# Crystal Basics

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(Dated: February 18, 2002)

Basic concepts about crystals with some mathematical details. I discuss how special wavevectors are important in periodic structures (the reciprocal lattice). This is applied to X-ray diffraction and the nature of electronic states in a solid. These notes complement your lecture notes but do not replace them.

## I. PERIODICITIES

### A. Reciprocal Lattice

A crystalline solid consists of a regular lattice of atoms. These atoms scatter photons and electrons. For instance, an injected electron would see a potential $U(\mathbf{r})$ which is periodic in space. This potential affects the motion of the electron in the solid, giving rise bands of allowed energies. You should understand how electron energy bands come about by the end of this course.

Similarly, the scattering of photons gives rise to regular patterns in the diffracted waves. X-ray crystallography makes use of this as an experimental probe of the crystal structure.

The periodicity of a crystalline lattice can be described by specifying how each unit cell repeats and what is in each unit cell. I will focus on just one atom per unit cell. Then the positions of the atoms in the lattice can be written as:

$$\mathbf{R} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3 \qquad (m_i \text{ integers}). \tag{1}$$

More importantly, the *relative* displacement between any two atoms can also be written in this form.

As mentioned above, these atoms present a periodic potential $U(\mathbf{r})$ to electrons in this solid. The periodicity of the potential means that $U(\mathbf{r})$ has the mathematical property:

$$U(\mathbf{r}+\mathbf{R}) = U(\mathbf{r}) \qquad \text{for all lattice vectors } \mathbf{R} \tag{2}$$

We now want to see how to describe an arbitrary periodic function by using simpler periodic functions that we understand. The simplest periodic function we know is, of course, the

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plane wave. It is specified by a wavelength $\lambda$ and a direction of travel. It is more convenient to use the wavevectors $\mathbf{G}$. The direction of $\mathbf{G}$ is the direction in which a periodic feature repeats itself. The magnitude of $\mathbf{G}$ is $|\mathbf{G}| = 2\pi/\lambda$. The plane wave can then be written as $\exp(i\mathbf{G}\cdot\mathbf{r})$.

To construct a general periodic function, we can put plane waves with different $\mathbf{G}$'s together. This is the mathematics of Fourier series. You have seen Fourier series in one dimension:

$$U(x) = \sum_K \left[A_K \cos(Kx) + B_K \sin(Kx)\right] , \qquad K = 2\pi n/a \quad (n = 0, 1, 2, \ldots) \tag{3}$$

for a function with period $a$. It is more convenient to write this as

$$U(x) = \sum_G U_G \, e^{iGx} , \qquad G = 2\pi n/a \quad (n = 0, \pm 1, \pm 2, \ldots) \tag{4}$$

The coefficients are related by: $A_K = (U_K + U_{-K})$ and $B_K = i(U_K - U_{-K})$.

Let us now extend this Fourier analysis to three dimensions:

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}} \, e^{i\mathbf{G}\cdot\mathbf{r}} \tag{5}$$

where the sum is over all allowed values of $\mathbf{G}$.

*Q1: What are the allowed wavevectors for a given lattice?*

Each plane-wave component of $U(\mathbf{r})$ in (5) must have the same periodic property (2) as the function itself:

$$\begin{aligned} e^{i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R})} &= e^{i\mathbf{G}\cdot\mathbf{r}} \\ \Rightarrow e^{i\mathbf{G}\cdot\mathbf{R}} &= 1 \qquad \text{for all lattice vectors } \mathbf{R} \end{aligned} \tag{6}$$

This reduces to what we know in one dimension (4): $G$ is an integer multiple of $2\pi/a$. (Recall that $e^{2\pi n i} = 1$ for integer $n$.)

In three dimensions, the condition (6) is satisfied for all lattice displacements $\mathbf{R}$ (see eqn (1)), if and only if $\mathbf{G}\cdot\mathbf{a}_i = 2\pi\times$(integer) for each of the lattice directions $i = 1, 2, 3$. This means that the $\mathbf{G}$'s themselves form a lattice, the **reciprocal lattice**:

$$\mathbf{G} = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3 \qquad (h_i \text{ integers}) \tag{7}$$

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij} \tag{8}$$

Explicitly, we can choose

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} , \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} , \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \tag{9}$$

*A1: The reciprocal lattice vectors* $\mathbf{G}$ *are the wavevectors allowed in the Fourier series for the periodic potential.* Any other plane-wave component with a different wavevector would be inconsistent with the periodicity of the lattice.

