

17/1/2018 (15/1/2018)

Rec. 7.8 Tight-binding with p-orbitals

Since s-orbitals are spherically symmetrically, we haven't had to worry about direction dependence of tight-binding matrix elements. Going beyond alkali ~~metals~~ metals we already start seeing the effects of higher 'l' orbitals. For instance, we'll consider presently the effect of p-orbitals on a site to the ~~band-structure~~ band-structure.

In the case of s-orbitals, the important quantity was  $V_{SS} = \langle \psi_1 | V_2 | \psi_2 \rangle$   
 $\equiv -t$  (126)

This defn. made in the orthogonal TBM, holds for any lattice made up of s-orbitals.

If instead a lattice site has p-orbitals, then we would have to consider 3 such orbitals with  $m_l = -1, 0, 1$ . It is convenient to use real orbitals instead of the complex spherical harmonics in our basis.

So instead of,  $Y_{10}(\theta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos \theta$ ,  $Y_{\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\varphi}$  (127)

we use,

$$\left. \begin{aligned} Y_{1z} &= Y_{10} = \sqrt{\frac{3}{4\pi}} \frac{z}{r} \\ Y_{1x} &= \frac{1}{\sqrt{2}} (-Y_{11} + Y_{1-1}) = \sqrt{\frac{3}{4\pi}} \frac{x}{r} \\ Y_{1y} &= \frac{i}{\sqrt{2}} (Y_{11} \pm Y_{1-1}) = \sqrt{\frac{3}{4\pi}} \frac{y}{r} \end{aligned} \right\} (128)$$

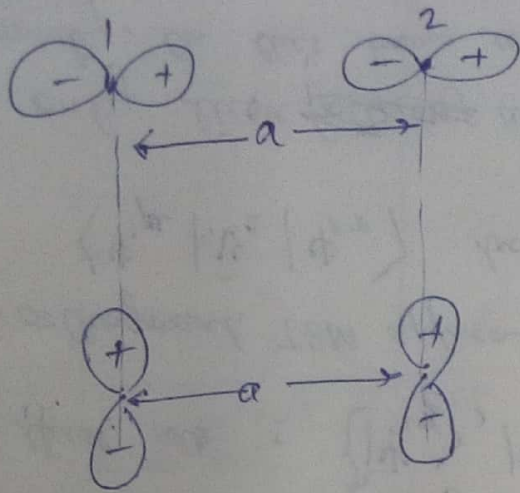
Hence, the real p-orbitals have x, y, z symmetry, respectively. i.e. they behave under rotations like x, y & z components of an ordinary vector.

Let's denote these as:  $\{ |\psi_{1x}\rangle, |\psi_{1y}\rangle, |\psi_{1z}\rangle \}_{i=1, N}$  (129)

In the orthogonal TBM approach we will need to use the integrals  $\langle \psi_{1\mu} | \hat{V}_2 | \psi_{2\nu} \rangle$  between 2 ~~neighboring~~ sites, where  $\mu, \nu = x, y, z$ .

Of these, only those ~~integrals~~ will be non-zero which involve  $\mu$  &  $\nu$  of same symmetry. On this basis we can anticipate 2 kinds of integrals:





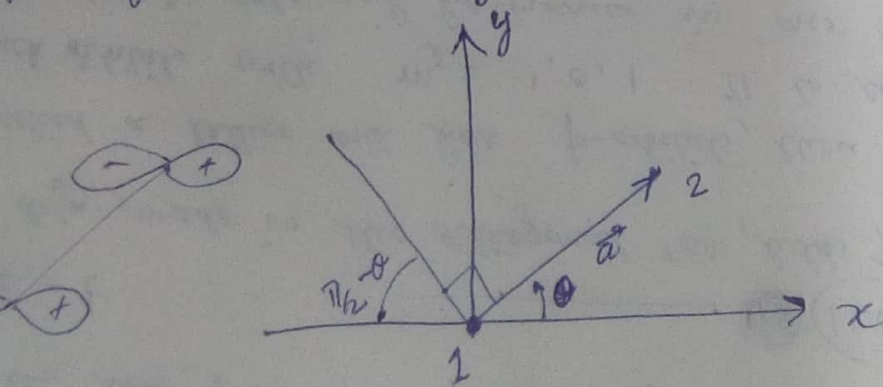
$$V_{pp\sigma} = \langle \psi_{1z} | \hat{V}_2 | \psi_{2z} \rangle \quad (130)$$

$$V_{pp\pi} = \langle \psi_{1y} | \hat{V}_2 | \psi_{1y} \rangle = \langle \psi_{1z} | \hat{V}_2 | \psi_{1z} \rangle$$

where  $\hat{V}_2(\vec{r}) = V(\vec{r}-\vec{a}) = V/|\vec{r}-\vec{a}|$  is spherically symmetric.

