

Lecture #6: $\vec{k} \cdot \vec{p}$ theory, effective mass, molecular bands

This is the final method we will describe. It is useful to find the band structure at small $|\vec{k} - \vec{k}_c|$, \vec{k}_c being a critical point. $\vec{k} \cdot \vec{p}$ theory is important because it highlights the interactions between bands and how it leads to effective masses much different from m_e .

Schrodinger eqn for Bloch states:

$$\left[\frac{\hat{p}^2}{2m} + U(\vec{r}) \right] u_{n\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}} = E_{n\vec{k}} u_{n\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}},$$

with $\vec{p} = \frac{\hbar}{i} \vec{\nabla}$. Apply this to the plane wave and eliminate it:

$$\left[\frac{1}{2m} \left| \frac{\hbar}{i} \vec{\nabla} + \hbar \vec{k} \right|^2 + U(\vec{r}) \right] u_{n\vec{k}}(\vec{r}) = E_{n\vec{k}} u_{n\vec{k}}(\vec{r})$$

$$(H_0 + H_1 + H_2) u_{n\vec{k}}(\vec{r}) = E_{n\vec{k}} u_{n\vec{k}}(\vec{r})$$

$$\left\{ \begin{array}{l} H_0 = \frac{p^2}{2m} + U(\vec{r}) \\ H_1 = \frac{\hbar}{m} \vec{k} \cdot \vec{p} \\ H_2 = \frac{\hbar^2 k^2}{2m} \end{array} \right. \quad \text{Use perturbation theory on } H_1, H_2.$$

The unperturbed basis is given by:

$$\left[\frac{p^2}{2m} + U(\vec{r}) \right] u_{n_0}(\vec{r}) = E_{n_0} u_{n_0}(\vec{r}) \quad \text{with periodic boundary conditions:}$$

$$u_{n_0}(\vec{r} + \vec{P}) = u_{n_0}(\vec{r})$$

↑
unit cell boundary.

2)

$$\text{From } \int d^3\vec{r} \psi_{n\vec{k}}^*(\vec{r}) \psi_{m\vec{k}}(\vec{r}) = \frac{1}{V} \sum_{\vec{R}} \int_{\text{cell}} d^3\vec{r} u_{n0}^*(\vec{r}) u_{m0}(\vec{r}) = \delta_{nm}$$

$$V = NV_{\text{cell}} \Rightarrow \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d^3\vec{r} u_{n0}^*(\vec{r}) u_{m0}(\vec{r}) = \delta_{nm}$$

Perturbation theory: To 1st order

$$|u_{m\vec{k}}\rangle = |u_{m0}\rangle + \frac{\hbar}{m} \sum_{m \neq n} \frac{\vec{k} \cdot \langle u_{m0} | \vec{p} | u_{n0} \rangle}{(E_{m0} - E_{n0})} |u_{n0}\rangle \quad (*)$$

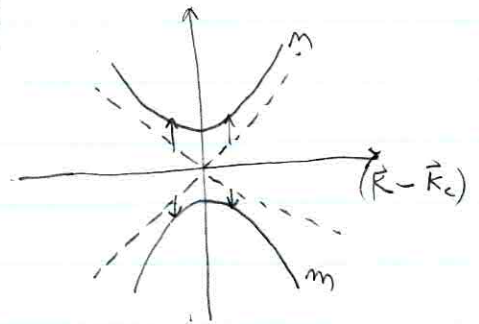
$$E_{m\vec{k}} = E_{m0} + \frac{\hbar}{m} \vec{k} \cdot \langle u_{m0} | \vec{p} | u_{m0} \rangle, \text{ go to 2nd order:}$$

$$\text{because } \left. \frac{\partial E_{m\vec{k}}}{\partial \vec{k}} \right|_{\vec{k}=0} = 0 = \frac{\hbar}{m} \langle u_{m0} | \vec{p} | u_{m0} \rangle$$

$$E_{m\vec{k}} = E_{m0} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{m \neq n} \frac{|\vec{k} \cdot \langle u_{m0} | \vec{p} | u_{n0} \rangle|^2}{E_{m0} - E_{n0}} + \mathcal{O}(k^3) \quad (**)$$

Level repulsion!

Note that bands far away in energy have little effect on each other.



Now, show from (*) and (**) that

$$\langle \psi_{m\vec{k}} | \vec{p} | \psi_{m\vec{k}} \rangle = \frac{\hbar}{m} \nabla_{\vec{k}} E_{m\vec{k}} = m \vec{N}_g$$

electron does any momentum, but the momentum is different from $\hbar\vec{k}$. Note: \vec{N}_g is not separate of momentum

$$\langle \psi_{m\vec{k}} | \vec{p} | \psi_{m\vec{k}} \rangle = \hbar\vec{k} + \langle u_{m\vec{k}} | \vec{p} | u_{m\vec{k}} \rangle = \hbar\vec{k} + \frac{\hbar}{m} \sum_{m \neq n} \left[\frac{\vec{k} \cdot \langle u_{m0} | \vec{p} | u_{n0} \rangle}{E_{m0} - E_{n0}} \langle u_{n0} | \vec{p} | u_{m0} \rangle \right]$$

But this is identical to $\nabla_{\vec{k}} (**)$!

