

4 Lattice Periodicity

4.1 Lattice Periodicity

In part 3 we saw that the many-body problem can be reduced exactly to the self-consistent solution of effective single-particle equations:

$$h\varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i}\varphi_{o_i}(\mathbf{r}) \quad (4.1)$$

with

$$h = -\frac{\hbar^2}{2m}\nabla^2 + v^{\text{eff}}(\mathbf{r}) \quad . \quad (4.2)$$

In the effective potential, the electrostatic potential of the nuclei depends on the atomic positions, whereas the Hartree and the exchange-correlation potential are determined by the charge density of the electrons. Since the densities depend on the positions of the atoms, the symmetry properties of $v^{\text{eff}}(\mathbf{r})$ are determined by the arrangement of the lattice components (nuclei), i.e., by the symmetry of $v(\mathbf{r})$. Note that this does not always mean that the symmetry of $v^{\text{eff}}(\mathbf{r})$ has to be the *same* as that of any given system of nuclei. In principle, the charge density (and thus, $v^{\text{eff}}(\mathbf{r})$) could have a lower symmetry than a given arrangement of nuclei.¹ However, this will typically lead to residual forces on the nuclei, “pulling” them into the same (lower) symmetry state as $v^{\text{eff}}(\mathbf{r})$. In general, the symmetries of $v(\mathbf{r})$, $n(\mathbf{r})$ and $v^{\text{eff}}(\mathbf{r})$ will thus be consistent with one another when the nuclei are at their equilibrium position. Since the operator ∇^2 is invariant with respect to translation, rotation and inversion in real space, the symmetry of h is determined only by $v^{\text{eff}}(\mathbf{r})$. Now we will see what we can learn from such investigations of the symmetry. In order to study the properties depending on the periodic arrangement of the atoms, we first have to introduce several definitions. The fundamental property of a *crystal* or a crystalline solid is the regular arrangement of its constituents, i.e., the nuclei. “Periodicity” and “order” are not synonyms, and the most recent definition by the “International Union of Crystallography” therefore reads: “A crystal is a solid having an essentially discrete diffraction pattern.” Periodic crystals form a subset. At this point we note that in nature crystals are more frequent than expected: Not only diamond and quartz are crystals. Also metals often have a crystalline structure, although their outer shape usually is not so pronounced as, e. g., for salts or for minerals.

¹So-called spin or charge density waves in periodic crystals are an example for cases where the nuclei may have a different (higher) translational symmetry (see below) than the resulting $v^{\text{eff}}(\mathbf{r})$. Examples are the so-called *Peierls instability*, or the magnetic ground state of Cr, where the periodicity of the electronic spin density extends over many unit cells of the actual nuclear subsystem.

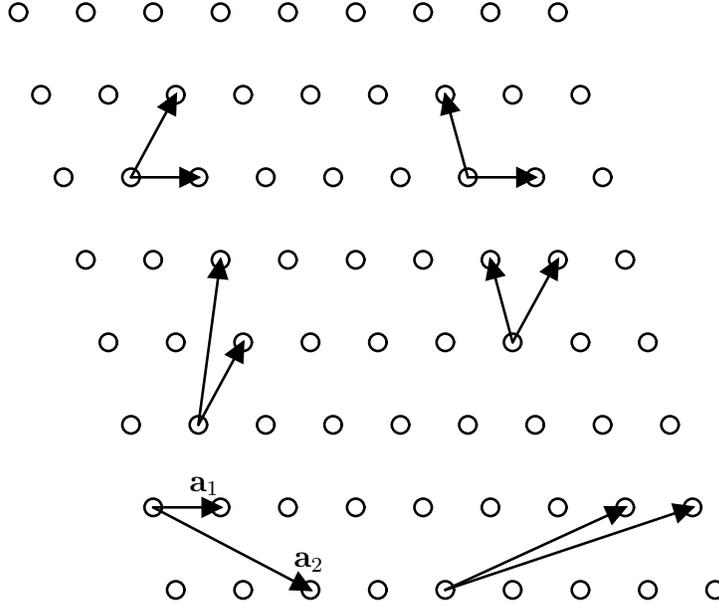


Figure 4.1: A two-dimensional Bravais lattice. The choice of the primitive vectors $\mathbf{a}_1, \mathbf{a}_2$ is not unique.

A periodic crystal is characterized by the fact that by a certain translation it is mapped onto itself. A translation is defined by a vector

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad , \quad (4.3)$$

where $n_i \in \mathbb{Z}$ and the vectors \mathbf{a}_i are linearly independent. For the translation operator we have

$$T_{\mathbf{R}_n} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}_n) \quad , \quad (4.4)$$

where $f(\mathbf{r})$ is an arbitrary function. We have

$$T_{\mathbf{R}_n} v^{\text{eff}}(\mathbf{r}) = v^{\text{eff}}(\mathbf{r} + \mathbf{R}_n) = v^{\text{eff}}(\mathbf{r}) \quad (4.5)$$

and

$$T_{\mathbf{R}_n} \nabla^2 f(\mathbf{r}) = \nabla^2 f(\mathbf{r} + \mathbf{R}_n) = \nabla^2 T_{\mathbf{R}_n} f(\mathbf{r}) \quad . \quad (4.6)$$

This means that $T_{\mathbf{R}_n}$ and h commute: Then for the Hamilton operator h we have

$$T_{\mathbf{R}_n} h \varphi_{o_i}(\mathbf{r}) = h \varphi_{o_i}(\mathbf{r} + \mathbf{R}_n) = h T_{\mathbf{R}_n} \varphi_{o_i}(\mathbf{r}) = \epsilon_{o_i} \varphi_{o_i}(\mathbf{r} + \mathbf{R}_n) \quad . \quad (4.7)$$

The vectors \mathbf{a}_i introduced above are called primitive vectors. The set of *points* defined by $\{\mathbf{R}_n\}$ is called a *Bravais lattice* (cf. Fig. 4.1). For obvious reasons the term Bravais lattice is often also used for the set of *vectors* $\{\mathbf{R}_n\}$. The choice of the primitive vectors is not unique, generally the shortest primitive translations are chosen. The points of the Bravais lattice do not need to correspond to the positions of individual atoms. As a warning we mention that not every apparently symmetric set of points constitutes a Bravais lattice (cf. the example in Fig. 4.2). Apart from translations, which shift all points in space, generally the structure of a crystal is also invariant with respect to symmetry operations that keep at least one point fixed, so-called *point symmetries* (details will be given later).

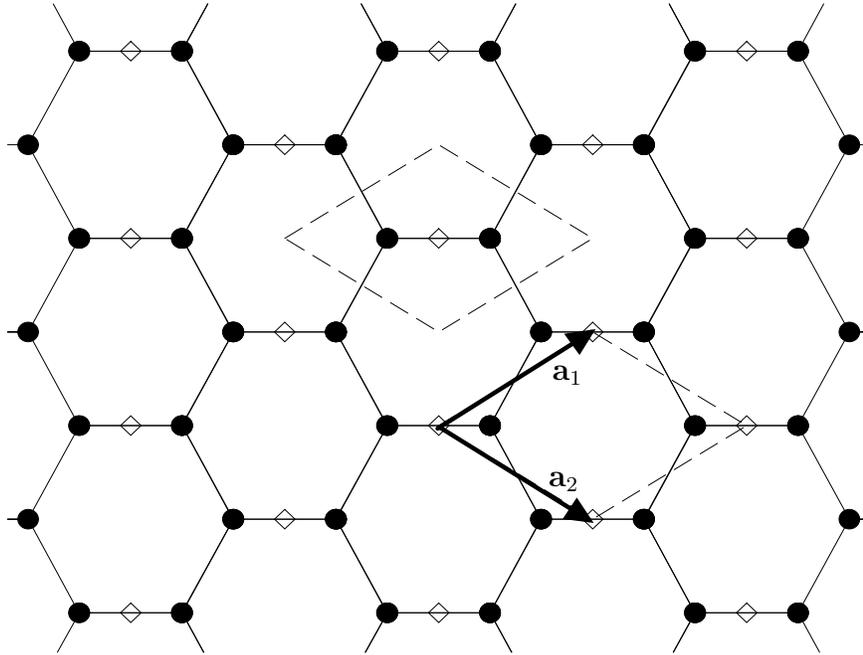


Figure 4.2: The crossing points of the honeycomb structure do not form a Bravais lattice, but the centers of the dumbbells do. Thus, the hexagonal structure is also called a *Bravais lattice with basis*, i.e., for each point of the Bravais lattice in this case there are two atoms, which in this context are called basis.

The smallest structural unit of a crystal is called the *primitive cell* or the *primitive unit cell*. If the *primitive unit cell* is shifted by all vectors of the Bravais lattice, the full space is filled without gaps or overlap. Similar to the definition of primitive vectors the definition of the primitive unit cell is not unique. A primitive unit cell contains exactly one point of the Bravais lattice. Thus, a possible choice for the primitive unit cell would be the body spanned by the shortest primitive vectors. This choice has the disadvantage that the primitive unit cell defined this way often does not have the same symmetry (point symmetry) as the Bravais lattice. But there is always a primitive unit cell which has the same symmetry with respect to reflection, rotations and inversion as the Bravais lattice. This is the *Wigner-Seitz cell*: It consists of the region, which is closer to a certain Bravais lattice point than to all other Bravais lattice points. The Wigner-Seitz cell has the same symmetry as the Bravais lattice. For the construction of the Wigner-Seitz cell, one starts with an arbitrary point of the Bravais lattice. The surface is obtained by connecting this lattice point with its nearest neighbors. In the middle of the connecting line a plane perpendicular to this line is constructed. A two-dimensional example is shown in Fig. 4.3, and some three-dimensional examples are shown in Fig. 4.4.

Often it is more illustrative to construct a crystal structure not from the primitive cell but from larger unit cells instead, so-called “*conventional unit cells*”. Four important examples for Bravais lattices are the sc (simple cubic), fcc (face-centered cubic), bcc (body-centered cubic) and the hexagonal Bravais lattice (cf. Fig. 4.4).

