ is also a lattice vector. Clearly $\mathbf{R}(T) \in \mathcal{G}_0^{max}$ if and only if $\mathbf{R}(T)\mathbf{a}_j$ is a lattice vector for $j = 1, 2, 3$

There are essentially 14 different types of crystal lattice. They are known as the "Bravais lattices". These will be described briefly, but no attempt will be made to give a logical derivation or to show that there are no others (In this context two types of lattice are regarded as being different if they have different maximal point groups, even though one type is a special case of the other For example, as may be seen from Table 7.1, the simple cubic lattice Γ_c is a special case of the simple tetragonal lattice Γ_q with $a = b$, but $\mathcal{G}_0^{max} = O_h$ for Γ_c, whereas $\mathcal{G}_0^{max} = D_{4h}$ for Γ_q)

Lattices with the same maximal point group are said to belong to the same "symmetry system", there being only seven different symmetry systems. Complete details are given in Table 7 1, in which the notation for point groups is that of Schönfliess (1923) (A full specification of these and the other crystallographic point groups may be found in Appendix C)

The cubic system is probably the most significant, the body-centred and face-centred lattices occurring for a large number of important solids The basic lattice vectors of the cubic lattices are shown in Figures 7 1, 7 2 and 7.3 The lattice points of the simple cubic lattice Γ_c merely form a repeated cubic array, and the basic lattice vectors lie along three edges of a cube For the body-centred cubic lattice Γ_c^v the basic lattice vectors join a point at the centre of a cube to three of the vertices of the cube, so that the lattice points form a repeated cubic array with lattice points also occurring at every cube centre. For the face-centred lattice Γ_c^f the lattice points again form a repeated cubic array with additional points also occurring at the midpoints of every cube face, the basic lattice vectors then joining a cube vertex to the midpoints of the three adjacent cube faces.

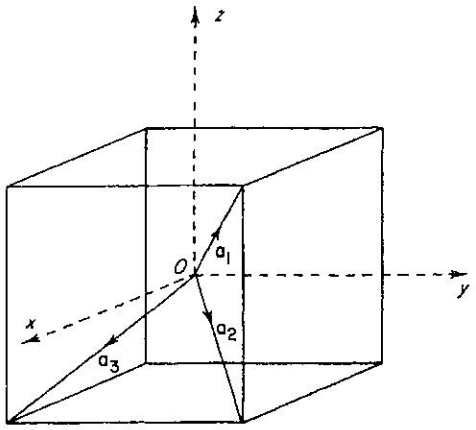

Figure 7 2 Basic lattice vectors of the body-centred cubic lattice, Γ_c^v

A symmetry system α may be regarded as being "subordinate" to a symmetry system β if $\mathcal{G}_0^{max}$ for α is a subgroup of $\mathcal{G}_0^{max}$ for β and at least one lattice of β is a special case of a lattice of α. The complete subordination scheme is then

triclinic < monoclinic < orthorhombic < tetragonal < cubic,
monoclinic < rhombohedral, orthorhombic < hexagonal,
(Here $\alpha < \beta$ indicates that α is subordinate to β)

For a perfect crystalline solid the group of the Schrödinger equation is a crystallographic space group, which contains rotations as well as pure primitive translations. The crystallographic space groups will be investigated in detail in Section 6 However, it is very enlightening, as a first stage in their study, to limit attention to the subgroup $\mathcal{T}$ of pure primitive translations of the relevant lattice. Only the translational symmetry is then being taken into account

In particular, the energy eigenfunctions must transform according to the irreducible representations of this subgroup, which is equivalent to saying that they satisfy Bloch's Theorem, as will be demonstrated in Section 3. Bloch's Theorem has now become so much an essential part of the theory of solids that it is sometimes forgotten that it is basically a group theoretical result. The elementary energy band theory based upon Bloch's Theorem itself requires no knowledge of group theory and so is presented in most textbooks on solid state theory. However, the neglect of rotational symmetries in this elementary theory does mean that some phenomena are overlooked, and, in particular, it cannot predict the extra degeneracies which can occur in electronic energy levels Moreover, it is only by taking into account the rotational symmetries that it is possible to reduce the numerical work in energy band calculations to a manageable amount and still produce accurate results

(1) Triclinic symmetry system ($\mathcal{G}_0^{max} = C_i$):
  (i) simple triclinic lattice, Γ_t $\mathbf{a}_1, \mathbf{a}_2$ and $\mathbf{a}_3$ arbitrary.

