Reciprocal Lattice

From Quantum Mechanics we know that symmetries have kinematic implications. Each symmetry predetermines its specific quantum numbers and leads to certain constraints (conservation laws/selection rules) expressed in terms of these quantum numbers. In this chapter, we consider kinematic consequences of the discrete translation symmetry. The shortest way to introduce the relevant quantities— *the vectors of reciprocal lattice*—is to consider the Fourier analysis for crystal functions.

**Fourier analysis for crystal functions**

Let $A(r)$ be some function featuring discrete translation symmetry:

$$A(r + T) = A(r),$$  

where $T$ is any translation vector of a certain translation group $\mathcal{G}_T$. We want to expand $A(r)$ in a Fourier series of functions respecting translation symmetry (i.e. obeying translation symmetry with the same group $\mathcal{G}_T$). Without loss of generality, we confine the coordinate $r$ to a unit cell of the Bravais lattice of the group $\mathcal{G}_T$. Hence, we work with the *vector space* of functions defined within the unit cell and satisfying the periodicity condition (1). Within this vector space, we want to construct the orthogonal basis of functions that would be eigenfunctions of continuous translations. These functions are the plane waves $e^{iG \cdot r}$ with the wavevector $G$ constrained by the condition (1). Clearly, the constraint reduces to

$$G \cdot T = 2\pi \times \text{integer} \quad \text{(for any } G \text{ and } T).$$  

From (2) we immediately see that the set of vectors $G$ is a *group*, $\mathcal{G}_G$, with the vector addition as a group operation. The group $\mathcal{G}_G$ can be interpreted as a group of translations and visualized with corresponding Bravais lattice referred to as *reciprocal lattice*. Noticing that the condition (2) is symmetric with respect to the vectors $T$ and $G$, we conclude that the Bravais lattice of the group $\mathcal{G}_T$ (referred to in this context as the direct lattice) is reciprocal with respect to the Bravais lattice of the group $\mathcal{G}_G$. In other words, the two lattices are mutually reciprocal.

A simple way of proving the orthogonality of the plane waves,

$$\int_{\text{cell}} dV e^{i(G_1 - G_2) \cdot r} = V_c \delta_{G_1, G_2},$$
is to make sure that they are the eigenfunctions of a certain Hermitian (dif-
ferential) operator with a discrete non-degenerate spectrum.\(^1\) For example,
the operator \(i\nabla\) does the job, because for the functions defined within the
primitive cell and featuring the translation invariance (1) the operator \(\nabla\)
is anti-Hermitian—checked by doing the inner-product integral by parts\(^2\)—
and \(i\nabla e^{i\mathbf{G} \cdot \mathbf{r}} = -\mathbf{G} e^{i\mathbf{G} \cdot \mathbf{r}}\), meaning that different plane waves have different
eigenvalues. It is convenient to include the factor \(1/V_c\) in the definition of
the inner product of functions:

\[
\langle A|B \rangle = (1/V_c) \int_{\text{cell}} A^\ast(\mathbf{r}) B(\mathbf{r}) \, dV .
\]

(4)

In this case, the set of the functions

\[
|\mathbf{G}\rangle \equiv e^{i\mathbf{G} \cdot \mathbf{r}}
\]

becomes normalized, and we arrive at the Fourier series in the form

\[
A(\mathbf{r}) = \sum_{\mathbf{G}} \langle \mathbf{G}|A\rangle |\mathbf{G}\rangle \equiv \sum_{\mathbf{G}} A_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}},
\]

(6)

where

\[
A_{\mathbf{G}} \equiv \langle \mathbf{G}|A \rangle = (1/V_c) \int_{\text{cell}} e^{-i\mathbf{G} \cdot \mathbf{r}} A(\mathbf{r}) \, dV .
\]

(7)

Talking of an explicit evaluation of the Fourier coefficients \(A_{\mathbf{G}}\) we note that
any integral over the primitive cell can be parametrized in terms of the
coordinates—in a general case, non-Cartesian ones—with respect to a given
primitive set \((a_1, a_2, a_3)\):

\[
\mathbf{r} = \xi_1 a_1 + \xi_2 a_2 + \xi_3 a_3 , \quad \xi_1, \xi_2, \xi_3 \in [0, 1],
\]

(8)

\[
(1/V_c) \int_{\text{cell}} dV (\ldots) = \int_0^1 d\xi_1 \int_0^1 d\xi_2 \int_0^1 d\xi_3 (\ldots) .
\]

(9)

The volume \(V_c\) cancels with the Jacobian of the transformation of integration
variables.