The Fourier coefficients, $U_{\mathbf{G}}$, are given by:

$$U_{\mathbf{G}} = \frac{1}{\Omega} \int_{\substack{\text{unit}\\\text{cell}}} U(\mathbf{r})\, e^{-i\mathbf{G}\cdot\mathbf{r}} d^3\mathbf{r} \tag{10}$$

where $\Omega = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ is the volume of the (real-space) unit cell. You can check that this reduces to the familiar answer in one dimension. You can also check that this reduces to what you might expect for a cubic lattice.

*Q2: What do the different wavevectors correspond to geometrically?*

The plane wave is called a plane wave for a good reason. The set of points $\mathbf{r}$ where the function $\exp(i\mathbf{G}\cdot\mathbf{r})$ has the same phase (*i.e.*, $\mathbf{G}\cdot\mathbf{r} = \phi$ constant) consists of parallel planes in three dimensions. (In two dimensions, these are lines, such as the water ripples along a beach.) The vector $\mathbf{G}$ is the normal to these planes. The separation of the planes is the wavelength of the plane wave: $\lambda = 2\pi/|\mathbf{G}|$.

From (6), we see that $\mathbf{G}\cdot\mathbf{R} = 2\pi\times(\text{integer})$. This means that the function $\exp(i\mathbf{G}\cdot\mathbf{r})$ has the same phase (modulo $2\pi$) at all atomic positions ($\mathbf{r} = \mathbf{R}$) on the lattice. So, we see that each $\mathbf{G}$ represents a way of grouping atoms in the solid into a parallel set of planes. These are called **Bragg planes**. A shorthand for specifying these planes is to use the integer coefficients of $\mathbf{G}$ in (7). They are the **Miller indices**: $[h_1, h_2, h_3]$.

*A2: Each wavevector* $\mathbf{G}$ *can be associated with a set of atomic planes.*

However, this association is not unique. More precisely, *a set of Bragg planes is represented by a set of* $\mathbf{G}$*'s along a line in reciprocal space through the origin.* This is because, if every constant-phase plane for $\exp(i\mathbf{G}\cdot\mathbf{r})$ contains atoms, then the constant-phase planes of $\exp(2i\mathbf{G}\cdot\mathbf{r})$ have half the period and only every other one intersects atomic positions. Similarly, for $3\mathbf{G}$, $4\mathbf{G}$, and so on. This is why we have to divide out any common factors in the Miller indices in order to have a *unique* definition of the Bragg planes: $[1, 2, 2]$ is legitimate, but not $[2, 4, 4]$ or $[3, 6, 6]$.

So, suppose we specify a set of Bragg planes with Miller indices $[h_1, h_2, h_3]$, then the set of reciprocal lattice vectors associated with it are:

$$\mathbf{G} = N(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3) \qquad \text{for non-zero integer } N. \tag{11}$$

The idea of Bragg planes is useful for understanding X-ray diffraction in crystals (see later).

## B. Brillouin zones

The result above picks out special wavectors $\mathbf{G}$ in the space of all possible vectors $\mathbf{k}$. They form a lattice in this $\mathbf{k}$-space or "reciprocal space". We can define a unit cell for this reciprocal lattice.

The Brillouin zone is a particular choice of unit cell. It is the one constructed from the Wigner-Seitz method. The particular Wigner-Seitz cell that contains the origin $\mathbf{k} = 0$ is called the first Brillouin zone. Other unit cells/Brillouin zones are copies of the first Brillouin zone, translated by a reciprocal lattice vector $\mathbf{G}$. This means that, for any wavevector

$\mathbf{q}$, there is a wavevector $\mathbf{k}$ in the first Brillouin zone related to it by $\mathbf{k} = \mathbf{q} - \mathbf{G}$. So, $\exp(i\mathbf{q}\cdot\mathbf{R}) = \exp(i\mathbf{k}\cdot\mathbf{R})$ for any displacement vector on the real-space lattice $\mathbf{R}$. In other words, if we perform only lattice translations, we cannot tell the difference between $\mathbf{k}$ and $\mathbf{q}$. We will make use of this later.

## II. BRAGG DIFFRACTION

X-ray crystallography relies on the scattering of X-rays from a crystal. How does the structure of the crystal affect the scattering?