(2) Monoclinic symmetry system ($\mathcal{G}_0^{max} = C_{2h}$):
  (i) simple monoclinic lattice, Γ_m
    $\mathbf{a}_3$ perpendicular to both $\mathbf{a}_1$ and $\mathbf{a}_2$;
  (ii) base-centred monoclinic lattice, Γ_m^b
    $\mathbf{a}_1 = (a, b, 0)$, $\mathbf{a}_2 = (a, -b, 0)$, $\mathbf{a}_3 = (c, 0, d)$.

(3) Orthorhombic symmetry system ($\mathcal{G}_0^{max} = D_{2h}$):
  (i) simple orthorhombic lattice, Γ_o
    $\mathbf{a}_1 = (a, 0, 0)$, $\mathbf{a}_2 = (0, b, 0)$, $\mathbf{a}_3 = (0, 0, c)$,
  (ii) base-centred orthorhombic lattice, Γ_o^b
    $\mathbf{a}_1 = (a, b, 0)$, $\mathbf{a}_2 = (a, -b, 0)$, $\mathbf{a}_3 = (0, 0, c)$,
  (iii) body-centred orthorhombic lattice, Γ_o^v
    $\mathbf{a}_1 = (a, b, c)$, $\mathbf{a}_2 = (a, b, -c)$, $\mathbf{a}_3 = (a, -b, -c)$,
  (iv) face-centred orthorhombic lattice, Γ_o^f
    $\mathbf{a}_1 = (a, b, 0)$, $\mathbf{a}_2 = (0, b, c)$, $\mathbf{a}_3 = (a, 0, c)$

(4) Tetragonal symmetry system ($\mathcal{G}_0^{max} = D_{4h}$).
  (i) simple tetragonal lattice, Γ_q
    $\mathbf{a}_1 = (a, 0, 0)$, $\mathbf{a}_2 = (0, a, 0)$, $\mathbf{a}_3 = (0, 0, b)$;
  (ii) body-centred tetragonal lattice, Γ_q^v.
    $\mathbf{a}_1 = (a, a, b)$, $\mathbf{a}_2 = (a, a, -b)$, $\mathbf{a}_3 = (a, -a, b)$

(5) Cubic symmetry system ($\mathcal{G}_0^{max} = O_h$):
  (i) simple cubic lattice, Γ_c.
    $\mathbf{a}_1 = (a, 0, 0)$, $\mathbf{a}_2 = (0, a, 0)$, $\mathbf{a}_3 = (0, 0, a)$;
  (ii) body-centred cubic lattice, Γ_c^v.
    $\mathbf{a}_1 = \frac{1}{2}a(1, 1, 1)$, $\mathbf{a}_2 = \frac{1}{2}a(1, 1, -1)$, $\mathbf{a}_3 = \frac{1}{2}a(1, -1, -1)$,
  (iii) face-centred cubic lattice, Γ_c^f.
    $\mathbf{a}_1 = \frac{1}{2}a(1, 1, 0)$, $\mathbf{a}_2 = \frac{1}{2}a(0, 1, 1)$, $\mathbf{a}_3 = \frac{1}{2}a(1, 0, 1)$

(6) Rhombohedral (or trigonal) symmetry system ($\mathcal{G}_0^{max} = D_{3d}$)
  (i) simple rhombohedral lattice, Γ_{rh}:
    $\mathbf{a}_1 = (a, 0, b)$, $\mathbf{a}_2 = (\frac{1}{2}a\sqrt{3}, -\frac{1}{2}a, b)$, $\mathbf{a}_3 = (-\frac{1}{2}a\sqrt{3}, -\frac{1}{2}a, b)$

(7) Hexagonal symmetry system ($\mathcal{G}_0^{max} = D_{6h}$)
  (i) simple hexagonal lattice, Γ_h.
    $\mathbf{a}_1 = (0, 0, c)$, $\mathbf{a}_2 = (a, 0, 0)$, $\mathbf{a}_3 = (-\frac{1}{2}a, -\frac{1}{2}a\sqrt{3}, 0)$

Table 7.1: The Bravais lattices (The real parameters a, b, c and d are arbitrary.)

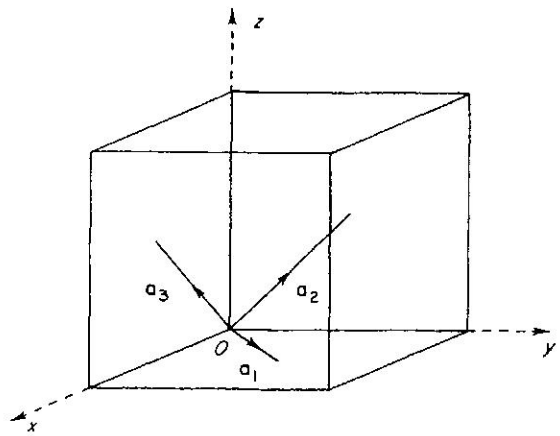

Figure 7.3: Basic lattice vectors of the face-centred cubic lattice, Γ_c^f.