\(^1\)This will also guarantee the completeness of the set.

\(^2\)Since the integral is over a finite region, the surface term appears, and one has to show
that its contribution is zero. This is conveniently done by extending the integration over
a large cluster consisting of \(N \gg 1\) adjacent cells. By periodicity, the bulk integral then
equals to \(N\) times the integral over a single cell, while the surface integral, if non-zero,
has to grow with \(N\) as \(N\) to a power smaller than 1. Since \(N\) can be arbitrarily large, this
proves that the surface contribution is identically zero.
**Primitive set for reciprocal lattice**

To find explicit expressions for the vectors of the reciprocal lattice we need to construct a primitive set. It turns out that there is a one-to-one correspondence between primitive sets of the direct and reciprocal lattices. To reveal this correspondence, let us take a primitive set \((a_1, a_2, a_3)\) of the direct lattice and construct the following three vectors:

\[
\begin{align*}
    c_1 &= a_2 \times a_3, \quad c_2 = a_1 \times a_3, \quad c_3 = a_1 \times a_2.
\end{align*}
\] (10)

By construction, the three vectors are not coplanar, and thus any vector \(G\) can be expressed, in a unique way, as their linear combination:

\[
G = \eta_1 c_1 + \eta_2 c_2 + \eta_3 c_3. \tag{11}
\]

Multiplying both sides of (11) by \(a_j\) \((j = 1, 2, 3)\) and applying (2), we see that

\[
\eta_j = \frac{(2\pi/V_c) \times \text{integer}}{(a_j \cdot (a_2 \times a_3))} \quad (j = 1, 2, 3). \tag{12}
\]

Furthermore, the requirement (12) straightforwardly implies (2), and we conclude that (12) and (2) are equivalent. This yields a primitive set \((b_1, b_2, b_3)\) of the reciprocal lattice:

\[
\begin{align*}
    b_1 &= 2\pi \frac{a_2 \times a_3}{a_1 \cdot (a_2 \times a_3)}, \\
    b_2 &= 2\pi \frac{a_1 \times a_3}{a_2 \cdot (a_1 \times a_3)}, \\
    b_3 &= 2\pi \frac{a_1 \times a_2}{a_3 \cdot (a_1 \times a_2)}.
\end{align*}
\] (13) (14) (15)

Each \(G\) is then associated with the three integers \((m_1, m_3, m_3)\):

\[
G = m_1 b_1 + m_2 b_2 + m_3 b_3. \tag{16}
\]

The 2D case readily follows from the 3D one by formally introducing \(a_3 = \hat{z}\), where \(\hat{z}\) is the unit vector perpendicular to the \(xy\) plane of the primitive set \((a_1, a_2)\). The relevant vectors of the reciprocal lattice are \((b_1, b_2)\), since both lie in the \(xy\) plane. The vector \(b_3\) is perpendicular to the \(xy\) plane and thus can be safely neglected.
The symmetry of the correspondence between the primitive sets of the direct and reciprocal lattices becomes obvious by noticing that the explicit relations (13)-(15) can be written in an equivalent implicit form

\[ \mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}. \]  

(17)

With equations (17) it is easy to see a simple relation between the volume \( V_c \) of the primitive cell of the direct lattice and the volume \( V_{c(\text{rcpr})} \) of the primitive cell of the reciprocal lattice:

\[ V_{c(\text{rcpr})} = (2\pi)^d/V_c. \]  

(18)

Indeed, write (17) in the matrix form (we do it for \( d = 3 \)),

\[
\begin{bmatrix}
  a_{1x} & a_{1y} & a_{1z} \\
  a_{2x} & a_{2y} & a_{2z} \\
  a_{3x} & a_{3y} & a_{3z}
\end{bmatrix}
\begin{bmatrix}
  b_{1x} & b_{2x} & b_{3x} \\
  b_{1y} & b_{2y} & b_{3y} \\
  b_{1z} & b_{2z} & b_{3z}
\end{bmatrix}
= \begin{bmatrix}
  2\pi & 0 & 0 \\
  0 & 2\pi & 0 \\
  0 & 0 & 2\pi
\end{bmatrix},
\]

and take the determinant of both sides recalling that the determinant of a product of matrices equals to the product of determinants.