Apart from translations $T_{\mathbf{R}_n}$, there may be further *symmetry operations of the crystal*:

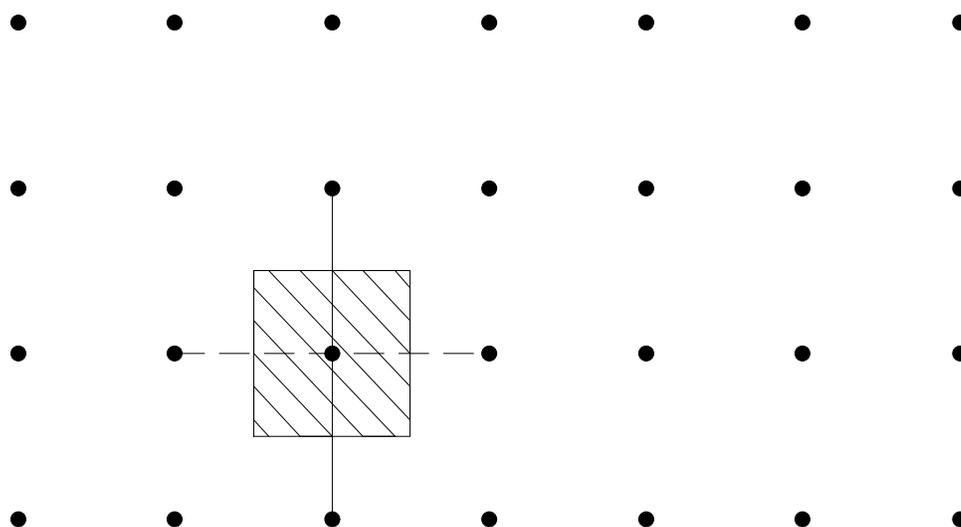


Figure 4.3: The Wigner-Seitz cell of a square net of points.

- 1) R_ϕ rotation
 - 1a) C_n normal rotation by $\phi = \frac{2\pi}{n}$
 - 1b) S_n improper rotation
- 2) σ reflection
- 3) $i = S_2$ inversion
- 4) \widehat{TR}_ϕ screw rotation
- 5) $\widehat{T}\sigma$ glide reflection

Generally, the term “rotation” includes “normal rotations” as well as improper rotations. An improper rotation is the following combination of operations: First, rotate about a certain axis by the angle ϕ and then reflect at the plane perpendicular to this axis. Screw rotation and glide reflection are combinations of rotations and reflections and non-primitive translations. The example of a glide reflection is shown in Fig. 4.5.

If we want to distinguish between proper and improper rotations, instead of the symbol R_ϕ we use the following symbols: Operator of the normal rotation: C_n . Operator of the improper rotation: S_n . The letter C results from “cyclic”. The Index n gives the rotation angle ϕ as $\phi = 2\pi/n$.

The operation of inversion at the origin, i.e., $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$ is labeled by the letter i , and we have $i = S_2$. Reflections are labeled by the letter σ . They can be composed of a rotation and an improper rotation: $\sigma = C_n^{-1} \otimes S_n$.

It can easily be seen that the set of symmetry operations of a body has group properties. Therefore, we have the four laws (O,A,N,I):

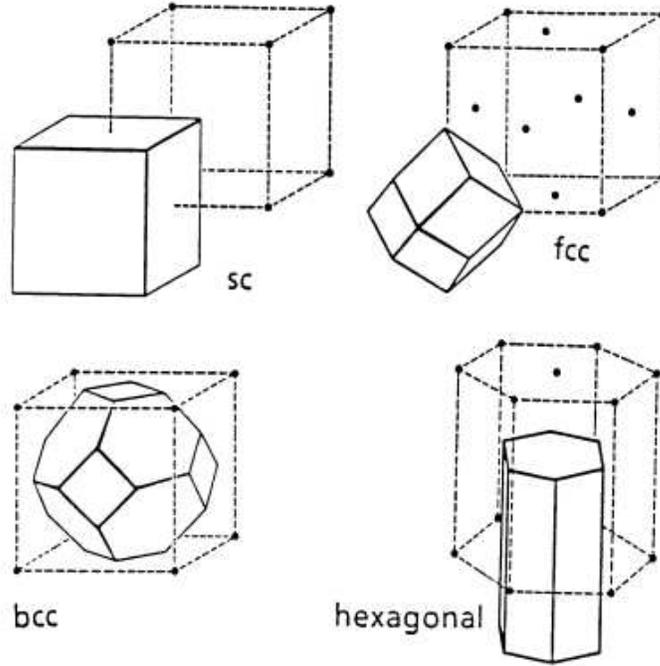


Figure 4.4: Some Bravais lattices and the corresponding Wigner-Seitz cells.

1) There is an operation \otimes :

$$a, b \in \mathbf{G} \rightarrow a \otimes b = c \in \mathbf{G}$$

2) The associative law is valid:

$$a \otimes (b \otimes c) = (a \otimes b) \otimes c$$

3) There is a neutral element E :

$$a \otimes E = E \otimes a = a$$

4) For each element in \mathbf{G} there is an inverse element:

$$a \otimes a^{-1} = E = a^{-1} \otimes a$$

For the elements of the Bravais lattice, i.e., for the translations, additionally we have the commutative law $a \otimes b = b \otimes a$:

$$T_{\mathbf{R}_m} + T_{\mathbf{R}_n} = T_{\mathbf{R}_n} + T_{\mathbf{R}_m} = T_{\mathbf{R}_n + \mathbf{R}_m} \quad (4.8)$$

Thus, the translational group is Abelian.

A subset \mathbf{U} of \mathbf{G} , that is closed with respect to the operation \otimes and itself has group properties, is called a *subgroup*. The set of elements, which is generated by operating all elements of \mathbf{U} on a given element a of the group, is called a *coset* (notation $a \otimes \mathbf{U}$). The

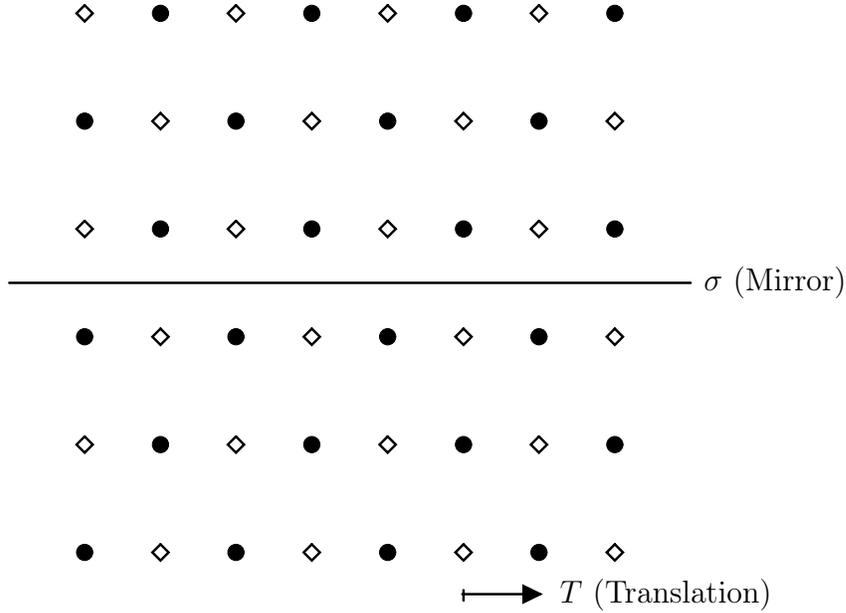


Figure 4.5: The system of two atom types is mapped on itself by a combination of translation T and reflection (glide reflection symmetry). The translation T and the reflection σ alone would not be symmetry operations. In this example the glide reflection is identical to a screw rotation. For the screw rotation a translation and a rotation (here by 180°) are combined.

cosets themselves are not groups. For non-Abelian groups one has to distinguish between right ($\mathbf{U} \otimes a$) and left cosets ($a \otimes \mathbf{U}$). If, in a special case, right and left cosets of a subgroup \mathbf{U} are the same, the subgroup \mathbf{U} is called a *normal divisor* of \mathbf{G} .

As an example for a point symmetry, we now investigate the point group of a cube. The group is labeled O_h , the letter O referring to “octahedra”. This point group is rather important. Many important crystals have this point symmetry or at least the symmetry of a subgroup of O_h . The sc, fcc, and bcc Bravais lattices have O_h symmetry.

In Table 4.1 the symmetry operations are described. Reflections do not appear explicitly in the table, but they are included in the symmetry operations of O_h . We have $\sigma_v = i \otimes C_2$ and $\sigma_d = i \otimes C_2'$. The index at σ indicates if the plane is crossing the cube vertically (v) or diagonally (d).

Another term we introduce is the *class of conjugate elements* (often just called class). Two symmetry operations a and b are part of such a class if there is an element c of this group, so that we have

$$a = c^{-1}bc . \quad (4.9)$$

The group elements a and b are then called “similar symmetry operations” or “conjugate operations”. Symmetry operations of the “same kind” are in one class. In Table 4.1 we already intuitively summarized the symmetry operations according to classes. Only in the last row we considered 5 classes together. This can easily be validated. The group O_h has 10 classes. The group O (this is the subgroup of O_h , which does not contain i) has 5 classes. The neutral element is always a class by itself.

symbol	operation	number
E	unit operation	1
C_4	rotation around the x -, $-x$ -, y -, $-y$ -, z - or $-z$ -axis by $2\pi/4$	6
C_2	rotation around the x -, y - or z -axis by $2\pi/2$	3
C_2	rotation around the six axes cutting the edges of the cube in the middle by $2\pi/2$	6
C_3	rotation around the four space diagonals by $\pm 2\pi/3$	8
$\otimes i$	all operations given up to here $\otimes i$	24

Table 4.1: The 48 symmetry operations of the cube, i.e., the point group O_h .