Consider what happens when a light wave with wavevector $\mathbf{k}_{\text{in}}$ encounters a single atom. The scattering cross-section is typically small. Most of the wave will not be affected, but there is a small chance that it will be scattered. The scattered part will have a different wavevector $\mathbf{k}_{\text{out}}$. If the photon energy does not match any atomic transitions, the scattering will be *elastic*, *i.e.* there is no transfer of energy between the atom and the photon. Since the photon energy is $\hbar\omega = c|\mathbf{k}_{\text{in}}|$, the incoming and outgoing wavevectors must have the same magnitudes (see Fig. 1a):

$$|\mathbf{k}_{\text{out}}| = |\mathbf{k}_{\text{in}}| \tag{12}$$

The change of momentum $\hbar\mathbf{q} \equiv \hbar(\mathbf{k}_{\text{out}} - \mathbf{k}_{\text{in}})$ can be anything as long as it obeys the elastic condition above. In terms of $\mathbf{q}$, this condition is

$$\begin{aligned} \mathbf{k}_{\text{out}}^2 = (\mathbf{k}_{\text{in}} + \mathbf{q})^2 &= \mathbf{k}_{\text{in}}^2 \\ \Rightarrow \qquad 2\mathbf{k}_{\text{in}}\cdot\mathbf{q} + \mathbf{q}^2 &= 0 \end{aligned} \tag{13}$$

for a given incoming wave $\mathbf{k}_{\text{in}}$.

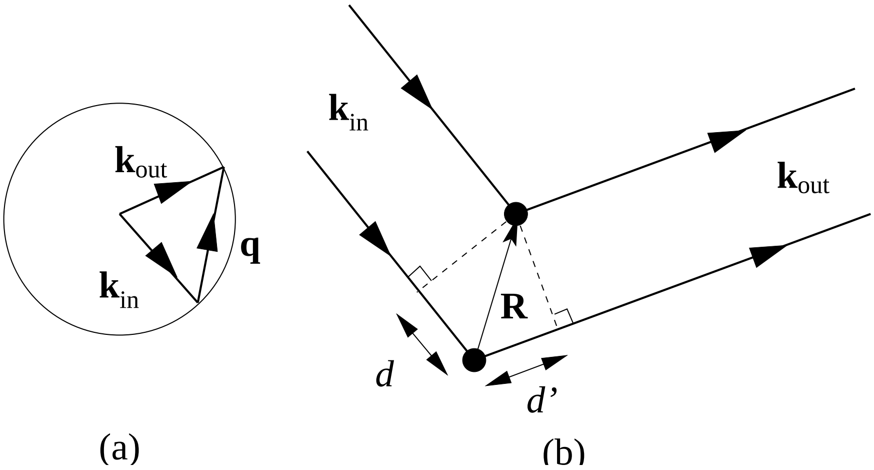

FIG. 1: (a) Momentum diagram. The incoming and outgoing momenta have the same magnitude. (b) Scattering of plane wave from two atoms. The distances labelled in the diagram are $d = -\hat{\mathbf{n}}_{\text{in}}\cdot\mathbf{R}$ and $d' = \hat{\mathbf{n}}_{\text{out}}\cdot\mathbf{R}$ where $\hat{\mathbf{n}}_{\text{in}} = \mathbf{k}_{\text{in}}/|\mathbf{k}_{\text{in}}|$ and $\hat{\mathbf{n}}_{\text{out}} = \mathbf{k}_{\text{out}}/|\mathbf{k}_{\text{out}}|$ are the unit vectors in the incoming and outgoing directions. The total path difference between the two rays is $D = d + d'$.

Now let us consider the scattering of the wave by two identical atoms one at the origin and the other at $\mathbf{R}$. The scattering cross-sections are the same, but the scattered wave have different phases. To see this, we notice there is a difference $D$ in the distance travelled by the two rays. This leads to a phase difference of $\Delta\phi(\mathbf{R}) = -2\pi(D/\lambda)$ between the ray scattered from $\mathbf{R}$ compared to the one from the origin. ($\lambda$ is the wavelength.) This is negative because the scattered wave from $\mathbf{R}$ lags behind in phase compared to the one from the origin. In other words, $\Delta\phi = -|\mathbf{k}_{\text{in}}|D$. From Fig. 1b and using (12), we can see that the phase difference between the two scattered rays is

$$\Delta\phi = -(\mathbf{k}_{\text{out}} - \mathbf{k}_{\text{in}}) \cdot \mathbf{R} = -\mathbf{q} \cdot \mathbf{R} \tag{14}$$

So, waves scattered off different atoms *interfere* with each other. The total scattered wave at wavevector $\mathbf{k}_{\text{out}}$ from scattering off all the atoms in the crystal would be:

$$\delta\psi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{k}_{\text{out}}\cdot\mathbf{r}} \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} \tag{15}$$

