

Electronic structure for crystals

The reciprocal space and Bloch theorem

Ling-Ti Kong

EEmail: konglt@sjtu.edu.cn

School of Materials Science and Engineering, Shanghai Jiao Tong University

Nov 09, 2022



Outline

- 1 Fourier transformation
- 2 Lattice and Reciprocal Lattice
- 3 Particles in a periodic potential
- 4 Further readings

Preliminary: δ -function

δ -function

- Dirac δ -function

$$\delta(x - x_0) = \begin{cases} \infty & \text{if } x = x_0 \\ 0 & \text{otherwise} \end{cases}$$

- Kronecker δ -function

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases}$$

Definition of Dirac δ -function

$$\begin{aligned} \delta(x - x_0) &= \int_{-\infty}^{\infty} e^{2\pi i(x-x_0)\xi} d\xi \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(x-x_0)\omega} d\omega \\ \delta_{mn} &= \frac{1}{N} \sum_k e^{2\pi i \frac{k}{N}(n-m)} \end{aligned}$$

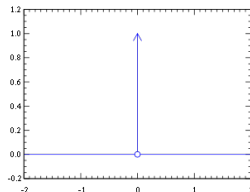
Properties of δ -function

$$\delta(-x) = \delta(x); \quad \delta(ax) = \frac{1}{|a|} \delta(x)$$

$$\int_{-\infty}^{\infty} \delta(x - x_0) dx = 1$$

$$\int_{-\infty}^{\infty} f(x) \delta(x - x_0) dx = f(x_0)$$

$$\sum_j x_j \delta_{i,j} = x_i$$



Fourier transformation

Fourier Transformation (FT)

$$f(t) \Rightarrow F(\omega) : F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{-i\omega t} dt, \quad \text{forward}$$

$$F(\omega) \Rightarrow f(t) : f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) e^{i\omega t} d\omega. \quad \text{inverse}$$

If $g(t) = f(t + T)$, $f(t) \Rightarrow F(\omega)$, $g(t) \Rightarrow G(\omega)$ (translation/shift theorem)

$$G(\omega) = \frac{1}{\sqrt{2\pi}} \int f(t + T) e^{-i\omega t} dt = \frac{1}{\sqrt{2\pi}} \int f(\tau) e^{-i\omega(\tau - T)} d\tau = e^{i\omega T} F(\omega).$$

For $f(t)$, $t \in (-\infty, \infty)$, if $f(t) = f(t + T)$

$$f(t) = \sum_{n=-\infty}^{\infty} c_n e^{i\omega_n t}, \quad c_n = \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} f(\tau) e^{-i\omega_n \tau} d\tau, \quad \omega_n = \frac{2\pi}{T} n.$$

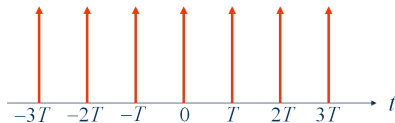
$F(\omega)$ for $f(t) = f(t + T)$

$$f(t) = f(t + T) \Rightarrow F(\omega) = e^{i\omega T} F(\omega) \Rightarrow e^{i\omega T} = 1 \Rightarrow \omega = \omega_n = \frac{2\pi}{T} n.$$

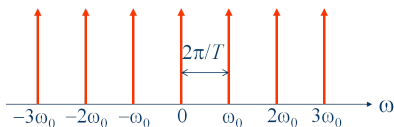
$$\Rightarrow f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(\omega) e^{i\omega t} d\omega = \sum_{n=-\infty}^{\infty} c_n e^{i\omega_n t}.$$

FT of periodical δ -function

$$\begin{aligned}f(t) &= \sum_{n=-\infty}^{\infty} \delta(t - nT) \\&= \frac{1}{T} \sum_{n=-\infty}^{\infty} e^{i\omega_n t} \\&\quad \omega_n = \frac{2\pi}{T}n\end{aligned}$$



$$\begin{aligned}F(\omega) &= \frac{1}{\sqrt{2\pi}} \frac{1}{T} \sum_{k=-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i(\omega - \omega_k)t} dt \\&= \frac{\sqrt{2\pi}}{T} \sum_{k=-\infty}^{\infty} \delta(\omega - \omega_k) \\&\quad \omega_k = \frac{2\pi}{T}k\end{aligned}$$