For crystallographic purposes, it is convenient to work with dimensionless vectors of direct and reciprocal lattices, \( \mathbf{T} \) and \( \mathbf{G} \), respectively, introduced as

\[ \mathbf{T} = a\tilde{\mathbf{T}}, \quad \mathbf{G} = (2\pi/a)\tilde{\mathbf{G}}, \]

(19)

where \( a \) is a convenient unit of length, normally the length of one of the vectors of the primitive set. For the dimensionless lattices, the relations (2) and (17) simplify to

\[ \tilde{\mathbf{G}} \cdot \tilde{\mathbf{T}} = \text{integer} \quad \text{(for any } \tilde{\mathbf{G}} \text{ and } \tilde{\mathbf{T}}), \]

(20)

\[ \tilde{\mathbf{a}}_i \cdot \tilde{\mathbf{b}}_j = \delta_{ij}. \]

(21)

Dimensionless primitive sets are very convenient for establishing the types of the reciprocal lattices. As an instructive example, see the calculation in Kittel’s book establishing the fact that \( fcc \) and \( bcc \) lattices are reciprocal with respect to each other.

**Working with non-primitive sets and unit cells. Symmetry factors**
In cases when the Bravais lattice features rectangular symmetries—fcc and bcc lattices being most typical and important 3D examples\(^3\)—it is very convenient to use non-primitive unit cells with corresponding non-primitive sets of translation vectors. The advantage is the simplification of geometric description and nomenclature. For example, for fcc and bcc lattices we simply start with geometry and nomenclature of simple cubic lattice and then add extra lattice points converting the sc lattice into fcc or bcc one. Yet another alternative is to start with some simple lattice (say, simple cubic lattice) and erase some points to arrive at a less trivial Bravais lattice. (Recall obtaining the sodium chloride lattice from the simple cubic one by using alternating coloring.)

It turns out that the two approaches—using non-primitive unit cells and erasing certain lattice points are dual in the following sense. If a direct lattice is parameterized with a non-primitive unit cell then the reciprocal lattice can be naturally obtained as a lattice reciprocal to the Bravais lattice of non-primitive units of the direct lattice, upon applying the constraint that some points of this ‘fake’ reciprocal lattice should be removed to produce the actual reciprocal lattice; and there is a general prescription of how to calculate the coefficients—the so-called symmetry factors—explicitly telling us which points of the ‘fake’ reciprocal lattice are fake and which are real. Below we develop corresponding tools.

We start with formalizing the problem. We are given a direct Bravais lattice associated with the group of translations \(G_T\) consisting of translation vectors \(T\). By introducing a non-primitive unit cell of our lattice \(G_T\) (from now on we use ‘lattice \(G_G\)’ as a short version of ‘Bravais lattice associated with the group \(G_G\)’), we actually introduce a new group of translations, \(G'_T\), consisting of the allowed translations vectors \(T'\) of the non-primitive unit cell. Clearly, each \(T' \in G'_T\) also belongs to \(G_T\), that is the group \(G'_T\) is a subgroup of \(G_T\):

\[
G'_T \subset G_T. \tag{22}
\]

The two reciprocal lattices, \(G_G\) and \(G'_G\), are defined by the conditions

\[
G \cdot T = 2\pi \times \text{integer} \quad \text{for any } T \in G_T, \tag{23}
\]

\[
G' \cdot T' = 2\pi \times \text{integer} \quad \text{for any } T' \in G'_T. \tag{24}
\]

\(^3\)In 2D, the analog is the centered rectangular lattice. And also the hexagonal lattice which in the context of the present discussion can be treated as nothing but a special case of the centered rectangular lattice.
The property (22) guaranties that any \( G \) satisfying (23) and thus belonging to \( G_G \) belongs also to \( G_{G'} \), by (24). Hence,

\[ G_G \subset G_{G'} . \tag{25} \]

In plain words, Eqs. (22) and (25) say that while the lattice \( G_T \) is obtained from the lattice \( G_{T'} \) by adding extra points to the basis, the lattice \( G_G \) is obtained from the lattice \( G_{G'} \) by removing certain lattice points. Not a bad deal! Instead of directly constructing reciprocal to fcc or bcc lattices, we work with corresponding simple cubic lattice \( G_{T'} \) that readily yields \( G_{G'} \). The latter is also a simple cubic lattice; with the straightforward relationship between the primitive sets:

\[ b_j' = \frac{2\pi a_j}{|a_j'|^2} \quad \text{ (for a cubic unit cell)} . \tag{26} \]