+ $\mathcal{O}(k^2)$

○ Rewrite (***) as:

$$E_{m\vec{k}} = E_{m0} + \sum_{ij} \frac{\hbar^2}{2} M_{ij}^{-1} k_i k_j$$

$$M_{ij}^{-1} = \frac{\delta_{ij}}{m_e} + \frac{2}{m_e^2} \sum_{m \neq n} \frac{\langle u_{m0} | p_i | u_{n0} \rangle \langle u_{n0} | p_j | u_{m0} \rangle}{(E_{m0} - E_{n0})}$$

"renormalized mass tensor"
or Effective mass tensor

For isotropic bands:

$$E_{m\vec{k}} = E_{m0} + \frac{\hbar^2 k^2}{2m^*}$$

$$\frac{1}{m^*} = \frac{1}{m_e} + \frac{2\hbar^2}{m_e^2} \sum_m \frac{|P_{mm}|^2}{E_{m0} - E_{m0}}$$

Bands and bands

➔ It is no accident that a band is usually either completely filled or empty.

The number of band states (# of \vec{k} 's in the BZ) equals $2 \times$ the # of unit cells (because of spin degeneracy); The # of electrons is the sum of valence electrons in each unit cell ("core" electrons are inert).

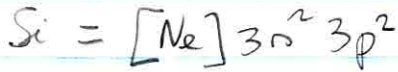
$$\Rightarrow N_e = \left(\sum_i N_i \right) \times N_{\text{cells}} \Rightarrow \begin{cases} \sum_i N_i \text{ even} \Rightarrow \text{All bands completely filled} \Rightarrow \text{INSULATOR} \\ \sum_i N_i \text{ odd} \Rightarrow \text{Top-most band half-filled} \Rightarrow \text{METAL} \end{cases}$$

Assuming no band overlap!

④ Examples: $Cu = [Ar] 3d^9 4s^1 \Rightarrow$ Metal with half-filled "s" conduction band (band overlaps not expected because $E_{4s} < E_{3d}$!)
 But life is not that simple: Consider $Fe = [Ar] 3d^6 4s^2 \Rightarrow$ even # but is a metal
 \Rightarrow Because of magnetism, the electrons prefer to be $\uparrow\uparrow\uparrow\uparrow\uparrow$ (Fermi)
 \Rightarrow Here e-e interaction plays a role!

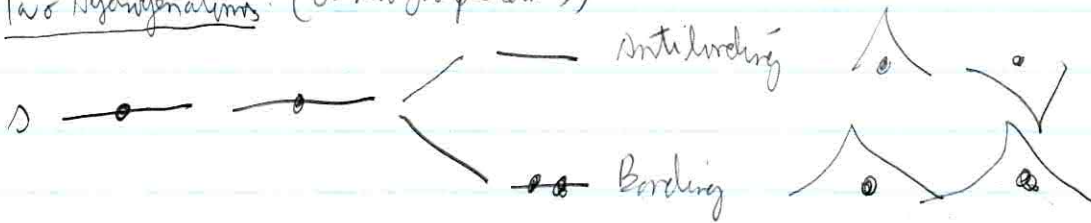
Lecture #7 Classification of solids

Often each atom has a number of degenerate valence orbitals:

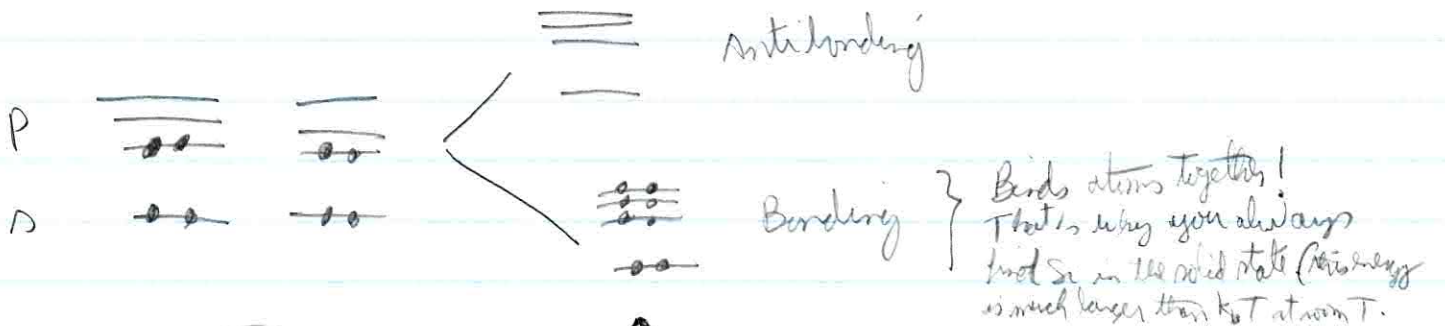


In this case it is more convenient to talk about molecular orbitals instead of atomic orbitals.

