

Electrons in Crystals

We are going to apply the 5-point scheme to determine the properties of electrons in crystals.

Recall that we need to use an appropriate Hamiltonian and make approximations to find the quasiparticles and their dispersion curves. Next, interactions between electrons and other elementary excitations are introduced. The physical properties of the solid such as optical and transport properties can be described in terms of response functions that measure the response of the solid to external probes.

The General Hamiltonian

The starting point will be based on the first model of a solid, i.e., a collection of ion cores and itinerant valence electrons.

→ Assumptions and considerations

- The electronic core states are atomic-like in character, which means undeformable and tightly bound to the nuclei.
 - Each core which consists of a nucleus and core electrons, can be treated as a single particle.
- There is a Coulomb interaction between the positive cores and the valence electrons
 - Near a nucleus, a negative test charge experiences an attractive potential corresponding to all the protons in the nucleus.
 - Outside the core effective charge of the core is reduced by the number of core electrons. For example Si, [Ne]3s²3p², then the charge near the nucleus is +14|e|, while the core charge is +4|e|.

→ The total Hamiltonian (H_T) for the cores and valence electrons is

$$H_T = \sum_i \frac{\hat{p}_i^2}{2m} + \sum_n \frac{\hat{p}_n^2}{2M_n} + \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{2} \sum_{nn'} \frac{\sum_l Z_n Z_{n'} e^2}{|\vec{R}_n - \vec{R}_{n'}|} + \sum_n V_n(\vec{r}_i - \vec{R}_n) + H_R$$

$\sum_i \frac{\hat{p}_i^2}{2m}$: Kinetic energy of the valence electrons

$\sum_n \frac{\hat{p}_n^2}{2M_n}$: Kinetic energy of the cores

$\frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$: Coulomb interaction between electrons.

$\frac{1}{2} \sum_{nn'} \frac{Z_n Z_{n'} e^2}{|\vec{R}_{n'} - \vec{R}_n|}$: Coulomb interaction between cores.

$\sum_{in} V_{in}(\vec{r}_i - \vec{R}_n)$: Interaction between electrons and cores.

H_R : Relativistic corrections, including spin-orbit coupling.

\sum' : Primed sum means $i \neq j$ or $n \neq n'$.

\vec{r}_i , \vec{p}_i , e , and m : electrons positions, momentum, charge, and mass.

\vec{R}_n , \vec{p}_n , eZ_n , and M_n : cores positions, momentum, charge, and mass.

- Straight forward approach to solve this Hamiltonian is not practical
- An exact solution means handling $\sim 10^{23}$ quantum #s to describe the problem
- Even if available, these quantum #s are too many for any useful use, and most of them are likely to have obscure or non useful physical meaning.

- Approximations are necessary and must be introduced from the start.

In what follows we introduce three basic approximations.

The Born-Oppenheimer Approximation

- The cores in a solid are much heavier than electrons, $\frac{m}{M} \sim 10^{-3} - 10^{-5}$
- For typical solid densities, the cores behave like classical particles while the electrons form an electron gas (spin-degenerate).
- There is a significant difference between the kinetic energy between both species. At a temperature T $E_m^{\text{kin}} \ll E_e^{\text{kin}}$.
- The difference in the mass and kinetic energy means that within the time that characterizes the motion of the cores, the electrons will be able to accommodate almost **instantaneously** to the position of the cores.
- These conditions are suitable for the **adiabatic approximation**, which stipulates that for a time dependent Hamiltonian $H(t)$ that changes adiabatically (indefinitely slow) and for which at every time instant t the eigenvalues of $H(t)$ are non-degenerate,

$$E_j(t) \neq E_k(t), \quad \forall t, \text{ and all } j \text{ and } k,$$

the system will always stay in the same eigenket $|j\rangle$ when evolving in time. We only need to consider instantaneous eigenvalues and vectors of $H(t) \forall t$. Let us rewrite the general Hamiltonian as

$$H = H_c + H_e + H_{ec}, \text{ where}$$

$$H_c = \sum_n \frac{\hat{p}_n^2}{2M_n} + \frac{1}{2} \sum_{nn'} \frac{Z_n Z_{n'} e^2}{|\vec{R}_n - \vec{R}_{n'}|}$$

$$H_e = \sum_i \frac{\hat{p}_i^2}{2m} + \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + H_R$$

$$H_{ec} = \sum_{i,n} V_n(\vec{r}_i - \vec{R}_n) = - \sum_{i,n} \frac{Z_n e^2}{|\vec{r}_i - \vec{R}_n|}$$

Recall that the ionic positions $\vec{R}_n = \vec{R}_n(t)$ change adiabatically in comparison to the fast movement of the electrons. In molecular and in Condensed Matter systems, this adiabatic approximation is referred to as the Born-Oppenheimer approximation, BOA.

→ In BOA, we initially drop $H_c \ll H_e + H_{ec}$, and we solve the Schrödinger equation corresponding to the instantaneous Hamiltonian for the electrons,

$$(H_e + H_{ec}) |\Psi_j(\vec{x}, \vec{R})\rangle = E_j^e(\vec{R}) |\Psi_j(\vec{x}, \vec{R})\rangle$$

$\vec{x} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ and $\vec{R} = (\vec{R}_1, \vec{R}_2, \dots, \vec{R}_N)$, freezing the position of the cores at every time t . Notice that eliminating H_c demotes the variables \vec{R}_i to parameter status in the electrons Hamiltonian.

→ Having solved for the electronic eigenkets $\{|\Psi_j(\vec{x}, \vec{R})\rangle\}$ and eigenvalues $\{E_j^e\}$, we can now obtain the eigenfunction of the full Hamiltonian, using the product ansatz

$$|\Psi(\vec{x}, \vec{R})\rangle = |\Psi(\vec{x}, \vec{R})\rangle |\Phi(\vec{R})\rangle$$

where $|\Phi(\vec{R})\rangle$ is the wavefunction associated with the motion of the cores. Recall that the electrons are initially in the state $|\Psi_j(\vec{r}, \vec{R})\rangle$, then they remain in this state as the system evolves. Let us assume that the system was initially in the ground state, then $|\Psi_j(\vec{r}, \vec{R})\rangle \rightarrow |\Psi_0(\vec{r}, \vec{R})\rangle$.

→ The total Hamiltonian is $H = H_e + H_{ec} + H_c$

We first act with $H_e + H_{ec}$ on $|\Psi(\vec{x}, \vec{R})\rangle$

$$(H_e + H_{ec}) |\Psi_0(\vec{x}, \vec{R})\rangle |\Phi(\vec{R})\rangle = |\Psi_0(\vec{x}, \vec{R})\rangle E_0^e(\vec{R}) |\Phi(\vec{R})\rangle$$

Next is $H_c = \sum_n \frac{\vec{p}_n^2}{2M_n} + \frac{1}{2} \sum_{nn'} \frac{2\pi^2 n^2 e^2}{|R_n - R_{n'}|^3}$,

so let us first act with the potential on $|\Psi(\vec{x}, \vec{R})\rangle$

$$\frac{1}{2} \sum_{n=1}^{\infty} \frac{Z_n Z_{n+1}}{2M_n} |\Psi(\vec{x}, \vec{R})\rangle |\Phi(\vec{R})\rangle = |\Psi_0(\vec{x}, \vec{R})\rangle |U_0(\vec{R})\rangle |\Phi(\vec{R})\rangle$$

Next is the kinetic energy term in \mathcal{H}_c . Recall that in $\sum_n \frac{\hat{P}_n^2}{2M_n}$, the operator \hat{P}_n^2 is