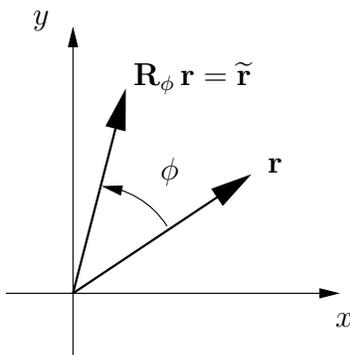


Figure 4.6: Operator R_ϕ . Here: Rotation about the z -axis by the angle ϕ .

The total of all symmetry operations (translations, point symmetries, and combinations of both), which map the Bravais lattice (including a possibly existing basis) on itself, form the *space group* of the crystal. If we label the operator of a rotation (by the angle ϕ) with R_ϕ (cf. Fig. 4.6), an arbitrary element of the space group can be labeled by $(R_\phi; T_{\mathbf{D}})$. We have:

$$(R_\phi; T_{\mathbf{D}})f(\mathbf{r}) = f(\tilde{\mathbf{r}} + \mathbf{D}) , \quad (4.10)$$

with $\tilde{\mathbf{r}} = R_\phi \mathbf{r}$. Because \mathbf{D} appears in a combination of rotation and translation operations, it is not necessarily an element of the Bravais lattice (cf. Fig. 4.5).

It can be shown that the space group contains the required group properties. In particular it has to be closed with respect to all operations, which are defined as:

$$(R_{\phi_2}; T_{\mathbf{D}_2})(R_{\phi_1}; T_{\mathbf{D}_1}) = (R_{\phi_2}R_{\phi_1}; T_{R_{\phi_2}\mathbf{D}_1 + \mathbf{D}_2}) . \quad (4.11)$$

For the inverse element we have:

$$(R_\phi; T_{\mathbf{D}})^{-1} = (R_\phi^{-1}; T_{-R_\phi^{-1}\mathbf{D}}) . \quad (4.12)$$

For Bravais lattices we have: The total number of the different² symmetry operations is finite: There are, e.g. only four rotations: C_2 , C_3 , C_4 , and C_6 . In periodic solids there is no rotational axis with a 5-fold symmetry or a symmetry of higher than 6 (due to translational invariance).

² The operations $T_{\mathbf{R}_n}$ and $NT_{\mathbf{R}_n}$ or C_n and $2C_n, 3C_n, \dots$ are considered the same.

Proof:

The vectors of the Bravais lattice are

$$\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \quad . \quad (4.13)$$

Further, the crystal shall have (at least) one rotational axis C_n , and for the moment we leave it open, what n may be. $C_n\mathbf{R}_n$ then also is an element of the Bravais lattice. The vectors

$$\mathbf{R}'_n = \mathbf{R}_n - C_n\mathbf{R}_n \quad (4.14)$$

are perpendicular to the rotational axis and are of course also part of the Bravais lattice. The shortest of these vectors shall be labeled with \mathbf{a}_1 . The vectors $(kC_n)\mathbf{a}_1$ with $k = 1 \dots n$ are then also elements of the Bravais lattice; (kC_n) means that the rotation is performed k -times. They all have the same length as \mathbf{a}_1 . Now we consider two vectors of different lengths:

$$|\mathbf{a}_1 - (kC_n)\mathbf{a}_1| = L_1 \quad (4.15)$$

and

$$|\mathbf{a}_1 + (kC_n)\mathbf{a}_1| = L_2 \quad . \quad (4.16)$$

Because \mathbf{a}_1 is the shortest vector perpendicular to the rotational axis, we have

$$L_1 \geq |\mathbf{a}_1| \quad (4.17)$$

and

$$L_2 \geq |\mathbf{a}_1| \quad . \quad (4.18)$$

Alternatively, it would be possible that L_1 or L_2 are zero. In Fig. 4.7 it can be seen that for $k = 1 \dots n$

$$\left| \sin\left(\frac{k\pi}{n}\right) \right| = \frac{L_1}{2|\mathbf{a}_1|} \quad (4.19)$$

and

$$\left| \cos\left(\frac{k\pi}{n}\right) \right| = \frac{L_2}{2|\mathbf{a}_1|} \quad . \quad (4.20)$$

With condition (Eq. (4.17)) follows:

$$\left| \sin\left(\frac{k\pi}{n}\right) \right| = \frac{L_1}{2|\mathbf{a}_1|} \geq \frac{1}{2} = \sin(30^\circ) \quad (4.21)$$

for all numbers $k \leq n$. This means that we must have $\frac{k\pi}{n} \geq \pi/6$, i.e., n must not be larger than 6.

From Eq. (4.18) we obtain

$$\left| \cos\left(\frac{k\pi}{n}\right) \right| \geq \frac{1}{2} = \cos(60^\circ) \quad (4.22)$$

If we set $k = 2$, we obtain a contradiction; thus $n = 5$ is also impossible. Therefore, we have proven that for a Bravais lattice only point symmetries with rotations $C_2, C_3, C_4,$

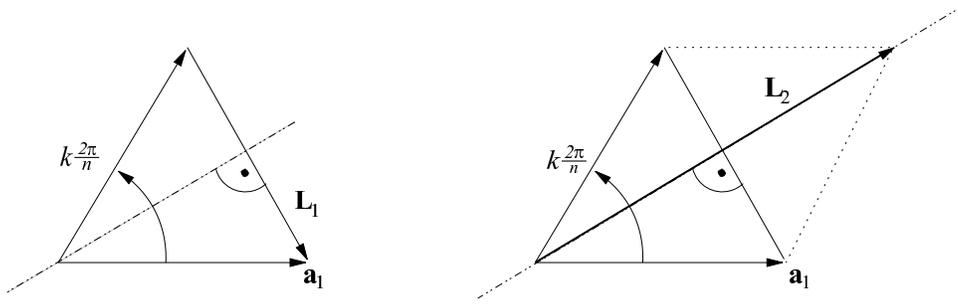


Figure 4.7: Visualization of Equations (4.19) and (4.20).

\tilde{G}_1	A_1	A_2	...	A_N
A_1	$A_1 \otimes A_1$	$A_1 \otimes A_2$...	$A_1 \otimes A_N$
A_2	$A_2 \otimes A_1$
\vdots
A_N	$A_N \otimes A_1$	$A_N \otimes A_N$

Table 4.2: Multiplication table of a group \tilde{G}_1 consisting of N elements. Each product $A_i \otimes A_j$ is equal to an element of the group, i.e., $A_i \otimes A_j = A_k$.

and C_6 can exist.

A cell with C_5 or one with C_n and $n > 6$ cannot fill space completely or without overlap. This was noted already in 1619 by Johannes Kepler. However, in 1984 in rapidly cooled aluminium-manganese-melts diffraction images of 5-fold symmetry were measured (Phys. Rev. Letters, **53**, 1951 (1984)) and also 12-fold (Phys. Rev. Letters, May 1988) symmetries were found. These are not periodic crystals although these are ordered systems. These “new lattices” are called quasi-crystals (cf. e.g. Physikalische Blätter 1986, S. 373 and S. 368, Fig. 3). A certain analogy to the three-dimensional quasi crystals in two dimensions are the so-called Penrose-patterns (cf e.g. Spektrum der Wissenschaft, Juli 1999). This effect is also known from tiling walls or floors. When tiles of five-fold symmetry are used one also needs other tiles to fill some areas.

From the very limited number of possible rotation axes for Bravais lattices it follows: For Bravais lattices there are only 7 different point groups (7 crystal systems). We first have to explain what is meant by the term “different”, or what is meant by the term “the same”. Two groups are equivalent, if they contain the same number of elements and if their multiplication tables are identical. The multiplication table of a point group is defined in Table 4.2. Instead of the term “point group of the Bravais lattice” we also use the term “crystal system” as a synonym. One of the 7 point groups, i.e., the group O_h , has already been examined.

In Table 4.3 the 7 crystal systems are listed, where we reduce the symmetry of the sample body (with the exception of the hexagonal point group) when going from row N to $N + 1$. When considering the space groups one finds that for Bravais lattices (with mono-atomic

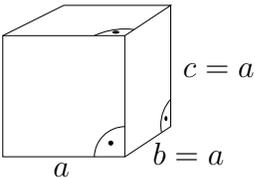
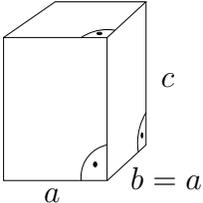
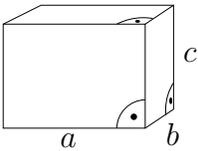
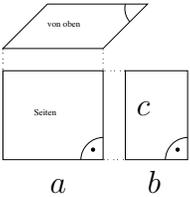
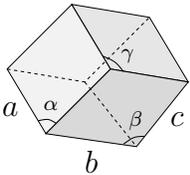
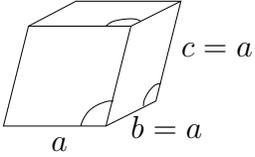
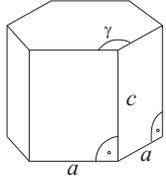
crystal system	crystal axes	example	Bravais lattice
cubic	$\alpha = \beta = \gamma = 90^\circ$ $a = b = c$		sc, fcc, bcc,
tetragonal	$\alpha = \beta = \gamma = 90^\circ$ $a = b \neq c$		simple tetragonal, centered tetragonal,
orthorhombic (rhombic)	$\alpha = \beta = \gamma = 90^\circ$ $a \neq b \neq c$		simple, face centered, body centered, face centered, (Basis: upper/lower facet)
monoclinic	$\alpha = \gamma = 90^\circ \neq \beta$ $a \neq b \neq c$		simple monoclinic, centered monoclinic,
triclinic	$\alpha \neq \beta \neq \gamma$ $a \neq b \neq c$	 Parallelepiped (Spat), opposite facets are parallel	simple triclinic,
trigonal	$\alpha = \beta = \gamma \neq 90^\circ$ $a = b = c$		simple trigonal,
hexagonal	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ $a = b \neq c$		simple hexagonal.