We have assumed here the internuclear axis to be x. But this is arbitrary. When the overlap involves orbitals w/ 0 projection along internuclear axis we denote it as  $\sigma$ . When the projections involved are  $\pm 1$ , we denote it as  $\pi$ .

Given two p orbitals at two sites connected by a lattice transformation  $\vec{a}$  lying on the xy plane we have:



The 2 direction cosines of  $\vec{a}$  are given by

$$\left. \begin{aligned} c_x &= \cos \theta \\ c_y &= \sin \theta \end{aligned} \right\} (131)$$

$$\left. \begin{aligned} c_x &= \vec{e}_{||} \cdot \hat{i} \\ c_y &= \vec{e}_{||} \cdot \hat{j} \end{aligned} \right\} (132)$$

where,  $\vec{e}_{||} = c_x \hat{i} + c_y \hat{j}$  (133)

in terms of unit vectors along x, y axis and the bond direction  $\vec{a}$

$$\vec{e}_1 = -c_y \hat{i} + c_x \hat{j} \quad \text{--- (134)}$$

Note that

$$\underline{\underline{c_x^2 + c_y^2 = 1}}$$

$$\Rightarrow \begin{cases} \hat{i} = c_x \vec{e}_{11} - c_y \vec{e}_1 \\ \hat{j} = c_y \vec{e}_{11} + c_x \vec{e}_1 \end{cases} \quad \text{(135)}$$

Thus, we can resolve the orbital contribution in these directions,

$$\begin{cases} |\psi_{1x}\rangle = c_x |\psi_{111}\rangle - c_y |\psi_{11\perp}\rangle \\ |\psi_{1y}\rangle = c_y |\psi_{111}\rangle + c_x |\psi_{11\perp}\rangle \end{cases} \quad \text{(136)}$$

|| → along bond  
⊥ → ⊥ to bond.

& similarly for  $|\psi_{2x}\rangle$  &  $|\psi_{2y}\rangle$ .

Hence,

$$\begin{aligned} \langle \psi_{1x} | \hat{V}_2 | \psi_{2x} \rangle &= (c_x |\psi_{111}\rangle - c_y |\psi_{11\perp}\rangle)^\dagger \hat{V}_2 (c_x |\psi_{211}\rangle - c_y |\psi_{21\perp}\rangle) \\ &= c_x^2 V_{pp\sigma} + c_y^2 V_{pp\pi} \\ &= c_x^2 V_{pp\sigma} + (1 - c_x^2) V_{pp\pi} \quad \text{--- (137)} \end{aligned}$$

$$\langle \psi_{1x} | \hat{V}_2 | \psi_{2y} \rangle = c_x c_y (V_{pp\sigma} - V_{pp\pi}) \quad \text{--- (138)}$$

$$\langle \psi_{1z} | \hat{V}_2 | \psi_{2z} \rangle = V_{pp\pi} \quad \text{--- (139)}$$

$$\langle \psi_{1x} | \hat{V}_2 | \psi_{2z} \rangle = \langle \psi_{1y} | \hat{V}_2 | \psi_{2z} \rangle = 0 \quad \text{--- (140)}$$

More general expressions can be found for  $\vec{a}$  in any general direction

$$\vec{e}_{11} = c_x \hat{i} + c_y \hat{j} + c_z \hat{k} \quad \text{--- (141)}$$



For a p-band we consider 3 Bloch sums:

$$|\psi_{\mathbf{k},\alpha}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n} |\psi_{n,\alpha}\rangle \quad \text{--- (142)}$$

where  $\alpha = x, y, z$ .