$\hat{P}_n^2 = -i\hbar^2 \nabla_{R_n}^2$. We are going to use the following convention, when \hat{P}_n acts on $|\Phi(\vec{R})\rangle$ we will keep the implicit operator form, since \hat{P}_n is the cores momentum. When \hat{P}_n acts on $|\Psi_0(\vec{x}, \vec{R})\rangle$ we take $\hat{P}_n = -i\hbar \nabla_{R_n}$. Then when we act with \hat{P}_n^2 on $|\Psi(\vec{x}, \vec{R})\rangle$ we get

$$\begin{aligned} \hat{P}_n^2 |\Psi_0(\vec{x}, \vec{R})\rangle |\Phi(\vec{R})\rangle &= (-\hbar^2 \nabla_{R_n}^2 |\Psi_0(\vec{x}, \vec{R})\rangle) |\Phi(\vec{R})\rangle + |\Psi_0(\vec{x}, \vec{R})\rangle \hat{P}_n^2 |\Phi(\vec{R})\rangle \\ &\quad - 2i\hbar \nabla_{R_n} |\Psi_0(\vec{x}, \vec{R})\rangle \cdot \hat{P}_n |\Phi(\vec{R})\rangle \end{aligned}$$

Then we can write

$$\begin{aligned} \mathcal{H} |\Psi(\vec{x}, \vec{R})\rangle &= |\Psi_0(\vec{x}, \vec{R})\rangle \left[- \sum_n \frac{\hbar^2 \nabla_{R_n}^2}{2M_n} + U_0(\vec{R}) + E_0(\vec{R}) \right] |\Phi(\vec{R})\rangle \\ &\quad - \sum_n \left[\frac{i\hbar}{M_n} (\nabla_{R_n} |\Psi_0(\vec{x}, \vec{R})\rangle) \cdot \hat{P}_n + \nabla_{R_n}^2 |\Psi_0(\vec{x}, \vec{R})\rangle \right] |\Phi(\vec{R})\rangle \end{aligned}$$

Operating by $\langle \Psi_0(\vec{x}, \vec{R}) |$ on $\mathcal{H} |\Psi(\vec{x}, \vec{R})\rangle$ we get

$$\mathcal{H}_{eff,c} |\Phi(\vec{R})\rangle = \left[\sum_n \frac{1}{2M_n} (\hat{P}_n - \hbar A_0)^2 + U(\vec{R}) \right] |\Phi(\vec{R})\rangle$$

where $A_0 = i \sum_n \langle \Psi_0(\vec{x}, \vec{R}) | \nabla_{R_n} |\Psi_0(\vec{x}, \vec{R})\rangle$

$$U_1(\vec{R}) = \sum_n \frac{\hbar^2}{2M_n} \langle \Psi_0(\vec{x}, \vec{R}) | \nabla_{R_n}^2 |\Psi_0(\vec{x}, \vec{R})\rangle$$

$$U(\vec{R}) = U_0(\vec{R}) + E_0(\vec{R}) - U_1(\vec{R}) - A_0^2 \sum_n 1/2M_n$$

The term A_0 is known as the Berry's vector potential.

for a normalized state

$$\nabla_{\vec{R}_n} \langle \Psi_0(\vec{x}, \vec{R}) | \Psi_0(\vec{x}, \vec{R}) \rangle = 0$$

$$= \langle \nabla_{\vec{R}_n} \Psi_0(\vec{x}, \vec{R}) | \Psi_0(\vec{x}, \vec{R}) \rangle + \langle \Psi_0(\vec{x}, \vec{R}) | \nabla_{\vec{R}_n} \Psi_0(\vec{x}, \vec{R}) \rangle$$

$$= 2 \operatorname{Re} \langle \Psi_0(\vec{x}, \vec{R}) | \nabla_{\vec{R}_n} \Psi_0(\vec{x}, \vec{R}) \rangle$$

which makes $A_0 = 0$ since the ground state has to be real (TR-symmetry).

Then the effective Hamiltonian for the cores is

$$H_{\text{eff},c} = \sum_n \frac{\hat{p}_n^2}{2Mn} + \frac{1}{2} \sum_{n \neq n'} \frac{Z_n Z_{n'} e^2}{|\vec{R}_n - \vec{R}_{n'}|} + U_2(\vec{R})$$

$$\text{where } U_2(\vec{R}) = E_0^c + U_1(\vec{R}), \text{ where } U_1(\vec{R}) = - \sum_n \frac{\hbar^2}{2Mn} \langle \Psi_0(\vec{x}, \vec{R}) | \nabla_{\vec{R}_n}^2 | \Psi_0(\vec{x}, \vec{R}) \rangle$$

for the contribution of U_1 , we assume the extreme case where the electrons are tightly bound to the cores $\rightarrow \vec{x}_i \simeq \vec{R}_j$ for some i and j . Then we can make an estimate

$$-\frac{\hbar^2}{2M} \sum_n \langle \Psi_0(\vec{x}, \vec{R}) | \nabla_{\vec{R}_n}^2 | \Psi_0(\vec{x}, \vec{R}) \rangle \simeq -\frac{\hbar^2}{2M} \sum_i \langle \Psi_0(\vec{x}, \vec{R}) | \nabla_{\vec{R}_i}^2 | \Psi_0(\vec{x}, \vec{R}) \rangle$$

$$= \frac{m_e}{M} E_{\text{kin}}^c \ll |E_0^c|$$

then we can neglect this term, and we get

$$H_{\text{eff},c} |\Phi(\vec{R})\rangle = \left[\sum_n \frac{\hat{p}_n^2}{2Mn} + U(\vec{R}) \right] |\Phi(\vec{R})\rangle$$

$$\text{where } V(\vec{R}) = \frac{1}{2} \sum_{n_1 n_2} \frac{Z_{n_1} Z_{n_2} e^2}{|\vec{R}_{n_1} - \vec{R}_{n_2}|} + E_o(\vec{R})$$

- The BOA provides the important step of separating the electronic and core degrees of freedom
- The electronic part leads primarily to the determination of the properties of electrons, holes, excitons, plasmons, and magnons.
- The core part is used to determine the cores motion and phonons.
- When the phonons are coupled to the electrons including terms in the general Hamiltonian that go beyond the electronic and core parts we can examine polarons, superconductivity and other properties of solids.

Now we focus on the electronic Hamiltonian.

The mean-field Approximation

$$H_{el} = H_e + H_{ec} = \sum_i \left[\frac{\hat{p}_i^2}{2m} + \sum_n V_n (\vec{r}_i - \vec{R}_n) \right] + \frac{1}{2} \sum_{ij} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + H_R$$

- The electronic Hamiltonian does not include the cores dynamical variables
- H_{el} still contains a very large # of particles, mainly, all the valence electrons.
- Another approximation is needed.
- The simplest approximation is the Hartree mean-field approximation

The Hartree Approximation assumes that each electron moves in the average field (mean field) created by the cores together with all other electrons.

→ The electronic wavefunction of all valence electrons is approximated by a product of one electron wavefunctions, and each one is characterized by some one-electron spatial and spin quantum #s.

→ The effects of the Pauli exclusion principle are taken into account by requiring that no pairs of one electron wavefunctions (orbitals) in the product have identical sets of quantum #s.

→ Demanding that the ground state has the lowest energy for the electronic system results into a set self consistent Euler-Lagrange equations (the Hartree equations) for the one electron orbitals and energies with potential $V(\vec{r}, \{\vec{R}_n\})$.

→ The Hartree approximation accomplishes the important task of separating HeI into a sum of one electron Hamiltonians

$$H_{el} = \sum_i H(\vec{r}_i, \{\vec{R}_n\}) \text{ where } H(\vec{r}, \{\vec{R}_n\}) = \frac{\hat{p}^2}{2m} + V(\vec{r}, \{\vec{R}_n\})$$

→ Another mean-field approach is the Hartree-Fock approximation.

→ This approach approximates the wave function by a determinant (Slater determinant) → All the symmetry required by the Pauli principle are satisfied

The Periodic Potential Approximation

$$H_{el} = \sum_i H(\vec{r}_i, \{\vec{R}_n\}) \text{ where } H(\vec{r}, \{\vec{R}_n\}) = \frac{\hat{p}^2}{2m} + V(\vec{r}, \{\vec{R}_n\})$$

The potential $V(\vec{r}, \{\vec{R}_n\})$ is a one-electron potential that describes the interactions acting on the one electron labeled by the coordinate \vec{r} .

→ It depends on the one-electron states occupied by all other electrons, because of the Pauli principle (Slater determinant).

→ Depends parametrically on the "fixed" positions of the cores $\{\vec{R}_n\}$.

