3.23 Electrical, Optical, and Magnetic Properties of Materials
Fall 2007

3.23 Fall 2007 – Lecture 8

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Please see: M. C. Escher. "Ascending and Descending." 1960.

Last time

$T-V$ $\quad\quad$ $T+V$

1. Newtonian, Lagrangian, and Hamiltonian formulations
2. 1-dim monoatomic and diatomic chain. Acoustic and optical phonons. $\longrightarrow [\cdot] \Longrightarrow [\cdot\ \cdot]$
3. Bravais lattices and lattices with a basis
4. Point groups and group symmetries
5. Primitive unit cell, conventioanl unit cell, periodic boundary conditions $\vec{a}$
6. $\boxed{\text{Reciprocal lattice}}$ $\Rightarrow \{\vec{G}_i\}$ $\quad e^{i\vec{G}_i\cdot\vec{r}}$

$$\vec{R}_l = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$$

3.23 Electronic, Optical and Magnetic Properties of Materials - Nicola Marzari (MIT, Fall 2007)

Study

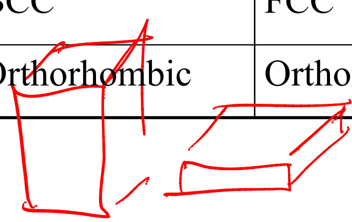
- Chapter 2 of Singleton textbook – "Band theory and electronic properties of solids"
- Start reading Chapter 3
- Problem sets from same book are excellent examples of "Exam Material"

Examples of reciprocal lattices

$(a,0,0)$
$(0,a,0)$
$(0,0,a)$

$(\frac{2\pi}{a},0,0)$
$(0,\ldots)$
$(0,0,\frac{2\pi}{a})$

Direct lattice	Reciprocal lattice
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
Orthorhombic	Orthorhombic



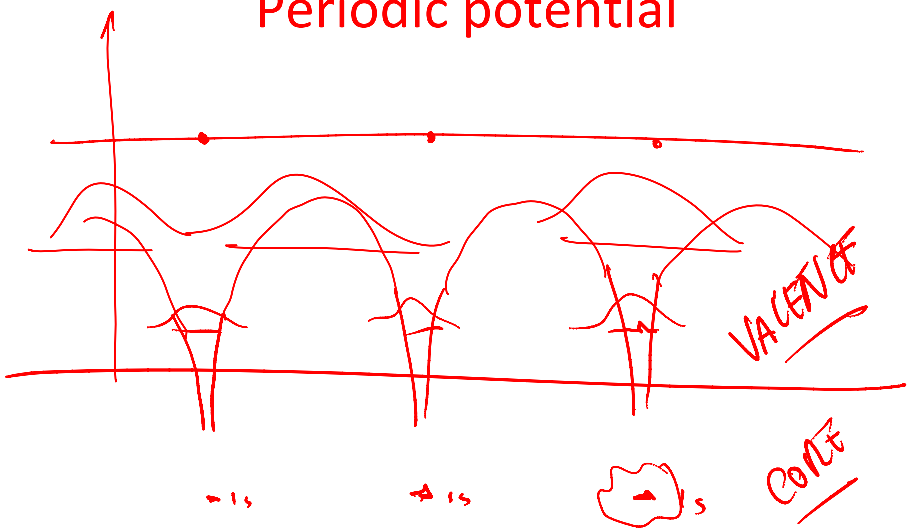
$\vec{b}_1 \quad 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$

$\vec{G}_i = l\vec{b}_1 + m\vec{b}_2 + n\vec{b}_3$

$\vec{a}_i \cdot \vec{b}_j = 2\pi\,\delta_{ij}$

$$V(\vec r) = \sum_{\vec R} -\frac{Z}{|r+R|} = V(\vec r + \vec R) \qquad -\frac{Z}{r}$$

Periodic potential



Bloch Theorem

$$\hat H = \hat T + \hat V(r) \qquad V(\vec r) = V(\vec r + \vec R)$$

$$\boxed{\psi_{n\vec k}(\vec r) = e^{i\vec k\cdot\vec r}\underbrace{u_{n\vec k}(\vec r)}_{\text{PERIODIC}}} \qquad (\mathrm{I})$$

$$u_{n\vec k}(\vec r + \vec R) = u_{n\vec k}(\vec r)$$

$$\psi_{n\vec k}(\vec r + \vec R) = e^{i\vec k\cdot(\vec r + \vec R)}\, u_{nk}(\vec r + \vec R) =$$

$$e^{i\vec k\cdot\vec R}\,\psi_{nk}(\vec r) = e^{i\vec k\cdot\vec R}\, e^{i\vec k\cdot\vec r}\, u_{nk}(\vec r) =$$

BLOCH (I)

