

Advanced Solid State Physics

Elective course

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Materials:

Blackboard

Overview of the lecture course

- Electrons in crystalline lattice
- Scattering in metals
- Transport in metals
- Phonons
- Magnetism
- Landau theory of phase transitions
- Macroscopic theory of superconductivity
- Notion of microscopic theory
- Ginzburg-Landau equations. Critical fields
- Ginzburg-Landau equations. Vortices.
- Strongly correlated systems

Electrons in crystalline lattice: Outline

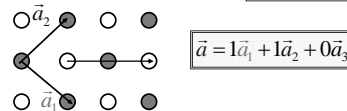
- Crystalline lattice
- Electrons in a periodic potential
- Bloch states
- Energy bands
- Electrons in a weak periodic potential
- Tight-binding model
- Metals vs insulators
- Free electron gas

Crystalline lattice

Crystalline lattice – a (sometimes complicated) periodic potential $U(\vec{r})$

Periodic: $U(\vec{r} + \vec{a}) = U(\vec{r})$ \vec{a} - a lattice period

Can be expanded in a basis: $\vec{a} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$



Also may be invariant under some rotations and reflections: symmetry transformations $\hat{S}U(\vec{r}) = U(\vec{r}) \Rightarrow$ **Theory of symmetry**

Electron in a periodic potential

Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + U(\vec{r})\psi(\vec{r}) = E\psi(\vec{r})$$

Is the solution $\psi(\vec{r} + \vec{a}) = \psi(\vec{r})$? No!!

$\psi(\vec{r} + \vec{a})$ must be a solution with the same energy.

$$\psi(\vec{r} + \vec{a}) = C(\vec{a})\psi(\vec{r}) \quad (\text{provided the level is nondegenerate; if not - diagonalize})$$

Normalization: $|C|^2 = 1$ $C(\vec{a}) = e^{i\vec{p}\cdot\vec{a}}$

Two translations: must be multiplicative $C(\vec{a}_1)C(\vec{a}_2) = C(\vec{a}_1 + \vec{a}_2)$

$$C(\vec{a}) = e^{i\vec{p}\cdot\vec{a}/\hbar}$$

Bloch waves

Solution: Bloch waves $\psi(\vec{r}) = e^{i\vec{p}\cdot\vec{r}/\hbar}u(\vec{r})$

u - periodic $u(\vec{r} + \vec{a}) = u(\vec{r})$

\vec{p} - quasimomentum Not defined uniquely!!!

$\vec{p} + \hbar\vec{K}$ Corresponds to the same wave function provided $\vec{K}\vec{a}_n = 2\pi l$

Solutions: $\vec{K} = m_1\vec{K}_1 + m_2\vec{K}_2 + m_3\vec{K}_3$ Form reciprocal lattice!!

Have the same symmetry as the crystalline lattice.

\vec{p} is equivalent to $\vec{p} + \hbar\vec{K}$

It is enough to consider a unit cell of a reciprocal lattice

Energy bands

What about energies?

For each value of \vec{p} - (infinitely) many solutions of the Schrödinger equation

$$\boxed{\varepsilon_i(\vec{p})}$$

Properties:

- Periodic in the reciprocal lattice: $\varepsilon_i(\vec{p} + \hbar\vec{K}) = \varepsilon_i(\vec{p})$
- Even (follows from the time-reversal symmetry): $\varepsilon_i(\vec{p}) = \varepsilon_i(-\vec{p})$

Each of the functions $\varepsilon_i(\vec{p})$ must attain a minimum and a maximum in the unit cell of the reciprocal lattice



Energy bands!

Energy bands

How do we calculate band structure in real metals?

- Standard theoretical models:
 - Weak periodic potential;
 - Tight-binding model.

Only describe very special materials, but good for illustrative purposes

- Approximate numerical methods:
 - Orthogonalized plane waves;
 - Pseudopotential;
 - Augmented plane waves;
 - Greens' functions (Korringa – Kohn – Rostoker);
 - ...

More powerful, but less illustrative

- First-principles calculations

Very powerful and technically very difficult

Electrons in a weak periodic potential

General idea:

Periodic potential is weak \Rightarrow Can be treated as perturbation

When can this be good?

