Electronic structure for crystals

The reciprocal space and Bloch theorem

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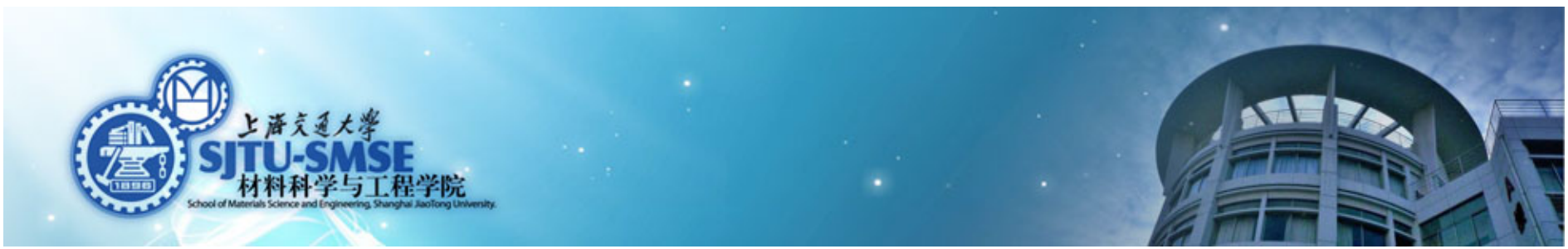


Outline

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

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

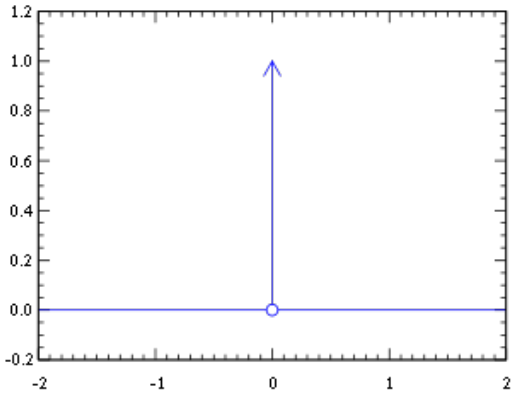
Properties of δ-function

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

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

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

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



Fourier transformation

Fourier Transformation (FT)

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

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

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

$$f(t) = \sum_{n=-\infty}^{\infty} \delta(t - nT)$$

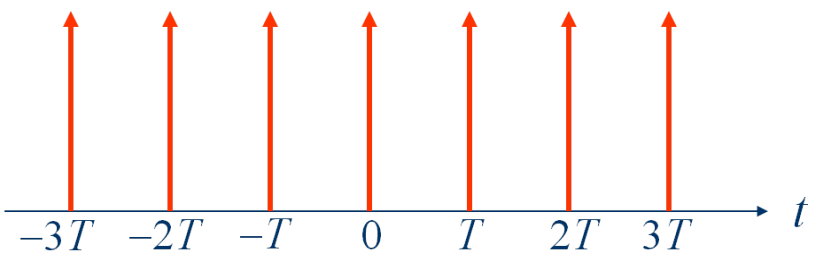
$$= \frac{1}{T} \sum_{n=-\infty}^{\infty} e^{i\omega_n t}$$

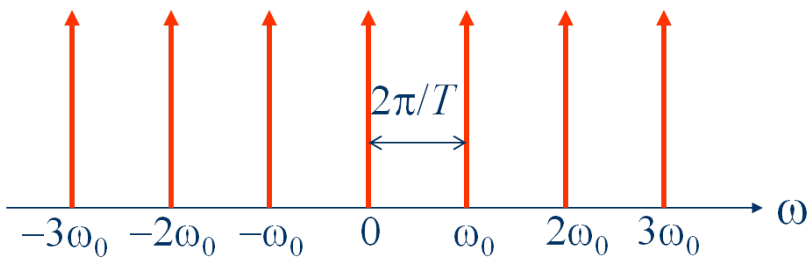
$$\omega_n = \frac{2\pi}{T} n$$

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \frac{1}{T} \sum_{k=-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-i(\omega-\omega_k}$$

$$= \frac{\sqrt{2\pi}}{T} \sum_{k=-\infty}^{\infty} \delta(\omega - \omega_k)$$

$$\omega_k = \frac{2\pi}{T} k$$





Fourier transformation

Discrete Fourier Transformation (DFT)