→ Even though the evaluation is reduced to one-electron at a time, it must

be done self-consistently to account for the electrons and core configurations.

→ Experiments tell us that in a **crystalline solid** the cores (to a good approximation) form an **ordered periodic array**.

→ We can take the starting point as a perfect crystal with core positions $\{\vec{R}_n\}$ determined by X-rays, crystallography or other means.

→ We also assume (at this stage) that there are no defects or surfaces, and we also assume temporarily an infinite # of atoms in the crystal.

→ With fixed $\{\vec{R}_n\}$ we can write $V(\vec{r}, \{\vec{R}_n\}) = V(\vec{r})$, where $V(\vec{r})$ has the symmetry of the periodic crystal arrangement.

→ Because of the periodicity an electron at \vec{r} feels the same potential as an electron at \vec{r}' which is related to \vec{r} by the periodicity and the symmetry of the lattice.

→ $V(\vec{r})$ describes the chemical composition of the crystal, the crystal structure and its relevant parameters, the equilibrium positions of the cores, and the averaged potential acting on an electron produced by all the others.

→ We have arrived at the one-electron periodic potential model.

→ With this model we can answer many questions about the properties and behavior of electrons in a solid at a mean-field level.

The crystal as a Broken-Symmetry State

A crystal is a special state of spontaneously broken translation symmetry.

Consider

$$H_{el} = \sum_i \left[\frac{\vec{p}_i^2}{2m} + \sum_n V_n(\vec{r}_i - \vec{R}_n) \right]$$

and recall that $V_n(\vec{r}_i - \vec{R}_n)$ depends on $|\vec{r}_i - \vec{R}_n|$

→ The Hamiltonian is invariant under translation symmetry. That is, if

$$\vec{r}_i \rightarrow \vec{r}_i + \vec{\delta} \text{ and } \vec{R}_n \rightarrow \vec{R}_n + \vec{\delta} \quad \forall i \text{ and } n.$$

then \hat{H} is unchanged.

→ \hat{H} is also invariant under rotations by an arbitrary angle Θ

$$\vec{r}_i \rightarrow \hat{\Theta}(\Theta) \vec{r}_i \text{ and } \vec{R}_n \rightarrow \hat{\Theta}(\Theta) \vec{R}_n \quad \forall i \text{ and } n$$

→ and space inversion (or parity)

$$\vec{r}_j - \vec{R}_n \rightarrow -(\vec{r}_j - \vec{R}_n) \quad \forall n \text{ and } j.$$

→ In a uniform liquid, the time-averaged density of particles $\langle \rho(\vec{R}) \rangle$ is constant (independent of \vec{R}), symmetric under T , Θ , and P .

→ In a crystal $\langle \rho(\vec{R}) \rangle$ becomes non constant but periodic

→ $\langle \rho(\vec{R}) \rangle$ is now invariant under discrete translations but not a general one.

→ The state of the crystal has less symmetry than its Hamiltonian. This phenomenon is known as Spontaneously broken symmetry.

→ Crystallization occurs because the particles arrange themselves in special positions to minimize the potential energy.

→ With few exceptions, quantum condensed matter systems form crystalline solids at zero temperature ($T=0$) because it minimizes the total energy.

→ There is no rigorous proof that a crystal is the optimum arrangement that to minimize $\langle H \rangle$, but experiments show that this is often the case (quasicrystals are an exception).

→ Helium, low atomic mass, weak interactions, the quantum zero point energy leaves the system as a liquid at $T=0$.

→ Heating up a metal restores the full T_c , Θ and P through one or more melting transitions → at high temperatures the system will be in the liquid phase with no ordering.

→ **The order parameter**: Is a quantity that measures the degree to which a symmetry is broken. It transforms non-trivially under a symmetry operation and thus it characterizes **how (structure) and how much (magnitude)** the symmetry is broken.

→ The order parameter of ferromagnets is magnetization \vec{M} . \vec{M} breaks spin rotation symmetry and transforms as a vector under R . R is broken when $\vec{M} \neq 0$, and $|\vec{M}|$ quantifies the degree to which R is broken.

→ What is the order parameter that measures broken translation symmetry?

Consider the Fourier transform of the density

$$\langle \rho(\vec{k}) \rangle = \frac{1}{V} \int d^3 \vec{r} \langle \rho(\vec{r}) \rangle e^{i \vec{k} \cdot \vec{r}}$$

V is the volume of the system.

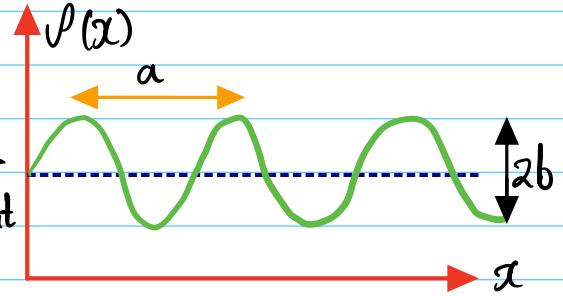
For a uniform liquid, $\langle \rho(\vec{r}) \rangle = \bar{\rho}$ which implies that

$$\langle \rho(\vec{k}) \rangle = 0 \quad \forall \vec{k} \neq 0, \text{ and } \langle \rho(\vec{k}=0) \rangle = \bar{\rho}$$

for a crystal the situation is different. Consider a simple 1D example.

$$\langle \rho(x) \rangle = \bar{\rho} + b \cos\left(\frac{2\pi x}{a} - \theta\right)$$

a is the lattice constant, b measures the strength of the ordering and θ is the phase that determines where the density peaks are.



We also notice a discrete translation symmetry $x \rightarrow x + na + n \in \mathbb{Z}$.

$$\rho(\vec{k}) = \lim_{L \rightarrow \infty} \frac{1}{L} \int dx \left[\bar{\rho} + \frac{b}{2} \left(e^{2\pi i x/a} e^{i\theta} + e^{-2\pi i x/a} e^{i\theta} \right) e^{i k x} \right]$$

$$\rightarrow \rho(\vec{k}) = \bar{\rho} \delta_{k,0} + \frac{b}{2} \left\{ e^{i\theta} \delta_{k, \frac{2\pi}{a}} + e^{i\theta} \delta_{k, -\frac{2\pi}{a}} \right\}$$

$\rho(\vec{k})$ at $k = \pm \frac{2\pi}{a}$ is an order parameter. Under translations θ changes and hence $\rho(\vec{k})$ changes.

→ The order parameter is characterized by

1) The magnitude b . Similar to $|\vec{M}|$ in ferromagnets

2) The phase angle which is a quantity that transforms non-trivially under Tr. Similar to \vec{M} in ferromagnets (non-trivial under R).

3) The wavevector \vec{k} . (not present in FMs since $\vec{k}=0$ for \vec{M}).

Translational Symmetry, Periodicity, and Lattices

$$H_{el} = \sum_i H(\vec{r}_i, \vec{R}_n \vec{y}) \quad \text{where} \quad H(\vec{r}, \vec{R}_n \vec{y}) = \frac{\vec{p}^2}{2m} + V(\vec{r}, \vec{R}_n \vec{y})$$

$$V(\vec{r}, \vec{R}_n \vec{y}) = V(\vec{r})$$

The crystal potential $V(\vec{r})$ describes a perfect crystal.

→ A perfect crystal: Collection of electrons and static cores in a perfect periodic arrangement.

→ Given an arbitrary point \vec{r} in the crystal, there is an infinite array of points $\vec{r} + \vec{R}_n$ such that (without change of orientation) the crystal appears exactly the same regardless from which point the arrangement is viewed from.

$$V(\vec{r} + \vec{R}_n) = V(\vec{r})$$

→ The collection of all vectors $\{\vec{R}\}$ form a set of discrete points called a **Bravais Lattice**. In 3D a Bravais lattice is a set of points of the form

$$\vec{R}_{\vec{n}} = \vec{R}_{n_1, n_2, n_3} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3,$$

where the vectors \vec{a}_i are not coplanar

$$(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3 \neq 0,$$

and $n_1, n_2, n_3 = 0, \pm 1, \pm 2, \dots$.