Table 4.3: The 7 Crystal Systems and 14 Bravais Lattices.

crystal system	number of Bravais lattices	number of point groups	name of the point groups
cubic	3	5	O_h, O, T_h, T, T_d
tetragonal	2	7	$C_4, S_4, C_{4h}, D_4, C_{4v}, D_{2d}, D_{4h}$
orthorhombic	4	3	D_2, C_{2v}, D_{2h}
monoclinic	2	3	C_2, C_S, C_{2h}
triclinic	1	2	C_1, C_i
trigonal	1	5	$C_3, C_{3i}, D_3, C_{3v}, D_{3d}$
hexagonal	1	7	$C_6, C_{6h}, D_6, C_{6v}, D_{3h}, D_{6h}, C_{3h}$
	$\Sigma = 14$	$\Sigma = 32$	

Table 4.4: Bravais lattices and point groups of the crystal structures.

basis) there are only 14 different space groups. This has been investigated by Frankheim in 1842, but he made a mistake (he found 15), in 1845 Bravais found the correct number.

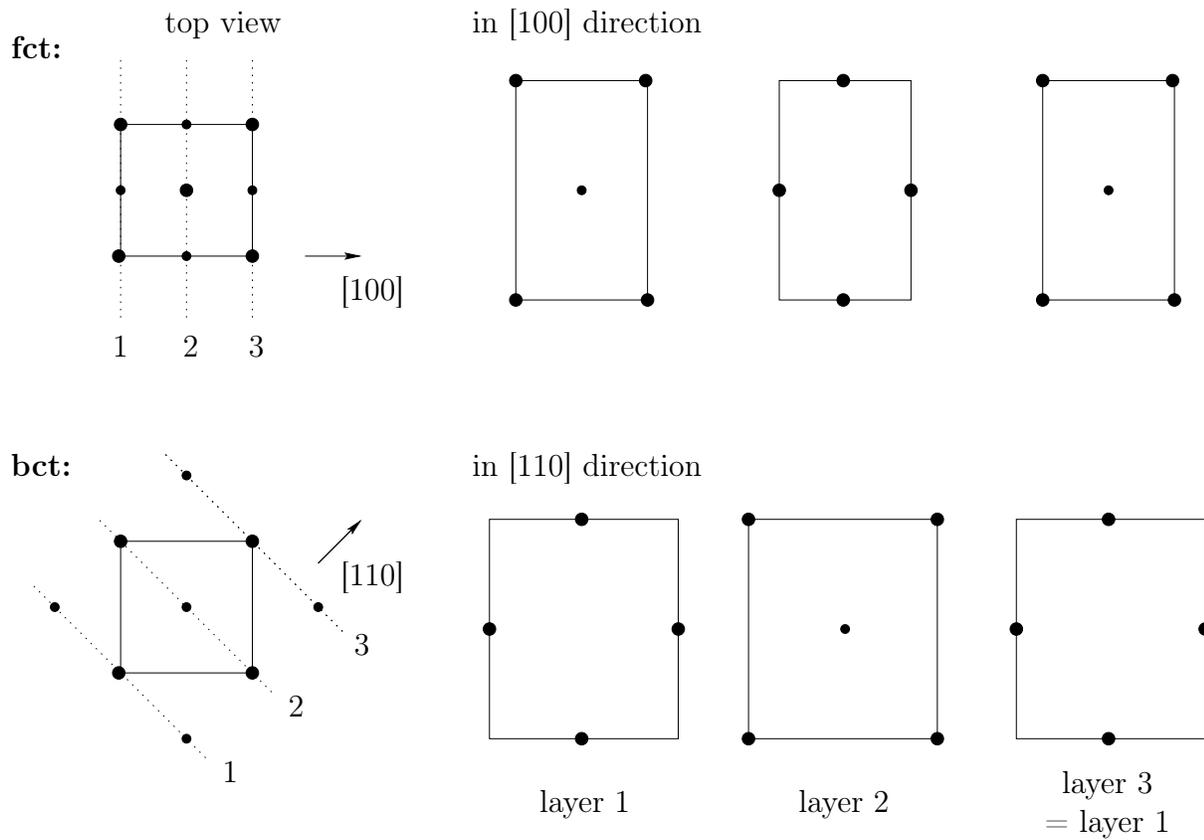


Figure 4.8: Layer sequence of a fct and of a bct lattice (at the left: projection onto the (001) plane). Both lattices can be represented as a ct lattice.

There are further Bravais lattices that may come to mind analogous to sc-, fcc-, and bcc-lattices. They are not included in the table, because they are equivalent to the ones listed. For example, a face-centered and a body-centered tetragonal Bravais lattice are identical (cf. Fig. 4.8).

This is a first crude classification of all possible periodic crystals in the 14 Bravais lattices. For each crystal there is a Bravais lattice and a crystal system. In case each point of the Bravais lattice has an inner structure (e.g. the dumbbells of Fig. 4.2), i.e., if it has a basis, then the point symmetry of the crystal is lower than the symmetry of the Bravais lattice. Generally, we have: The point group of a crystal is a subgroup of the *crystal system*. For the cubic crystal system O_h , e.g. there are 5 subgroups, which can be present in real crystals. These are the groups O_h , O (like O_h , but without inversion i), T_d (the point group of a tetrahedron: $E, 8C_3, 3C_2, 6\sigma_d, 6S_4$), T (the point group of a tetrahedron, without reflection symmetry: $E, 3C_2, 4C_3^+, 4C_3^-$), the group $T_h = T \otimes i$, which in addition to T contains also the operations $i, 8S_6, 3\sigma_d$. We have used $\sigma_d = C_2 \otimes i$ and $S_4 = C_4 \otimes i$. Thus, if the “inner atomic structure” of the individual points of the Bravais lattice are taken into account, one finds: There are 32 crystalline point groups, which are compatible with the translational properties of a crystal (cf. Table 4.4) and there are 230 space groups.

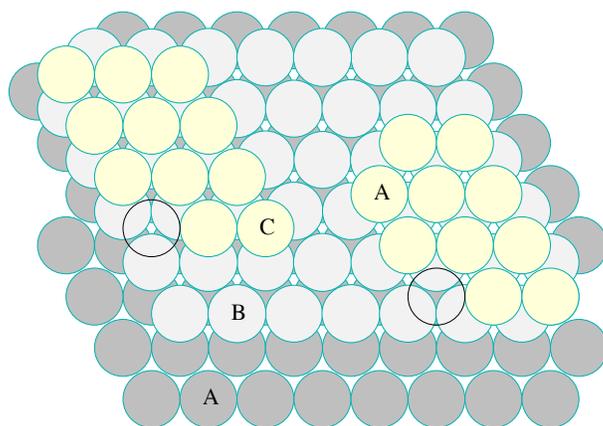


Figure 4.9: Close-packed structures hcp (left, layer sequence ABCABC...) and fcc (right, layer sequence ABAB...).

If one thinks of the crystal as being composed of hard spheres and these spheres are close-packed, one obtains a structure with the first two layers as shown in Fig. 4.9. The first layer has a 6-fold symmetry and each sphere has 6 neighbors. The spheres of the second layer are located in the hollow sites of the first layer. For the third layer there are two different possibilities: The spheres could be on top of the gaps (site b) or above the spheres of the second-last layer (site a). In the second case the arrangement of the third layer is equal to the first, and we obtain a layer sequence ABABAB... . This is the hcp-structure. In case b) a layer sequence of ABC... can be obtained. This is the fcc-structure.

fcc- and hcp-structures are mostly adopted by systems without directional bonds between structural elements (in simple Bravais lattices without basis these are the atoms). Then energetically it will be favored if each structural element can form bonds to as many

neighbors as possible. In the fcc- and hcp-structure each structural element has twelve nearest neighbors.

In Fig. 4.10 some important crystal structures are listed (from Ashcroft-Mermin). Further some crystals adopting these structures and their lattice constants are given. Except for the last example, the hexagonal structure, these are all cubic crystal systems.

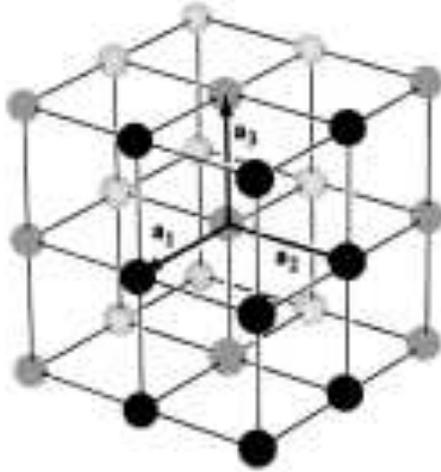
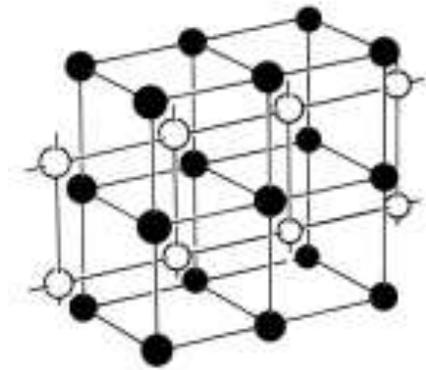
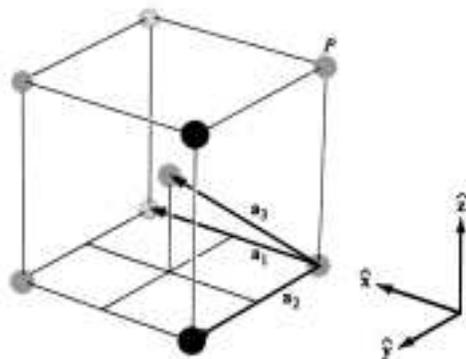


Figure 4.10: Some important crystal structures. a) Simple cubic (sc) Bravais lattice, (e.g. α -Polonium).