How does the sum over all the phase factors behave? Let us start with the one-dimensional case with atoms at $R = na$ for $n = 0, \pm 1, \pm 2, \ldots, \pm N$. We will then take the limit of infinite $N$. Then the sum of phase factors is:

$$\begin{aligned}
S_N(qa) = \sum_{n=-N}^{N} e^{-iqx} &= \sum_{n=-N}^{N} z^n \qquad\qquad \text{where } z = e^{-iqa} \\
&= z^{-N} \sum_{n=0}^{2N} z^n = z^{-N} \frac{1 - z^{2N+1}}{1 - z} \qquad \text{(geometric series)} \\
&= \frac{z^{-(N+\frac{1}{2})} - z^{N+\frac{1}{2}}}{z^{-\frac{1}{2}} - z^{\frac{1}{2}}} = \frac{\sin[(2N+1)qa/2]}{\sin(qa/2)}
\end{aligned} \tag{16}$$

We can see that $S_N(q)$ is a strongly oscillatory function. It is of order unity everywhere, except for sharp peaks when $qa/2 = 0, \pm\pi, \pm 2\pi, \ldots$, *i.e.* when $q$ is a reciprocal lattice vector $G = 2\pi n/a$. This is when all the terms in the summation in $S_n$ are equal to unity, *i.e.*, the path difference between any two rays is a whole number of wavelengths. The height of these peaks is $2N + 1$ and so it grows with the number of atoms in the system. The width of the peaks is proportional to $1/N$ and so the peaks become perfectly sharp as $N \to \infty$. Away from these peaks, the scattering amplitude is negligible by comparison as $N \to \infty$. This is a result we know from diffraction gratings with parallel slits at a spacing of $a$.

We have seen that $S_\infty(qa)$ picks out $qa = 2\pi\times$ (integer). To generalize this result to three dimensions, we can separate the variables into three one-dimensional sums:

$$\begin{aligned}
\sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} &= \sum_{m_1,m_2,m_3} e^{-i\mathbf{q}\cdot(m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3)} = \sum_{m_1,m_2,m_3} e^{-im_1\mathbf{q}\cdot\mathbf{a}_1}\, e^{-im_2\mathbf{q}\cdot\mathbf{a}_2}\, e^{-im_3\mathbf{q}\cdot\mathbf{a}_3} \\
&= S_\infty(\mathbf{q}\cdot\mathbf{a}_1)\, S_\infty(\mathbf{q}\cdot\mathbf{a}_2)\, S_\infty(\mathbf{q}\cdot\mathbf{a}_3)
\end{aligned} \tag{17}$$

The natural coordinate system for $\mathbf{q}$ is to use the reciprocal lattice directions defined in (9): $\mathbf{q} = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3$. This is because the relations (8) gives us $\mathbf{q} \cdot \mathbf{a}_i = 2\pi h_i$. So, the above equation means that the scattering is strong when $h_1, h_2, h_3$ are all integers. From (7), we find that $\mathbf{q}$ is a reciproical lattice vector.

To summarize:

- The scattered rays interfere constructively when $\mathbf{q}$ is a reciprocal lattice vector $\mathbf{G}$.
- When $\mathbf{q}$ is not a reciprocal lattice vector, the rays interfere destructively. The scattering amplitude for these events can be ignored when the array of scatterers becomes infinite.

*Photons are scattering by a crystal in a set of discrete directions. The possible momentum changes for the photons are* $\hbar\mathbf{q} = \hbar\mathbf{G}$ *for any reciprocal lattice vector* $\mathbf{G}$ *which satisfies the elastic collision condition (13):* $2\mathbf{k}_{\text{in}} \cdot \mathbf{G} + \mathbf{G}^2 = 0$.

The simplest way to make sure that the elastic collision condition is satisfied is to use the *Ewald method.* Take the diagram in Fig. 1a with the tip of the vector $\mathbf{k}_{\text{in}}$ at a point on the reciprocal lattice. A possible $\mathbf{k}_{\text{out}}$ is found if the sphere intersects another point on the reciprocal lattice.

As we know from previous sections, the atoms in the crystal can be organized into a set of Bragg planes normal to $\mathbf{q} = \mathbf{G}$. From Fig. 2, we can see that the X-rays can be regarded as reflecting specularly off these planes. This is the original interpretation by Bragg.