A proof of Bloch's Theorem that involves only an elementary application of the ideas of the previous chapters is given is Section 3. Sections 4 and 5 are then devoted to a brief account of the elementary electronic energy band theory that is based on this theorem. Section 8 then describes, for the case of symmorphic space groups, how this theory is modified when the full space group is introduced in place of its translational subgroup $\mathcal{T}$. It will be seen there that the concepts introduced in Sections 4 and 5 still play a fundamental role.

2 The cyclic boundary conditions

Strictly speaking, a real crystalline solid cannot possess any translational symmetry because it is necessarily finite in extent. Consequently any translation will shift some electron or nucleus from just inside some surface to the outside of the body, that is, to a completely different environment.

On the other hand, for a normal sample the inter-nuclear spacing is so much smaller than the dimensions of the sample and the interactions that directly affect each electron or nucleus are of such short range, that for electrons and nuclei well inside the body the situation is almost exactly as if the solid were infinite in extent. Moreover, the evidence of X-ray crystallography is that the nuclei within a solid can be ordered as if they were based on an infinite lattice, except near the surfaces. As most of the properties of a solid depend only on the behaviour of the vast majority of electrons or nuclei that lie in the interior, it is a very reasonable approximation to idealize the situation by working with models based on infinite lattices. The translational symmetry possessed by such models then permits a considerable simplification of the analysis.

However, the symmetry groups based on infinite lattices are necessarily of infinite order, and it is easier to work with groups of finite order This can be achieved by imposing "cyclic" boundary conditions on the infinite lattice

For the electrons it may be assumed that for every energy eigenfunction $\phi(\mathbf{r})$

$$\phi(\mathbf{r}) = \phi(\mathbf{r} + N_1\mathbf{a}_1) = \phi(\mathbf{r} + N_2\mathbf{a}_2) = \phi(\mathbf{r} + N_3\mathbf{a}_3), \tag{7 2}$$

where N_1, N_2 and N_3 are very large positive integers and $\mathbf{a}_1, \mathbf{a}_2$ and $\mathbf{a}_3$ are the basic lattice vectors of the lattice This implies that the infinite crystal is considered to consist of a set of basic blocks in the form of parallelepipeds having edges $N_1\mathbf{a}_1$, $N_2\mathbf{a}_2$ and $N_3\mathbf{a}_3$, and that the physical situation is identical in corresponding points of different blocks. These boundary conditions cannot affect the behaviour of electrons well inside each basic block to any significant extent, so the bulk properties are again unchanged The integers N_1, N_2 and N_3 may be taken to be as large as desired.

The integration involved in the inner product (ϕ, ψ) defined in Equation (1 19) must now be taken as being over just one basic block of the crystal, B. For any pure primitive translation T the operators $P(T)$ retain the unitary property of Equation (1 20), provided all functions involved satisfy Equation (7 2). This follows because $(P(T)\phi, P(T)\psi)$ is equal to

$$\int\int\int_B \phi(\mathbf{r} - \mathbf{t}(T))^*\psi(\mathbf{r} - \mathbf{t}(T))\, dxdydz = \int\int\int_{B'} \phi(\mathbf{r})^*\psi(\mathbf{r})\, dxdydz,$$

where B' is obtained from B by a translation $-\mathbf{t}(T)$. As every part of B' can be mapped into a part of B by an appropriate combination of translations through $N_1\mathbf{a}_1$, $N_2\mathbf{a}_2$ and $N_3\mathbf{a}_3$, by Equations (7 2) the last integral becomes (ϕ, ψ).

The conditions in Equations (7 2) are often referred to as the "Born cyclic boundary conditions", as they are the analogues for electronic states of the vibrational boundary conditions first proposed by Born and von Karman (1912). They imply that

$$P(\{\mathbf{1}|N_j\mathbf{a}_j\}) = P(\{\mathbf{1}|\mathbf{0}\}) \tag{7.3}$$

for every function of interest and for $j = 1, 2, 3$. (Of course $P(\{\mathbf{1}|\mathbf{0}\})$ is merely the identity operator) Consequently

$$P(\{\mathbf{1}|\mathbf{t}_\mathbf{n} + l_1N_1\mathbf{a}_1 + l_2N_2\mathbf{a}_2 + l_3N_3\mathbf{a}_3\}) = P(\{\mathbf{1}|\mathbf{t}_\mathbf{n}\})$$