→ **Lattice Vectors**: The vectors \vec{R}_n are called lattice vectors or translation vectors.

→ The vectors \vec{a}_i are called the **primitive lattice vectors** or primitive translation vectors.

→ The parallelepiped defined by the 3 lattice vectors \vec{a}_1, \vec{a}_2 , and \vec{a}_3 has a volume V_p given by

$$V_p = |(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3|$$

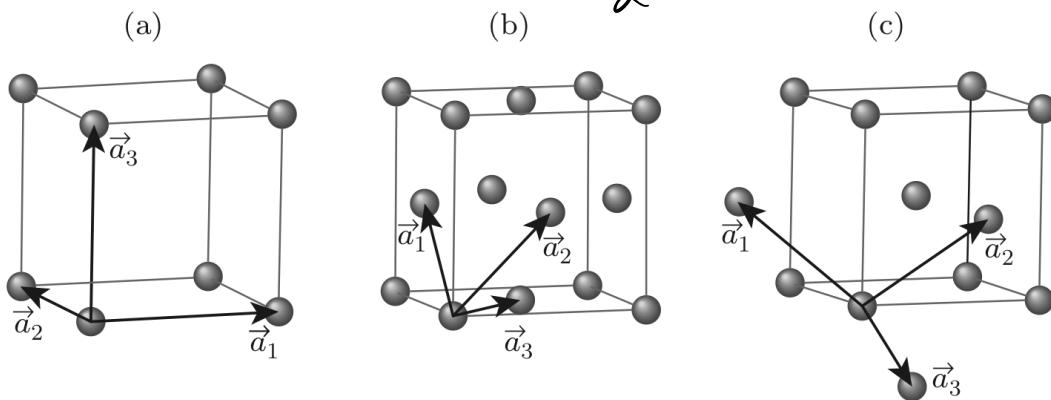
and the lattice points in a Bravais lattice have a density $1/V_p$

Common examples in 3D

a) Simple cubic lattice : $\vec{a}_1 = a\hat{i}$, $\vec{a}_2 = a\hat{j}$, $\vec{a}_3 = a\hat{k}$

b) Face-centered cubic lattice : $\vec{a}_1 = \frac{a}{2}(\hat{j} + \hat{z})$, $\vec{a}_2 = \frac{a}{2}(\hat{z} + \hat{x})$,
 $\vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{j})$

c) Body-centered cubic lattice : $\vec{a}_1 = \frac{a}{2}(\hat{j} + \hat{z} - \hat{x})$, $\vec{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{j})$,
 $\vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{j} - \hat{z})$.

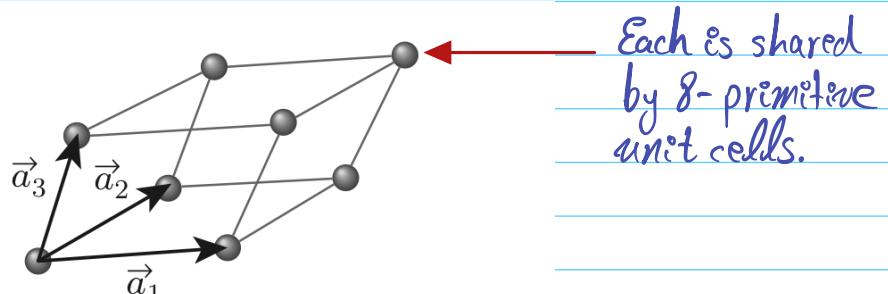


Every lattice site in a Bravais lattice has the same # of nearest neighbours. This is called the **coordination number**. (6, 12, 8).

→ **Primitive Cell**: Is a region in space that, when translated by all the vectors in the Bravais Lattice, exactly fills all the space of the crystal without voids or overlaps.

Each primitive cell contains only one lattice point.

The volume of the primitive cell is Nq , and the parallelepiped is one kind of choice of primitive cell.



This choice gives a 1 to 1 correspondence between the primitive cell and

the lattice sites.

Although the volume of the primitive unit cell is constant, its shape is arbitrary (it can consist of disconnected parts).

→ **Unit Cell**: is a region in space which, when translated by a subset of vectors of the Bravais lattice, exactly fill the space of the crystal with no voids or overlap.

The volume of the unit cell satisfies

$$\int u = v \int p, v=1,2,3,\dots$$

Then the primitive cell is a unit cell of minimum volume.

→ **Basis**: A basis is the set of atoms and their coordinates within the unit cell which form the crystal.

The basis for a primitive cell is smaller than the basis for the unit cell. The bases of the primitive cell are the minimal bases.

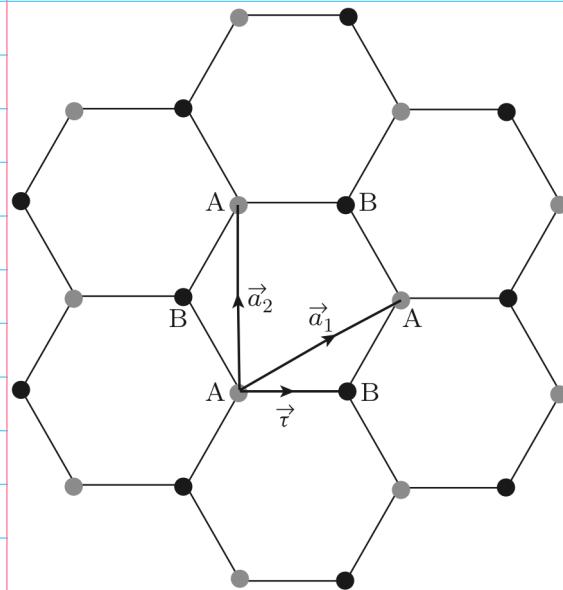
A basis must contain an integral number of the formula units that characterize the crystal.

Mathematically, a basis is given by a finite set of vectors $\{\vec{t}_m\}, m=1,2,\dots, N_b$ where N_b is the number of atoms in the basis.

Because the origin of the unit cell is arbitrary, two bases, which differ by a constant displacement, $\{\vec{t}_m\}$ and $\{\vec{t}_m + \vec{r}_n\} + M$ define the same crystal.

The change of any basis vector by a translation vector ($\vec{t}_m + \vec{r}_n$) yields a different basis and a different unit cell, but still describe the same crystal.

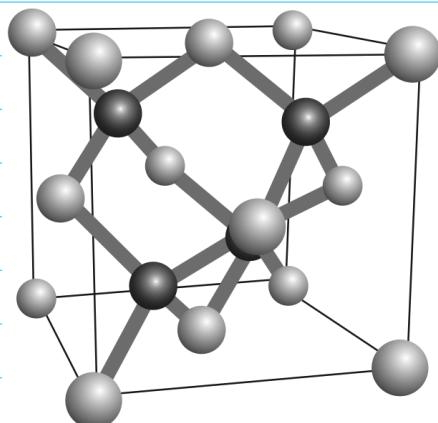
Examples of lattices with basis:



The vector $\vec{\tau}$ connecting neighboring atoms is not a translation primitive translation vector.

The underlying Bravais lattice is a triangular lattice.

The honeycomb lattice can be viewed as a triangular lattice with 2-point basis, or two interpenetrating triangular lattices formed by the A and the B sites.



Diamond, Silicon, and Germanium have 2-atoms/unit cell.

The underlying Bravais lattice is FCC and $\vec{\tau}$ is along the diagonal of the cube with one quarter length of the diagonal $\rightarrow \vec{\tau} = \frac{c}{4} (\hat{i} + \hat{j} + \hat{k})$.

