

Chapter 1

Atomic Structure

1.1 Crystals and lattices

Ordered matter is in the form of a crystal, a structure or pattern repeated periodically in three dimensions. For the periodic structure, one can define an underlying **lattice**, which is a **purely geometrical** object, whereas by the crystal, we mean the matter (electrons and nuclei) that have a periodic structure. Lattices are **classified according to their symmetry**, and there are 7 types of them. They are called “Bravais” lattices. A lattice is defined by its set of translation, or primitive vectors ($\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3$), also called basis vectors. A general vector of the lattice can be written as $\mathbf{R} = n_1\mathbf{R}_1 + n_2\mathbf{R}_2 + n_3\mathbf{R}_3$ with (n_1, n_2, n_3) integer numbers. We will denote the angles between the basis vectors by $\alpha = (\widehat{\mathbf{R}_2, \mathbf{R}_3}), \beta = (\widehat{\mathbf{R}_1, \mathbf{R}_3}), \gamma = (\widehat{\mathbf{R}_1, \mathbf{R}_2})$. These three vectors define a volume called the unit cell. The same lattice can be represented by different sets of primitive vectors, but they all will naturally have the same volume for their unit cell. Within the unit cell, there is an atomic “pattern” which is identically repeated outside in other cells. The symmetry of a crystal is defined by its geometric lattice as well as the symmetry of this pattern. Note also that the position of the lattice with respect to the atoms can be arbitrary, and we need not put atoms at the corner of a cell.

$$\text{Crystal} = \text{Geometric lattice} + \text{Atomic pattern}$$

What we probe, or what we see, is the atomic pattern. Given this pattern, how can we deduce the lattice and its translation vectors? The answer is

trivial for a mono-atomic crystal, as in this case, what we see is just the Bravais lattice. The question might be harder to answer when there are many identical but inequivalent atoms in the unit cell. A translation vector of the lattice must take an atom to the same atom placed in the neighboring cell, but any vector connecting two atoms is not necessarily a translation vector! The lattice can be deduced by inspecting along which directions the atomic pattern is repeated.

Bravais lattices are classified as: ¹

Triclinic: with the three basis vectors are of arbitrary length and directions. It only has inversion symmetry.

Monoclinic: where one basis vector is orthogonal to the plane of the other two, their lengths is still arbitrary. Monoclinic lattices can be either **primitive** or **base-centered**. Their point group is C_{2h} , and they are defined with 4 parameters (R_1, R_2, R_3, γ).

Orthorhombic: with the three basis vectors being perpendicular ($\alpha = \beta = \gamma = \pi/2$). They are thus defined by only 3 parameters (R_1, R_2, R_3), and their point group is D_{2h} . They can either be **primitive**, **base-centered**, **body-centered** or **face-centered**.

Tetragonal: with the three basis vectors being perpendicular ($\alpha = \beta = \gamma = \pi/2$), and the base being a square ($R_1 = R_2$). They are thus defined by only 2 parameters (R_1, R_3), and their point group is D_{4h} . They can either be **primitive** or **body-centered**.

Trigonal or Rhombohedral: the three basis vectors form a rhombus ($\alpha = \beta = \gamma; R_1 = R_2 = R_3$), They are defined by 2 parameters (R_1, α), and their point group is D_{3d} .

¹For completeness, below, we give the definition of the point groups:

The mirror symmetries with their plane perpendicular to the rotation axis are called σ_h (h for horizontal) and mirror symmetries with their plane containing the rotation axis are called σ_v (v for vertical).

- C_n is the group of rotations of angle multiples of $2\pi/n$ ($n = 2, 3, 4, 6$) (n elements)

- S_n is the group of elements $\sigma_h \times C_n$ (n elements)

- C_{nh} is created by adding σ_h to C_n ($2n$ elements)

- C_{nv} is created by adding σ_v to C_n ($2n$ elements - non Abelian)

- D_n is created by adding C_2 to C_n with its axis perpendicular to the axis of C_n ($2n$ elements - non Abelian)

- D_{nh} is created by adding σ_h to D_n with its axis perpendicular to the axis of C_n ($4n$ elements)

- D_{nd} is created by adding σ_d to D_n with its plane containing the axis of C_n and bisecting the angle between two adjacent C_2 axes. ($4n$ elements - non Abelian)

Hexagonal: defined by $(\alpha = \beta = \pi/2; \gamma = 2\pi/3)$, and $(R_1 = R_2)$. Their point group is D_{6h} .