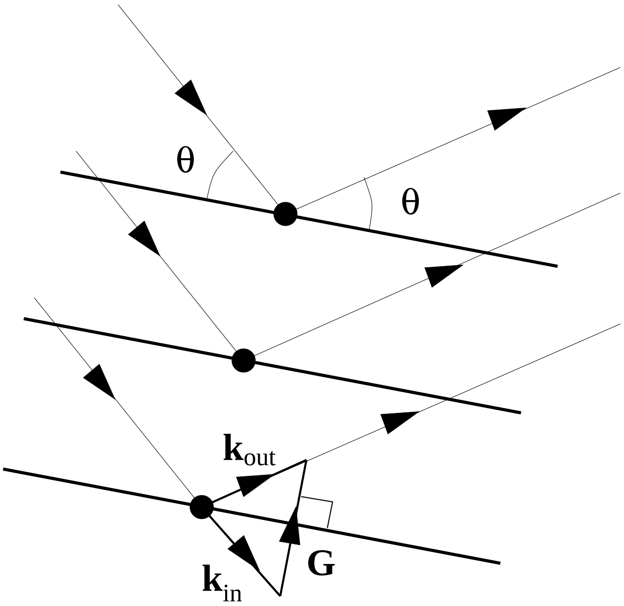

FIG. 2: Bragg planes. The wavevector $\mathbf{G}$ specifies a set of Bragg planes normal to it. The vectors $\mathbf{k}_{\text{in}}$, $\mathbf{k}_{\text{out}}$ and $\mathbf{G}$ form an isosceles triangle. This means that the X-rays reflect off these planes at the same angle as their angle of incidence (specular reflection). Denote this angle by $\theta$, then the angle between $\mathbf{k}_{\text{in}}$ and $\mathbf{k}_{\text{out}}$ is $2\theta$. This is the change in direction of the X-rays. Note also that the angle between $\mathbf{k}_{\text{in}}$ and $\mathbf{G}$ is $\pi/2 - \theta$, and so, $\mathbf{k}_{\text{in}} \cdot \mathbf{G} = -|\mathbf{k}_{\text{in}}|\,|\mathbf{G}|\sin\theta$.

Bragg expressed the diffraction condition in terms of the wavelength $\lambda$ of the X-rays, $\lambda = 2\pi/|\mathbf{k}_{\text{in}}|$ and the separation of the Bragg planes $d$. From our discussion on Bragg planes (11), we know that a set of Bragg planes correspond a set of reciprocal lattice vectors along a line in reciprocal space. The reciprocal lattice vectors have magnitude $|\mathbf{G}| = 2\pi N/d$ for some integer $N$. Suppose the X-rays approach the Bragg planes at an angle $\theta$ as defined in Fig. 2. From the diffraction condition (13), we see that $2|\mathbf{k}_{\mathrm{in}}|\,\sin\theta = |\mathbf{G}|$. Subsituting for $d$ and $\lambda$, we find the Bragg version of the diffraction condition:

$$\boxed{2d\,\sin\theta = N\lambda \qquad \text{for positive integer } N} \tag{18}$$

In summary, we have shown that the scattering of photons by a crystal occurs only when the change in momentum is $\hbar\mathbf{G}$. This gives rise to *discrete* set of scattering angles. This is the basis of crystallography. Crystallographers work backwards, using the set of scattering angles they observe for a given crystal to deduce the periodic structure of the crystal. Combined with information of the chemical constituents of the crystal, they can tell how all the atoms are arranged in each unit cell. This applies not only to simple inorganic compounds, such as NaCl, but also complex biological molecules, such as DNA (the famous double helix that Watson and Crick discovered in 1953) and large proteins.

## III. BLOCH'S THEOREM

### A. The Theorem

The diffraction analysis for photons can also be applied to the scattering of electrons. So, one might wonder what happens to electron plane waves which live in the crystal. They are also strongly scattered. This means that a plane wave with wavevector $\mathbf{q}$ is mixed up with a plane wave with $\mathbf{q} + \mathbf{G}$. Notice that all these scattered wavevectors are related to the *same* wavevector $\mathbf{k}$ if they are translated back into the first Brillouin zone by a reciprocal lattice translation. This means that, although the electron momentum $\hbar\mathbf{q}$ is not conserved, we can define a "crystal momentum" $\hbar\mathbf{k}$ in the first Brillouin zone that is conserved. A more precise statement of this conservation law is Bloch's theorem.

In a crystal, an electron moves in the periodic potential $U$. The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \tag{19}$$

What can we say about the eigenstates in this periodic potential? This is the subject of Bloch's theorem.