The tight-binding Hamiltonian can be written as:

$$H = \sum_{\substack{\langle nn' \rangle \\ \alpha\alpha'}} |\psi_{n,\alpha}\rangle H_{n\alpha, n'\alpha'} \langle \psi_{n',\alpha'}| \quad \text{--- (143)}$$

The on-site elements are  $H_{n\alpha, n'\alpha'} = \tilde{\epsilon}_p^{\alpha} \delta_{\alpha\alpha'} \quad \text{--- (144)}$

Consider an f.c.c. lattice of  $N$  atoms.

The hopping matrix elements can be calculated w.r.t one site at the origin & the sites at one of the 6 nn, ( $\vec{a}_i$ ;  $i=1,2,3$ ).

$$\rightarrow \underbrace{\frac{a}{2}(0,1,1); \frac{a}{2}(0,1,\bar{1})}_{\text{plane } yz}; \underbrace{\frac{a}{2}(1,0,1); \frac{a}{2}(1,0,\bar{1})}_{\text{plane } xz} \quad \left. \vphantom{\frac{a}{2}(0,1,1)} \right\} \text{(145)}$$

$$\& \underbrace{\frac{a}{2}(1,1,0); \frac{a}{2}(1,\bar{1},0)}_{\text{plane } xy}$$

The other 6 nn can be obtained from these.

$$\text{Let } \langle \psi_{0\alpha} | \tilde{V}_i | \psi_{i\alpha'} \rangle = V_{\alpha\alpha'}^i \quad \text{--- (146)}$$

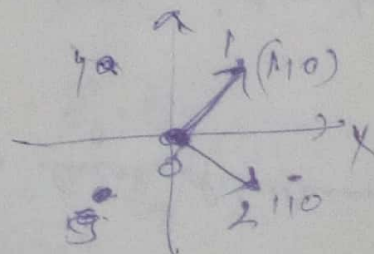
$i=1,2 \rightarrow \text{nn neighbours}$

Let's consider the xy plane first.

$$V_{xx1} = c_x^2 V_{pp\sigma} + (1-c_x^2) V_{pp\pi} \quad \text{--- (147)}$$

$$c_x = \frac{1}{\sqrt{2}} (1,1,0) \cdot (1,0,0) = \frac{1}{\sqrt{2}}$$

$$\therefore V_{xx1} = \frac{(V_{pp\sigma} + V_{pp\pi})}{2} \quad \text{--- (148)}$$



$$V_{xy1} = c_x c_y (V_{pp\sigma} - V_{pp\pi})$$

$$= \frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{2}} (V_{pp\sigma} - V_{pp\pi}) = \frac{(V_{pp\sigma} - V_{pp\pi})}{2} \quad (149)$$

$$V_{zz1} = V_{pp\pi}$$

$$V_{xz1} = \cancel{\frac{1}{2}(V_{pp\sigma} - V_{pp\pi})} V_{yz1} = 0 \quad (150)$$

All other matrix elements can be obtained by symmetry.

or,  $\langle \psi_{\vec{k}, \alpha} | \hat{H} | \psi_{\vec{k}', \alpha'} \rangle = \delta_{\vec{k}\vec{k}'} \langle \psi_{\vec{k}, \alpha} | \hat{H} | \psi_{\vec{k}, \alpha} \rangle \equiv \delta_{\vec{k}\vec{k}'} H_{\alpha\alpha'}(\vec{k}) \quad (151)$

This is because the  $\hat{H}_z$  commutes w/  $\hat{T}_{\vec{a}}$  & is hence diagonal in  $\vec{k}$ .  
 At each  $\vec{k}$ -value the matrix  $H_{\alpha\alpha'}(\vec{k})$  is a 3x3 matrix that has to be diagonalized to find eigenvalues & eigenvectors.

$$H_{\alpha\alpha'}(\vec{k}) = \frac{1}{N^0} \sum_{lm} e^{i\vec{k} \cdot (\vec{R}_m - \vec{R}_l)} \langle \psi_{\alpha\alpha} | \left( \sum_{\substack{np \\ pp}} |\psi_{np}\rangle H_{np, np'} \langle \psi_{n'p'} | \right) | \psi_{m\alpha'} \rangle$$

$$= \sum_{i=1}^{12} e^{i\vec{k} \cdot \vec{a}_i} \langle \psi_{0\alpha} | \hat{V}_i | \psi_{i\alpha'} \rangle + \tilde{\epsilon}_p^0 \delta_{\alpha\alpha'} \quad (152)$$

where  $\vec{a}_i \rightarrow 12 \text{ n.n.}$

~~We have used  $\sum_{\vec{R}_n} e^{i\vec{k} \cdot \vec{R}_n}$~~

or,  $H_{xx}(\vec{k}) = \tilde{\epsilon}_p^0 + \frac{a}{2} \cos(k_x a)$   
 For ex.  $\frac{a}{2} (0, 1, 1) : c_x = 0, c_y = \frac{1}{\sqrt{2}} = c_z$   
 $\frac{a}{2} (0, \bar{1}, \bar{1}) : c_x = 0, c_y = c_z = -\frac{1}{\sqrt{2}}$   
 etc.