Fourier transformation

Discrete Fourier Transformation (DFT)

$$x_n \Rightarrow X_k : X_k = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} x_n e^{-j\frac{2\pi}{N}kn}, \quad \text{forward}$$

$$X_k \Rightarrow x_n : x_n = \frac{1}{\sqrt{N}} \sum_{k=0}^{N-1} X_k e^{j\frac{2\pi}{N}kn}. \quad \text{inverse}$$

- Completeness $\mathcal{F} : \mathbb{C} \rightarrow \mathbb{C}$;
- Orthogonality

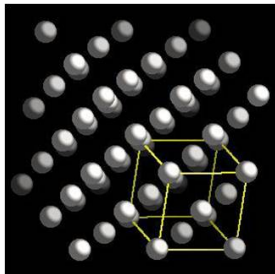
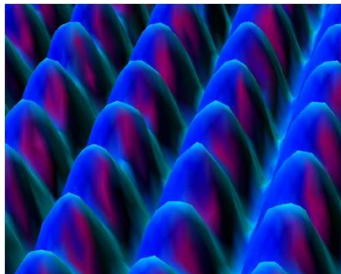
$$\sum_{n=0}^{N-1} e^{j\frac{2\pi}{N}kn} e^{-j\frac{2\pi}{N}k'n} = N\delta_{kk'}$$

- Periodicity $X_k = X_{k+N}$, $x_n = x_{n+N}$, $X_{-k} = X_{N-k} = X_k^*$
- ...

Crystal and crystal lattice

Definition

A **crystal** or crystalline solid is a **solid** material whose constituent atoms, molecules, or ions are arranged in an **orderly repeating** pattern extending in **all** three spatial dimensions.



Crystal and crystal lattice

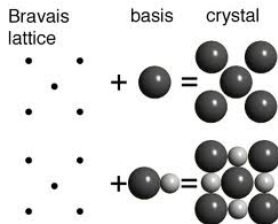
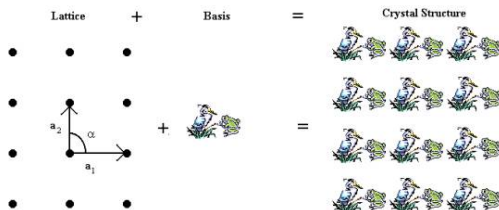
Definition

A **lattice** is an infinite array of points in space, in which each point has identical surroundings to all other points.

$$\mathbf{T} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

Definition

A **basis** is an atom, ion, or collection of atoms or ions (e.g. a molecule).



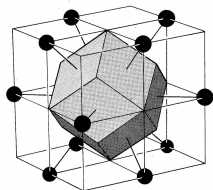
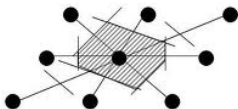
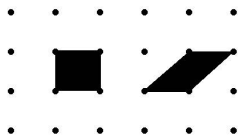
Crystal and crystal lattice

Definition

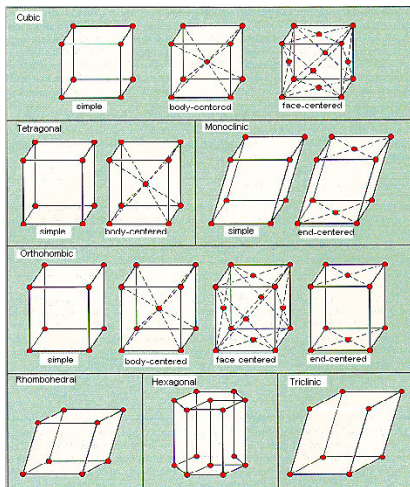
A **unit cell** is a region of space that when repeated fills all space.