Cubic: defined by $(\alpha = \beta = \gamma = \pi/2)$, and $(R_1 = R_2 = R_3)$. Their point group is O_h . They can either be **primitive**, **body-centered** or **face-centered**.

1.1.1 Fourier expansion in one dimension

Physical quantities such as the electron density or potential energy in an ideal crystal are a periodic function. They can therefore be Fourier expanded. For simplicity, in one dimension, we can write:

$$V(x) = \sum_{n=-\infty}^{\infty} \hat{V}_n e^{i2\pi nx/a}$$

where a is the lattice parameter and the Fourier coefficients \hat{V}_n are defined as: $\hat{V}_n = \frac{1}{a} \int_0^a V(x) e^{-i2\pi nx/a} dx$. This can be verified by putting back the above expression for the Fourier coefficients in the expansion:

$$\begin{aligned} V(x) &= \sum_{n=-\infty}^{\infty} \left[\frac{1}{a} \int_0^a V(y) e^{-i2\pi ny/a} dy \right] e^{i2\pi nx/a} & (1.1) \\ &= \int_0^a V(y) \sum_{n=-\infty}^{\infty} e^{i2\pi n(x-y)/a} \frac{dy}{a} \\ &= \int_0^a V(y) \sum_m \delta(x - y - ma) dy = V(x) \end{aligned}$$

by virtue of the Poisson summation formula: $\sum_n e^{i2\pi nt/a} = \sum_m a\delta(t - ma)$, which is really the Fourier expansion of the “comb” function. Well this statement was just equivalent to the original Fourier expansion! An easier verification can come by substituting the Fourier expansion of $V(x)$ in the definition of \hat{V} :

$$\begin{aligned} \hat{V}_n &= \frac{1}{a} \int_0^a \left[\sum_{m=-\infty}^{\infty} \hat{V}_m e^{i2\pi mx/a} \right] e^{-i2\pi nx/a} dx & (1.2) \\ &= \sum_{m=-\infty}^{\infty} \hat{V}_m \frac{1}{a} \int_0^a e^{i2\pi(m-n)x/a} dx \\ &= \sum_{m=-\infty}^{\infty} \hat{V}_m \frac{e^{i2\pi(m-n)} - 1}{i2\pi(m-n)} \end{aligned}$$

$$= \sum_{m=-\infty}^{\infty} \hat{V}_m \delta_{m,n} = \hat{V}_n$$

We have of course assumed that the sums and integrals were uniformly convergent and thus could be interchanged.

1.1.2 Fourier expansion and reciprocal space

As the concept of reciprocal space is trivial in one dimension, we will now proceed to generalize the Fourier expansion to 3 space dimensions. A periodic function in 3D has the following property:

$$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r} + n_1 \mathbf{R}_1 + n_2 \mathbf{R}_2 + n_3 \mathbf{R}_3)$$

with (n_1, n_2, n_3) arbitrary integers. So, if we can expand the vector \mathbf{r} in the $(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$ basis as $\mathbf{r} = x_1 \mathbf{R}_1 + x_2 \mathbf{R}_2 + x_3 \mathbf{R}_3$ with x_i real numbers, then the above 1D definition of the Fourier series can be written for each x_i :

$$\begin{aligned} V(x_1, x_2, x_3) &= \sum_{m_1=-\infty}^{\infty} \hat{V}_{m_1}(x_2, x_3) e^{i2\pi m_1 x_1} \\ &= \sum_{m_1, m_2=-\infty}^{\infty} \hat{V}_{m_1, m_2}(x_3) e^{i2\pi(m_1 x_1 + m_2 x_2)} \\ &= \sum_{m_1, m_2, m_3=-\infty}^{\infty} \hat{V}_{m_1, m_2, m_3} e^{i2\pi(m_1 x_1 + m_2 x_2 + m_3 x_3)} \end{aligned} \quad (1.3)$$