$$\begin{aligned}
 H_{xx}(\vec{k}) = & \tilde{E}_p^0 + e^{i \frac{(k_y + k_z)a}{2}} V(0, 1, 1)_{xx} + e^{-i \frac{(k_y + k_z)a}{2}} V(0, \bar{1}, \bar{1})_{xx} \\
 & + e^{i \frac{(k_y - k_z)a}{2}} V(0, 1, \bar{1})_{xx} + e^{-i \frac{(k_y - k_z)a}{2}} V(0, \bar{1}, 1)_{xx} \\
 & + e^{i \frac{(k_x + k_z)a}{2}} V(1, 0, 1)_{xx} + e^{-i \frac{(k_x + k_z)a}{2}} V(\bar{1}, 0, \bar{1})_{xx} \\
 & + e^{i \frac{(k_x - k_z)a}{2}} V(1, 0, \bar{1})_{xx} + e^{-i \frac{(k_x - k_z)a}{2}} V(\bar{1}, 0, 1)_{xx} \\
 & + e^{i \frac{(k_x + k_y)a}{2}} V(1, 1, 0)_{xx} + e^{-i \frac{(k_x + k_y)a}{2}} V(\bar{1}, \bar{1}, 0)_{xx} \\
 & + e^{i \frac{(k_x - k_y)a}{2}} V(1, \bar{1}, 0)_{xx} + e^{-i \frac{(k_x - k_y)a}{2}} V(\bar{1}, 1, 0)_{xx}
 \end{aligned} \quad (153)$$

where  $V(0, \pm 1, \pm 1)_{xx} = V_{pp\pi}$

$$V(\pm 1, 0, \pm 1)_{xx} = V(\pm 1, \pm 1, 0)_{xx} = \frac{1}{2} (V_{pp\sigma} + V_{pp\pi})$$

$$\Rightarrow H_{xx}(\vec{k}) = \tilde{E}_p^0 + 4 \cos \frac{k_y a}{2} \cos \frac{k_z a}{2} V_{pp\pi}$$

$$+ 2 \left( \cos \frac{k_x a}{2} \cos \frac{k_z a}{2} + \cos \frac{k_x a}{2} \cos \frac{k_y a}{2} \right) \frac{1}{2} (V_{pp\sigma} + V_{pp\pi})$$

$$= \tilde{E}_p^0 + 4 \cos \left( \frac{k_y a}{2} \right) \cos \left( \frac{k_z a}{2} \right) V_{pp\pi} + 2 \cos \left( \frac{k_x a}{2} \right) \left( \cos \left( \frac{k_z a}{2} \right) + \cos \left( \frac{k_y a}{2} \right) \right) (V_{pp\sigma} + V_{pp\pi})$$

(154)

& the expression for  $H_{yy}(\vec{k})$  &  $H_{zz}(\vec{k})$

$$\begin{aligned} \text{Now } V_{xy}(\vec{a}) &= c_x c_y (V_{p\sigma} - V_{p\pi}) \\ V_{xz}(\vec{a}) &= c_x c_z (V_{p\sigma} - V_{p\pi}) \end{aligned} \quad \left. \vphantom{\begin{aligned} V_{xy}(\vec{a}) \\ V_{xz}(\vec{a}) \end{aligned}} \right\} \text{--- (155)}$$

and cyclic permutation.