Two Hydrogen atoms: (or two group I atoms):

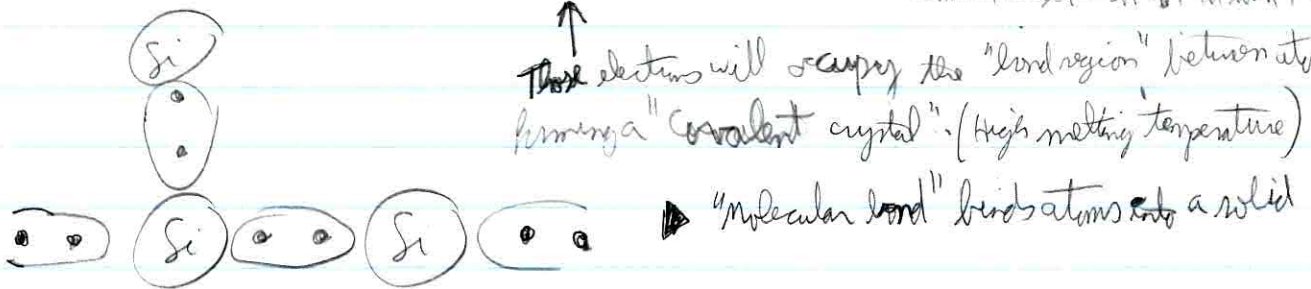


Two atoms with partially filled s and p orbitals (e.g. group III such as Si):



Binds atoms together!
 That is why you always find Si in the solid state (bond energy is much larger than kT at room T.)

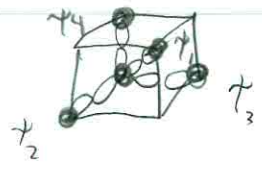
These electrons will occupy the "bond region" between atoms, forming a "covalent crystal". (high melting temperature).



Bonds and crystal symmetry:
 "s p³ hybridization"

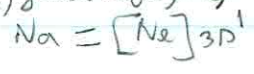
$$\begin{cases} |T_1\rangle = \frac{1}{2} [|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle] \\ |T_2\rangle = \frac{1}{2} [|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle] \\ |T_3\rangle = \frac{1}{2} [|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle] \\ |T_4\rangle = \frac{1}{2} [|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle] \end{cases}$$

The four sp^3 states fit naturally into a cube
 \Rightarrow group IV materials, group III-V, etc... all have tetragonal symmetry (diamond, zincblende, etc).

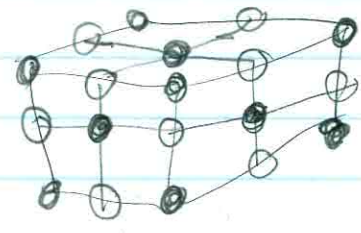
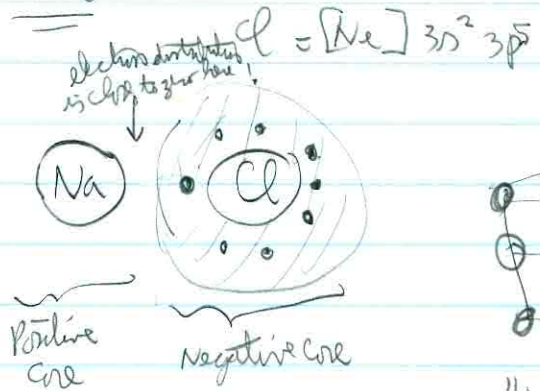


Ionic crystals

NaCl:



Basic entities are ions, not atoms!

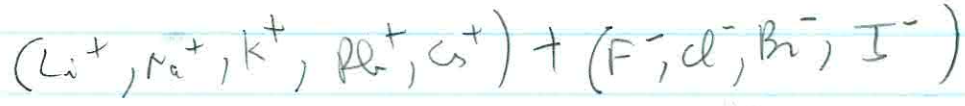


"NaCl" structure: Cubic lattice with two different kinds of atoms (fcc with 2 atom basis)

\Rightarrow Electrostatics binds the atoms together into a solid

(I-VII):

Alkali halides: NaCl, LiF, NaF, CsI, ...

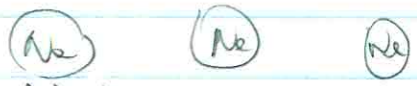


\Rightarrow all are insulators

Molecular crystals

Basic entities are molecules, not atoms!

Example: Solid Hydrogen, solid noble gases such as Ne, Ar, Kr, Xe (Exists only at Low Temperatures and high pressures!)



Single atom but it's called a molecule here

\Rightarrow Van der Waals forces binds the molecules together.

