Lec 9. <u>Tight-binding approach for Si</u>

<u>Lattice with a basis</u>

So far we have considered only Bravais lattices where every lattice point is associated w/ one atom only. Most semiconductor crystals have a lattice with a basis. The simplest example is that of Si. Si crystallizes in an F.C.C. lattice formed out of 2 atoms per lattice point. (Diamond lattice

F.C.C. primitive cell: $\frac{a}{2}(0,1,1)$, $\frac{a}{2}(1,0,1)$ & $\frac{a}{2}(1,1,0)$

volume $= \frac{a^3}{4}$.

Si : 2 atoms in the unit cell: at $(0,0,0)$ & $\frac{a}{4}(1,1,1$

Let $\vec{u}_\ell$ represent the position of the basis atoms in a unit cell with respect to the cells origin.

for Silicon $\vec{u}_1 = (0,0,0)$ & $\vec{u}_2 = (\frac{a}{4}, \frac{a}{4}, \frac{a}{4})$

If there were only 1 s orbital per atom then the Bloch sum would be written as :

$$|\varphi_{\vec{k},\ell}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot(\vec{R}_n + \vec{u}_\ell)} |\psi_{n\ell}\rangle. \quad \boxed{16.1}$$

for each basis atom. The functions are eigenstates of $\hat{T}_{\vec{a}_i}$ w/ the same eigenvalue $e^{i\vec{k}\cdot\vec{a}}$.

$$\hat{T}_{\vec{a}}|\varphi_{\vec{k},\ell}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot(\vec{R}_n + \vec{u}_\ell)} \hat{T}_{\vec{a}}|\psi_{n+1,\ell}\rangle$$

$\downarrow$ pushed along $\vec{a}_i$.

$$= e^{i\vec{k}\cdot\vec{a}} |\varphi_{\vec{k},\ell}\rangle \quad \boxed{16.2}$$

Let $\ell = 1, N_b.$ $\longrightarrow \boxed{16.3}$

Thus, we have N_b degenerate Bloch states (for $\hat{T}_a$). The resulting bands can be found by diagonalizing an $N_b \times N_b$ matrix.

For 3 p orbitals per site it will be a $3N_b \times 3N_b$ matrix.

Si crystal : A minimal atomic basis set for Si consists of the 3s & 3p orbitals $\rightarrow$ $|s\rangle, |p_x\rangle, |p_y\rangle, |p_z\rangle$, centered one the atomic sites. Thus, we are looking at an 8×8 problem on the diamond lattice.

The integrals we would need as $V_{ss\sigma}, V_{sp\sigma}, V_{pp\sigma}, V_{pp\pi}$ (4 parameters)

It is convenient (although not necessary) to use hybrid orbitals as a basis.

A Hybrid orbitals $\rightarrow$ ~~Symmon~~ Special linear combination of basis orbitals (usually symmetry adapted).
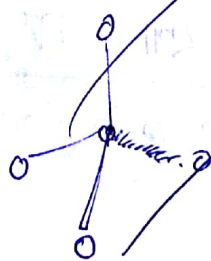
$s \& p \rightarrow sp, sp^2, sp^3$ hybrids.

Principle of maximum overlap — Hybrids maximize the hopping coupling (bonding interaction) along special directions. For instance, sp^3 hybrids do so along the directions of the bonds in the diamond lattice.

The 4 sp^3 hybrid orbitals are given by :

$$|sp^3\rangle = \begin{cases} |h_1\rangle = \frac{1}{2}\left(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle\right) \\ |h_2\rangle = \frac{1}{2}\left(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle\right) \\ |h_3\rangle = \frac{1}{2}\left(|s\rangle + |p_x\rangle - |p_y\rangle + |p_z\rangle\right) \\ |h_4\rangle = \frac{1}{2}\left(|s\rangle + |p_x\rangle + |p_y\rangle - |p_z\rangle\right) \end{cases} \quad - \; (163)$$

They point in the 4 directions $(111), (\bar{1}11), (1\bar{1}1) \& (11\bar{1})$ respectively. i.e 4 directions of the vertices of a tetrahedron relative to the centre of the object.