This expression is clearly invariant if any of the x_i is shifted to $x_i + n_i$ (or \mathbf{r} to $\mathbf{r} + \mathbf{R}_i$). In order to be able to write more simply the exponent as $i\mathbf{r} \cdot \mathbf{G}$, we have to introduce 3 new basis vectors $(\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3)$ such that $\mathbf{G} = m_1 \mathbf{G}_1 + m_2 \mathbf{G}_2 + m_3 \mathbf{G}_3$ and

$$\mathbf{G}_i \cdot \mathbf{R}_j = 2\pi \delta_{i,j}$$

The newly introduced vectors form the **basis of the reciprocal space**. The expression for the Fourier expansion can now be written as:

$$V(\mathbf{r}) = \sum_{m_1, m_2, m_3=-\infty}^{\infty} \hat{V}_{m_1, m_2, m_3} e^{i\mathbf{G}_{m_1, m_2, m_3} \cdot \mathbf{r}} = \sum_{\mathbf{G}} \hat{V}_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} \quad (1.4)$$

with

$$\hat{V}_{\mathbf{G}} = \frac{1}{\Omega_c} \int_{unit\ cell} V(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d\mathbf{r} \quad (1.5)$$

As expected, Ω_c is the volume of the unit cell: $\Omega_c = \mathbf{R}_1 \cdot (\mathbf{R}_2 \times \mathbf{R}_3)$. Thus, we see that the \mathbf{G} vectors of the reciprocal lattice naturally appear as they are needed for the Fourier expansion of any periodic function of the lattice. Similar to the 1D case, eq. ??, we have the following relation satisfied for an arbitrary vector \mathbf{k} :

$$\frac{1}{\Omega_c} \int_{unit\ cell} e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} = \delta_{\mathbf{k},\mathbf{G}}$$

where δ (with subscripts) is the Kroenecker delta function, as opposed to $\delta(x)$ (with arguments) which is the Dirac delta function. The Poisson summation formula, which is equivalent to the definition of a Fourier expansion is written as:

$$\sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} = \Omega_c \sum_{\mathbf{R}} \delta(\mathbf{r} - \mathbf{R})$$

Physicists also sometimes use it as:

$$\sum_{\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} = N \delta_{\mathbf{r},\mathbf{R}}$$

where N is the infinite number of cells or \mathbf{R} (or \mathbf{G}) vectors in the lattice. Clearly, when \mathbf{r} is a lattice vector, all terms in the sum are equal to 1 and the result is N , else, the result is zero due to destructive interference effects.

1.1.3 Indexing of planes in the lattice: the Miller indices

Given a Bravais lattice with primitive vectors \mathbf{R}_i , we can consider a plane passing through the end of 3 translation vectors as: $(n_1\mathbf{R}_1, n_2\mathbf{R}_2, n_3\mathbf{R}_3)$. The inverses of the 3 integers define the Miller indices. However as the inverse is not necessarily an integer, the **Miller indices** are the smallest integers with the same ratio as $(1/n_1, 1/n_2, 1/n_3)$. They are usually labeled as (hkl) . Clearly a given (hkl) refers to a *family of parallel planes*. One can show that the vector $\mathbf{r} = \sum_{i=1,3} x_i \mathbf{R}_i$ belongs to a plane with Miller indices (hkl) if and only if $\mathbf{r}\cdot\mathbf{G} = integer$ with $\mathbf{G} = h\mathbf{G}_1 + k\mathbf{G}_2 + l\mathbf{G}_3$. Each value of the integer refers to \mathbf{r} belonging to one plane in the family.

Crystalline “directions” use a different convention. A direction defined by $\mathbf{R} = n_1\mathbf{R}_1 + n_2\mathbf{R}_2 + n_3\mathbf{R}_3$ is labeled as $[n_1n_2n_3]$.

A family of planes related to the (hkl) planes by a rotational symmetry operation of the lattice are denoted by $\langle hkl \rangle$.

$\{hkl\}$ refers to all the planes parallel to the direction $[hkl]$.

1.1.4 Wigner-Seitz cell and Brillouin zones

The Wigner-Seitz cell is defined as the cell obtained by bisecting the smallest translation vectors of the same origin, by planes perpendicular to these vectors. The remaining volume limited by these planes is called the Wigner-Seitz cell. Similar to the unit cell, this cell also, if repeated periodically by translations of the primitive vectors, will cover the whole space without leaving any voids. Its volume is equal to that of the unit cell Ω_c .

The first Brillouin zone is the WS cell of the reciprocal space.