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

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

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

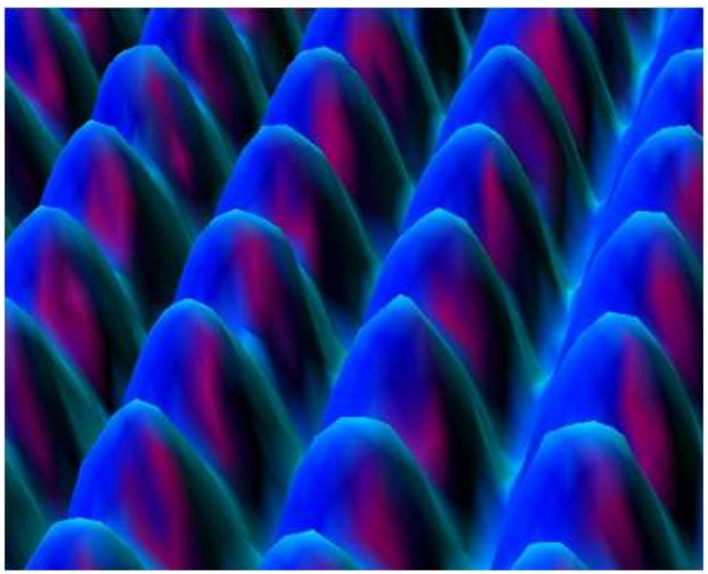
$$\sum_{n=0}^{N-1} e^{i\frac{2\pi}{N}kn} e^{-j\frac{2\pi}{N}k'n} = N\delta_{kk'}$$

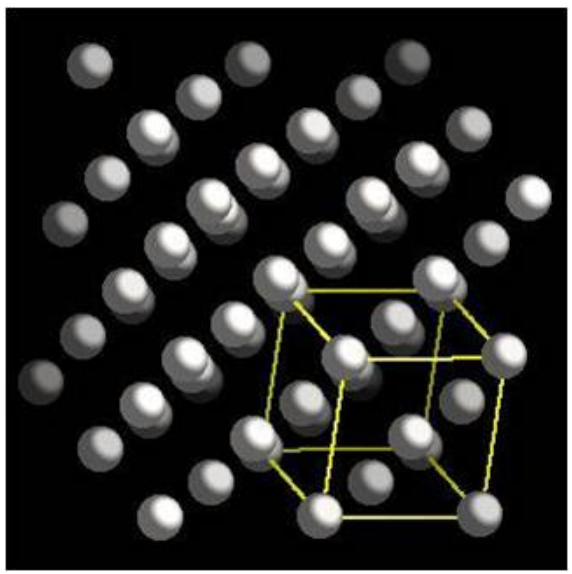
- Periodicity $X_k = X_{k+N}, x_n = x_{n+N}, \; X_{-k} = X_{N-k} = X_k^*$
- ...