Principle of orthogonality:

Note that $\langle \cos \beta | \sin \beta \rangle = \ldots$

$$\langle h_i | h_j \rangle = \delta_{ij} \quad\quad - \text{(164)}$$

Construction of $\perp^r$ orthogonal hybrids:

Let $|h_1\rangle = N(|s\rangle + \lambda|p_1\rangle)$ & $|h_2\rangle = N(|s\rangle + \lambda|p_2\rangle) \quad - \text{(165)}$

be 2 equivalent hybrids on the same atom (i.e. they only differ in their orientation).

$$N = \frac{1}{\sqrt{1+\lambda^2}} \quad - \text{(166)}$$

Orthogonality requirement $\Rightarrow \langle h_1 | h_2 \rangle = N^2(1 + \lambda^2 \langle p_1 | p_2 \rangle) \quad - \text{(166)}$

$$= 0$$

$\Rightarrow$ Let $\langle p_1 | p_2 \rangle = \cos\theta_{12}$.

$$\Rightarrow \lambda^2 = -1/\cos\theta_{12}. \quad - \text{(167)}$$

0.1) sp hybrids: $s + p_z$. $\quad |h_1\rangle = \frac{1}{\sqrt{2}}(|s\rangle + p_z)$

$\theta_{12} = \cos\pi \Rightarrow \cos\theta_{12} = -1 \Rightarrow \lambda = \pm 1$.

To maximize overlap we'll choose p_1 & p_2 to have opposite signs $\Rightarrow \theta_{12} = 180° \Rightarrow \lambda = \mp F$

$\therefore |h_1\rangle =$

1) sp-hybrids: if we choose $|p_1\rangle = |p_x\rangle$ & $|p_2\rangle = -|p_x\rangle$

$\Rightarrow \theta_{12} = \pi \Rightarrow \lambda = 1$ & $N = 1/\sqrt{2}$

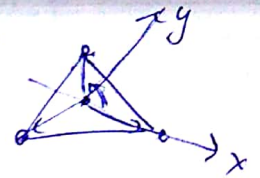$\therefore |h_1\rangle = \frac{1}{\sqrt{2}}(|s\rangle + |p_x\rangle)$

$|h_2\rangle = \frac{1}{\sqrt{2}}(|s\rangle - |p_x\rangle)$ $\quad \text{(168)}$

2 p-orbitals are left unchanged (p_y, p_z)

2) sp²-hybrids: The angle we want between any 2 p-orientation is ~~120°~~ $\frac{2\pi}{3}$.

$\Rightarrow \cos\theta =$

$$|h_1\rangle = \left(|s\rangle + \frac{1}{\sqrt{2}}|p_x\rangle\right)\frac{1}{\sqrt{3}}$$
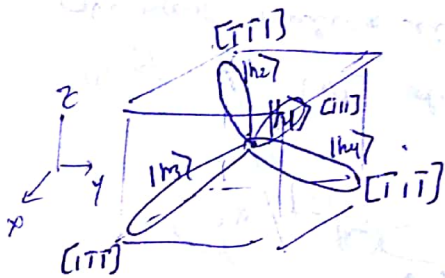
$$|h_2\rangle = \frac{1}{\sqrt{3}}\left(|s\rangle - \frac{|p_x\rangle}{\sqrt{2}} + \frac{\sqrt{3}}{\sqrt{2}}|p_y\rangle\right)$$

$$|h_3\rangle = \frac{1}{\sqrt{3}}\left(|s\rangle - \frac{|p_x\rangle}{\sqrt{2}} - \frac{\sqrt{3}}{\sqrt{2}}|p_y\rangle\right)$$

(169)

$|p_z\rangle$ is left unchanged.

3) sp³ hybrids:

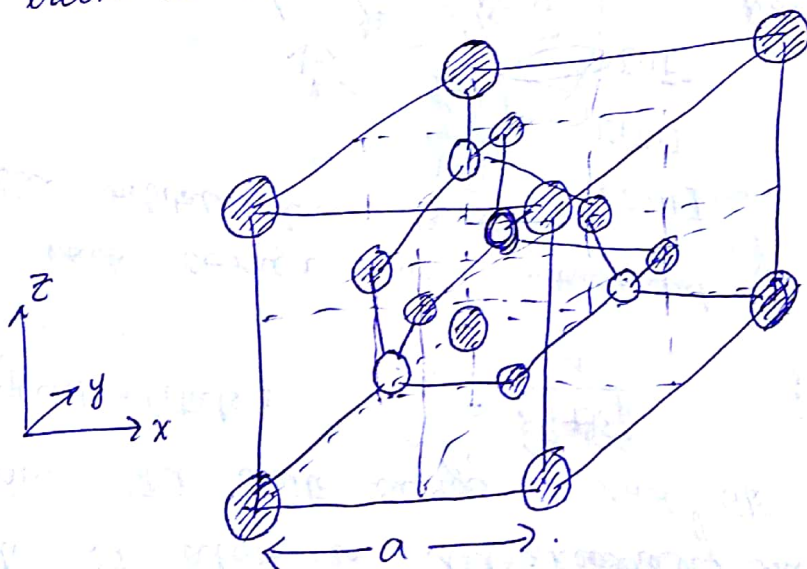$$|h_1\rangle = \frac{1}{2}\left(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle\right)$$