Bravais Lattices in 1D and 2D

(a)	Linear	(b)	Square	(c)	Rectangular
	$ a $		$ a = b , \varphi = 90^\circ$		$ a \neq b , \varphi = 90^\circ$
(d)	Oblique	(e)	Hexagonal	(f)	Centered Rectangular
	$ a \neq b , \varphi \neq 90^\circ$		$ a = b , \varphi = 120^\circ$		$ a \neq b , \varphi = 90^\circ$

Bravais lattices in 3D

cubic:
simple



body centered



cubic:
all sides equal
all angles 90°

tetragonal:



simple

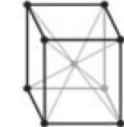


tetragonal:
only two of three side lengths equal
all angles 90°

orthorhombic:



simple



body centered



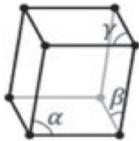
face centered



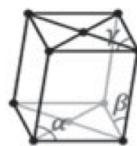
base centered

orthorhombic:
no two sides equal
all angles 90°

simple
monoclinic

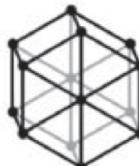


base
centered
monoclinic

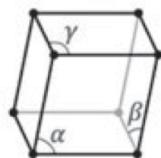
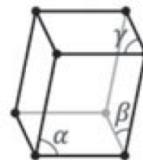


monoclinic:
angles between primitive
lattice vectors :
 $\alpha = 90^\circ$ $\gamma = 90^\circ$
 $\beta \neq 90^\circ$
only two right angles

hexagonal



triclinic:
no right angles
no two sides equal



rhombohedral:
all side lengths equal.
all angles equal, but not right angles.

→ **Wigner-Seitz Cell**: The Wigner-Seitz cell is a special primitive cell.
It is built by: 1) Drawing a line from the origin of the Bravais lattice to

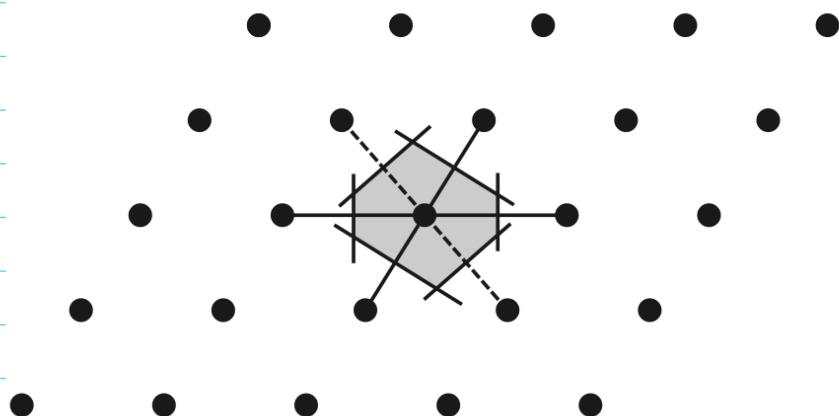
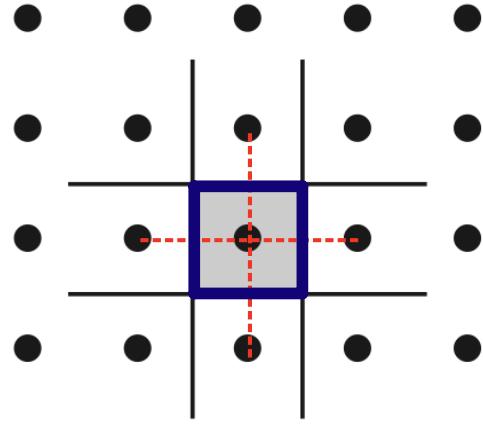
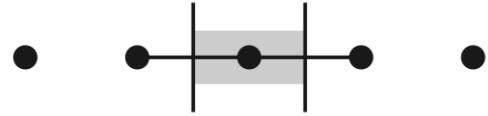
the nearest neighbor lattice points

2) Construct all the planes of that bisect and are perpendicular to the lines.

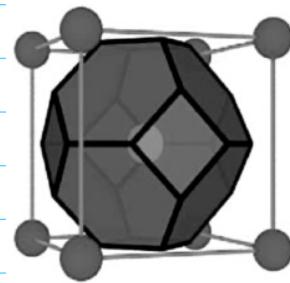
3) The smallest polyhedron that remains at the origin is the Wigner-Seitz cell.

The Wigner-Seitz cell is the most compact of all primitive cells and exhibits the maximum number of symmetries.

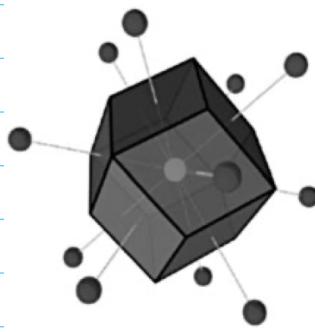
Examples :



Wigner-Seitz Cell in 3D

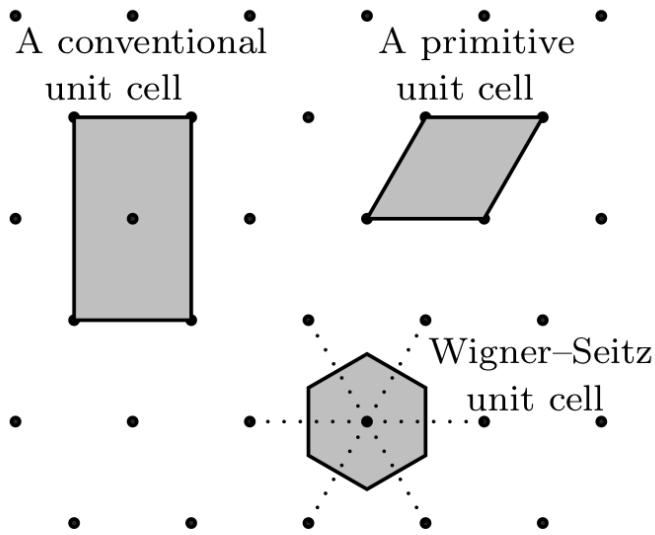


BCC

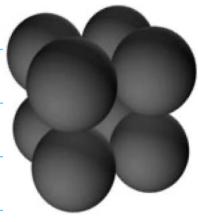


FCC

The 3-different Cells



→ Atoms Per Unit Cell and the Atomic Packing factor



SC 1-atom



BCC 2-atoms



FCC 4-atoms



Atomic Packing factor = APF = $\frac{N_{atc} V_a}{V_c}$; V_a = Volume of the atom

V_c = Volume of the cell

N_{atc} = # of atoms / cell

$$SC - APF = \frac{1 \cdot \frac{4}{3}\pi r^3}{(2r)^3} = \frac{\frac{4}{3}\pi r^3}{8r^3} = \frac{\pi}{6}$$

$$FCC - APF = \frac{4 \cdot \frac{4}{3}\pi r^3}{(2\sqrt{2}r)^3} = \frac{\frac{4}{3}\pi r^3}{16r^3} = \frac{\pi}{6\sqrt{2}}$$

$$BCC - APF = \frac{2 \cdot \frac{4}{3}\pi r^3}{(\frac{4r}{\sqrt{3}})^3} = \frac{\frac{8}{3}\pi r^3}{\frac{64r^3}{27}} = \frac{27\pi}{64}$$

→ Lattice Symmetries in addition to Discrete Translations

Rotations by angles $2\pi/n$ ($n \in \mathbb{Z}$), along certain axes (in 3D, in 2D an axis reduces to a point).

These axes are referred to as *n-fold rotation axes*.

Example: Each lattice site of a square lattice is a 4-fold rotation axis and so is the center of each square.

Inversion about a special point known as an inversion center. This is specific to 3D in 2D an inversion is equivalent to a π rotation about an inversion center, and thus it is not an independent symmetry. But because of its importance people sometimes specify whether a 2D crystal has an inversion center or not. Crystals with at least one inversion center are called *centrosymmetric*, otherwise they are called *non-centrosymmetric*.

Example: Each lattice site of a Bravais lattice is an inversion center, thus all Bravais lattices are centrosymmetric.

Reflection about a plane (in 3D, in 2D it reduces to a line)

Examples : Each lattice point that connects a lattice point to its nearest (or next-nearest) neighbour is a mirror line on a square or triangular lattice.

Combinations of all the above along with a translation (not necessarily by a lattice vector).

→ **Reciprocal Lattice** : Is a mathematical construction to study quantum mechanical properties of solids.