Alkali metals (Li, Na, K, Rb, Cs) – “favorite metals of a theorist”

Generally, **all s- and p- metals** (Examples: Cu, Ag, Al) – reasonably good for certain bands

No good: **d- and f- metals** (examples: Fe, Co, Cr, Mn)

Energy bands in 1D

Unperturbed wave functions: $\psi_p(x) = \frac{1}{\sqrt{L}} e^{ipx/\hbar}$

Energies: $\varepsilon^{(0)}(p) = p^2 / 2m$

External potential: Perturbation $U(x) = \sum_n U_n e^{2\pi i n x / a}$

Matrix elements: $\langle p | U | p' \rangle = U_n$ provided $p - p' = 2\pi n \hbar / a$

First-order correction: $\Delta\varepsilon_1(p) = \langle p | U | p \rangle = U_0$



Not interesting – renormalization of all energies

Second-order correction:

$$\Delta\varepsilon_2(p) = \sum_{p'} \frac{|\langle p | U | p' \rangle|^2}{\varepsilon(p) - \varepsilon(p')} = \sum_{n \neq 0} \frac{|U_n|^2}{\varepsilon(p) - \varepsilon(p - 2\pi n \hbar / a)} \quad \text{Diverges!}$$

Energy bands in 1D

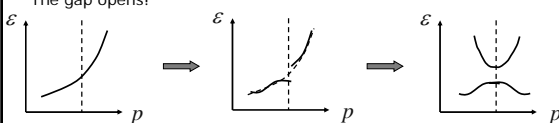
Need to use perturbation theory for degenerate states $p \approx p' \approx \pi n \hbar / a$

- Write the wave function as $\psi = a_p \psi_p + a_{p'} \psi_{p'}$.
- Insert into Schrödinger equation
- Solve the resulting secular equation

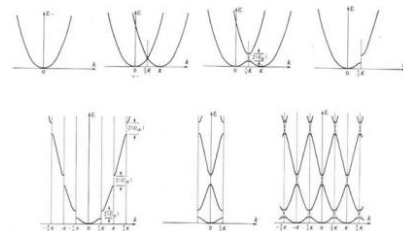
Solutions:

$$\varepsilon = \frac{\varepsilon_p + \varepsilon_{p'}}{2} \pm \sqrt{\left(\frac{\varepsilon_p - \varepsilon_{p'}}{2}\right)^2 + |U_n|^2}$$

The gap opens!



Energy bands



1D: Bands do not overlap
2D and 3D: Bands can overlap

Tight-binding model

Unperturbed states: Electrons localized in isolated atoms

Perturbation: Overlap of electron shells of neighboring atoms

$$V(x) = \sum_n U(x-na)$$

Exact solutions of Schrödinger equation: Bloch waves $\psi(x) = e^{ipx/\hbar} u(x)$

Extended states: inconvenient for the perturbation theory.

Define Wannier states $w_n(x) = N^{-1/2} \sum_p e^{-ipna/\hbar} \psi_p(x)$ in 1D

$w_n(x)$ is localized on the site $x \approx na$ $w_n(x) = w_0(x-na)$
(for instance, without the Bloch modulation, $w_n(x) = \delta(x-na)$)

Tight-binding model

Substitute into Schrödinger equation:

$$\sum_n \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x-na) \right) e^{ipna/\hbar} w_n(x) + \sum_n h(x) e^{ipna/\hbar} w_n(x) = \epsilon_p \sum_n e^{ipna/\hbar} w_n(x); \quad h(x) \equiv \sum_{m \neq n} U(x-ma)$$

Perturbation: Term with h (only contains overlap between different atomic states)

Unperturbed: $w_0(x) = \varphi(x)$ Atomic functions

$\epsilon_p = \epsilon_0$ Atomic energies

Tight-binding model

First-order correction:

$$\epsilon_p = \epsilon_0 + \frac{\sum_n h(n) \exp(ipna/\hbar)}{\sum_n I(n) \exp(ipna/\hbar)}$$

$$\epsilon_p = \epsilon_0 + h(0) + 2[h(1) - h(0)I(1)] \cos pa/\hbar$$

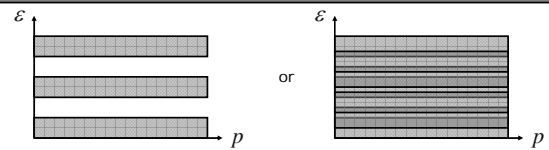
$$h(n) = \int dx \varphi^*(x) h(x) \varphi(x-na) \quad I(n) = \int dx \varphi^*(x) \varphi(x-na)$$

$$h(1) \ll h(0), \quad I(1) \ll I(0) = 1$$

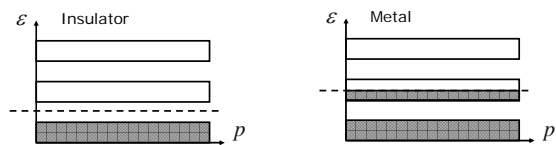
Narrow sinusoidal band

3D: Qualitatively the same; details depend on the symmetry of the lattice. Always narrow bands.