Let the eigenstates be $\psi(\mathbf{r})$. Bloch's theorem tells us that these wavefunctions are also periodic. In other words, they are plane-wave-like states. More specifically, Bloch tells us that the wavefunction changes only by a plane-wave phase factor when we go from one lattice site to another. So we can label the states by the wavevector $\mathbf{q}$ associated with the plane-wave phase factor.

$$\hat{T}\psi_{\mathbf{q}}(\mathbf{r}) \equiv \psi_{\mathbf{q}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{q}\cdot\mathbf{R}}\,\psi_{\mathbf{q}}(\mathbf{r}) \tag{20}$$

Another way of saying this is that the wavefunction transform in the same way as a plane wave under a lattice translation operation $\hat{T}$. This is of course true for any vector $\mathbf{R}$ for a pure plane wave which describes electrons moving in the vacuum. For electrons in a periodic potential, however, this is only true if we restrict $\mathbf{R}$ to the lattice translations specified in (1).

The theorem tells us that the eigenfunctions of $H$ are also eigenfunctions of the translation operator $\hat{T}_{\mathbf{R}}$, with eigenvalue $t_{\mathbf{R}} = \exp(i\mathbf{q}\cdot\mathbf{R})$. In the vacuum, this is equivalent to saying that momentum $\mathbf{p} = \hbar\mathbf{q}$ is a good quantum number, so that we can classify the eigenstates of the Hamiltonian (with $U = 0$) by the eigenvalues of the momentum operator. Simiarly, in the periodic lattice, we can classify the states by the eigenvalues of $\hat{T}$. This is why we label the states by $\mathbf{q}$.

However, the choice of $\mathbf{q}$ is not unique for a given eigenvalue of $t_{\mathbf{R}}$ — we can always replace $\mathbf{q}$ by $\mathbf{q} - \mathbf{G}$ for some reciprocal lattice vector $\mathbf{G}$ and $t_{\mathbf{R}}$ will remain unchanged because of eq. (6). This means that, as far as this classification scheme is concerned, any vector $\mathbf{q}$ is equivalent to another vector $\mathbf{k}$ in the first Brilluoin zone. So, a more appropriate form of Bloch's theorem is to use $\mathbf{k}$ to label the solutions and allow for multiple eigenstates with the same $\mathbf{k}$ (but not the same energy). The multiplicity will be labelled by a "band index" $n$:

$$\boxed{\hat{T}\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\,\psi_{n\mathbf{k}}(\mathbf{r}) \qquad (\mathbf{k} \in \text{1st BZ})} \tag{21}$$

Given Bloch's result, it is natural to factor out the plane-wave part from $\psi_{n\mathbf{k}}$. Then, an equivalent statement of the theorem is that the eigenstates in a periodic potential can be written as:

$$\boxed{\psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}} \qquad \text{with} \qquad u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R})} \tag{22}$$

for some function $u_{n\mathbf{k}}(\mathbf{r})$ which has the same periodicity of the potential.

### B. Proof

We will now prove the result (21). I follow the proof in Ashcroft and Mermin.

Consider the action of $\hat{T}_{\mathbf{R}}$ and $\hat{H}$ on any function $f(\mathbf{r})$:

$$\hat{T}_{\mathbf{R}}[\hat{H}(\mathbf{r})f(\mathbf{r})] = \hat{H}(\mathbf{r}+\mathbf{R})f(\mathbf{r}+\mathbf{R}) \qquad \text{by definition of } \hat{T}$$

But the Hamiltonian is invariant under a lattice translation and $f(\mathbf{r}+\mathbf{R}) = \hat{T}_{\mathbf{R}}f(\mathbf{r})$. So,

$$\hat{T}_{\mathbf{R}}\hat{H}f(\mathbf{r}) = \hat{H}\,\hat{T}_{\mathbf{R}}f(\mathbf{r}) \quad \text{for any } f \qquad \Rightarrow \qquad \hat{T}_{\mathbf{R}}\hat{H} = \hat{H}\,\hat{T}_{\mathbf{R}} \tag{23}$$

It is a general result in quantum mechanics that, if two operators commute, then they can have simultaneous eigenstates. Another illustration of this property is that eigenstates of a particle in free space can be labelled by all three components of the momentum, $p_{x,y,z}$ because $-i\partial/\partial x$, $-i\partial/\partial y$ and $-i\partial/\partial z$ commute with each other. On the other hand, eigenstates of $p_x$ are not eigenstates of position $x$ because they do not commute: $[x, p] = i\hbar$. This is, of course, the content of the Heisenberg uncertainty principle.