A price that we have to pay for the luxury is that we need to figure out which points of the lattice \( G_{G'} \) have to be removed to produce \( G_G \). This is conveniently done with the symmetry factors \( S_{G'} \) such that

\[ S_{G'} = \begin{cases} 1, & G' \in G_G, \\ 0, & G' \notin G_G . \end{cases} \tag{27} \]

An easy way to establish the symmetry factors is to compare Fourier coefficients \( F_G \) and \( F_{G'} \)—corresponding to the translation groups \( G_T \) and \( G_{T'} \), respectively—for some generic periodic function \( F(r + T) = F(r) \). The simplest \( F(r) \) is given by delta-functions centered on the sites of the Bravais lattice:

\[ F(r) = \sum_T \delta(r - T) \equiv \sum_{T'} \sum_{\nu=1}^{\nu_0} \delta(r - T' - R_{\nu}) . \tag{28} \]

Here the identity represents the same function in terms of the nomenclature of the lattice \( G_{T'} \), in which case there are \( \nu_0 \) points in the unit cell; we enumerate them with the subscript \( \nu \), and characterize their positions by corresponding vectors \( R_{\nu} \) (for definiteness, we select \( R_1 = 0 \)). Doing the integrals (7), we find

\[ \mathcal{F}_G = \frac{1}{V_c}, \quad \mathcal{F}_{G'} = \frac{1}{V'_c} \sum_{\nu=1}^{\nu_0} e^{-iG' \cdot R_{\nu}} , \tag{29} \]

where \( V_c \) and \( V'_c \) are the volumes of primitive cells of the lattices \( G_T \) and \( G_{T'} \), respectively (note that \( V'_c = \nu_0 V_c \)). Comparing the two Fourier series,

\[ \sum_G e^{iG \cdot r} \mathcal{F}_G \equiv \mathcal{F}(r) \equiv \sum_{G'} e^{iG' \cdot r} \mathcal{F}_{G'} , \tag{30} \]
we see that
\[ \frac{1}{V_c} \sum_{\nu_0} e^{-i\mathbf{G}' \cdot \mathbf{R}_\nu} = \mathcal{F}_{G'} = \begin{cases} \mathcal{F}_{G'} = 1/V_c, & G' \in \mathcal{G}_G, \\ 0, & G' \notin \mathcal{G}_G, \end{cases} \]  
(31)

and conclude that
\[ S_{G'} = \frac{1}{\nu_0} \sum_{\nu_0} e^{-i\mathbf{G}' \cdot \mathbf{R}_\nu}. \]  
(32)

Let us evaluate the symmetry factors for bcc and fcc lattices, both represented with the simple-cubic lattice \( \mathcal{G}_{T'} \), for which the primitive set is given by unit Cartesian vectors, \((\hat{x}, \hat{y}, \hat{z})\). The vectors \( \mathbf{R}_\nu \) are \( \nu_{0}^{(\text{bcc})} = 2 \) and \( \nu_{0}^{(\text{fcc})} = 4 \):

\[ \mathbf{R}_2^{(\text{bcc})} = \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right), \]
\[ \mathbf{R}_2^{(\text{fcc})} = \left( \frac{1}{2}, \frac{1}{2}, 0 \right), \]
\[ \mathbf{R}_3^{(\text{fcc})} = \left( \frac{1}{2}, 0, \frac{1}{2} \right), \]
\[ \mathbf{R}_4^{(\text{fcc})} = \left( 0, \frac{1}{2}, \frac{1}{2} \right). \]  
(34)

The lattice \( \mathcal{G}_{G'} \), reciprocal to the \( \mathcal{G}_{T'} \) lattice is sc, with the primitive set \((2\pi \hat{x}, 2\pi \hat{y}, 2\pi \hat{z})\), so that \( G' = 2\pi(m_1 \hat{x} + m_2 \hat{y} + m_3 \hat{z}) \). For the symmetry factors we then get

\[ S_{m_1 m_2 m_3}^{(\text{bcc})} = \left[ 1 + e^{-i\pi(m_1 + m_2 + m_3)} \right] / 2, \]  
(35)
\[ S_{m_1 m_2 m_3}^{(\text{fcc})} = \left[ 1 + e^{-i\pi(m_2 + m_3)} + e^{-i\pi(m_1 + m_3)} + e^{-i\pi(m_1 + m_2)} \right] / 4. \]  
(36)

It is straightforward to see that non-zero \( S_{m_1 m_2 m_3}^{(\text{bcc})} \) corresponds to a fcc lattice, while non-zero \( S_{m_1 m_2 m_3}^{(\text{fcc})} \) corresponds to a bcc lattice.