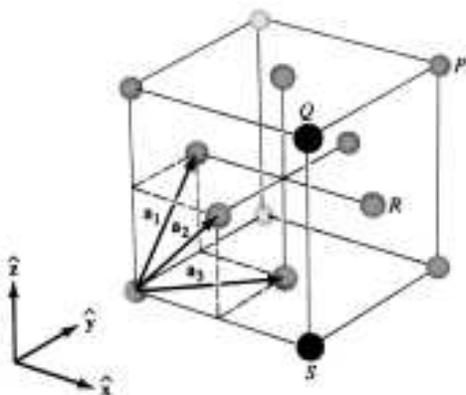
CRYSTAL	a (Å)	CRYSTAL	a (Å)
CsCl	4.12	TlCl	3.83
CsBr	4.29	TlBr	3.97
CsI	4.57	TlI	4.20

Fig. 4.10 – b) CsCl structure (sc with a diatomic basis).



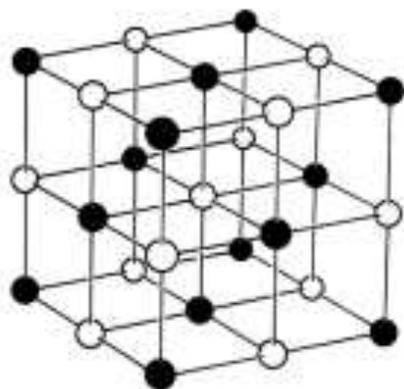
ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ba	5.02	Li	3.49 (78 K)	Ta	3.31
Cr	2.88	Mo	3.15	Tl	3.88
Cs	6.05 (78 K)	Nu	4.23 (5 K)	V	3.02
Fe	2.87	Nb	3.30	W	3.16
K	5.23 (5 K)	Rb	5.59 (5 K)		

Fig. 4.10 – c) body-centered cubic Bravais lattice (bcc).



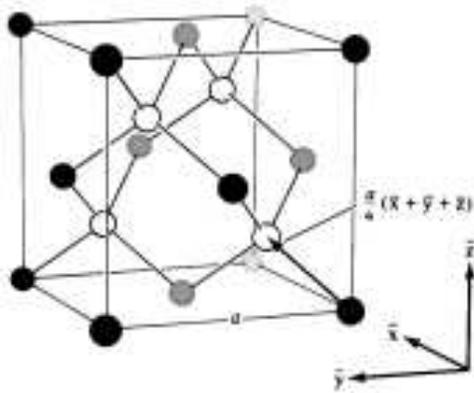
ELEMENT	a (Å)	ELEMENT	a (Å)	ELEMENT	a (Å)
Ar	5.26 (4.2 K)	Ir	3.84	Pt	3.92
Ag	4.09	Kr	5.72 (58 K)	δ -Pu	4.64
Al	4.05	La	5.30	Rh	3.80
Au	4.08	Ne	4.43 (4.2 K)	Sc	4.54
Cu	5.58	Ni	3.52	Sr	6.08
Ce	5.16	Pb	4.95	Th	5.08
β -Co	3.55	Pd	3.89	Xe (58 K)	6.20
Cu	3.61	Pr	5.16	Yb	5.49

Fig. 4.10 – d) face-centred cubic Bravais lattice (fcc).



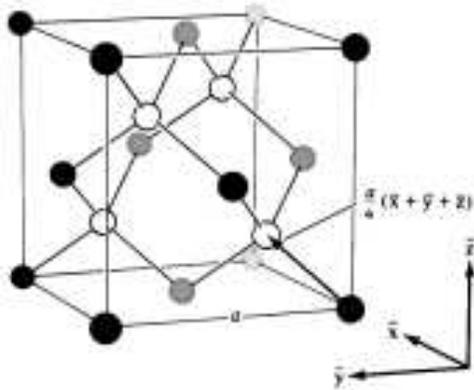
CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
LiF	4.02	RbF	5.64	CaS	5.69
LiCl	5.13	RbCl	6.58	CaSe	5.91
LiBr	5.50	RbBr	6.85	CaTe	6.34
LiI	6.00	RbI	7.34	SrO	5.16
NaF	4.62	CsF	6.01	SrS	6.02
NaCl	5.64	AgF	4.92	SrSe	6.23
NaBr	5.97	AgCl	5.55	SrTe	6.47
NaI	6.47	AgBr	5.77	BaO	5.52
KF	5.35	MgO	4.21	BaS	6.39
KCl	6.29	MgS	5.20	BaSe	6.60
KBr	6.60	MgSe	5.45	BaTe	6.99
KI	7.07	CuO	4.81		

Fig. 4.10 – e) NaCl structure (fcc with a diatomic basis),



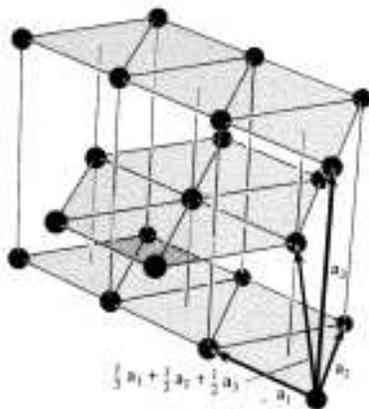
ELEMENT	CUBE SIDE a (Å)
C (diamond)	3,57
Si	5,43
Ge	5,66
α -Sn (grey)	6,49

Fig. 4.10 – f) Diamond structure (fcc with a diatomic basis).



CRYSTAL	a (Å)	CRYSTAL	a (Å)	CRYSTAL	a (Å)
CuF	4.26	ZnS	5.41	AlSb	6.13
CuCl	5.41	ZnSe	5.67	GaP	5.45
CuBr	5.69	ZnTe	6.09	GaAs	5.65
CuI	6.04	CdS	5.82	GaSb	6.12
AgI	6.47	CdTe	6.48	InP	5.87
BeS	4.85	HgS	5.85	InAs	6.04
BeSe	5.07	HgSe	6.08	InSb	6.48
BeTe	5.54	HgTe	6.43	SiC	4.35
MnS (red)	5.60	AlP	5.45		
MnSe	5.82	AlAs	5.62		

Fig. 4.10 – g) Zincblende structure (fcc with a diatomic basis of different species).



ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α -Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	3.57	5.83	1.63	Tl	3.46	5.53	1.60
Hf	3.20	5.06	1.58	Tm	3.54	5.55	1.57
Ho	3.58	5.62	1.57	Y	3.65	5.73	1.57
La	3.75	6.07	1.62	Zn	2.66	4.95	1.86
Lu	3.50	5.55	1.59	Zr	3.23	5.15	1.59
Mg	3.21	5.21	1.62				
Nd	3.66	5.90	1.61	"Ideal"			1.63

Fig. 4.10 – h) Hexagonal closed packed structure (hcp, hexagonal Bravais lattice with a diatomic basis). The table lists the lattice parameters for some elements with hexagonal closed-packed structure (hcp), cf. Fig. 4.9.

	Bravais lattice	crystal structure
point symmetry	7 crystal systems	32 crystalline point groups
point symmetry and translational symmetry	14 Bravais lattices	230 crystalline space groups

Table 4.5: The space groups.

4.2 The Bloch Theorem

What can we learn from the symmetry properties of $v^{\text{eff}}(\mathbf{r})$ for the solution of the Kohn-Sham equation? In this paragraph we take into account (at first) the translational invariance of the periodic crystal. For the Kohn-Sham equation the Hamilton operator of the crystal and the translations of the Bravais lattice commute (cf. Eq. (4.7)).

Thus, the functions $\varphi_{o_i}(\mathbf{r})$ and $T_{\mathbf{R}_n}\varphi_{o_i}(\mathbf{r})$ are both eigenfunctions of h , and they have the same eigenvalue. In order to analyze this we will distinguish two cases:

- a) The eigenvalue ϵ_{o_i} is non-degenerate.

Then the functions $\varphi_{o_i}(\mathbf{r})$ and $T_{\mathbf{R}_n}\varphi_{o_i}(\mathbf{r})$ are physically equivalent. They can differ by a phase factor only:

$$T_{\mathbf{R}_n}\varphi_{o_i}(\mathbf{r}) = e^{i\alpha}\varphi_{o_i}(\mathbf{r}) \quad , \quad (4.23)$$

where α is an arbitrary real number, which can depend on \mathbf{R}_n .

In order to investigate the properties of the function $\alpha(\mathbf{R}_n)$ in more detail, we apply two translational operators \mathbf{R}_n and \mathbf{R}_m and obtain

$$T_{\mathbf{R}_m}T_{\mathbf{R}_n}\varphi_{o_i}(\mathbf{r}) = e^{i\alpha(\mathbf{R}_m)}e^{i\alpha(\mathbf{R}_n)}\varphi_{o_i}(\mathbf{r}) \quad . \quad (4.24)$$

Further we have

$$T_{\mathbf{R}_m+\mathbf{R}_n}\varphi_{o_i}(\mathbf{r}) = e^{i\alpha(\mathbf{R}_m+\mathbf{R}_n)}\varphi_{o_i}(\mathbf{r}) \quad . \quad (4.25)$$

For the phase function α we obtain

$$\alpha(\mathbf{R}_m + \mathbf{R}_n) = \alpha(\mathbf{R}_m) + \alpha(\mathbf{R}_n) \quad , \quad (4.26)$$

and we have

$$\alpha(j\mathbf{R}_n) = j\alpha(\mathbf{R}_n) \quad (4.27)$$

with j being an arbitrary integer number. The function $\alpha(\mathbf{R}_n)$ therefore is linear in \mathbf{R}_n . Thus, it has the form

$$\alpha(\mathbf{R}_n) = \mathbf{k}\mathbf{R}_n \quad . \quad (4.28)$$

Therefore, we have

$$T_{\mathbf{R}_n}\varphi_{o_i}(\mathbf{r}) = \varphi_{o_i}(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k}\mathbf{R}_n}\varphi_{o_i}(\mathbf{r}) \quad (4.29)$$

This is the eigenvalue equation of the translation operator. The eigenvalues of $T_{\mathbf{R}_n}$ are $e^{i\mathbf{k}\mathbf{R}_n}$. The introduced vector \mathbf{k} labels the eigenvalues of $T_{\mathbf{R}_n}$ and thus also the eigenfunctions of $\varphi_{o_i}(\mathbf{r})$.

b) The eigenvalue ϵ_{o_i} shall be degenerate.