for any lattice vector $\mathbf{t}_\mathbf{n}$ and any set of integers l_1, l_2 and l_3, so that *only* $N = N_1N_2N_3$ of these operators are *distinct* The set of distinct operators may be taken to be $P(\{\mathbf{1}|n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3\})$ with

$$0 \leq n_j < N_j, \quad j = 1, 2, 3. \tag{7.4}$$

Moreover, as $P(\{\mathbf{1}|N_j\mathbf{a}_j\}) = P(\{\mathbf{1}|\mathbf{a}_j\})^{N_j}$, it follows from Equation (7 3) that

$$P(\{\mathbf{1}|\mathbf{a}_j\})^{N_j} = P(\{\mathbf{1}|\mathbf{0}\}), \quad j = 1, 2, 3 \tag{7.5}$$

Thus this set of distinct operators forms a *finite* group $\mathcal{T}$ of order $N = N_1N_2N_3$. Henceforth this group $\mathcal{T}$ will be used in place of the infinite group of pure primitive translations $\mathcal{T}^\infty$.

Incidentally, as it remains true that

$$P(\{\mathbf{1}|\mathbf{t}_\mathbf{n}\})\, P(\{\mathbf{1}|\mathbf{t}_{\mathbf{n}'}\}) = P(\{\mathbf{1}|\mathbf{t}_\mathbf{n}\}\{\mathbf{1}|\mathbf{t}_{\mathbf{n}'}\})$$

for any two lattice vectors $\mathbf{t}_\mathbf{n}$ and $\mathbf{t}_{\mathbf{n}'}$ of a lattice, the mapping $\phi(\{\mathbf{1}|\mathbf{t}_\mathbf{n}\}) = P(\{\mathbf{1}|\mathbf{t}_\mathbf{n}\})$ is a homomorphic mapping of $\mathcal{T}^\infty$ onto $\mathcal{T}$ The kernel $\mathcal{K}$ of this mapping is the infinite set of pure primitive translations of the form $\{\mathbf{1}|l_1N_1\mathbf{a}_1 + l_2N_2\mathbf{a}_2 + l_3N_3\mathbf{a}_3\}$, where l_1, l_2 and l_3 are any set of integers.

3 Irreducible representations of the group $\mathcal{T}$ of pure primitive translations and Bloch's Theorem

As the group $\mathcal{T}$ is a finite Abelian group of order $N = N_1N_2N_3$, it possesses N inequivalent irreducible representations, all of which are one-dimensional (see Chapter 5, Section 6). These are easily found, for $\mathcal{T}$ is isomorphic to the direct product of three cyclic groups.

Consider a particular one-dimensional irreducible representation $\mathbf{\Gamma}$ of $\mathcal{T}$ and suppose that $\mathbf{\Gamma}(\{\mathbf{1}|\mathbf{a}_j\}) = [c_j]$, for $j = 1, 2, 3$ Then, from Equation (7 5), it follows that

$$c_j^{N_j} = 1, \tag{7 6}$$

so that

$$c_j = \exp(-2\pi i p_j/N_j), \quad j = 1, 2, 3.$$

where p_j is an integer As $\exp(-2\pi i(p_j + N_j)/N_j) = \exp(-2\pi i p_j/N_j)$, there are only N_j *different* values of c_j allowed by Equation (7 6) and each of these, by convention, may be taken to correspond to a p_j having one of the values $0, 1, 2, \ldots, N_j - 1$ Then

$$\mathbf{\Gamma}(\{\mathbf{1}|n_j\mathbf{a}_j\}) = [\exp(-2\pi i p_j n_j/N_j)]$$

and hence

$$\Gamma(\{\mathbf{1}|\mathbf{t}_\mathbf{n}) = [\exp(-2\pi i\{(p_1n_1/N_1) + (p_2n_2/N_2) + (p_3n_3/N_3)\})], \tag{7 7}$$

where $\mathbf{t}_\mathbf{n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$. There are $N = N_1N_2N_3$ sets of integers (p_1, p_2, p_3) allowed by the above convention which can be used to label the N different irreducible representations of $\mathcal{T}$.