**Bragg diffraction: Basic principles**

Consider a problem of elastic perturbative scattering of a quantum particle from a crystal. We remind that elastic means that the state of the crystal does not change after the scattering. Perturbative means that the probability of the process is much smaller than unity, so that we can rely on the perturbation theory (Fermi Golden Rule). For our theoretical purposes, the specific type of the particle does not matter. In practice, very important are X-ray quanta (photons), neutrons, and electrons, with (de Broglie) wavelength comparable to the crystal lattice period. Let the initial
state of the quantum particle be the plane wave with the wavevector $k$. We are interested in the **kinematic structure** of the probability amplitude $M_{kk'}$ of finding the particle in the plane-wave state with the momentum $k'$ as a result of the scattering event. By kinematic structure we mean selection rules imposed on $k$ and $k'$ by the periodicity of the crystal. These selection rules, known as **Bragg conditions**, deal only with the direction of $k'$ (as well as the direction of $k$), but not its absolute value, since $k' = k$ by elasticity of the process. The expression for the probability amplitude is

$$M_{kk'} = \langle \text{final state} | U_{\text{int}} | \text{initial state} \rangle, \quad (37)$$

where

$$| \text{initial state} \rangle = |k \rangle |\text{crystal} \rangle, \quad |k \rangle \equiv e^{ik \cdot r}, \quad (38)$$

$$| \text{final state} \rangle = |k' \rangle |\text{crystal} \rangle, \quad |k' \rangle \equiv e^{ik' \cdot r}, \quad (39)$$

and $U_{\text{int}}$ is the Hamiltonian of interaction between the particle and the crystal; the ket $|\text{crystal} \rangle$ stands for the wavefunction of the crystal (the same in the initial and final states). Hence, $M_{kk'}$ can be written as the integral over the crystal,

$$M_{kk'} = \int_{\text{crystal}} e^{-iq \cdot r} A(r) dV, \quad (40)$$

with

$$q = k' - k, \quad (41)$$

and $A(r)$ being the result of averaging the interaction Hamiltonian over the wavefunction of the crystal:

$$A(r) = \langle \text{crystal} | U_{\text{int}}(r) | \text{crystal} \rangle. \quad (42)$$

In terms of the general kinematic constraints we are revealing, the details of the form of $A(r)$ are irrelevant, the only crucial property being the translation symmetry, Eq. (1), that $A(r)$ has to respect. Nevertheless, it is worth mentioning that for the X-ray scattering, $A(r)$ amounts to the expectation value of the density of electrons at the point $r$ times the coupling constant.

In view of the periodicity of $A(r)$, the integral (40) over the crystal reduces to the sum of the integral over the primitive cell with exponential pre-factors:

$$M_{kk'} = S_q \sum_n (\text{crystal}) e^{-iq \cdot T_n}, \quad (43)$$
\[ S_q = \int_{\text{cell } n=0} e^{-i\mathbf{q}\cdot\mathbf{r}} A(\mathbf{r}) \, dV. \] (44)

From (43) we see that \( M_{\mathbf{k}\mathbf{k}'} \) is sharply peaked when

\[ \mathbf{q} \equiv \mathbf{k}' - \mathbf{k} = \mathbf{G} \quad \text{(Bragg condition)}. \] (45)

Indeed, in this case, all the exponentials interfere constructively and

\[ M_{\mathbf{k}\mathbf{k}'} = S_{\mathbf{G}} N_{\text{cells}}, \] (46)

where \( N_{\text{cells}} \) is the (macroscopically large) number of primitive cells in the crystal. If \( \mathbf{q} \) is not macroscopically close to one of the vectors \( \mathbf{G} \), many exponentials in (43) interfere destructively and the value of \( M_{\mathbf{k}\mathbf{k}'} \) is much smaller than (46). For the wavevectors \( \mathbf{k} \) and \( \mathbf{k}' \) satisfying the Bragg condition (45), the scattering amplitude is linearly proportional to \( N_{\text{cells}} \). In accordance with the Golden Rule, the intensity of scattering—that is the probability density of having a scattering event with given \( \mathbf{k} \) and \( \mathbf{k}' \)—scales as the square of the scattering amplitude, and thus is \( \propto N_{\text{cells}}^2 \); this is the manifestation of enhancement of quantum-mechanical elementary processes by constructive interference of the amplitudes.