Given a crystal and its Bravais lattice defined by three primitive translation vectors \vec{a}_1 , \vec{a}_2 , and \vec{a}_3 we define the reciprocal lattice as

$$\vec{g}_m \equiv m_1 \vec{g}_1 + m_2 \vec{g}_2 + m_3 \vec{g}_3 \quad (m_1, m_2, m_3 = \text{integers})$$

such that for any translation vector \vec{R}_n

$$\vec{g} \cdot \vec{R}_n = 2\pi v \quad (v = \text{integer})$$

for any m_1, m_2, m_3 . Then, we can easily show that

$$\vec{g}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{(\vec{a}_i \times \vec{a}_j) \cdot \vec{a}_k}$$

where $(i \rightarrow j \rightarrow k) = (1 \rightarrow 2 \rightarrow 3)$, in cyclic in order, satisfies the requirements with $v = n_1 m_1 + n_2 m_2 + n_3 m_3$.

The magnitude of \vec{a}_i is in units of length, typically Å or Bohr radius a_0 , the magnitudes of \vec{g}_i are measured in units of Å^{-1} or a_0^{-1} . This space of inverse length where we define the reciprocal lattice is called the **reciprocal space**.

→ **Periodic functions** : Any function $U(\vec{r})$ that has the periodicity of the lattice

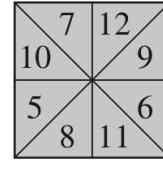
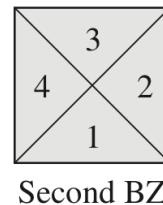
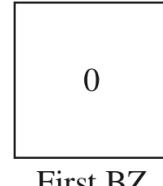
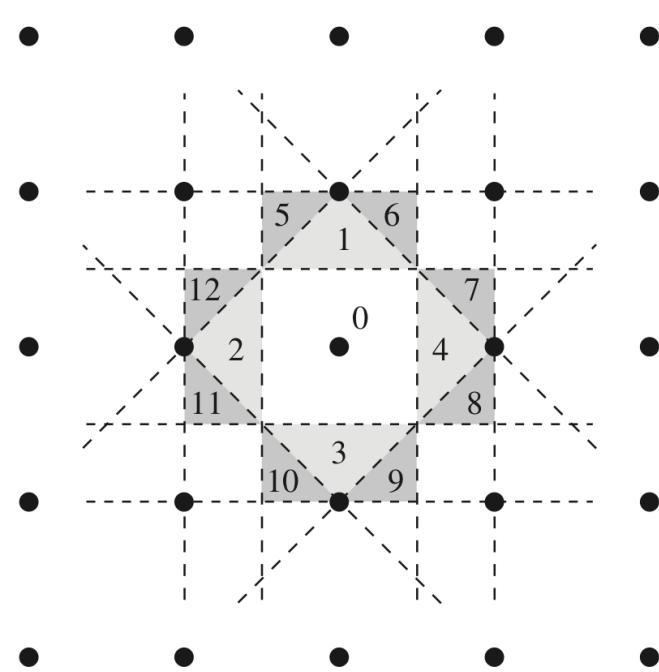
$$U(\vec{r} + \vec{R}_n) = U(\vec{r})$$

can be expressed in a "discrete" Fourier expansion

$$U(\vec{r}) = \sum_m b_m e^{i\vec{g}_m \cdot \vec{r}},$$

where \vec{g}_m are the reciprocal lattice vectors.

→ **Brillouin Zone**: Since the reciprocal space is a lattice we may define cells and primitive cells similar to real space.
If we follow the same prescription followed by the Wigner-Seitz we obtain a polyhedron in reciprocal space. This cell is known as the BZ



for 3D the BZ volume is

$$V_{BZ} = |(\vec{g}_1 \times \vec{g}_2) \cdot \vec{g}_3| = 8\pi^3 / [(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3] = 8\pi^3 / V_p$$

A second higher zone can be defined by regions in space between the bisecting planes. These regions are mapped back in the 1st BZ by reciprocal lattice vectors

$$\vec{k} = \vec{k} - \vec{g}_m$$

→ **Periodic Boundary Conditions**: All crystals even perfect ones are finite. The finiteness of a crystal is essential for defining the crystal volume \sqrt{x} and the finiteness has important physical consequences. The presence of a crystal surface or boundary destroys the periodicity of the crystal, and many concepts defined above lose their meaning.

This situation is solved with the aid of a mathematical tool that makes the crystal finite and periodic. This tool is periodic boundary conditions.

Periodic boundary conditions state that a crystal closes onto itself and that the last atom on the right is followed, without loss of periodicity, by the first atom on the left. Similar conditions apply to other n -dimensional crystals. (This corresponds to replacing a line by a circle, a plane by a torus, and the whole crystal by a "super torus")

We eliminate finite crystal effects by considering a crystalline solid of volume \sqrt{x} containing N -primitive cells. Hence, for N primitive cells in the \vec{a}_i -direction ($i=1, 2, 3$ in 3D), any translation of the form $R_{\vec{a}_1}N_1, R_{\vec{a}_2}N_2, R_{\vec{a}_3}N_3$ where $N_i = \text{integer}$, takes the crystal back to itself, and leaves the crystal invariant. Therefore, there are $N \equiv N_1 \cdot N_2 \cdot N_3$ primitive cells and the crystal volume is $\sqrt{x} = N\sqrt{p}$.

Semiclassical Theory of X-ray Scattering

Let us begin by considering the scattering of X-rays from a free non-relativistic electron. We can ignore the nuclei because they are too massive to be perturbed by an electromagnetic field. The electron is assumed to have $v/c \ll 1$, so it couples primarily to the electric field \vec{E} rather than the magnetic field of the X-rays. Hence we can neglect the Lorentz force and we get

$$\vec{\delta r} = -\frac{e}{m_e} \vec{E}(\vec{r} + \vec{\delta r}, t),$$

where \vec{r} is the equilibrium position of the electron, and $\vec{\delta r}$ is the deviation.

tion caused by the external force. Consider a plane wave incident on the electron,

$$\vec{E}(\vec{r}, t) = \vec{E}_{in} e^{i\vec{k} \cdot \vec{r}} e^{i\omega t}$$

The oscillatory force induces a harmonically oscillating dipole

$$\vec{p}(t) = -e\delta(\vec{r}) = \frac{-e^2}{mc^2} \vec{E}_{in} e^{i\vec{k} \cdot \vec{r}} e^{i\omega t}$$

and we assumed that $\vec{k} \cdot \vec{r} \ll 1$ (small oscillations)

The electric field radiated by this oscillating dipole at position \vec{R} is

$$\vec{E}_a = \frac{e^2}{mc^2} [\hat{n} \times (\hat{n} \times \vec{E}_{in})] e^{i\vec{k} \cdot \vec{r}} e^{i\omega t} \frac{e^{iK|\vec{R}-\vec{r}|}}{|\vec{R}-\vec{r}|}$$

where $\hat{n} = \frac{(\vec{R}-\vec{r})}{|\vec{R}-\vec{r}|} \simeq \frac{\vec{R}}{|\vec{R}|}$ is the unit vector along the direction of radiation, $\frac{e^2}{mc^2} \equiv r_c$ is the "classical radius of the electron", $K = w/c$

The factor $|\vec{R}-\vec{r}|^{-1}$ gives the usual fall off of the amplitude for spherical waves due to energy conservation

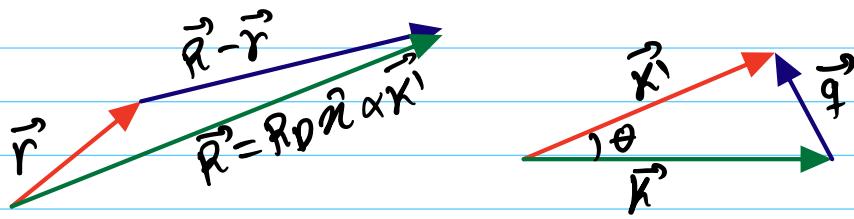
If we have more than one electron the waves from each electron will interfere. If the detector is far away at \vec{R}_D then

$$|\vec{R}-\vec{r}| \rightarrow R_D$$

then we can approximate

$$K|\vec{R}-\vec{r}| = K\sqrt{R_D^2 - 2\vec{r} \cdot \vec{R}_D + r^2}$$

$$\simeq KR_D \left[1 - \frac{\vec{r} \cdot \vec{R}_D}{R_D^2} + O\left(\frac{r^2}{R_D^2}\right) \right]$$



The direction of the detector determines the final state of momentum of the X-ray

$$\vec{k}' \equiv \vec{k} + \vec{q} = K \frac{\vec{R}_D}{R_D} = K \hat{n}$$

since if the target is far away all the beams reaching the detector are parallel.