Equation (7 7) can be simplified and given a simple geometric interpretation by introducing the following notation Define the "basic lattice vectors of the reciprocal lattice" $\mathbf{b}_1, \mathbf{b}_2$ and $\mathbf{b}_3$ by

$$\mathbf{a}_j.\mathbf{b}_k = 2\pi\delta_{jk}, \quad j, k = 1, 2, 3, \tag{7 8}$$

so that, explicitly,

$$\mathbf{b}_1 = 2\pi \mathbf{a}_2 \wedge \mathbf{a}_3 / \{\mathbf{a}_1 \cdot (\mathbf{a}_2 \wedge \mathbf{a}_3)\}, \tag{7.9}$$

with similar expressions for $\mathbf{b}_2$ and $\mathbf{b}_3$. Then define the so-called "allowed k-vectors" by

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3, \tag{7.10}$$

where $k_j = p_j / N_j$. Thus

$$\mathbf{k} \cdot \mathbf{t_n} = 2\pi i \{(p_1 n_1 / N_1) + (p_2 n_2 / N_2) + (p_3 n_3 / N_3)\},$$

so that Equation (7.7) becomes

$$\mathbf{\Gamma}^{\mathbf{k}}(\{\mathbf{1}|\mathbf{t_n}\}) = [\exp(-i\mathbf{k}.\mathbf{t_n})], \tag{7.11}$$

where the N irreducible representations are now labelled by the allowed **k**-vectors.

Suppose that $\phi_1^{\mathbf{k}}(\mathbf{r})$ is a basis function transforming as the first (and only) row of $\mathbf{\Gamma}^{\mathbf{k}}$. Then, by Equations (1.26) and (7.11),

$$P(\{\mathbf{1}|\mathbf{t_n}\})\phi_1^{\mathbf{k}}(\mathbf{r}) = \mathbf{\Gamma}^{\mathbf{k}}(\{\mathbf{1}|\mathbf{t_n}\})\phi_1^{\mathbf{k}}(\mathbf{r}) = \exp(-i\mathbf{k}.\mathbf{t_n})\phi_1^{\mathbf{k}}(\mathbf{r}) \tag{7.12}$$

However, by Equation (1.17),

$$P(\{\mathbf{1}|\mathbf{t_n}\})\phi_1^{\mathbf{k}}(\mathbf{r}) = \phi_1^{\mathbf{k}}(\{\mathbf{1}|\mathbf{t_n}\}^{-1}\mathbf{r}) = \phi_1^{\mathbf{k}}(\mathbf{r} - \mathbf{t_n}),$$

so that

$$\phi_1^{\mathbf{k}}(\mathbf{r} - \mathbf{t_n}) = \exp(-i\mathbf{k}.\mathbf{t_n})\phi_1^{\mathbf{k}}(\mathbf{r}).$$

Thus

$$\phi_1^{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}.\mathbf{r})u_{\mathbf{k}}(\mathbf{r}), \tag{7.13}$$

where $u_{\mathbf{k}}(\mathbf{r})$ is a function that has the periodicity of the lattice, that is, $u_{\mathbf{k}}(\mathbf{r} - \mathbf{t_n}) = u_{\mathbf{k}}(\mathbf{r})$ for any lattice vector $\mathbf{t_n}$.

Equation (7.13) is the statement of the theorem of Bloch (1928) in its usual form, for electronic energy eigenfunctions must be basis functions of the irreducible representations $\mathbf{\Gamma}^{\mathbf{k}}$ of $\mathcal{T}$. A function of the form in Equation (7.13) is therefore called a "Bloch function". The corresponding energy eigenvalue may be denoted by $\epsilon(\mathbf{k})$, so that

$$H(\mathbf{r})\phi_1^{\mathbf{k}}(\mathbf{r}) = \epsilon(\mathbf{k})\phi_1^{\mathbf{k}}(\mathbf{r}) \tag{7.14}$$

The notation for basis functions here follows the standard practice in which the irreducible representation is specified by a superscript (or set of superscripts) and the rows by a subscript (or set of subscripts). In particular, the wave vector **k** appears as a superscript with this convention. However, it should be pointed out that in most of the solid state literature **k** is written as a subscript, so that $\phi_1^{\mathbf{k}}(\mathbf{r})$ would be written as $\phi_{\mathbf{k}}(\mathbf{r})$ and Equation (8.20) would become $H(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r}) = \epsilon(\mathbf{k})\phi_{\mathbf{k}}(\mathbf{r})$.

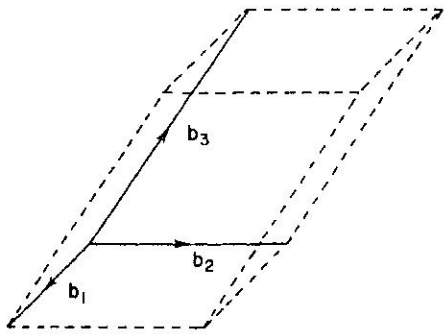

Figure 7.4 The basic parallelepiped of **k**-space.