Definition

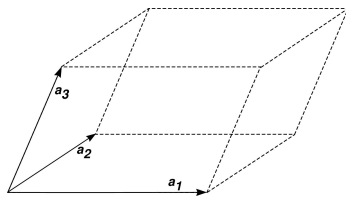
A **primitive cell** is a unit cell that has the minimum volume.



Crystal and crystal lattice



7 systems + 14 Bravais lattice



$$\mathbf{T} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

$$\mathbf{r} = \mathbf{r}' + \mathbf{T}$$

$$\mathcal{F}(\mathbf{r}) = \mathcal{F}(\mathbf{r} + \mathbf{T})$$

Reciprocal lattice

Lattice point distribution function

$$f(\mathbf{r}) = \sum_{\mathbf{T}} \delta(\mathbf{r} - \mathbf{T}) = \frac{1}{V} \sum_{\mathbf{k}} e^{i\mathbf{G}_k \cdot \mathbf{r}}, \quad \mathbf{T} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

FT of $f(\mathbf{r})$

$$F(\mathbf{G}) = \frac{\sqrt{(2\pi)^3}}{V} \sum_{\mathbf{k}} \delta(\mathbf{G} - \mathbf{G}_k)$$

where $V = \mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3$ and \mathbf{G}_k satisfies $e^{-i\mathbf{G}_k \cdot \mathbf{T}} = 1$.

Let $\mathbf{G}_k = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3$:

$$e^{-i\mathbf{G}_k \cdot \mathbf{T}} = e^{-i \sum_{\alpha} \sum_{\beta} k_{\alpha} n_{\beta} \mathbf{b}_{\alpha} \cdot \mathbf{a}_{\beta}} = 1$$

If $\mathbf{b}_{\alpha} \cdot \mathbf{a}_{\beta} = 2\pi \delta_{\alpha\beta}$, it will always be satisfied.

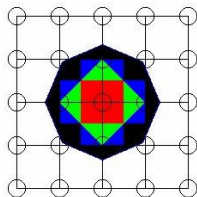
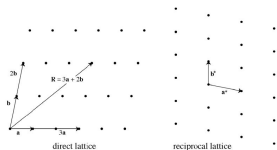
For a rigorous proof:

Reciprocal lattice

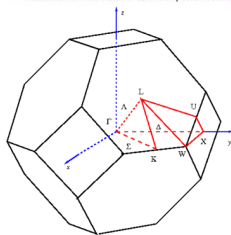
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$



First Four Brillouin Zones for a Square Lattice



$$|\mathbf{R}| = |h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3| \Rightarrow \text{Length of lattice vector}$$

$$|\mathbf{G}| = |h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3| = \frac{2\pi}{d_{hkl}} \Rightarrow \text{Lattice plane spacing}$$

Reciprocal lattice

$$f(\mathbf{r}) = f(\mathbf{r} + \mathbf{T})$$

$$f(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

where

$$n_{\mathbf{G}} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} f(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} d^3\mathbf{r}$$

$f(\mathbf{r})$:

- $n(\mathbf{r})$
- $v(\mathbf{r})$

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

However, ψ is *not* one of these $f(\mathbf{r})$'s.

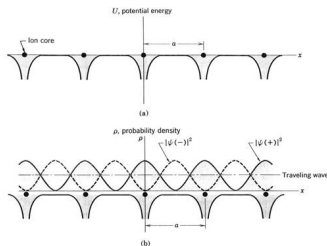


Figure 3 (a) Variation of potential energy of a conduction electron in the field of the ion cores of a linear lattice. (b) Distribution of probability density ρ in the lattice for $|\psi(-)|^2 \propto \sin^2 \pi x/a$; $|\psi(+)|^2 \propto \cos^2 \pi x/a$; and for a traveling wave. The wavefunction $\psi(+)$ piles up electronic charge on the cores of the positive ions, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave. The wavefunction $\psi(-)$ piles up charge in the region between the ions and removes it from the ion cores; thereby raising the potential energy in comparison with that seen by a traveling wave. This figure is the key to understanding the origin of the energy gap.