$$|h_2\rangle = \frac{1}{2}\left(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle\right)$$

$$|h_3\rangle = \frac{1}{2}\left(|s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle\right)$$

$$|h_4\rangle = \frac{1}{2}\left(|s\rangle - |p_x\rangle - |p_y\rangle + |p_z\rangle\right)$$

(170)

Coming back to Si. we can draw the unit cell as follows:

We see that there are 2 kinds of atoms in the cell. (shaded & unshaded). The same structure is true for Ⅲ-Ⅴ semiconductors like GaAs. The structure is called diamond structure when the 2 sites have the same atom and zinc blende when the atoms are different.

Each Si atom is tetrahedrally surrounded by 4 other Si atom. The onsite energy at each site is the energy of the hybrid orbitals:

$$\varepsilon_h^0 = \frac{\tilde{\varepsilon}_s^0 + 3\tilde{\varepsilon}_p^0}{4} \quad ; \quad \varepsilon_h^0 = -9.38 \, eV \qquad \text{(1)}$$

(Harrison, Elementary Electronic structure)

At each corner the arrangement of the orbitals looks as follows:
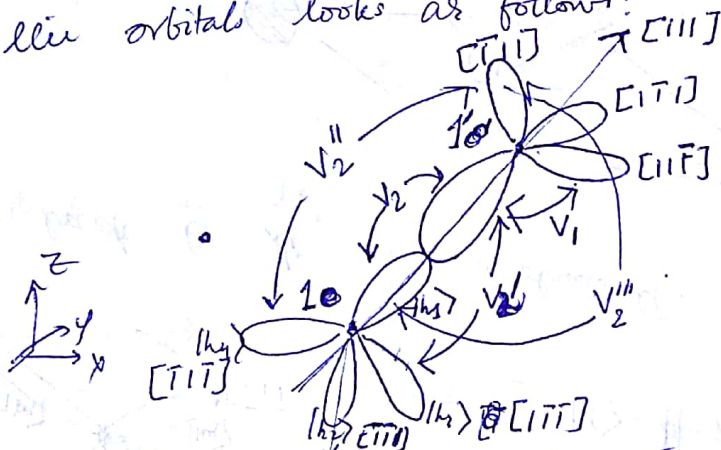
Note that the states on 1' and 1 are inverted (for maximum overlap).

Along the [111] direction we have the strongest overlap and hence the strongest matrix element.

$$-V_2 \equiv \langle h_1 | \Delta \hat{H} | h_1' \rangle = \langle h_1 | \hat{v}' | h_1' \rangle$$

$$= \frac{1}{4} \left(\langle s | + \langle p_x | + \langle p_y | + \langle p_z | \right) \hat{v}' \left(-|s\rangle \mp |p_x\rangle \mp |p_y\rangle \mp |p_z\rangle \right)$$

$$= -\frac{1}{4} \left(V_{ss\sigma} - \frac{2}{\cancel{3}}\sqrt{3}\, V_{sp\sigma} - 3 V_{pp\sigma} \right) \qquad \text{(172.)}$$

$$|V_2| \rightarrow \text{covalent energy.}$$

the The coupling between the along state $|h_1\rangle$ and $|h_2\rangle$, $|h_3\rangle$ or $|h_4\rangle$ (or v.v.) is smaller in magnitude than V_2. These couplings are all exactly equal due to symmetry & given by:

$$V_2'^{\,\prime o} = -\frac{1}{4}\left(V_{ss\sigma} - \frac{2\sqrt{3}}{3}V_{sp\sigma} + V_{pp\sigma}\right) \quad —(173)$$

For Ⅲ-Ⅴ semiconductors since the onsite energies on the 2 sites will differ, we also define a polar energy: $V_3 = \dfrac{\mathcal{E}_{h+} - \mathcal{E}_{h-}}{2} \quad —(174)$

where $\mathcal{E}_{h\pm}$ refers to the cation/anion site.