$T_{\vec{R}} f(\vec{r}) = f(\vec{r}+\vec{R})$

$T_R H \psi = H(\vec{r}+\vec{R})\psi(\vec{r}+\vec{R}) =$

$= H(\vec{r}) T_{\vec{R}} \psi \Rightarrow T_R H \psi = H T_R \psi$

T_R, H COMMUTE $\Rightarrow$ COMMON SET OF EIGENSTATES

$T_R T_{R'} \psi = \psi(r+R+R') = T_{R'} T_R \psi =$

$= T_{R+R'} \psi \qquad T_R T_{R'} = T_{R'} T_R = T_{R+R'}$

$H\psi = E\psi \qquad T_R \psi = c(R)\psi$

$T_R T_{R'} \psi = T_R\, c(R')\psi = c(R)c(R')\psi$

$= T_{R+R'}\psi = c(R+R')\psi$

$c(R+R') = c(R)c(R')$

$c(a_i) = e^{i 2\pi x_i}$

$\psi \to \|T\psi\|^2 = \|\psi\|^2$

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

$$c(\vec{R}) = c(n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3) =$$

$$= c(\underbrace{a_1 + a_1 + a_1 \ldots}_{n_1} + \underbrace{a_2 \ldots}\; + \underbrace{a_3 \ldots}) =$$

$$= c(a_1)^{n_1} c(a_2)^{n_2} c(a_3)^{n_3}$$

$$c(a_1) = e^{i 2\pi x_1} \quad c(a_2) = e^{i 2\pi x_2} \quad c(a_3) = e^{i 2\pi x_3}$$

$$\boxed{c(\vec{R}) = e^{i \vec{k} \cdot \vec{R}}} \qquad \vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$$

$$\vec{k} \cdot \vec{R} = n_1 2\pi x_1 + n_2 2\pi x_2 + n_3 2\pi x_3$$

$$\underbrace{T_R \psi} = e^{i \vec{k} \cdot \vec{R}} \psi$$

$$\boxed{\psi(r+R) = e^{i \vec{k} \cdot \vec{R}} \psi} \quad \text{BLOCH (II)}$$

$e^{-ik \cdot R} \quad e^{-ik \cdot r}$

PERIODIC $= \; = u_k(r)$

$$e^{-ik(\vec{r}+\vec{R})} \psi(\vec{r}+\vec{R}) = \underbrace{\psi(\vec{r}) e^{-i\vec{k} \cdot \vec{r}}}$$

Bloch Theorem

The one-particle effective Hamiltonian $\hat{H}$ in a periodic lattice commutes with the lattice-translation operator $\hat{T}_{\mathrm{R}}$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

$$[\hat{H}, \hat{T}_{\mathrm{R}}] = 0 \quad \Rightarrow \quad \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}$$

- *n, k* are the quantum numbers (band index and crystal momentum), *u* is periodic
- From two requirements: a translation can't change the charge density, and two translations must be equivalent to one that is the sum of the two

Bloch Theorem

$$[\hat{H}, \hat{T}_{\mathrm{R}}] = 0 \quad \Rightarrow \quad \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\Psi_{n\vec{k}}\left(\vec{r} + \vec{R}\right) \quad \exp\left(i\vec{k}\bullet\vec{R}\right)\Psi_{n\vec{k}}\left(\vec{r}\right) \quad =$$

Crystal momentum **k** (in the first BZ)

Periodic boundary conditions for the electrons: Born – von Karman

BvK

$$\psi(\vec{r} + N_i \vec{a}_i) = \psi(\vec{r})$$

Bloch

$$\psi_{n\vec{k}}(\vec{r} + N_i \vec{a}_i) = e^{i (N_i \vec{a}_i)\cdot \vec{k}}\, \psi_{n\vec{k}}(\vec{r})$$

$$e^{i N_i \vec{a}_i \cdot \vec{k}} = 1 \Rightarrow N_i \vec{a}_i \cdot (x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3) =$$

$$= N_1 x_1 \cancel{2\pi} = \cancel{2} n \pi$$

$$x_1 = \frac{n}{N_1}$$

Explicit proof of Bloch's theorem

$$H\psi = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi = \varepsilon\psi$$

$$V(\vec{r}) = \sum_G V_G\, e^{i \vec{G}\cdot\vec{r}}$$

$$\psi(\vec{r}) = \sum c_k\, e^{i\vec{k}\cdot\vec{r}} \qquad V_0 = 0$$

$$\sum_k \frac{\hbar^2 k^2}{2m} c_k e^{i\vec{k}\cdot\vec{r}} + \underbrace{\left(\sum_G V_G e^{i\vec{G}\cdot\vec{r}}\right)\left(\sum_k c_k e^{i\vec{k}\cdot\vec{r}}\right)} = E \sum_k c_k e^{i\vec{k}\cdot\vec{r}}$$

$$\sum_{G,k} V_G c_k e^{i(\vec{G}+\vec{k})\cdot\vec{r}}$$

$$V(r)\psi(r) = \boxed{\sum_{G,k} V_G c_{k-G} e^{i\vec{k}\cdot\vec{r}}}$$

$$\sum_k e^{i\vec{k}\cdot\vec{r}} \left(\underbrace{\left(\frac{\hbar^2 k^2}{2m} - E\right) c_k + \sum_G V_G c_{k-G}}_{=0} \right) = 0$$

$$\left(\frac{\hbar^2 k^2}{2m} - E\right) c_k + \sum_G V_G c_{k-G} = 0$$

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

$$\left(\frac{\hbar^2 (q-G')^2}{2m} - E\right) c_{q-G'} + \sum_{G''} V_{G''-G'} \underbrace{c_{q-G''}}_{q-G'\;\cancel{-G}}$$

~~$\Psi_{nk}(r)$ is not a momentum eigenstate~~

$$\psi_q = \sum_G c_{q-G}\, e^{i(q-G)\cdot\vec{r}}$$

$$= e^{i\vec{q}\cdot\vec{r}} \cdot \underbrace{\left(\sum_G c_{q-G}\, e^{-i\vec{G}\cdot\vec{r}} \right)}_{u_q(\vec{r})}$$