Particle in a periodical potential

Single particle Schrödinger equation

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r}) \right] \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})$$
$$v(\mathbf{r}) = v(\mathbf{r} + \mathbf{T})$$

If $\psi(\mathbf{r})$ is a solution, $\psi(\mathbf{r} + \mathbf{T})$ should also be a solution corresponding to the same energy.

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r} + \mathbf{T}) \right] \psi(\mathbf{r} + \mathbf{T}) = \epsilon \psi(\mathbf{r} + \mathbf{T})$$
$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r}) \right] \psi(\mathbf{r} + \mathbf{T}) = \epsilon \psi(\mathbf{r} + \mathbf{T})$$

$$\psi(\mathbf{r} + \mathbf{T}) = C \psi(\mathbf{r})$$

Bloch's theorem

Bloch's Theorem

If $v(\mathbf{r} + \mathbf{T}) = v(\mathbf{r})$, then $\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$, where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$.

In other words, there exist a vector \mathbf{k} , so that $\psi(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi(\mathbf{r})$.



Werner Heisenberg and Felix Bloch, around 1931. (DM)

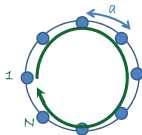
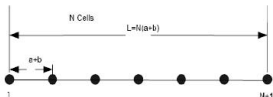
Assuming $\psi(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r})$ a solution, then:

$$\begin{aligned}\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) &= u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})e^{i\mathbf{k}\cdot(\mathbf{r} + \mathbf{T})} \\ &= u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot(\mathbf{r} + \mathbf{T})} \\ &= e^{i\mathbf{k}\cdot\mathbf{T}} \left[u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \right] \\ &= e^{i\mathbf{k}\cdot\mathbf{T}} \psi(\mathbf{r}).\end{aligned}$$

Born-von Karman boundary condition

Way to “model” infinite crystal

The **Born-von Karman** boundary condition requires that the wave functions at the two end points be equal to each other.



$$\psi(x + Na) = \psi(x)$$

$$\psi(\mathbf{r} + N_j \mathbf{a}_j) = \psi(\mathbf{r})$$

a : Microscopic periodicity
N · a : Macroscopic periodicity

Corollary

$$\begin{aligned}\psi(x + Na) &= C\psi(x + (N-1)a) \\ &= C^2\psi(x + (N-2)a) \\ &= C^N\psi(x) = \psi(x)\end{aligned}$$

$$\Rightarrow C^N = 1 \Rightarrow C = \exp\left(2\pi i \frac{n}{N}\right)$$

Bloch's theorem

BvK BC \Rightarrow

$$k_n = \frac{2\pi}{a} \frac{n}{N} \quad (1D)$$

$$\mathbf{k}_n = \sum_j \frac{n_j}{N_j} \mathbf{b}_j \quad (3D).$$

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\mathbf{r}}$$

Remarks: I

- $\psi_{\mathbf{k}}$ is a superposition of PWs with wavevectors differ by \mathbf{G}_n to maintain the PBC;
- $\psi_{\mathbf{k}}$ is not a momentum eigenstate, $\hbar\mathbf{k}$ is crystal momentum;
- For large $|\mathbf{k} + \mathbf{G}|$, $c_{\mathbf{k},\mathbf{G}} \rightarrow 0$.