As a second possibility we have to investigate the case that the eigenvalue is f -fold degenerate. For the f eigenfunctions φ_l we have: The functions $\varphi_l(\mathbf{r})$ and $T_{\mathbf{R}_n}\varphi_l(\mathbf{r})$ with $l = 1 \dots f$ have the same energy eigenvalue ϵ_{o_i} . This means:

$$T_{\mathbf{R}_n}\varphi_l(\mathbf{r}) = \sum_{m=1}^f \Gamma_{m,l}\varphi_l(\mathbf{r}) \quad (4.30)$$

The matrices $\Gamma_{m,l}$ are called representation of the translational group:

$$\Gamma_{m,l} = \langle \varphi_m | T_{\mathbf{R}_n} | \varphi_l \rangle \quad (4.31)$$

The translations $T_{\mathbf{R}_n}$ form an Abelian group. This means: Since the group of the $T_{\mathbf{R}_n}$ is Abelian, in the space $\{\varphi_l\}$ with $l \in \{1 \dots f\}$ there is a similarity transformation of $\varphi_l(\mathbf{r})$ to $\tilde{\varphi}_l(\mathbf{r})$ and thus of $\Gamma_{m,l}$ to $\tilde{\Gamma}_{m,l}$, such that the matrix $\tilde{\Gamma}_{m,l}$ is diagonal.³ This is also formulated as follows: The irreducible representation of an Abelian group is one-dimensional. Then, we can write:

$$T_{\mathbf{R}_n}\tilde{\varphi}_l(\mathbf{r}) = \tilde{\Gamma}_{l,l}\tilde{\varphi}_l(\mathbf{r}) \quad (4.32)$$

Formally, this equation is the same as (4.29), and it follows that

$$\tilde{\Gamma}_{l,l} = e^{i\mathbf{k}\mathbf{R}_n} \quad (4.33)$$

We summarize:

The translational operators of the Bravais lattice commute with h . $T_{\mathbf{R}_n}$ and h therefore have the same eigenfunctions. The eigenfunctions and eigenvalues of h can be labeled by the eigenvalues of $T_{\mathbf{R}_n}$ or, better, by the vector \mathbf{k} : From now on we will write $\varphi_{\mathbf{k}}(\mathbf{r})$ and $\epsilon(\mathbf{k})$. \mathbf{k} contains three quantum numbers. This labeling is not necessarily complete. The statement that for the eigenfunctions of a crystal we have

$$T_{\mathbf{R}_n}\varphi_{\mathbf{k}}(\mathbf{r}) = \varphi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k}\mathbf{R}_n}\varphi_{\mathbf{k}}(\mathbf{r}) \quad (4.34)$$

is called *Bloch theorem*.⁴ In order to understand the meaning and the consequences of the Bloch theorem, we have a look at the equation

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \quad (4.35)$$

At first this is a very general ansatz for the eigenfunctions of h , because we have made no assumptions for $u_{\mathbf{k}}(\mathbf{r})$. We have:

$$T_{\mathbf{R}_n}\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}(\mathbf{r}+\mathbf{R}_n)}u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) \quad (4.36)$$

Because for $\varphi_{\mathbf{k}}(\mathbf{r})$ the Bloch's theorem is valid, we obtain

$$T_{\mathbf{R}_n}\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{R}_n}\varphi_{\mathbf{k}}(\mathbf{r}) \quad (4.37)$$

$$= e^{i\mathbf{k}\mathbf{R}_n}e^{i\mathbf{k}\mathbf{r}}u_{\mathbf{k}}(\mathbf{r}) \quad (4.38)$$

³For the proof of this we refer to text books on group theory (e.g. Tinkham).

⁴This was found by Bloch during his PhD thesis, which he carried out in the group of Seitz, but initially he was not aware of the importance of this result.

From this we obtain the equation

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = u_{\mathbf{k}}(\mathbf{r}) \quad (4.39)$$

The function $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the Bravais lattice. This can be formulated as follows: The solutions of the single-particle Schrödinger equation of a periodic crystal have the form of a plane wave that is modulated by a function with lattice periodicity. $\varphi_{\mathbf{k}}(\mathbf{r})$ generally does not have the periodicity of the lattice, but $|\varphi_{\mathbf{k}}(\mathbf{r})|^2$. This gives rise to a second formulation of Bloch's theorem: Due to the translational invariance of the Hamilton operator the eigenfunctions have the following form:

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad \text{with } u_{\mathbf{k}}(\mathbf{r}) \text{ having the periodicity of the Bravais lattice} \quad (4.40)$$

This form of the eigenfunctions of h gives a hint to the physical meaning of the vectors \mathbf{k} . When looking at the special case $v^{\text{eff}}(\mathbf{r}) = \text{constant}$ we know that the solutions are simple plane waves:

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_g}} e^{i\mathbf{k}\mathbf{r}} \quad (4.41)$$

I.e., in this case the function $u_{\mathbf{k}}(\mathbf{r})$ is constant. V_g is the volume of the base region. This means: When going to a constant potential (infinitesimal translational invariance) \mathbf{k} becomes identical to the wave vector. We note that the vector \mathbf{k} , as appearing here, (for crystals) is not uniquely defined. This is because different vectors \mathbf{k} yield the same eigenvalue $e^{i\mathbf{k}\mathbf{R}_n}$ of $T_{\mathbf{R}_n}$. This will be investigated more closely now.

4.3 The Reciprocal Lattice

Since the vector \mathbf{k} appears in a scalar product and in an exponent, it is not uniquely defined. We have

$$e^{i\mathbf{k}'\mathbf{R}_n} = e^{i\mathbf{k}\mathbf{R}_n} \quad \text{for } \mathbf{k}' = \mathbf{k} + \mathbf{G}_m \quad , \quad (4.42)$$

if

$$\mathbf{G}_m \mathbf{R}_n = 2\pi N \quad \text{with } N \text{ integer} \quad . \quad (4.43)$$

All vectors \mathbf{k}' defined by Eq. (4.42) label the same eigenvalue and the same eigenfunction of $T_{\mathbf{R}_n}$. How does the set of \mathbf{G} -vectors defined by (4.42) look like? We define:

$$\begin{aligned} \mathbf{b}_1 &= \frac{2\pi}{\Omega} (\mathbf{a}_2 \times \mathbf{a}_3) \\ \mathbf{b}_2 &= \frac{2\pi}{\Omega} (\mathbf{a}_3 \times \mathbf{a}_1) \\ \mathbf{b}_3 &= \frac{2\pi}{\Omega} (\mathbf{a}_1 \times \mathbf{a}_2) \end{aligned} \quad (4.44)$$

Here the vectors \mathbf{a}_i shall be the primitive vectors and $\Omega = \mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)$ is the volume of the primitive unit cell. The vectors \mathbf{G}_m then are

$$\mathbf{G}_m = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \quad (4.45)$$

direct lattice	reciprocal lattice
sc	sc
hexagonal	hexagonal
fcc	bcc
bcc	fcc

Table 4.6: Four important Bravais lattices in direct space and the corresponding Bravais lattices in reciprocal space.

with m_i being an integer number. This lattice of \mathbf{G}_m -vectors defined in \mathbf{k} space is called the reciprocal lattice. (Vectors in real space have the dimension length. Vectors in reciprocal space have the dimension 1/length.)

The vectors of the reciprocal lattice satisfy the condition (Eq. (4.43)), and the basis vectors of the reciprocal lattice are defined by Eq. (4.44), or by

$$\mathbf{a}_i \mathbf{b}_j = 2\pi \delta_{i,j} \quad . \quad (4.46)$$

The set $\{\mathbf{k} + \mathbf{G}_m\}$ with an arbitrary vector \mathbf{G}_m from reciprocal space labels the eigenfunctions and eigenvalues of the single-particle Schrödinger equation. In order to label this set we use the shortest vector of the set $\{\mathbf{k} + \mathbf{G}_m\}$. From the definition (4.45) we obtain that the reciprocal lattice is a Bravais lattice. Therefore we consider only those \mathbf{k} -vectors, which are closer to point $\mathbf{k} = 0$ (or $\mathbf{G} = 0$) than to any other point of the reciprocal lattice. Such a region of the reciprocal lattice is called “first Brillouin zone” (the corresponding region of the direct lattice is called the “Wigner-Seitz cell”). A two-dimensional example is shown in Fig. 4.11. The construction of Brillouin zones for three-dimensional Bravais lattices is somewhat more complex, but of course also just geometry.

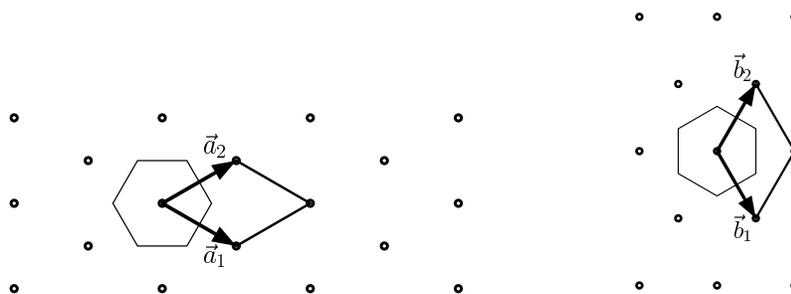


Figure 4.11: A two-dimensional rhombic point lattice. On the left the direct lattice and the Wigner-Seitz cell are shown, and on the right the corresponding reciprocal lattice with the first Brillouin zone.