At this point, it is very instructive to discuss the role of quantumness, which is actually two-fold: (i) the quantumness of the incident particle and (ii) the quantumness of the crystall. The first circumstance is necessary only for bringing about the issue of wave diffraction. In this respect, a classical field (say, classical electromagnetic filed instead of a single photon) would lead to the same effect. The quantumness of the crystal is far more important, since at any finite temperature, thermal fluctuations break translation symmetry of a classical crystal, thus suppressing the effect of perfect constructive interference. The situation with quantum crystal—to be discussed in detail in the chapter on phonons—is qualitatively different. The central for the whole discussion expressions (42)–(44) hold true at any temperature, the only effect of the latter being the suppression of the amplitude (44).

Our next goal is to understand the width of the Bragg peaks. We are mainly interested in the scaling of the peak width with the system size. The details of the form of the peak depend on the particular overall shape of the crystal and thus are not very instructive. We select the most convenient shape, which is the one prompted by the shape of the primitive parallelepiped. In this case (choosing the cell \( n = 0 \) to be in the corner of the crystal),

\[ \sum_{\mathbf{n}}^{(\text{crystal})} (\ldots) \equiv \sum_{n_1=0}^{L_1-1} \sum_{n_2=0}^{L_2-1} \sum_{n_3=0}^{L_3-1} (\ldots), \] (47)
Figure 1: The function $I(\chi, L)$, Eq. (51), in the vicinity of one of its narrow (at $L \gg 1$) peaks. The amplitude at the maximum is $I = L^2$, the width of the peak is $\Delta \chi \sim 2\pi/L$. 
where \( L_j \) is the number of primitive cells per translational dimension \( j \) \((L_1L_2L_3 = N_{\text{cells}})\), which is very convenient for evaluating the sum in (43) by reducing it to the product of three similar and simple factors,

\[
\sum_n e^{-iq \cdot T_n} = Q(\chi_1, L_1) Q(\chi_2, L_2) Q(\chi_3, L_3) \quad (\chi_j = q \cdot a_j),
\] (48)

that are nothing but partial sums of geometric series:

\[
Q(\chi, L) = \sum_{n=0}^{L-1} e^{-i\chi n} = \frac{1 - e^{-i\chi L}}{1 - e^{-i\chi}} = e^{-i\chi(L-1)/2} \frac{\sin(\chi L/2)}{\sin(\chi/2)}. \quad (49)
\]

The exponential pre-factor is irrelevant since the probability density for the scattering is given by the square of the absolute value of the scattering amplitude:

\[
|M_{kk}'|^2 = |S_q|^2 I(\chi_1, L_1) I(\chi_2, L_2) I(\chi_3, L_3),
\] (50)

\[
I(\chi, L) = |Q(\chi, L)|^2 = \frac{\sin^2(\chi L/2)}{\sin^2(\chi/2)}. \quad (51)
\]

The function \( I(\chi, L) \) is a \( 2\pi \)-periodic function of \( \chi \), with very sharp (at \( L \gg 1 \)) peaks of the amplitude \( L^2 \) and the width \( \Delta \chi \sim 2\pi/L \), see Fig. 1. Recalling that \( \chi_j = q \cdot a_j \), we conclude that, in the wavevector units, the width of the peak is on the order of the inverse linear system size.

Note that there are also satellite peaks of the same width and progressively decreasing amplitude. The shape of the function \( I(\chi, L) \) in the vicinity of the peak is readily revealed by expanding the sine in the denominator: \( \sin^2 \chi/2 \approx \chi^2/4 \) at \( |\chi| \ll 1 \):

\[
I(\chi, L) = |Q(\chi, L)|^2 = 4 \frac{\sin^2(\chi L/2)}{\chi^2}. \quad (52)
\]

With this formula we see that the amplitude of the \( m \)-th satellite peak decreases with \( m \) as \( 1/m^2 \).