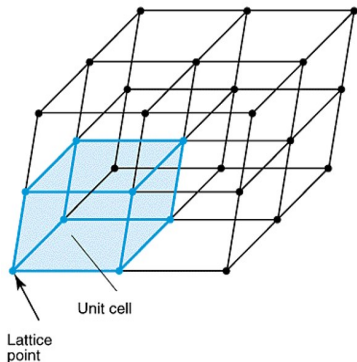
$$\begin{aligned} & \hat{p}\psi_{\mathbf{k}}(\mathbf{r}) \\ &= -i\hbar \nabla \psi_{\mathbf{k}}(\mathbf{r}) \\ &= -i\hbar \nabla \left[u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} \right] \\ &= \hbar\mathbf{k}\psi_{\mathbf{k}} - e^{i\mathbf{k}\mathbf{r}} i\hbar \nabla u_{\mathbf{k}}(\mathbf{r}) \\ &\neq p\psi_{\mathbf{k}} \end{aligned}$$

$$E_{\mathbf{k}} \propto |\mathbf{k} + \mathbf{G}|^2$$

Bloch's theorem

Remarks: II

- k can be limited to $|k| \leq G/2$ (FBZ).
- SE restricted to a *single* cell.



$$\begin{aligned}\psi_{\mathbf{k}+\mathbf{G}} &= u_{\mathbf{k}+\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} \\ &= (u_{\mathbf{k}+\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}) e^{i\mathbf{k}\cdot\mathbf{r}} \\ &= u'_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \\ &= \psi_{\mathbf{k}}\end{aligned}$$

$$E_{\mathbf{k}+\mathbf{G}} = E_{\mathbf{k}}$$

$$\begin{aligned}\mathbf{k}_n &= \sum_j \frac{n_j}{N_j} \mathbf{b}_j \Rightarrow \\ \text{number of } k\text{-points} &= \\ N_1 \cdot N_2 \cdot N_3 &= N \\ &= \text{number of cells in crystal.}\end{aligned}$$

Particle in a periodical potential

Kohn-Sham Equation

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

$$v_{\text{eff}}(\mathbf{r}) = \sum_m v_m e^{i\mathbf{G}_m \mathbf{r}}$$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_m c_m e^{i(\mathbf{k} + \mathbf{G}_m) \mathbf{r}} \equiv \sum_{\mathbf{q}_m} c_m |\mathbf{q}_m\rangle, \quad \mathbf{q}_m = \mathbf{k} + \mathbf{G}_m$$

Definition

$$\langle \cdot | \text{ bra} \quad | \cdot \rangle \text{ ket}$$

$$\langle \psi | \phi \rangle = \int \psi^*(x) \phi(x) dx$$

$$\langle \psi | \hat{A} | \phi \rangle = \int \psi^*(x) \hat{A} \phi(x) dx$$

Particle in a periodical potential

$$\langle \mathbf{q}_{m'} | \left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \sum_m c_m | \mathbf{q}_m \rangle = \langle \mathbf{q}_{m'} | \epsilon_i \sum_m c_m | \mathbf{q}_m \rangle$$

$$\sum_m c_m \langle \mathbf{q}_{m'} | -\frac{\hbar^2}{2m_e} \nabla^2 | \mathbf{q}_m \rangle + \sum_m c_m \langle \mathbf{q}_{m'} | v_{\text{eff}}(\mathbf{r}) | \mathbf{q}_m \rangle = \sum_m c_m \langle \mathbf{q}_{m'} | \epsilon_i | \mathbf{q}_m \rangle$$

$$\langle \mathbf{q}_{m'} | -\frac{\hbar^2}{2m_e} \nabla^2 | \mathbf{q}_m \rangle = \frac{\hbar^2 |\mathbf{k} + \mathbf{G}_m|^2}{2m_e} (2\pi)^3 \delta_{m,m'}$$

$$\langle \mathbf{q}_{m'} | v_{\text{eff}}(\mathbf{r}) | \mathbf{q}_m \rangle = \langle \mathbf{q}_{m'} | \sum_n v_n e^{i\mathbf{G}_n \mathbf{r}} | \mathbf{q}_m \rangle = (2\pi)^3 v_{m'-m}$$

$$\langle \mathbf{q}_{m'} | \epsilon_i | \mathbf{q}_m \rangle = (2\pi)^3 \epsilon_i \delta_{m,m'}$$

Particle in a periodical potential

Schrödinger Equation \Rightarrow Eigen problem

$$\sum_m \left[\frac{\hbar^2 |\mathbf{k} + \mathbf{G}_m|^2}{2m_e} \delta_{m,m'} + v_{m-m'} \right] c_{i,m} = \epsilon_i c_{i,m'}$$