7.1 Brillouin zones

The set of lattice vectors of the reciprocal lattice is defined by

$$\mathbf{K_m} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3, \tag{7.15}$$

where $\mathbf{m} = (m_1, m_2, m_3)$, m_1, m_2 and m_3 are integers, and $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ are the basic lattice vectors of the reciprocal lattice defined by Equation (7.8). They have the property that

$$\exp(i\mathbf{K_m}.\mathbf{t_n}) = 1 \tag{7.16}$$

for any $\mathbf{K_m}$ and $\mathbf{t_n}$. It is useful to note that

$$\sum_{\mathbf{t_n}} \exp(i\mathbf{k}\,\mathbf{t_n}) = \begin{cases} N, & \text{if } \mathbf{k} = \mathbf{K_m}, \\ 0, & \text{if } \mathbf{k} \neq \mathbf{K_m}, \end{cases} \tag{7.17}$$

where the sum is over all the lattice vectors of one basic block of Section 2, this result being a consequence of the fact that the left-hand side is a product of three simple geometric series. Similarly,

$$\sum_{\mathbf{k}} \exp(-i\mathbf{k}.\mathbf{t_n}) = \begin{cases} N, & \text{if } \mathbf{t_n} = \mathbf{0}, \\ 0, & \text{if } \mathbf{t_n} \neq \mathbf{0}, \end{cases}$$

the sum being over all allowed **k**-vectors.

In Section 3, N irreducible representations of $\mathcal{T}$ were found and described by the allowed k-vectors (Equation (7.10)). These **k**-vectors can be imagined as being plotted in the so-called "k-space" or "reciprocal space" defined by the reciprocal lattice vectors. The allowed **k**-vectors lie on a very fine lattice defined by Equation (7.10)) within and upon three faces of the parallelepiped having edges $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ that is shown in Figure 7.4.

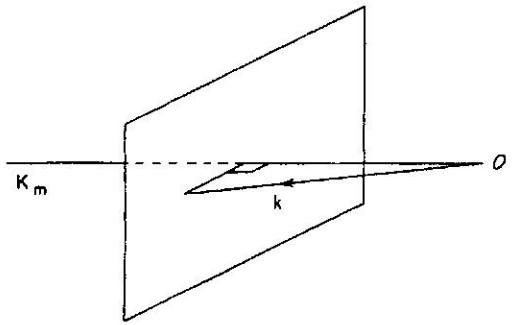

Figure 7.5: Construction of a Brillouin zone boundary

It is, however, more convenient to replot the allowed **k**-vectors into a more symmetrical region of k-space surrounding the point $\mathbf{k} = \mathbf{0}$. To do this consider the equation,

$$\mathbf{k}' = \mathbf{k} + \mathbf{K_m}, \tag{7.18}$$

where $\mathbf{K_m}$ is a reciprocal lattice vector. Two vectors **k** and **k**′ satisfying Equation (7.18) are said to be "equivalent", because $\exp(-i\mathbf{k}'.\mathbf{t_n}) = \exp(-i\mathbf{k}.\mathbf{t_n})$ by Equation (7.16), and hence

$$\Gamma^{\mathbf{k}'}(\{\mathbf{1}|\mathbf{t_n}\}) = \Gamma^{\mathbf{k}}(\{\mathbf{1}|\mathbf{t_n}\})$$

for every $\{\mathbf{1}|\mathbf{t_n}\}$ of $\mathcal{T}$. Thus the irreducible representation described by **k** could equally be described by **k**′. The more symmetrical region of **k**-space is called the "Brillouin zone" (or sometimes the "first Brillouin zone"), and it is defined to consist of all those points of k-space that lie closer to $\mathbf{k} = \mathbf{0}$ than to any other reciprocal lattice points. Its boundaries are therefore the planes that are the perpendicular bisectors of the lines joining the point $\mathbf{k} = \mathbf{0}$ to the nearer reciprocal lattice points, the plane bisecting the line from $\mathbf{k} = \mathbf{0}$ to $\mathbf{k} = \mathbf{K_m}$ having the equation

$$\mathbf{k}\,\mathbf{K_m} = \frac{1}{2}|\mathbf{K_m}|^2,$$

as is clear from Figure 7.5. For some lattices, such as the body-centred cubic lattice Γ_c^v, only *nearest* neighbour reciprocal lattice points are involved in the construction of the Brillouin zone, but for others, such as the face-centred cubic lattice Γ_c^f, *next-nearest* neighbours are involved as well. The irreducible representations of $\mathcal{T}$ then correspond to a very fine lattice of points inside the Brillouin zone and on one half of its surface.