Alternative forms and interpretations of Bragg conditions.
Ewald sphere and Brillouin zones

By conservation of energy we have \( k' = k \), and the complete set of equations expressing the kinematic constraints of the Bragg diffraction read

\[
k' = k, \quad k' - k = G \quad \text{(Bragg conditions, basic version).} \quad (53)
\]

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We have one scalar and one vector constraints. Mathematically, this is equivalent to a system of four scalar constraints. The constraints can be re-written in the following two important forms

\[ \mathbf{k} \cdot \mathbf{G} = \frac{G^2}{2}, \quad \mathbf{k}' = \mathbf{k} - \mathbf{G} \quad \text{(Bragg conditions, version A)}, \quad (54) \]

\[ \mathbf{k}' \cdot \mathbf{G} = \frac{G^2}{2}, \quad \mathbf{k} = \mathbf{k}' - \mathbf{G} \quad \text{(Bragg conditions, version B)}. \quad (55) \]

(These alternative forms of Bragg conditions are easily derived by taking squares of \( \mathbf{k}' = \mathbf{k} - \mathbf{G} \) and \( \mathbf{k} = \mathbf{k}' - \mathbf{G} \), respectively. Note that the sign of \( \mathbf{G} \) does not matter since \( -\mathbf{G} \in \mathcal{G} \).)

Geometrically, any scalar constraint on a three-dimensional vector yields a surface (a system of surfaces) in corresponding vector space. The scalar constraint \( \mathbf{k}' = \mathbf{k} \) means that the end of the vector \( \mathbf{k}' \) has to be in the sphere of the radius \( \mathbf{k} \) in the wavevector space. To visualize Eqs. (53), we draw this sphere together with the properly positioned reciprocal lattice, as shown in Fig. 8. This geometric construction is known as Ewald construction, in the context of which the sphere \( \mathbf{k}' = \mathbf{k} \) is referred to as Ewald sphere. With the Ewald construction we clearly see that Bragg diffraction requires a fine-tuning: It happens only if, in addition to the origin of the reciprocal lattice that belongs to the Ewald sphere by construction, there is yet another reciprocal lattice point on the sphere.

The necessity of fine-tuning is also seen with the first equation of Eqs. (54), imposing a scalar constraint on the vector \( \mathbf{k} \). To reveal the surfaces standing behind this constraint, rewrite it as

\[ \mathbf{k} \cdot \hat{\mathbf{e}}_{\mathbf{G}} = \frac{G}{2}, \quad (56) \]

where \( \hat{\mathbf{e}}_{\mathbf{G}} = \frac{\mathbf{G}}{G} \) is the unit vector in the direction of \( \mathbf{G} \). We see that the ends of the vectors \( \mathbf{k} \) satisfying the Bragg conditions live in special planes that are perpendicular bisectors of the reciprocal lattice vectors (for an illustration, see Fig. 9). There are infinitely many such planes. And these divide the wavevector space into infinitely many pieces called Brillouin zones. Of crucial importance is the first Brillouin zone—the one containing the origin of the reciprocal lattice. By construction it is nothing but the Wigner-Seitz cell of the reciprocal lattice. Now note that if we know the Wigner-Seitz cell, we can immediately restore the whole lattice by reflecting the origin against the boundaries, and then applying the procedure iteratively. Having restored the reciprocal lattice, we can pick up one of its primitive sets of translation vectors and construct corresponding set of

\textsuperscript{4}Recall that those planes are at the heart of the Voronoi-Wigner-Seitz construction!
the direct lattice. We thus arrive at the fundamental conclusion that Bragg scattering allows one to measure the Bravais lattice of the crystal structure.

There are two equivalent ways of measuring the shape of the first Brillouin zone. The above-discussed one deals with the condition (56) for the incident wave. Equation (55), identical to (54) up to replacement $k \leftrightarrow k'$, tells us that the same goal can be achieved by working with $k'$, in which case one reveals the first Brillouin zone of Bragg-scattered waves. For example, think of the experimental protocol when the incident particle beam is collimated but not monochromatic, while the detector measures the magnitude of $k'$ for a fixed direction. This way one obtains a discrete sequence of points of the reciprocal space, each point corresponding to the intersection of the chosen direction axes with the boundary of each Brillouin zone.