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

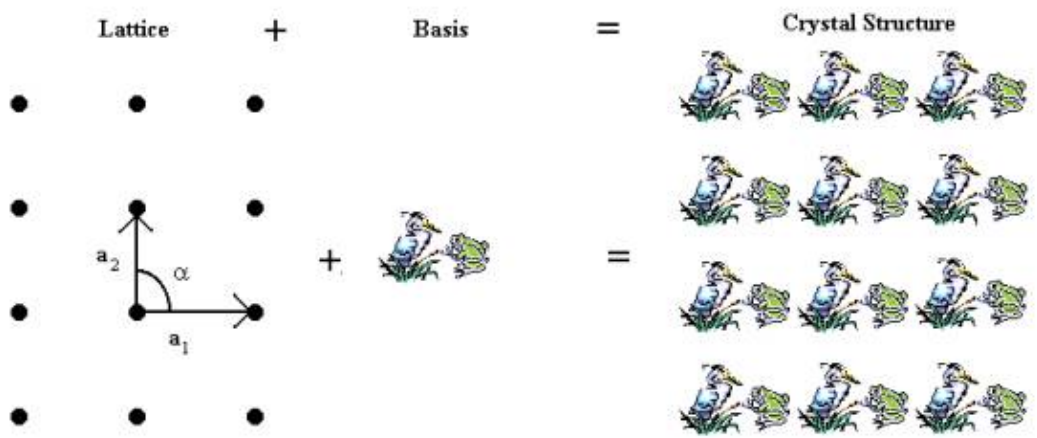
Definition

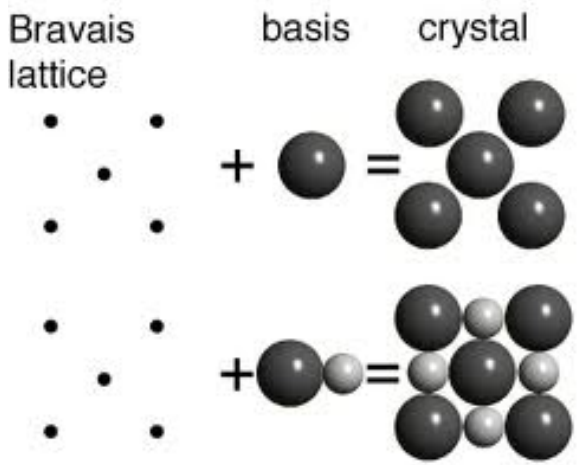
A lattice is an infinite array of points in space, in which each point has identical surroundings to all other points.

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

Definition

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





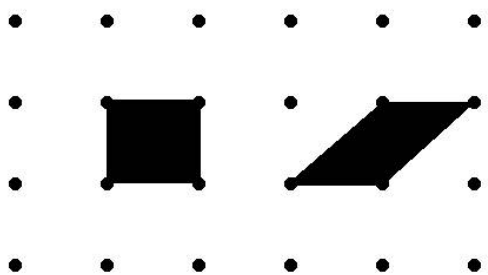
Crystal and crystal lattice

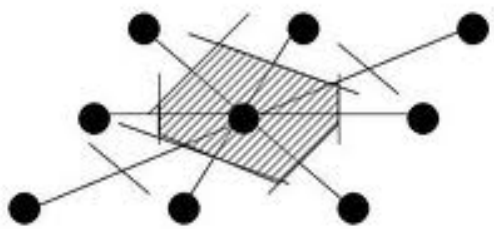
Definition

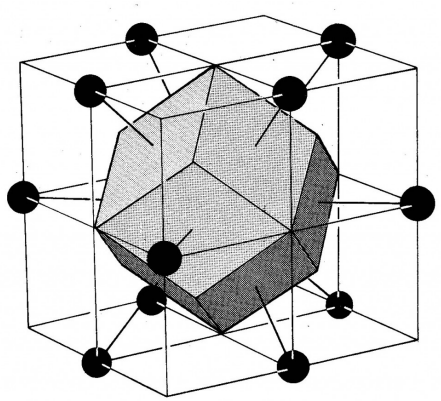
A unit cell is a region of space that when repeated fills all space.