We have proved that the energy eigenstates are also eigenstates of $\hat{T}_{\mathbf{R}}$. But why do the eigenvalues of $\hat{T}_{\mathbf{R}}$ have plane-wave properties? Let us look at the result of successive lattice translations, by $\mathbf{R}$ and then by $\mathbf{R}'$. This can of course be done by a single translation of $\mathbf{R}+\mathbf{R}'$: $\hat{T}_{\mathbf{R}+\mathbf{R}'} = \hat{T}_{\mathbf{R}'}\hat{T}_{\mathbf{R}}$. This implies that the eigenvalues $t$ of $\hat{T}$ for different translations must be related by:

$$t_{\mathbf{R}+\mathbf{R}'} = t_{\mathbf{R}}\, t_{\mathbf{R}'} \qquad \text{for any } \mathbf{R}, \mathbf{R}'$$

The logarithms of $t$ must therefore be additive. Let us write $t_{\mathbf{R}} = \exp(ig_{\mathbf{R}})$. Then, the $g$'s must obey

$$g_{\mathbf{R}+\mathbf{R}'} = g_{\mathbf{R}} + g_{\mathbf{R}'} \qquad \text{for any } \mathbf{R}, \mathbf{R}'$$

For an infinite system, this also means that $g$ must be a linear function of $\mathbf{R}$ and so can be written as

$$g_{\mathbf{R}} = \mathbf{k}\cdot\mathbf{R}$$

At the moment, $\mathbf{k}$ can be any complex vector. We need to show that it is real. It does not make sense to have an imaginary part to $\mathbf{k}$ because this would mean that $t_{\mathbf{R}}$, and hence the wavefunction, grows or decays exponentially with distance. We would expect the probability density $|\psi(\mathbf{r})|^2$ of finding an electron somewhere should be unchanged on a lattice translation because the environment at $\mathbf{r}$ and $\mathbf{r}+\mathbf{R}$ would be the same as far as the electron is concerned. Strictly speaking, this is only true for an infinite system. For a finite system, this argument would have to assume that the electron spends most of its time in the bulk of the crystal and that boundary effects do not affect the bulk properties of these states.

To see this more mathematically, we insist on a normalized wavefunction.

$$\int \psi^*(\mathbf{r})\psi(\mathbf{r})\, d^3\mathbf{r} = 1$$

In an infinite system, this also means that:

$$\begin{aligned} 1 &= \int \psi^*(\mathbf{r}+\mathbf{R})\psi(\mathbf{r}+\mathbf{R})\, d^3\mathbf{r} \\ &= \int t^*_{\mathbf{R}}\psi^*(\mathbf{r})\, t_{\mathbf{R}}\psi(\mathbf{r})\, d^3\mathbf{r} = |t_{\mathbf{R}}|^2 \end{aligned}$$

Therefore, $\mathbf{k}$ must be real and we have obtained Bloch's theorem. As discussed above, we can restrict $\mathbf{k}$ to the first Brillouin zone.

### C. Boundary Conditions and Counting States

The alert reader would complain that I should define the wavefunction for a finite volume $V$ and then take the system size to infinity. This is because I cannot really speak of a wavefunction that vanishes as $V^{-1/2}$ *at* the limit of $V = \infty$.

One way to take the infinite-volume limit is to use **periodic boundary conditions**:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n\mathbf{k}}(\mathbf{r}+N_i\mathbf{a}_i) \qquad \text{for } i = 1,2,3 \tag{24}$$

where $N_i$ is the number of atoms in the $\mathbf{a}_i$ direction in the whole lattice. In other words, pretend that the volume is infinite by repeating the sample beyond its boundaries, but insist that the wavefunction repeats itself. This will give a real $\mathbf{k}$. See Ashcroft and Mermin for more detailed discussion.

In fact, periodic boundary conditions quantizes $\mathbf{k}$. We see that (24) is satisfied if $N_i \mathbf{k} \cdot \mathbf{a}_i = 2\pi m_i$. It is convenient to write $\mathbf{k}$ in terms of the vectors $\mathbf{b}$ that define the reciprocal lattice (9). Using the orthogonality (8) between $\mathbf{a}$'s and $\mathbf{b}$'s, we get:

$$\mathbf{k} = \sum_i \frac{m_i}{N_i} \mathbf{b}_i \tag{25}$$

where $m_i$ are integers and $\mathbf{b}_i$ are the vectors that specify reciprocal lattice, as defined in (9). Since $\mathbf{k}$ is restricted to the first Brillouin zone, we have $m_i = N_i/2, N_i/2 - 1, \ldots, -N_i/2 + 1$ for even $N_i$ and $m_i = (N_i - 1)/2, \ldots, (-N_i + 1)/2$ for odd $N_i$. We can see that there is a total of $N_1 N_2 N_3$ possible $\mathbf{k}$'s for a given band index. In other words:

*The total number of electron states in each band is the total number of unit cells in the crystal. For a Bravais lattice, this is the same as the total number of atoms.*

It is important to note that the **density of states** in $\mathbf{k}$-space is uniform. In other words, the number of states $\delta\mathcal{N}$ in a volume element $\delta^3\mathbf{k}$ in the first Brillouin zone is

$$\delta\mathcal{N} = \frac{N_1 N_2 N_3 \, \delta^3\mathbf{k}}{|\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|} = \frac{V}{(2\pi)^3} \, \delta^3\mathbf{k} \tag{26}$$

where $V = N_1 N_2 N_3 |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ is the volume of the system. I have used that the fact that the volume of the Brillouin zone $\Omega_{\mathrm{BZ}} = |\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)|$ is related to the volume of the (real-space) unit cell $\Omega = |\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|$ by: $\Omega_{\mathrm{BZ}} = (2\pi)^3/\Omega$.

### D. Consequences

Bloch's theorem is a central theorem in solid-state physics because it explains why there are mobile electrons in a solid. This underpins our interpretation of the electrons as a "nearly free electron gas". Such a model is very successful in describing many physical properties of solids.

In fact, taken as a mathematical statement about non-interacting electrons in a perfect crystals, Bloch's theorem guarantees that the electrons do not get trapped inside the atoms, no matter how strong the ionic potentials $U(\mathbf{r})$ are. The electrons still retain wave-like properties and are mobile across the whole system. This allows us to use simple plane-wave ideas to explain why electrons conduct electricity in a metal. (For the reader who already knows about band gaps, this discussion only applies to metals, *i.e.* when the Fermi energy does not lie near or inside a band gap.)

Compare this with a classical particle going through a pin-ball machine. You would not expect it to come out with its momentum unchanged — it would collide off the pins and its trajectory would look more or less like a random walk. However, Bloch's theorem tells us that the quantum electron behaves quite differently. There is still a conserved quantity, namely $\hbar\mathbf{k}$ which is often referred to as the "crystal momentum". (Note that this is *not* the actual momentum of the electron because the eigenfunctions of $\hat{H}$ are not eigenstates of the momentum operator $-i\hbar\nabla$.)

Our classical intuition from the pin-ball machine seems to tell us that Bloch's theorem is too good to be true. The conservation of crystal momentum means that the electrons effectively do not scatter as they travel through the crystal. So, the Fermi gas in a periodic potential has zero resistance at all temperatures! This seems to fly in the face of experience.

This contradiction arises because we have only looked at a very simple model of a metal. There are many ingredients missing from our model which will give rise to resistance. I list some of them here:

- *Impurities/Defects.* Impurities and defects in the crystal structure (such as dislocations) are present in all solids. These are randomly positioned. So, the assumption of a periodic potential in Bloch's theorem is only approximately true for clean systems.
- *Phonons.* We have modelled the ions in the crystals as a static potential to the electron. (This is known as the Born-Oppenheimer approximation.) But these ions are not infinitely massive. They oscillate at finite temperature. The magnitude of the oscillations grow with temperature. These oscillations involve collective motion of all the ions (*i.e.* normal modes). They are known as phonons. They include the sound modes. Electrons scattering off oscillating atoms will gain/lose energy to them. This provides a mechanism of dissipation and resistance, especially at high temperatures when many phonon modes are excited.
- *Electron-electron interactions.* Two electrons can scatter off each other, changing their crystal momenta: $(\mathbf{k}_1, \mathbf{k}_2) \rightarrow (\mathbf{k}'_1, \mathbf{k}'_2)$. Most processes would conserve the total crystal momentum: $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}'_1 + \mathbf{k}'_2$. But, as we know, these momenta are only defined up to a reciprocal lattice vector. So, there are *Umklapp* processes where $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}'_1 + \mathbf{k}'_2 + \mathbf{G}$. Note that $\mathbf{G}$ is large compared with other vectors in the first Brillouin zone. So, two forward-going particles might scatter and end up both going backwards. This is obviously a way to dissipate current and give rise to resistance. In fact, strong interactions have even more drastic effects on the electron gas, giving rise to magnetism, superconductivity and other novel ground states for the electrons. This is the subject of continuing research.

## IV. BOOKS

- C. Kittel, *Introduction to Solid State Physics* (7th edition, John Wiley & Sons, 1995). Good on fundamentals, but relies on understanding of Fourier analysis.
- N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Saunders College Publishing, 1976). More thorough treatment of the fundamental principles than other texts.
- J.R. Hook and H.E. Hall, *Solid State Physics.* (John Wiley & Sons, 1991). Up-to-date topics.