$+ \rightarrow$ higher energy hybrid (less electronegative)

$- \rightarrow$ lower energy hybrid (more electronegative)

e.g. GaAs. $V_3 = 2.16$ eV.

Another coupling is between hybrids on the same site. This is called the metallic energy. $-V_1 = \dfrac{\tilde{\mathcal{E}}_p^o - \tilde{\mathcal{E}}_s^o}{4} \quad —(176)$.

Both V_1 & V_2' are inter-bond coupling. They result in broadening of the valence and conduction bands.
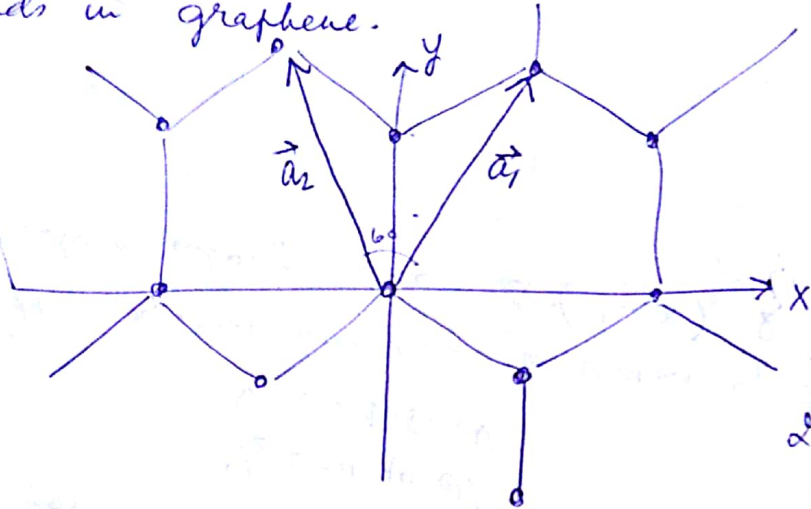
<u>H.W.</u>

① A simple model for Si is the Weaire-Thorpe model (Phys. Rev. B **4** , 2508 (1971)) where only V_2 & V_1 are taken to be non-zero. Reasonable values for them are (Elementary Electronic Structure, W. Harrison)

$$V_2 = -4.44 \text{ eV}$$
$$V_1 = -1.80 \text{ eV}.$$

Given the nearest neighbour vectors of Si, derive the band structure along the $\Delta \cdot (\Gamma - X)$ & $\Lambda (L-\Gamma)$ lines.

② π- bands in graphene.

primitive
translation
vectors

$$\vec{a_1} = a\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$$

$$\vec{a_2} = a\left(-\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$$

$$a = 2.45 \text{Å}$$

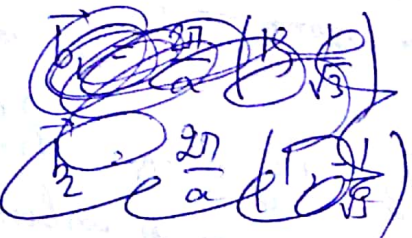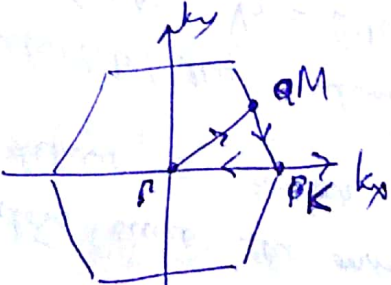2 atoms in the primitive
cell (conventional
hexagonal cell)

$$C \rightarrow sp^2 + p_z$$

3 hybrid bands well separated
from the π-bands formed by p_z.
These two sets do not interact with each other

∴ Hamiltonian at every k-point factors into a

(6×6) block and a (2×2) block.

$sp^2 \rightarrow \sigma$ - bands . gap $\sim 10 eV$ between
valence & conduction bands

Band structure around F.L is due to the π-bands

B.Z.

A) Give the reciprocal primitive translation vectors $\vec{b_1}$ & $\vec{b_2}$
& coordinates of K & M pts in units of $\frac{2\pi}{a}$

B) Compute the band-~~structure~~ dispersion along the path KΓMK. Use the orthogonal TBM with $V_{pp\pi} = -2.38\,eV$.

Comment on the gap structure you find.