**Structure factor and atomic form-factors**

In the Bragg diffraction context, the periodic function $A(r)$ often comes in the form of atomic decomposition,

$$A(r) = \sum_j f_j(r - r_j),$$  \hspace{1cm} (57)

where $r_j$ is the position of the $j$-th atom in the infinite space.$^5$

Clearly, there is only a finite number of different functions $f_j(r)$, forming sub-lattices of the global lattice; it is sufficient to consider just one of them (and then add similar contributions from the others). For a single sub-lattice we have $f_j(r) \equiv f(r)$, and that is what will be assumed from now on.

In this case, along with the Bragg interference responsible for the Bragg diffraction, there can take place additional interference within a primitive cell. This additional interference can either enhance or suppress the scattering amplitude, depending on $G$. Below we develop corresponding theory.

Given that diffraction peaks are macroscopically sharp while the function $S_\mathbf{q}$ defined by Eq. (44) is a smooth function of $\mathbf{q}$, we naturally confine our consideration with $\mathbf{q} = \mathbf{G}$. In the Bragg spectroscopy, $S_\mathbf{G}$ is called the structure factor. We have (the utility of the integration over the whole crystal volume $V$ will become clear later)

$$S_\mathbf{G} = \int_{\text{cell}} \int_{n=0} e^{-i\mathbf{G} \cdot \mathbf{r}} A(\mathbf{r}) \, dV \equiv \frac{1}{N_{\text{cells}}} \int_V e^{-i\mathbf{G} \cdot \mathbf{r}} A(\mathbf{r}) \, dV,$$  \hspace{1cm} (58)

$^5$To clearly see the origin of Eq. (57), think, e.g., of a neutron interacting with each nucleus individually: $U_{\text{int}}(r) = \sum_j U_{\text{int}}^{(j)}(r - r_j)$. 

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and comparing this to (7) we see that the structure factor is nothing but the Fourier coefficient of $A$ (up to the normalization of the latter which is a matter of convention):

$$S_G = V_c A_G.$$  \hfill (59)

Now we plug (57), with $f_j = f$, into the second integral of (58) and—understanding that the integration over the whole crystal volume of an essentially localized function $f$ can be upgraded to the infinite-space integration—obtain

$$S_G = \frac{f_G}{N_{\text{cells}}} \sum_j e^{-iG \cdot r_j}, \hfill (60)$$

with

$$f_G = \int e^{-iG \cdot r} f(r) dV \quad \text{(over all the space !)}. \hfill (61)$$

The quantity $f_G$ is called \textit{atomic form-factor}. The expression (60) is not yet the final answer. It can be further simplified by taking into account the translational symmetry. Let us take $j \equiv (n, \nu)$, where $n$ labels the cell (corresponding to the basis translated by $T_n$) and $\nu$ enumerates the atoms within the cell. (At this point it is worth noting that the treatment of this section does not imply that the cell is necessarily primitive.) Then

$$r_j = T_n + R_\nu, \hfill (62)$$

where $R_\nu$ is the position of the $\nu$-th atom in the basis cell, and

$$\sum_j e^{-iG \cdot r_j} = \sum_n \sum_{\nu=1}^{\nu_0} e^{-iG \cdot (T_n + R_\nu)} = \sum_n \sum_{\nu=1}^{\nu_0} e^{-iG \cdot R_\nu} = N_{\text{cells}} \sum_{\nu=1}^{\nu_0} e^{-iG \cdot R_\nu}.$$  

This brings us to the final answer

$$S_G = f_G \sum_{\nu=1}^{\nu_0} e^{-iG \cdot R_\nu}. \hfill (63)$$

We cannot but notice that the form of Eq. (63) is reminiscent of that of the symmetry coefficients, Eq. (32). Apart from the pre-factor $f_G$, the most important qualitative distinction is that $S_G$’s do not have to be zero for certain $G$’s. Indeed, if we are dealing with a primitive cell containing more than one atom (of the same sort or of different sorts), we will still have $\nu_0 > 1$ and thus summation over positions in (63), but no extra symmetries leading to exact cancellations of the terms for certain special $G$’s.
Additivity of the structure factor with respect to different sorts of atoms allows us to immediately generalize Eq. (63) to the case when there are different $f_j$’s:

$$S_G = \sum_{\nu=1}^{\nu_0} f_G^{(\nu)} e^{-iG \cdot R_{\nu}},$$  \hspace{1cm} (64)$$

the label $\nu$ standing now not only for the position of the atom in the primitive cell, but also reflecting the sort of the atom.