Definition

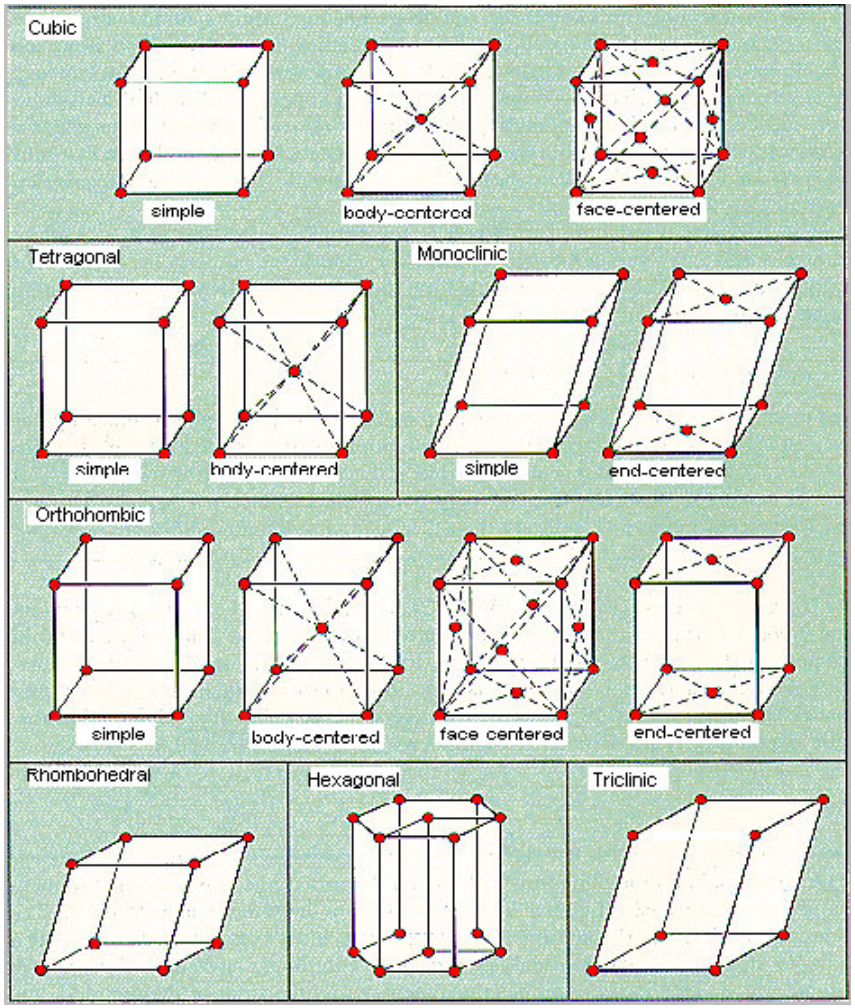
A primitive cell is a unit cell that has the minimum volume.



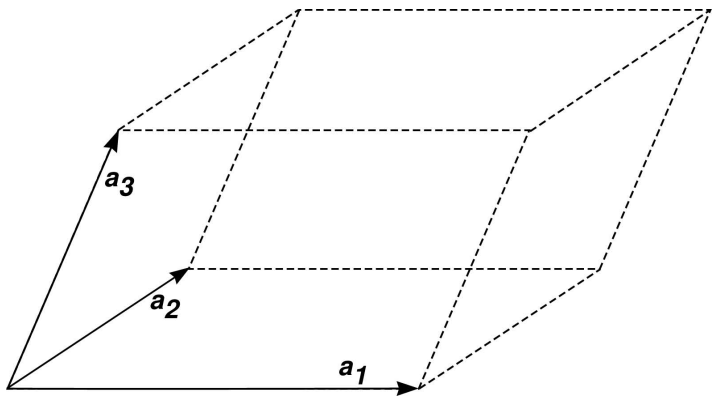




Crystal and crystal lattice



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

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

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

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

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

For a rigorous proof:

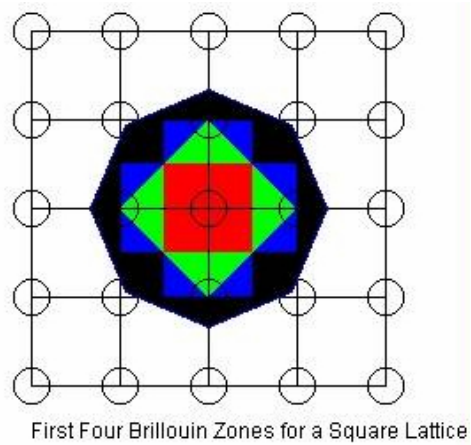
http://www.ece.rutgers.edu/~maparker/classes/581-chapters/Ch06-Structure-Phonons/Ch06Sec04ReciprlLatt.pdf