Matrix equation

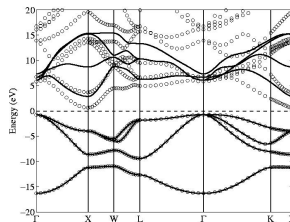
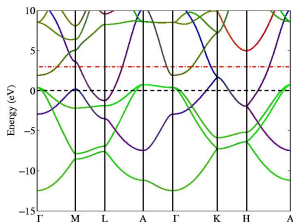
(here we have omitted the constants \hbar and m)

$$\begin{bmatrix} \frac{1}{2} (\mathbf{k})^2 & V_{\text{eff}}(\mathbf{G}_1) & V_{\text{eff}}(\mathbf{G}_2) & V_{\text{eff}}(\mathbf{G}_3) & \dots \\ V_{\text{eff}}(\mathbf{G}_1) & \frac{1}{2} (\mathbf{k} + \mathbf{G}_1)^2 & V_{\text{eff}}(\mathbf{G}_2 - \mathbf{G}_1) & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_1) & \dots \\ V_{\text{eff}}(\mathbf{G}_2) & V_{\text{eff}}(\mathbf{G}_2 - \mathbf{G}_1) & \frac{1}{2} (\mathbf{k} + \mathbf{G}_2)^2 & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_2) & \dots \\ V_{\text{eff}}(\mathbf{G}_3) & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_1) & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_2) & \frac{1}{2} (\mathbf{k} + \mathbf{G}_3)^2 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{bmatrix} = \epsilon \begin{bmatrix} c_0 \\ c_1 \\ c_2 \\ c_3 \end{bmatrix}$$

Particle in a periodical potential

$$\sum_m \left[\frac{\hbar^2 |\mathbf{k} + \mathbf{G}_m|^2}{2m_e} \delta_{m,m'} + v_{m-m'} \right] \mathbf{c}_m = \epsilon_i \mathbf{c}_{m'}$$

- Problem limited to **primitive cell**;
- **k 's** are **independent** to each other;
- For each k , one can get at most **M** eigen-states;
- $\epsilon_i(k)$ gives the **band structure**;
- Each band has $N_k = N_1 \cdot N_2 \cdot N_3$ states;

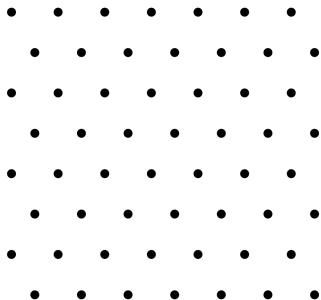


References and further readings

- ① W. Kohn, *Nobel Lecture: Electronic structure of matter—wave functions and density functionals*, *Rev. Mod. Phys.* **71**:1253-1266, 1999.
- ② C. Kittel, *Introduction to Solid State Physics*, 8th Ed.
- ③ J. Singleton, *Band Theory and Electronic Properties of Solids*, Oxford Univ Press, 2001.
- ④ J. Hafner, *Atomic-scale computational materials science*, *Acta Materialia* **48**:71-92, 2000.
- ⑤ <http://www.tcm.phy.cam.ac.uk/~mjr/bloch.pdf>
- ⑥ <http://www.physto.se/~arydh/CondMat/Lectures/Lect6.pdf>
- ⑦ <http://www.phy.duke.edu/~hx3/physics/symmetry&bloch/symmetry&bloch.pdf>
- ⑧ <http://www.kcl.ac.uk/content/1/c6/02/14/53/lecture6a.pdf>

Homework

- 1 Read/work through all the slides;
- 2 **Hand in:** Derive the Fourier transformation of the lattice point distribution shown in page 12;
- 3 **Hand in:** Draw the Wigner-Seitz cell and the first Brillouin zone for a two dimensional triangular lattice.



Due: **Nov 16th, 2022.**