The mapping of the parallelepiped of Figure 7.4 into the Brillouin zone can be quite complicated because different regions of the parallelepiped are mapped using different reciprocal lattice vectors. The following two-dimensional example shown in Figure 7.6 of a square lattice demonstrates

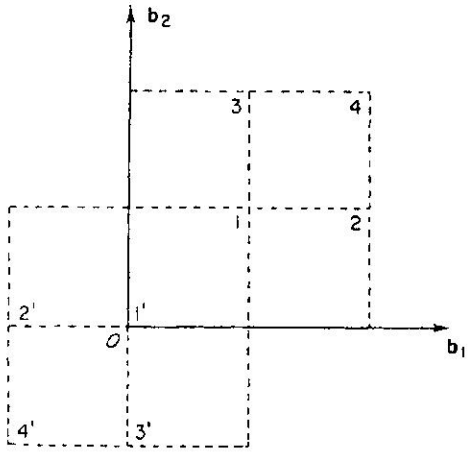

Figure 7.6: Construction of a two-dimensional Brillouin zone

this clearly. In this example the analogue of the three-dimensional parallelepiped of Figure 7.5 is the square with sides $\mathbf{b}_1$ and $\mathbf{b}_2$, which consists of four regions 1, 2, 3 and 4, and the analogue of the Brillouin zone is the square having $\mathbf{k} = \mathbf{0}$ at its centre, which consists of the four regions 1′, 2′, 3′ and 4′. The region 1 is mapped into 1′ by $\mathbf{K}_{(0,0,0)} = \mathbf{0}$, 2 is mapped into 2′ by $\mathbf{K}_{(-1,0,0)} = -\mathbf{b}_1$, 3 is mapped into 3′ by $\mathbf{K}_{(0,-1,0)} = -\mathbf{b}_2$, and 4 is mapped into 4′ by $\mathbf{K}_{(-1,-1,0)} = -\mathbf{b}_1 - \mathbf{b}_2$.

By construction, the volume of the Brillouin zone is the same as that of the parallelepiped from which it is formed, namely $\mathbf{b}_1\,(\mathbf{b}_2 \wedge \mathbf{b}_3)$. It follows from Equation (7.9) that this is equal to $(2\pi)^3/\{\mathbf{a}_1.(\mathbf{a}_2 \wedge \mathbf{a}_3)\}$, where $\mathbf{a}_1\,(\mathbf{a}_2 \wedge \mathbf{a}_3)$ is the volume of the parallelepiped whose sides are $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$.

For the simple cubic lattice Γ_c, the basic lattice vectors of the reciprocal lattice obtained from Table 7.1 and Equation (7.9) are

$$\mathbf{b}_1 = (2\pi/a)(1,0,0),\ \mathbf{b}_2 = (2\pi/a)(0,1,0),\ \mathbf{b}_3 = (2\pi/a)(0,0,1)$$

The Brillouin zone is given in Figure 7.7. The position vectors of the "symmetry points" are as follows: for Γ, $\mathbf{k} = (0,0,0)$, for X, $\mathbf{k} = (\pi/a)(0,0,1)$, for M, $\mathbf{k} = (\pi/a)(0,1,1)$, and for R, $\mathbf{k} = (\pi/a)(1,1,1)$. The significance of the term "symmetry point" will be explained in Section 7. The notation is that of Bouckaert *et al* (1936).

Similarly, for the body-centred cubic lattice Γ_c^v the basic lattice vectors of the reciprocal lattice are

$$\mathbf{b}_1 = (2\pi/a)(1,0,1),\ \mathbf{b}_2 = (2\pi/a)(0,1,-1),\ \mathbf{b}_3 = (2\pi/a)(1,-1,0),$$

the Brillouin zone being shown in Figure 7.8. The position vectors of the symmetry points are as follows: for Γ, $\mathbf{k} = (0,0,0)$; for H, $\mathbf{k} = (\pi/a)(0,0,2)$;

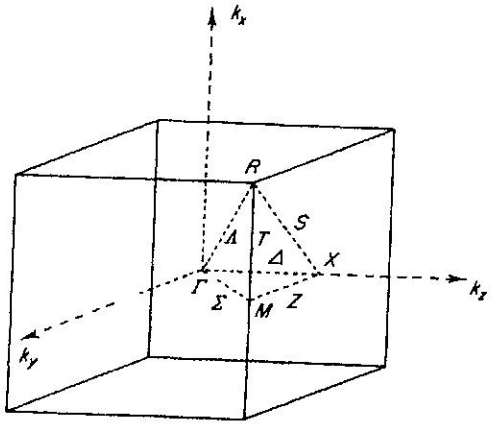

Figure 7.7. Brillouin zone corresponding to the simple cubic lattice Γ_c.