Reciprocal lattice

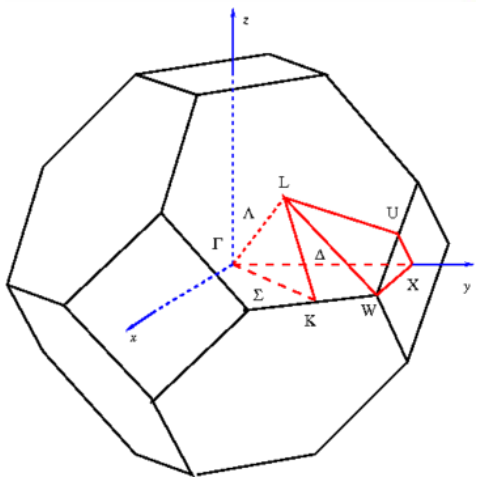
$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

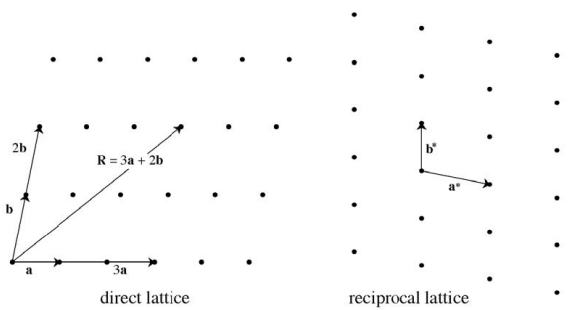
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3}$$

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



First Four Brillouin Zones for a Square Lattice





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

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

Reciprocal lattice

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

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

where

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

$f(\mathbf{r})$:

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

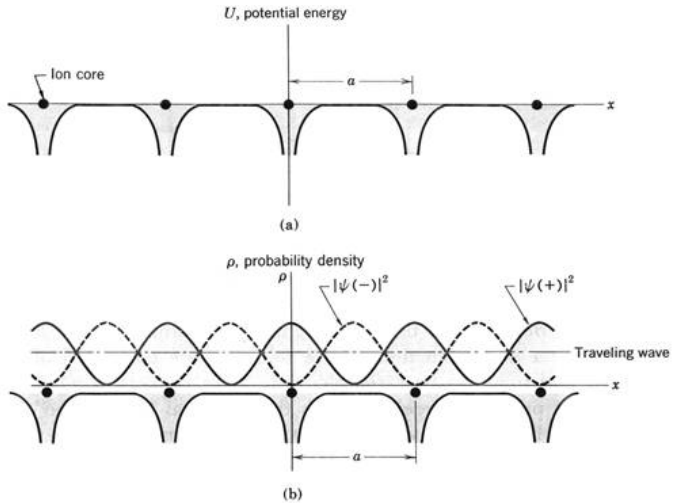


Figure 3 (a) Variation of potential energy of a conduction electron in the field of the ion cores of a linear lattice. (b) Distribution of probability density ρ in the lattice for $|\psi(-)|^2 \propto \sin^2 \pi x/a$; $|\psi(+)|^2 \propto \cos^2 \pi x/a$; and for a traveling wave. The wavefunction $\psi(+)$ 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.

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

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

Particle in a periodical potential

Single particle Schrödinger equation

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

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

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

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

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

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 k, so that $\psi(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}\mathbf{T}}\psi(\mathbf{r})$.

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

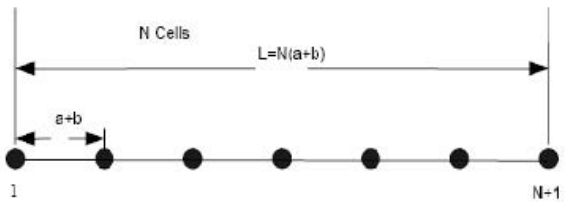
Assuming $\psi(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{k}\mathbf{r})$ a solution, then:

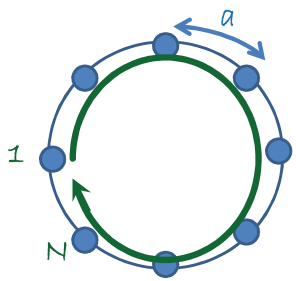
$$\begin{aligned}
\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{T}) &= u_{\mathbf{k}}(\mathbf{r}+\mathbf{T})e^{i\mathbf{k}(\mathbf{r}+\mathbf{T})} \\
&= u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}(\mathbf{r}+\mathbf{T})} \\
&= e^{i\mathbf{k}\mathbf{T}}\left[u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}\right]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

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

$N \cdot a$: Macroscopic periodicity

Corollary

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

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

Bloch's theorem

BvK BC $\Rightarrow$

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

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

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

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

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 $|\mathbf{k}+\mathbf{G}|$, $c_{\mathbf{k},\mathbf{G}} \to 0$.