It can easily be confirmed that the relations between the direct and the reciprocal lattice noted in Table 4.6 are valid. Fig. 4.12 shows the 1st Brillouin zone of four important direct lattices: sc, fcc, bcc, and hexagonal. The point $\mathbf{k} = 0$ is always called Γ . Other directions and points also have specific labels. Later we will need $\epsilon(\mathbf{k})$ for the full range of the Brillouin-Zone of the crystal. For this purpose it is often sufficient to investigate

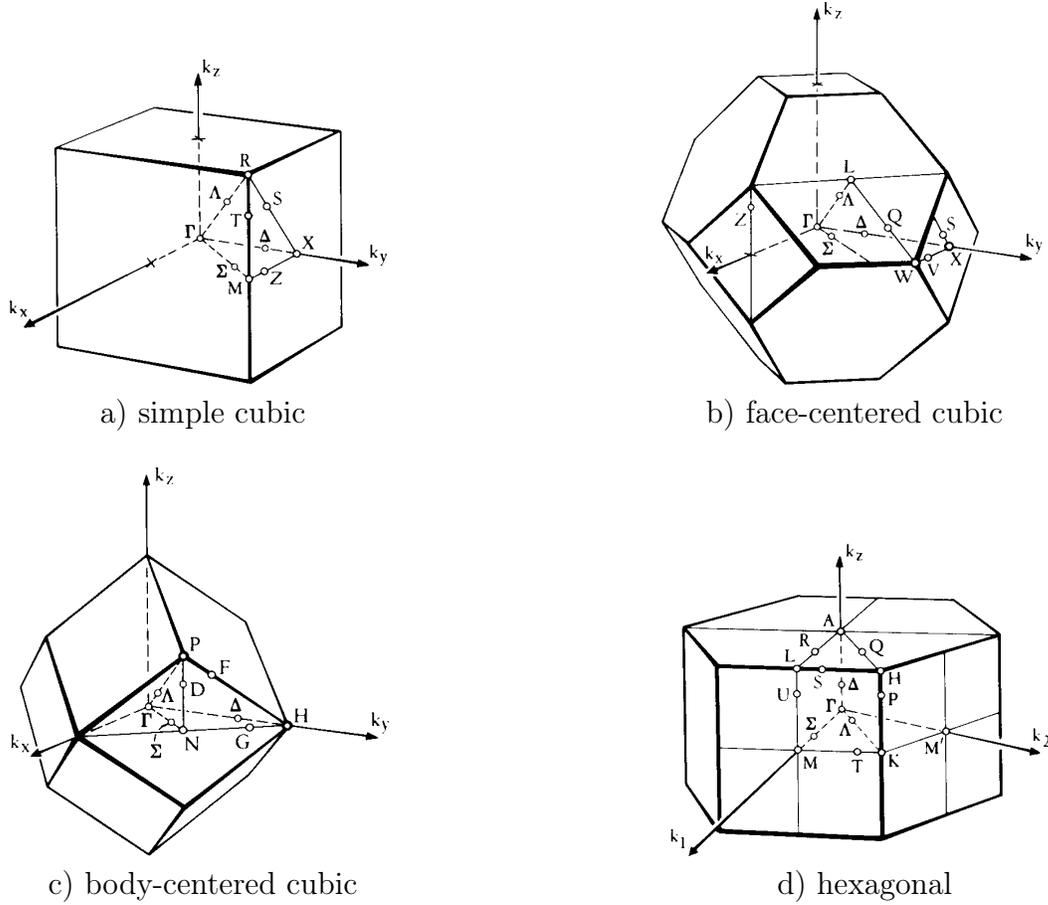


Figure 4.12: Brillouin zones for the simple cubic a), face-centered cubic b), body-centered cubic c), and hexagonal lattice d). The most important symmetry points and lines and their labels are shown.

the function along certain directions or in a small part of the 1st Brillouin zone. The rest is determined by the point symmetry of the lattice. This will be discussed later. Now we will investigate the physical meaning of the reciprocal lattice and of the 1. Brillouin zone for the wave functions of the effective single-particle Schrödinger equation. Due to the translational invariance for the effective potential, $v^{\text{eff}}(\mathbf{r} + \mathbf{R}_n) = v^{\text{eff}}(\mathbf{r})$, only the vectors of the reciprocal lattice appear in the Fourier expansion:

$$v^{\text{eff}}(\mathbf{r}) = \sum_l v^{\text{eff}}(\mathbf{G}_l) e^{i\mathbf{G}_l \mathbf{r}} \quad (4.47)$$

with $\mathbf{G}_l \mathbf{R}_n = 2\pi N$.

For the eigenfunctions of the Schrödinger equation we obtain in a similar way:

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \sum_m C_{\mathbf{G}_m}(\mathbf{k}) e^{i\mathbf{G}_m \mathbf{r}} \quad (4.48)$$

Then, the Kohn-Sham equation in reciprocal space is:

$$\begin{aligned} & \sum_m \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G}_m)^2 C_{\mathbf{G}_m}(\mathbf{k}) e^{i(\mathbf{k} + \mathbf{G}_m)\mathbf{r}} + \sum_l v^{\text{eff}}(\mathbf{G}_l) \sum_m C_{\mathbf{G}_m}(\mathbf{k}) e^{i(\mathbf{k} + \mathbf{G}_m + \mathbf{G}_l)\mathbf{r}} \\ &= \epsilon(\mathbf{k}) \sum_m C_{\mathbf{G}_m}(\mathbf{k}) e^{i(\mathbf{k} + \mathbf{G}_m)\mathbf{r}} \end{aligned} \quad (4.49)$$

For the $C_{\mathbf{G}_m}(\mathbf{k})$ this means:

$$\frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G}_n)^2 C_{\mathbf{G}_n}(\mathbf{k}) + \sum_m v^{\text{eff}}(\mathbf{G}_n - \mathbf{G}_m) C_{\mathbf{G}_m}(\mathbf{k}) = \epsilon(\mathbf{k}) C_{\mathbf{G}_n}(\mathbf{k}) \quad (4.50)$$

For any chosen $\mathbf{k}/$ vector of the 1st Brillouin zone this is a set of equations, which for a certain (given) \mathbf{k} allows for the calculation of the expansion coefficients $C_{\mathbf{G}_n}(\mathbf{k})$. Only those coefficients $C_{\mathbf{G}_n}(\mathbf{k})$ (or plane waves $e^{i(\mathbf{k} + \mathbf{G}_n)\mathbf{r}}$) are coupled by the periodic potential $v^{\text{eff}}(\mathbf{G}_n - \mathbf{G}_m)$, which differ by a reciprocal lattice vector. Equation (4.48) means that a plane wave $e^{i\mathbf{k}\mathbf{r}}$ in the solid does not exist alone, but due to diffraction at the periodic potential plane waves $e^{i(\mathbf{k} + \mathbf{G}_m)\mathbf{r}}$ are added. Equation (4.50) can also be written in matrix form:

$$\sum_m h_{n,m} C_{\mathbf{G}_m}(\mathbf{k}) = \epsilon(\mathbf{k}) C_{\mathbf{G}_n}(\mathbf{k}) \quad (4.51)$$

with

$$h_{n,m} = \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G}_n)^2 \delta_{n,m} + v^{\text{eff}}(\mathbf{G}_n - \mathbf{G}_m) \quad (4.52)$$

This means that for each vector \mathbf{k} one matrix equation has to be solved, which provides a number of eigenfunctions and eigenvalues. Therefore, next to \mathbf{k} another quantum number will be introduced and we write: $\varphi_{n,\mathbf{k}}(\mathbf{r}), \epsilon_n(\mathbf{k})$. We find that equation (4.50) or (4.51) and (4.52) are often quite useful for real systems and can be calculated. This is in particular pronounced if it is combined with the so-called pseudopotential theory (cf. part V). The main problem is the dimension of the matrix of Eq. (4.53), and in particular the calculation of the non-diagonal elements or the sums in Eq. (4.50). We find that $v^{\text{eff}}(\mathbf{G}_l)$ rapidly decreases with increasing length of the \mathbf{G}_l and often only the first terms in $v^{\text{eff}}(\mathbf{G}_l)$ differ from zero. If this is true, then the evaluation of Eq. (4.50) or (4.51) and (4.52) is possible, because the non-diagonal part of the matrix $h_{n,m}$ is then of finite size. We have introduced two quantum numbers: the vector \mathbf{k} , which is limited to the first Brillouin zone and the discrete index n . In order to illustrate this on a simple level, we examine a one-dimensional example and a very weakly varying potential. Then, the energies are

$$\epsilon_n(\mathbf{k}) \approx \frac{\hbar^2}{2m} (\mathbf{k} + \mathbf{G}_n)^2 \quad . \quad (4.53)$$

Figure 4.13 shows the parabola for $\mathbf{G} = 0$ as a dotted line. We have found that due to periodicity it is reasonable and sufficient to constrain \mathbf{k} to the first Brillouin zone. This is possible if we look at $\mathbf{k} + \mathbf{G}_n$, i.e., if we fold back parts, which are outside the first Brillouin zone, of the dotted curve, by a suitable vector \mathbf{G}_n . The part of Fig. 4.14 in the range of the 1st Brillouin zone, or the function $\epsilon_n(\mathbf{k})$ is called the “band structure”.

For the further discussion of the importance of the reciprocal lattice we have taken a side view at a crystal (cf. Fig. 4.14). We can see that the Bravais point lattice can also be

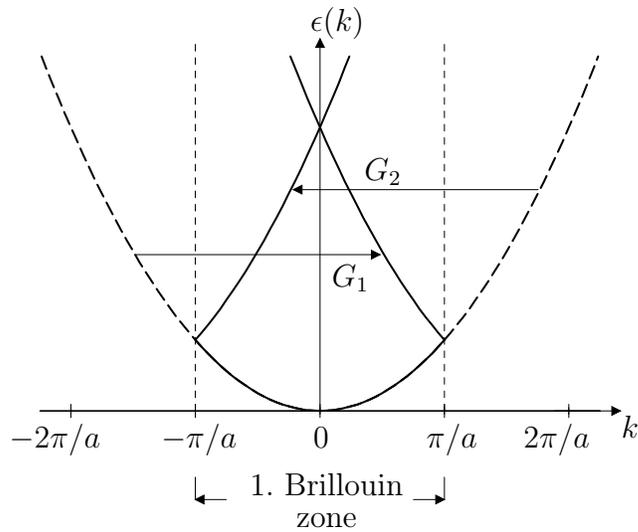


Figure 4.13: First Brillouin zone of a one-dimensional lattice of lattice constant a . \mathbf{G}_1 and \mathbf{G}_2 are the shortest non-zero reciprocal lattice vectors (length $2\pi/a$). The straight line gives the function $\epsilon_n(\mathbf{k})$.

regarded as a regular arrangement of planes. There is a close relation between the vectors of the reciprocal lattice and such parallel planes (the straight, the dashed-dotted and the dashed planes in Fig. 4.14): For each family of lattice planes being separated by a distance d there are reciprocal lattice vectors perpendicular to these planes. The shortest of these reciprocal lattice vectors has the length $2\pi/d$. The inverse of this statement is also true: For each reciprocal lattice vector \mathbf{G} there is a family of lattice planes perpendicular to \mathbf{G} . This close relation between planes of the crystal and the reciprocal lattice vectors implies that one generally can label the planes in the crystal lattice by the shortest reciprocal lattice vector being perpendicular to these planes.