Then

$$\frac{e^{iK|\vec{R}-\vec{r}|}}{|\vec{R}-\vec{r}|} \approx \frac{e^{iKR_D}}{R_D} e^{i(\vec{k}+\vec{q}) \cdot \vec{r}}$$

where $\vec{h}\vec{q}$ is the momentum taken from the crystal and transferred to the X-ray. Hence

$$\vec{E}_a \approx \frac{e^2}{mc^2} \frac{e^{iKR_D}}{R_D} [\vec{n} \times (\vec{n} \times \vec{E}_{in})] e^{iwt} e^{-i\vec{q} \cdot \vec{r}}$$

The factor $e^{-i\vec{q} \cdot \vec{r}}$ removes momentum $\vec{h}\vec{q}$ from an electronic wavefunction.

This factor arises from the electron moving from the origin to \vec{r} , which changes the phase of the incoming and scattered waves.

The sensitivity of the phase of the scattered wave to the position of the electron allows the deduction of the spatial structure of the electron to be detected by X-rays.

In the case of Z electrons we generalize the result by replacing $e^{-i\vec{q} \cdot \vec{r}}$ by

$$f(\vec{q}) = \sum_{j=1}^Z e^{i\vec{q} \cdot \vec{r}_j}$$

and f is known as the **atomic form factor**, which is usually written as

$$f(\vec{q}) = \int d^3\vec{r} e^{i\vec{q} \cdot \vec{r}} \rho(\vec{r})$$

and $\rho(\vec{r})$ is the density

$$\rho(\vec{r}) = \sum_{j=1}^Z \delta^3(\vec{r} - \vec{r}_j)$$

X-ray Scattering from a Crystal

for a lattice at zero temperature the electron density is periodic and it can be written as

$$\rho(\vec{r}) = \sum_i f_a(\vec{r}_i - \vec{R}_i)$$

where the sum is over the Bravais lattice sites and f_a is the atomic electron density (in the crystalline environment).

Let $F(\vec{q})$ be the form factor of the crystal

$$F(\vec{q}) = \int d^3\vec{r} e^{i\vec{q} \cdot \vec{r}} \sum_i f_a(\vec{r} - \vec{R}_i).$$

We can easily show that

$$F(\vec{q}) = f(\vec{q}) W(\vec{q})$$

where $f(\vec{q})$ describes how the charge is distributed in a single atom

$$f(\vec{q}) = \int d^3\vec{r}' e^{i\vec{q} \cdot \vec{r}'} f_a(\vec{r}')$$

and

$$W(\vec{q}) = \sum_{i=1}^N e^{i\vec{q} \cdot \vec{R}_i}$$

is the **crystal form factor**, which describes how N -atoms are distributed in the system.

It can be also shown that W vanishes for all \vec{q} that are not an element of the reciprocal space and when $\vec{q} = \vec{G}$ then $e^{i\vec{q} \cdot \vec{R}_i} = 1$, and

$$W(\vec{q}) = \sum_{l,m,n} e^{i\vec{q} \cdot (l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3)} = N \sum_{\vec{G}} \delta(\vec{q}, \vec{G})$$

We can also use the Poisson summation formula to get

$$W(\vec{q}) = \sum_{h,k,l} (2\pi)^3 \delta(2\pi h - \vec{q} \cdot \vec{a}_1) \delta(2\pi k - \vec{q} \cdot \vec{a}_2) \delta(2\pi l - \vec{q} \cdot \vec{a}_3)$$

$$W(\vec{q}) = \frac{1}{V_P} \sum_{\vec{G}} (2\pi)^3 \delta^3(\vec{q} - \vec{G}) ; V_P = (\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3$$

recall that for an orthorombic structure $V_P = a_1 a_2 a_3$

Side Note: The Poisson summation formula

Suppose we have a function of a real variable and we wish to sum the values of f on the sites of a uniform lattice of lattice constant a .

$$g = \sum_{n=-\infty}^{\infty} f(na).$$

It is possible to relate this sum to a sum on the reciprocal lattice

$$\sum_{n=-\infty}^{\infty} f(na) = \frac{1}{a} \sum_{l=-\infty}^{\infty} \tilde{f}(gl)$$

Go back to the original problem. The two results — and — are equivalent.

Summing $W(\vec{q})$ in — over \vec{q}

$$\sum_{\vec{q}} W(\vec{q}) = N.$$

Performing the integral of —

$$\frac{V}{(2\pi)^3} \int d^3\vec{q} \frac{1}{\sqrt{p}} (2\pi)^3 \delta^3(\vec{q}) = \frac{V}{\sqrt{p}} = N.$$

We have used $\frac{1}{V} \sum_{\vec{q}} \leftrightarrow \frac{1}{(2\pi)^3} \int d^3\vec{q}$ where V is the total volume

The physical interpretation of the results above. At the scattering angles where the wave-vector transfer lies on a reciprocal lattice, the interference from the scattering from different atoms (or planes of atoms) is constructive, and in all other directions it will be destructive and there will be no scattering.

Then we have found

$$F(\vec{q}) = f(\vec{q}) \frac{(2\pi)^3}{\sqrt{p}} \sum_{\vec{g}} \delta^3(\vec{q} - \vec{g})$$

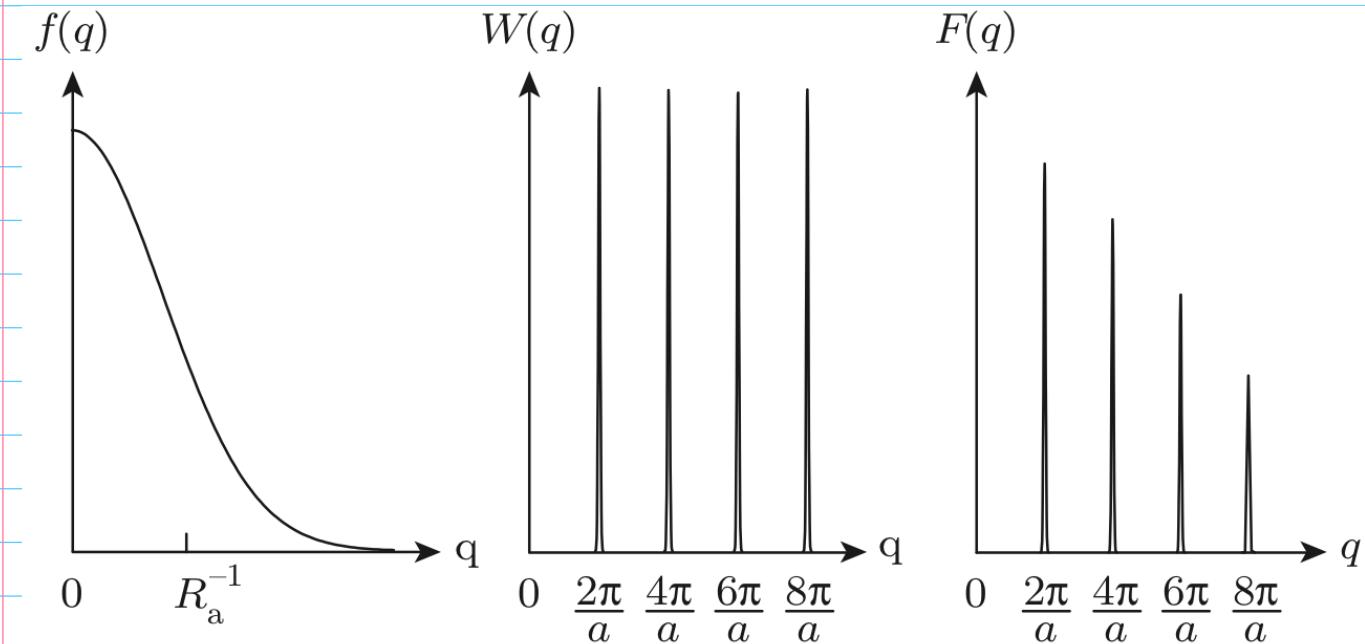
which tells us that the scattering from a crystal singles out only special allowed values of the wave vector and that the weight of the δ -function

is simply the atomic form factor of an individual atom.