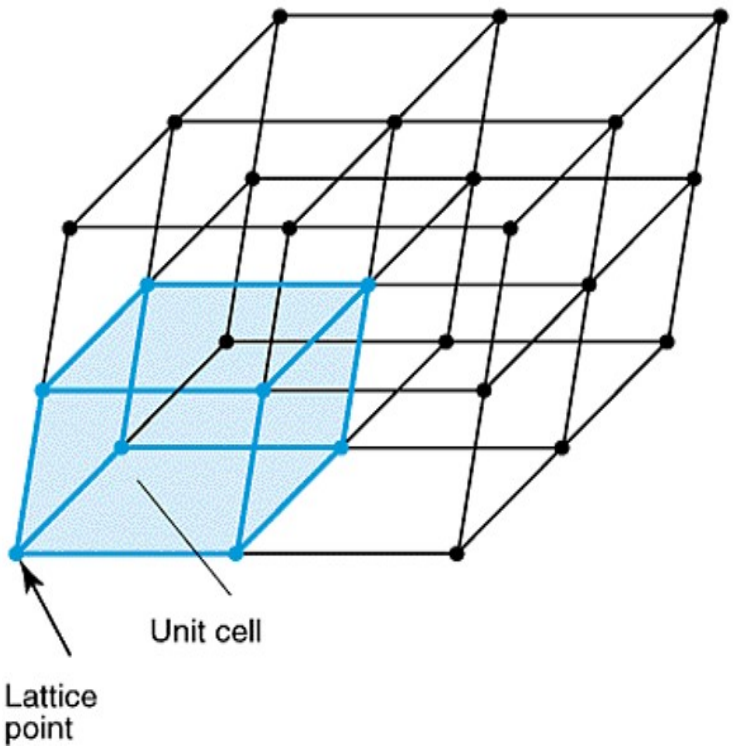
$$\begin{aligned} & \hat{p}\psi_{\mathbf{k}}(\mathbf{r}) \\ = \; & -i\hbar\nabla\psi_{\mathbf{k}}(\mathbf{r}) \\ = \; & -i\hbar\nabla\left[u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\mathbf{r}}\right] \\ = \; & \hbar\mathbf{k}\psi_{\mathbf{k}} - e^{i\mathbf{k}\mathbf{r}} i\hbar\nabla u_{\mathbf{k}}(\mathbf{r})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

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

Bloch's theorem

Remarks: II

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



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

$\mathbf{k_n} = \sum_j \frac{n_j}{N_j} \mathbf{b}_j \Rightarrow$
number of k-points $=$
$N_1 \cdot N_2 \cdot N_3 = N$
$=$ number of cells in crystal.

Particle in a periodical potential

Kohn-Sham Equation

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

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

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

Definition

$\langle\cdot|$ bra $\qquad$ $|\cdot\rangle$ 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

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

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

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

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

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

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

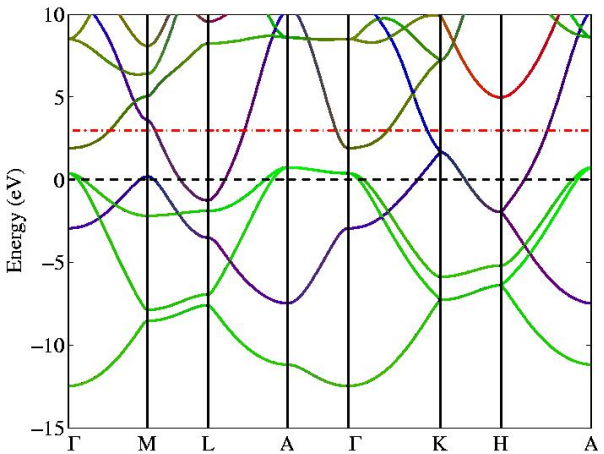
(here we have omitted the constants h and m)