One obtains  $H_{xy}(\vec{k}) = -2 \sin\left(\frac{k_x a}{2}\right) \sin\left(\frac{k_y a}{2}\right) (V_{p\sigma} - V_{p\pi})$  --- (158)

At  $\vec{k} = 0$  one obtains  $H_{xx}(0) = H_{yy}(0) = H_{zz}(0) = \tilde{E}_p^0 + 4V_{p\pi} + 4(V_{p\sigma} + V_{p\pi})$   
 $= \tilde{E}_p^0 + 8V_{p\pi} + 4V_{p\sigma}$  --- (157)

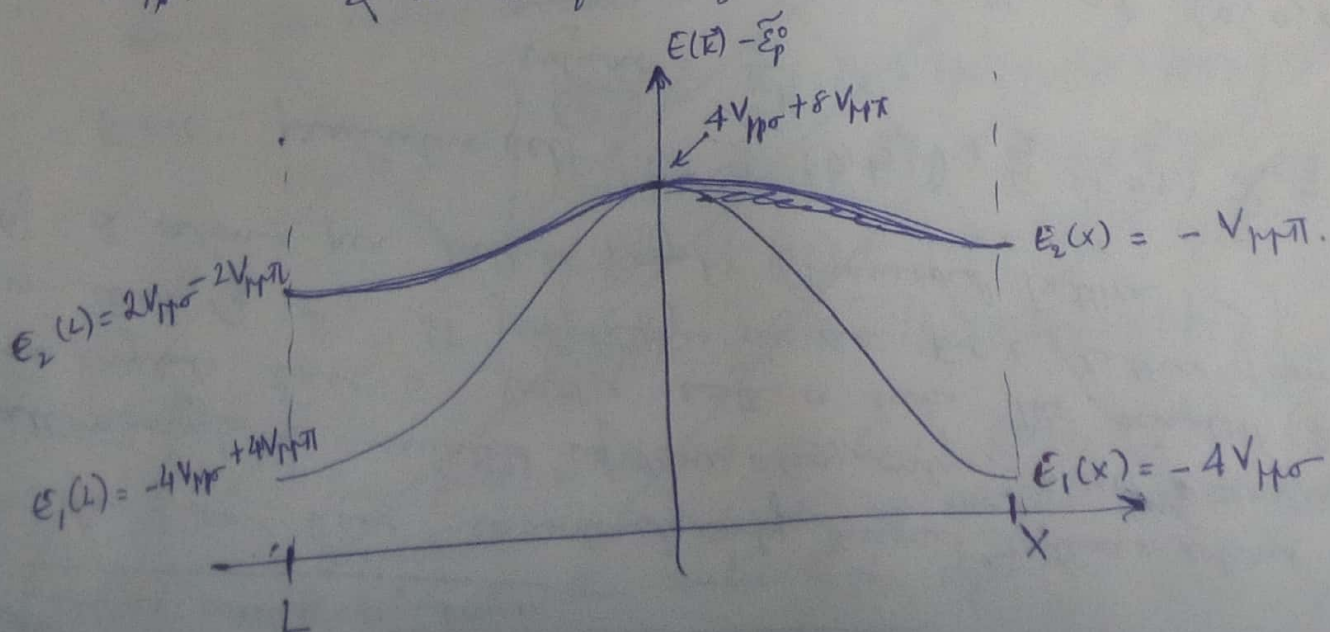
Along  $\Delta$   $(k_x, 0, 0)$  one has:

$$H_{xx}(k, 0, 0) = \tilde{E}_p^0 + 4V_{p\pi} + 4 \cos\left(\frac{k_x a}{2}\right) (V_{p\sigma} + V_{p\pi})$$
 --- (158)

$$H_{yy}(k, 0, 0) = H_{zz}(k, 0, 0) = \tilde{E}_p^0 + 4 \cos\left(\frac{k_x a}{2}\right) V_{p\pi} + 2 \left( \cos\left(\frac{k_x a}{2}\right) + 1 \right) \times (V_{p\sigma} + V_{p\pi})$$
 --- (159)

&  $H_{xy} = H_{xz} = H_{yz} = 0$ . --- (160)

At  $X$ : we have a 1-fold degenerate level  $E_1(X) = \tilde{E}_p^0 - 4V_{p\pi}$   
 & a 2-fold degenerate level  $E_2(X) = \tilde{E}_p^0 - 4V_{p\pi}$