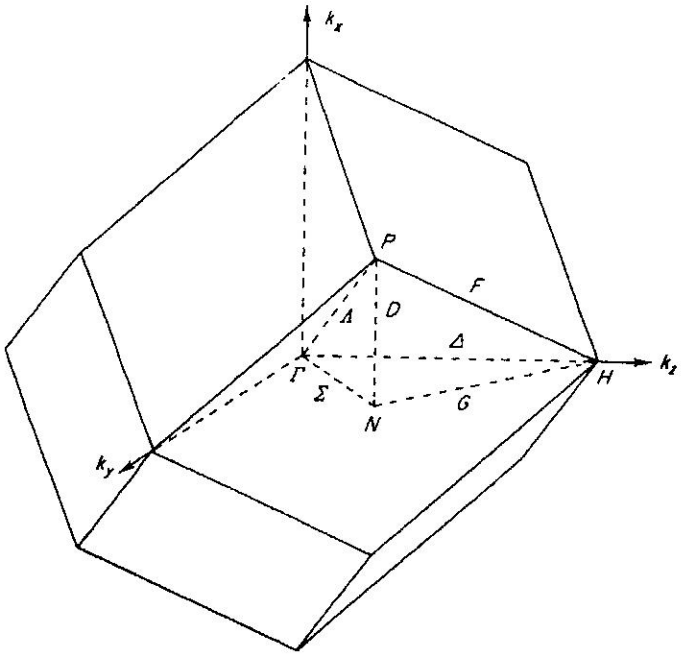

Figure 7.8: Brillouin zone corresponding to the body-centred cubic lattice Γ_c^v.

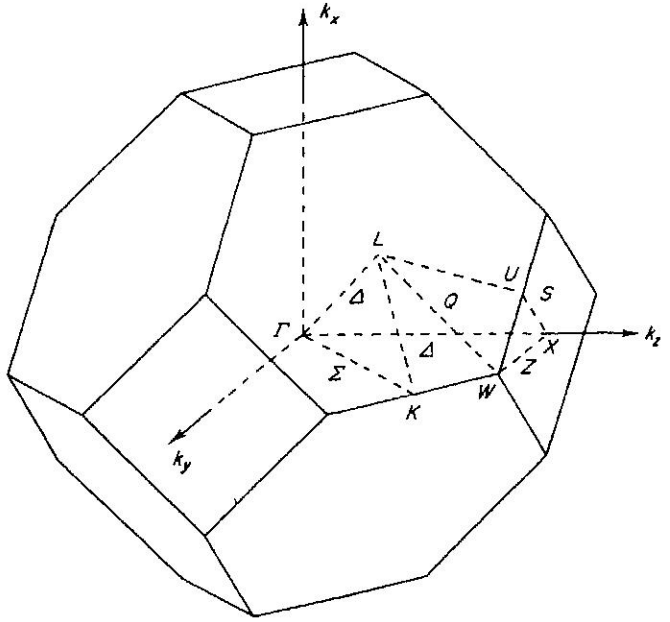

Figure 7.9. Brillouin zone corresponding to the face-centred cubic lattice Γ_c^f.

for N, $\mathbf{k} = (\pi/a)(0,1,1)$; and for P, $\mathbf{k} = (\pi/a)(1,1,1)$, the notation being that of Bouckaert *et al.* (1936)

Finally, for the face-centred cubic lattice Γ_c^f the basic lattice vectors of the reciprocal lattice are

$$\mathbf{b}_1 = (2\pi/a)(1,1,-1),\ \mathbf{b}_2 = (2\pi/a)(-1,1,1),\ \mathbf{b}_3 = (2\pi/a)(1,-1,1).$$

The Brillouin zone is given in Figure 7.9, the position vectors of the points indicated (in the notation of Bouckaert *et al.* (1936)) being: for Γ, $\mathbf{k} = (0,0,0)$; for K, $\mathbf{k} = (\pi/a)(0,\frac{3}{2},\frac{3}{2})$; for L, $\mathbf{k} = (\pi/a)(1,1,1)$; for U, $\mathbf{k} = (\pi/a)(\frac{1}{2},\frac{1}{2},2)$; for W, $\mathbf{k} = (\pi/a)(0,1,2)$, and for X, $\mathbf{k} = (\pi/a)(0,0,2)$.

The Brillouin zones corresponding to the other eleven Bravais lattices may be found in the review article by Koster (1957).

5 Electronic energy bands

The set of energy eigenvalues corresponding to an allowed k-vector may be denoted by $\epsilon_1(\mathbf{k}), \epsilon_2(\mathbf{k}), \ldots$, with the convention that

$$\epsilon_n(\mathbf{k}) \leq \epsilon_{n+1}(\mathbf{k}) \tag{7.19}$$