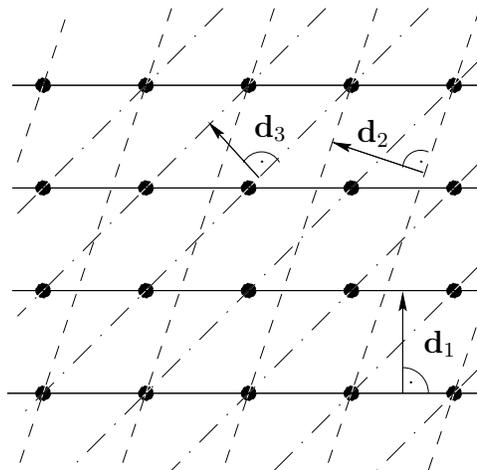


Figure 4.14: Side view of a crystal (i.e., of the Bravais point lattice)

These labels are called *Miller indices*. In general, they are defined by the coordinates of the shortest possible reciprocal lattice vector of the *Bravais lattice* perpendicular to this plane; by definition, they are always integer numbers and have no common factor. Note that,

usually, the Miller indices in any cubic lattice are referred to by the *conventional* (cubic) cell, which for the fcc- and bcc-lattices is a sc lattice with a basis. Figure 4.15 shows three important lattice planes for cubic crystals and their labels. In fcc and bcc lattices, this convention leads to a formal disconnection between lattice planes and actual reciprocal lattice vectors: Since the primitive cells (one atom per cell) of both lattices are smaller than the conventional cell (2 atomic for bcc, 4 atoms for fcc), some of their reciprocal lattice vectors appear to be missing when written down in a in the “simple cubic” notation. For example, for the bcc lattice we find that only (i, j, k) with $i + j + k = \text{even number}$ is allowed, for the fcc lattice the indices of reciprocal lattice vectors have to be either all odd or all even numbers. Thus, the fcc, bcc, and sc lattices all have (111) lattice planes as denoted by Miller indices and shown in Fig. 4.15, but the shortest corresponding reciprocal lattice vector in bcc would have the indices (222).

Now we have a look at the origin of a reflection of electrons at (or in) a crystal, the crystal being composed of planes. At first we imagine that a plane wave of electrons or X-rays propagates with wave vector \mathbf{k} . From the discussion of Eq. (4.48) we know that this wave is not a stationary state (eigenstate). This is obtained without solving the Schrödinger equation.

The wave is reflected at the crystal planes (cf. Fig. 4.16). We have constructive interference (Bragg reflection), if the path difference of the waves scattered at different planes is a multiple of the wave vector,

$$2d \sin \theta = m\lambda = m \frac{2\pi}{|\mathbf{k}|} \quad , \quad (4.54)$$

where m is an arbitrary integer number and λ the wave length of the plane waves.

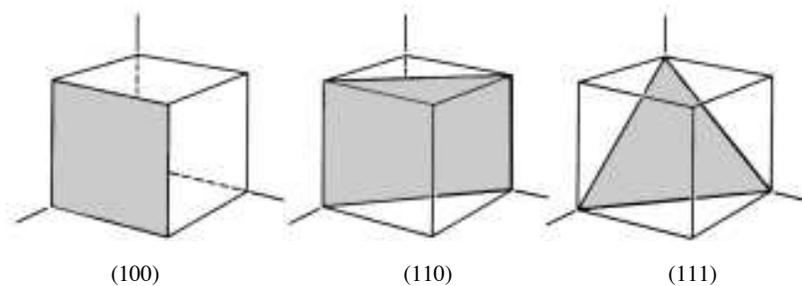


Figure 4.15: Important crystal planes in a cubic crystal

We rewrite this condition by using that there are reciprocal lattice vectors which are perpendicular to the planes of interest and which have the following length:

$$|\mathbf{G}_m| = m \frac{2\pi}{d} \quad (4.55)$$

From Eq. (4.54) we obtain

$$2d \frac{\mathbf{G}_m \mathbf{k}}{|\mathbf{G}_m| |\mathbf{k}|} = m \frac{2\pi}{|\mathbf{k}|} \quad . \quad (4.56)$$

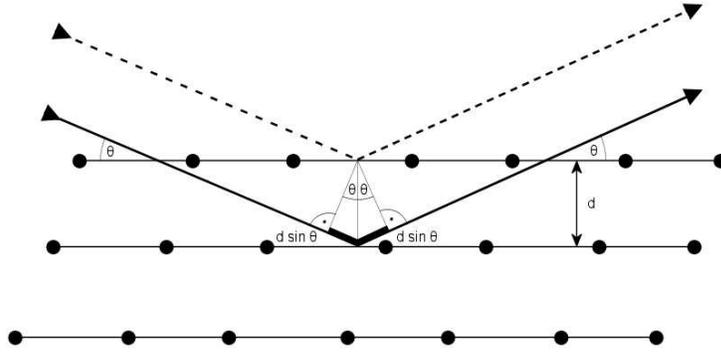


Figure 4.16: Bragg reflection at a crystal

Here, we use that

$$\mathbf{k} \cdot \mathbf{G}_m = |\mathbf{k}| |\mathbf{G}_m| \sin \theta \quad .$$

The condition for constructive interference (cf. Eq. (4.56)) can also be written as:

$$2\mathbf{k} \cdot \mathbf{G}_m = |\mathbf{G}_m|^2 \quad (4.57)$$

or

$$\mathbf{k}^2 = (\mathbf{k} - \mathbf{G}_m)^2 \quad . \quad (4.58)$$

This means: Waves with wave vectors \mathbf{k} fulfilling the requirement (Eq. (4.58)) (i.e., the Bragg condition), cannot propagate in the crystal. They are reflected in other directions. The condition (Eq. (4.58)) is obviously fulfilled at the border of the Brillouin zone, i.e., $\mathbf{k} = \frac{\mathbf{G}_m}{2}$.

4.4 Periodic Boundary Conditions

For many questions it is reasonable (without influencing the physical results),⁵ to use periodic boundary conditions. These have been discussed already in chapter 2. From now on we will assume that the crystal is sufficiently large, so that surface effects do not play a role. Then, also the shape of the crystal is not important. The dimensions of the crystal shall be $L_i \mathbf{a}_i$, with L_i being a large integer number. The volume of the base region is then

$$V_g = L_1 L_2 L_3 \Omega \quad (4.59)$$

with Ω , the volume of the primitive unit cell:

$$\Omega = \mathbf{a}_1 (\mathbf{a}_2 \times \mathbf{a}_3) \quad (4.60)$$

Periodic boundary conditions for the wave function then mean that we have:

$$\varphi_{n,\mathbf{k}}(\mathbf{r} + L_j \mathbf{a}_j) = \varphi_{n,\mathbf{k}}(\mathbf{r}) \quad . \quad (4.61)$$

⁵Problems arise if the boundary plays a role, e.g. for magnetic effects.

Due to the Bloch condition we have:

$$\varphi_{n,\mathbf{k}}(\mathbf{r} + L_j \mathbf{a}_j) = e^{iL_j \mathbf{a}_j \mathbf{k}} \varphi_{n,\mathbf{k}}(\mathbf{r}) \quad . \quad (4.62)$$

From (4.61) and (4.62) we obtain:

$$e^{iL_j \mathbf{a}_j \mathbf{k}} = 1 \quad \text{for } j = 1, 2, 3 \quad (4.63)$$

The possible \mathbf{k} vectors fulfill this condition

$$L_j \mathbf{a}_j \mathbf{k} = 2\pi M \quad (4.64)$$

with M being an arbitrary integer number. If we now write

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

we obtain

$$k_j = \frac{M}{L_j} \quad . \quad (4.65)$$

L_j is determined by the size of the base region. M is an arbitrary integer number. Therefore, we are dealing (because of periodic boundary conditions) with a discrete, but arbitrarily dense packed set of \mathbf{k} vectors. In direction \mathbf{b}_j the distance of two \mathbf{k} -points is $1/L_j$. The volume in \mathbf{k} -space referring to a \mathbf{k} -point then is

$$V_{\mathbf{k}} = \frac{\mathbf{b}_1}{L_1} \left(\frac{\mathbf{b}_2}{L_2} \times \frac{\mathbf{b}_3}{L_3} \right) \quad . \quad (4.66)$$

Since $\mathbf{b}_1(\mathbf{b}_2 \times \mathbf{b}_3)$ is the volume of the first Brillouin zone, we obtain

$$V_{\mathbf{k}} = \frac{(2\pi)^3}{L_1 L_2 L_3 \Omega} = \frac{(2\pi)^3}{V_g} \quad (4.67)$$

with V_g being the volume of the base region.

The density of \mathbf{k} -points then is $V_g/(2\pi)^3$. This is the same result as we obtained earlier for free electrons (cf. Eq. (2.7) and the following). Before, we have described the wave function as a simple plane wave. Here we have made no assumptions concerning the wave functions, but we have used the fact that they satisfy Bloch's theorem.