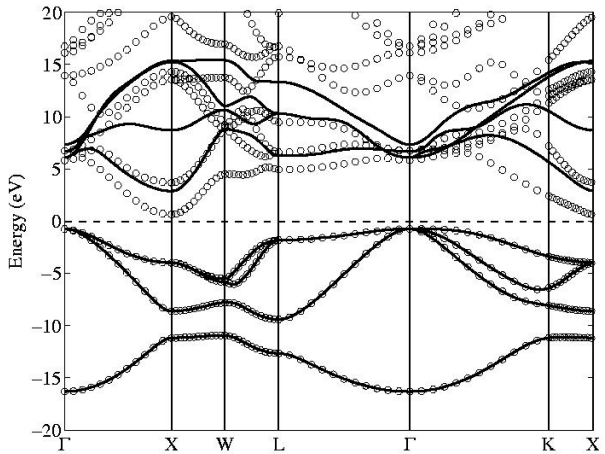
$$\begin{bmatrix} \frac{1}{2}(k)^2 & V_{eff}(G_1) & V_{eff}(G_2) & V_{eff}(G_3) & \dots \\ V_{eff}(G_1) & \frac{1}{2}(k+G_1)^2 & V_{eff}(G_2 - G_1) & V_{eff}(G_3 - G_2) & \dots \\ V_{eff}(G_2) & V_{eff}(G_2 - G_1) & \frac{1}{2}(k+G_2)^2 & V_{eff}(G_3 - G_2) & \dots \\ V_{eff}(G_3) & V_{eff}(G_3 - G_1) & V_{eff}(G_3 - G_2) & \frac{1}{2}(k+G_3)^2 & \dots \\ \dots & \dots & \dots & \dots & \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \end{bmatrix} = \varepsilon \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \end{bmatrix}$$

Particle in a periodical potential

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

- 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;





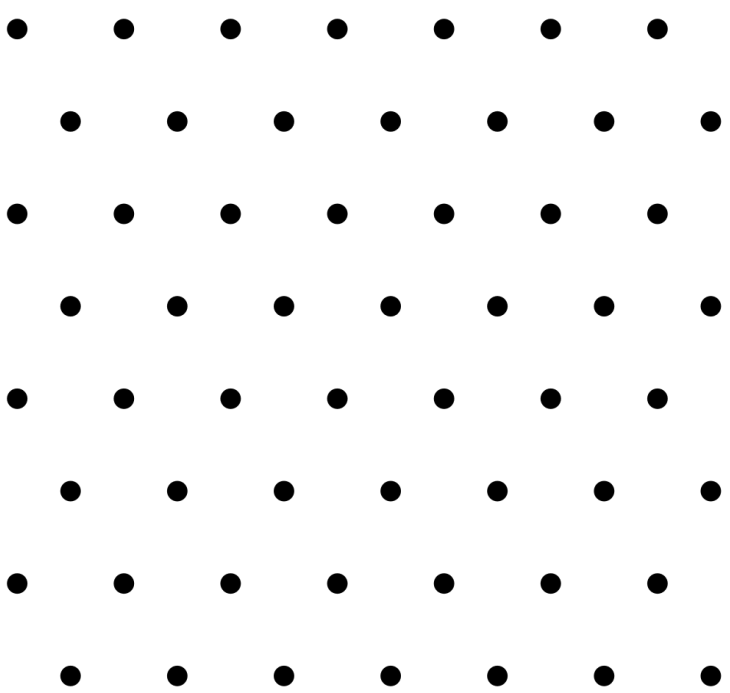
Band structure for MgB_2 (left) and SiC (right), respectively. Source: http://li.mit.edu/Archive/QO/data.html

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, 8^{th} 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
9. http://en.wikipedia.org/wiki/Bloch_wave

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: **Oct 20$^{\text{th}}$, 2021.**