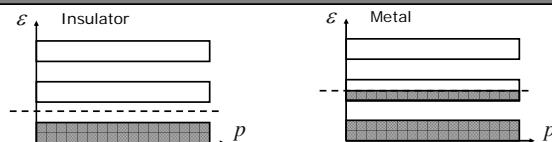
Metals vs insulators



Let us now fill the electron states.



Metals vs insulators



Metals can be charged at no energy cost.

Insulators can only be charged if energy is supplied (e.g. by temperature).

Semiconductors are insulators with a narrow gap, so that the free carriers can be easily created (temperature or doping).

Also: semimetals, various species of insulators, non-crystalline solids etc.

Periodic table

Periodic Table of the Elements																		
1A	2A	3A										4A	5A	6A	7A	8A	0	
H	He	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	Kr	Xe	
2	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	Kr	Xe
3	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	Kr	Xe
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	*La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	*Ac	Rf	Ha	106	107	108	109	110	111	112	113	114	115	116	117	118
* Lanthanide Series: Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu																		
* Actinide Series: Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr																		

Free electron gas: Fermi energy

Finite size system \implies Discrete quasimomentum

For large systems, the details should not depend on the boundary conditions

Take a sample $L_x \times L_y \times L_z$ and periodic boundary conditions:

$$e^{ip_x L_x / \hbar} = 1 \implies p_x L_x = 2\pi \hbar n_x \quad \text{spin } \psi(x) = \psi(x + L_x)$$

$$\text{How many states? } dn_x = L_x dp_x / 2\pi \hbar \implies dn = 2 \frac{d^3 p}{(2\pi \hbar)^3} V$$

Zero temperature: all states below p_F are occupied

$$\# \text{ of states: } N = 2 \int_0^{p_F} \frac{d^3 p}{(2\pi \hbar)^3} = 2V \frac{1}{(2\pi \hbar)^3} \frac{4\pi}{3} p_F^3 = \frac{V p_F^3}{3\pi^2 \hbar^3}$$

$$p_F = \hbar \left(3\pi^2 N / V \right)^{1/3} \quad \text{- determined only by electron concentration}$$

$$E_F = p_F^2 / 2m = \left(3\pi^2 N / V \right)^{2/3} \hbar^2 / 2m$$

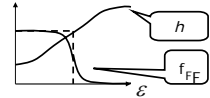
Free electron gas: Specific heat

Need to calculate energy of electron gas at finite temperature.

$$E = \frac{2V}{(2\pi \hbar)^3} \int f_F(p^2 / 2m) d^3 p \quad f_F(\epsilon) = (1 + \exp((\epsilon - \mu) / k_B T))^{-1}$$

Step 1: Integrate over angles $2 \frac{d^3 p}{(2\pi \hbar)^3} \rightarrow g(\epsilon) d\epsilon \quad \epsilon = p^2 / 2m$

$$g(\epsilon) = \frac{\sqrt{2}}{\pi^2 \hbar^3} m^{3/2} \sqrt{\epsilon} \quad \text{- density of states}$$



Step 2: Integrate over energy

$$\int d\epsilon h(\epsilon) f_F(\epsilon) = \int_0^{\mu} h(\epsilon) d\epsilon + \frac{\pi^2 k_B^2 T^2}{6} \left. \frac{\partial h}{\partial \epsilon} \right|_{\epsilon=\mu} \quad k_B T \ll \epsilon_F$$

Free electron gas: Specific heat

Step 2a: Calculate the number of particles and find the temperature dependence of the chemical potential

$$\mu(T) \approx \epsilon_F - \frac{\pi^2 k_B^2 T^2}{6} \frac{g'(\epsilon_F)}{g(\epsilon_F)}$$

Step 2b: Calculate the energy and the specific heat

$$C = \frac{1}{V} \left(\frac{\partial E}{\partial T} \right)_V = \frac{\pi^2}{3} k_B T g(\epsilon_F)$$

Only electrons close to the Fermi surface are thermally excited

Width of the energy strip: $k_B T$

Only properties of electrons at the Fermi surface are relevant!!!