The requirement $\vec{q} = \vec{G}$ is called the **Lau diffraction condition**.

The intense diffraction peaks at $\vec{q} = \vec{G}$ are known as **Bragg peaks**.

In a 1-D Bravais lattice



Now that we have established that the only possible X-ray reflections correspond to momentum transfers of $\hbar\vec{G}$, we should see under what conditions such transfers are allowed by **Kinematics**?

If the initial wave vector is \vec{k} and the final wave vector is $\vec{k} + \vec{G}$, energy conservation requires

$$|\vec{k} + \vec{G}|^2 = |\vec{k}|^2$$

or

$$\vec{G}^2 + \vec{k}^2 + 2\vec{k} \cdot \vec{G} = \vec{k}^2$$

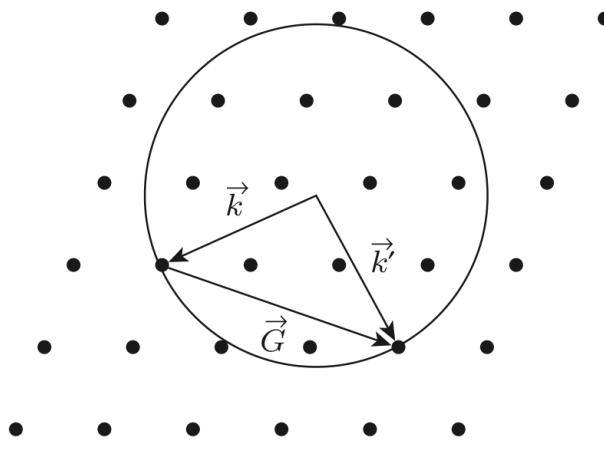
$$\vec{G}^2 + 2\vec{k} \cdot \vec{G} = 0$$

which means that \vec{k} must lie on a **BZ boundary**, which bisects

the reciprocal lattice vector.

The Ewald construction is a graphical method to determine allowed reflections. 1) We draw the reciprocal lattice space. 2) Place the incoming wavevector \vec{k} with the tip of the vector at a reciprocal lattice point. 3) Draw a circle \vec{K} centered at the base of \vec{k} . This circle gives the final wave vectors with the correct energy. 4) If the circle intersects any lattice points, then those points are allowed reflections, since there exist a \vec{G} such that $|\vec{k} + \vec{G}| = |\vec{K}|$.

Generally one has to adjust \vec{k} to find a reflection. This is done by rotating the sample relative to the α -ray, using powder sample consisting of randomly oriented crystallites, or by using non-monochromatic light.



Equivalence of Laue condition and Bragg's Law

Let us start by recalling that

$$\vec{G} \cdot \vec{R}_n = 2\pi v \quad (v = \text{integer})$$

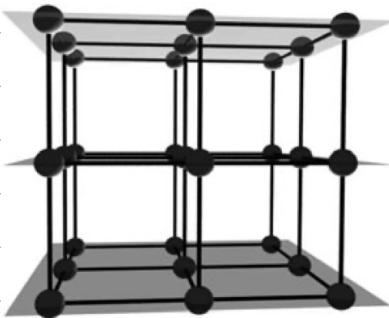
$$\vec{R}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$$\vec{G} = m_1 \vec{g}_1 + m_2 \vec{g}_2 + m_3 \vec{g}_3$$

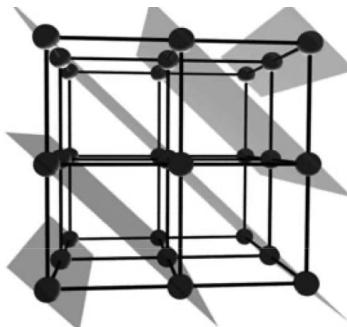
We can also understand reciprocal space in terms of lattice planes.

Lattice plane : contains at least 3-non collinear points of a lattice

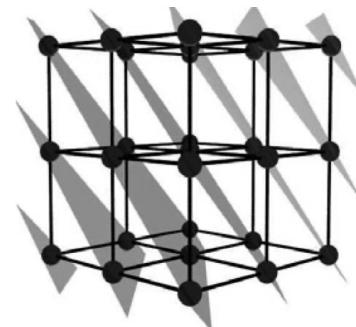
family of lattice planes : is an infinite set of equally separated parallel lattice planes which taken together contain all points of the lattice.



(010) family of lattice planes



(110) family of lattice planes



(111) family of lattice planes

The spacing between planes in a family is

$$d_{hkl} = \frac{2\pi}{|\vec{g}_{(hkl)}|}$$

Here we have written \vec{g} in terms of the Miller indices

$$\vec{g}_{(hkl)} = h\vec{g}_1 + k\vec{g}_2 + l\vec{g}_3, \text{ then}$$

$$|\vec{g}_{(hkl)}| = \sqrt{h^2 |\vec{g}_1|^2 + k^2 |\vec{g}_2|^2 + l^2 |\vec{g}_3|^2}$$

We can construct \vec{g}_1 , \vec{g}_2 and \vec{g}_3 such that $\vec{g}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$

$$|\vec{g}_{(hkl)}| = 2\pi \sqrt{\left(\frac{h}{a_1}\right)^2 + \left(\frac{k}{a_2}\right)^2 + \left(\frac{l}{a_3}\right)^2}$$

$$d_{hkl} = \left[\left(\frac{h}{a_1}\right)^2 + \left(\frac{k}{a_2}\right)^2 + \left(\frac{l}{a_3}\right)^2 \right]^{\frac{1}{2}}$$

Now, recall that Laue condition requires

$$\vec{q} = \vec{k} - \vec{k}' = \hat{\vec{G}}$$

$$\text{recall } \vec{k} = \frac{2\pi}{\lambda} \vec{R}$$

$$\frac{2\pi}{\lambda} (\vec{k} - \vec{k}') = \hat{\vec{G}} \text{ and let us dot by } \hat{\vec{G}}$$

$$\frac{2\pi}{\lambda} \hat{\vec{G}} \cdot (\vec{k} - \vec{k}') = \hat{\vec{G}} \cdot \hat{\vec{G}} = |\hat{\vec{G}}|$$

$$\frac{2\pi}{|\hat{\vec{G}}|} (\sin(\theta) - \sin(\theta')) = \lambda$$

$$2d \sin(\theta) = \lambda \quad (\text{Bragg Condition}).$$

In general

$$2d_{hkl} \sin(\theta_{hkl}) = \lambda$$

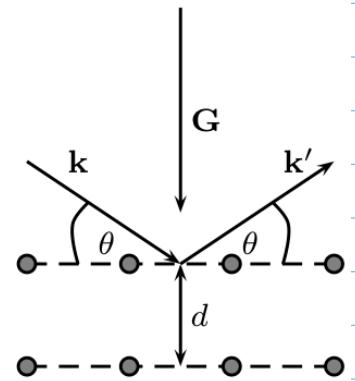
Final note on X-ray Scattering

We have been implicitly ignoring the possibility of a multi-basis in a crystal.

If there are m -atoms in the unit cell then $f(\vec{q})$ is replaced by

$$f(\vec{q}) = \sum_{s=1}^m e^{i \vec{q} \cdot \vec{r}_s} f_s(\vec{q})$$

where f_s is the atomic form factor of the s th atom located at \vec{r}_s in the unit cell.



In this of multi-atom basis, it sometimes happens that, for certain values of \vec{G} , $f(\vec{G})$ vanishes due to destructive interference.

This occurs for instance e.g. diamond and silicon, where we have 2-identical atoms in the unit cell (So that $f_1 = f_2$). These so called "forbidden reflections" can cause confusion in structural determination.