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Lec. 9. Tight-binding approach for Si

lattice with a basis

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  $\vec{u}_1$  represent the position of the basis atoms in a unit cell with respect to the cell's 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:

$$|\Psi_{\vec{k},l}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k} \cdot (\vec{R}_n + \vec{u}_1)} |\Psi_{nl}\rangle \quad \text{--- (161)}$$

for each basis atom. The functions are eigenstates of  $\hat{T}_{\vec{a}_1}$  w/ the same eigenvalue  $e^{i\vec{k} \cdot \vec{a}_1}$ .

$$\hat{T}_{\vec{a}_1} |\Psi_{\vec{k},l}\rangle = \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k} \cdot (\vec{R}_n + \vec{u}_1)} \hat{T}_{\vec{a}_1} |\Psi_{n+1,l}\rangle$$
$$= \frac{1}{\sqrt{N}} e^{i\vec{k} \cdot \vec{a}_1} |\Psi_{\vec{k},l}\rangle \quad \text{--- (162) pushed along } \vec{a}_1$$

let  $l = 1, N_b \rightarrow$  (163)



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 on the atomic sites. Thus, we ~~with~~ are looking at an 8x8 problem on the diamond lattice.

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

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

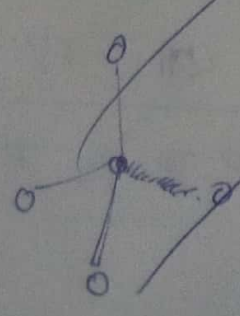
A hybrid orbital  $\rightarrow$  ~~special~~ special linear combination of basis orbitals (usually symmetry adapted).

s & p  $\rightarrow$  sp,  $sp^2$ ,  $sp^3$  hybrids.

Principle of minimum 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:

~~$$|sp^3\rangle = \begin{cases} \psi_1 = \frac{1}{2}(|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle) \\ \psi_2 = \frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle + |p_z\rangle) \\ \psi_3 = \frac{1}{2}(|s\rangle + |p_x\rangle - |p_y\rangle - |p_z\rangle) \\ \psi_4 = \frac{1}{2}(|s\rangle - |p_x\rangle + |p_y\rangle + |p_z\rangle) \end{cases}$$~~

~~~~

~~They point in the 4 directions (111), (1-1-1), (-11-1) & (-1-11) respectively, i.e. 4 directions of the vertices of a tetrahedron relative to the centre of the object.~~

principle of orthogonality.

Note that

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \quad (164)$$

Construction of orthogonal hybrids:

Let  $|\psi_1\rangle = N(1s) + \lambda|p_z\rangle$  &  $|\psi_2\rangle = N(1s) + \lambda|p_z\rangle$  (165)  
 be 2 equivalent hybrids on the same atom (i.e. they only differ in their orientation).  
 $N = \frac{1}{\sqrt{1+\lambda^2}}$  (166)

Orthogonality requirement  $\Rightarrow \langle \psi_1 | \psi_2 \rangle = N^2(1 + \lambda^2 \langle p_z | p_z \rangle) = 0$  (166)

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

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

1) sp hybrids:

$s + p_z$

$|\psi_1\rangle = \frac{1}{\sqrt{2}}(1s + p_z)$

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

To maximize overlap we'll choose

~~the~~  $p_1$  &  $p_2$  to have opposite signs  $\Rightarrow \theta_{12} = 180^\circ \Rightarrow \lambda = \mp 1$

$\therefore |\psi_1\rangle =$

1) sp-hybrids:

we choose  $|p_1\rangle = |p_z\rangle$  &  $|p_2\rangle = -|p_z\rangle$

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

$\therefore |\psi_1\rangle = \frac{1}{\sqrt{2}}(1s + |p_z\rangle)$

$|\psi_2\rangle = \frac{1}{\sqrt{2}}(1s - |p_z\rangle)$

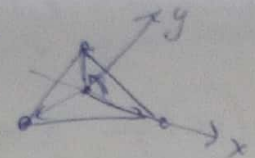
(168)

2 orbitals are left unchanged ( $\psi_3, \psi_4$ )



2) sp<sup>3</sup> hybrids:

The angle we want between any 2 p-orientation is  $\frac{2\pi}{3}$ .



$$\Rightarrow \cos \theta = \frac{1}{\sqrt{3}}$$

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

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

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

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$|p_z\rangle$  is left unchanged

3) sp<sup>3</sup> hybrids:

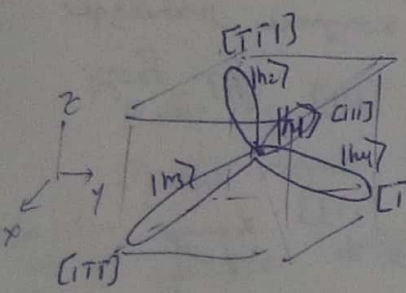
$$|h_1\rangle = \frac{1}{2} ( |s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle )$$

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

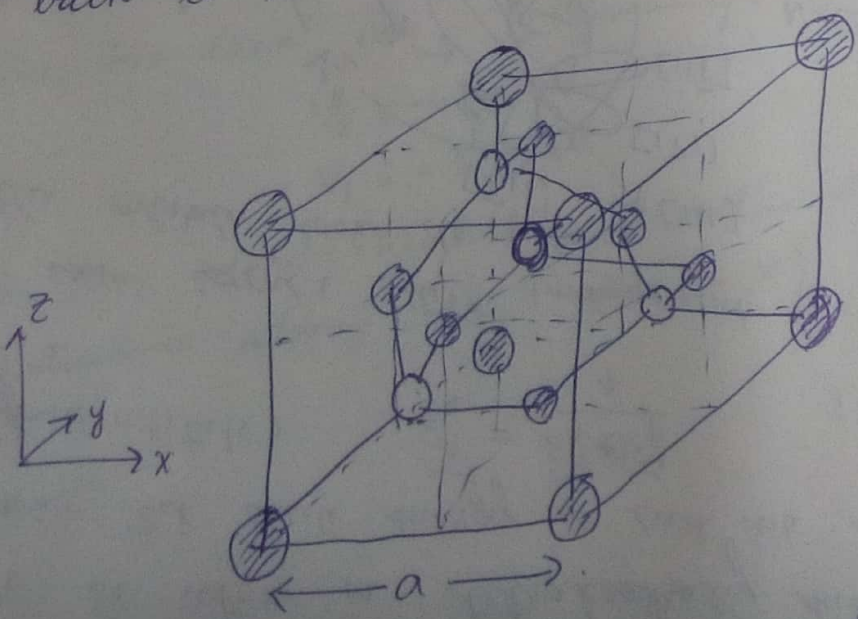
$$|h_3\rangle = \frac{1}{2} ( |s\rangle - |p_x\rangle + |p_y\rangle - |p_z\rangle )$$

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

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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 atoms. The onsite energy at each site is the energy of the hybrid orbitals:

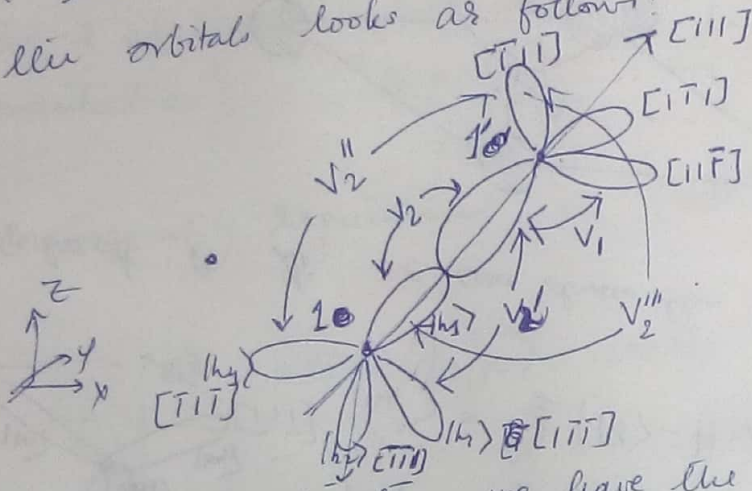
$$\tilde{\epsilon}_h^0 = \frac{\tilde{\epsilon}_s^0 + 3\tilde{\epsilon}_p^0}{4}$$

$$\epsilon_h^0 = -9.38 \text{ eV}$$

(Harrison, Elementary Electronic Structure)

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At each corner the arrangement of the orbitals looks as follows:



Note that the orbitals on 1' and 1 are inverted (for maximum overlap).

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

$$\begin{aligned}
 -V_2 &\equiv \langle h_1 | \hat{H} | h_1' \rangle = \langle h_1 | \hat{U}' | h_1' \rangle \\
 &= \frac{1}{4} (\langle s | + \langle p_x | + \langle p_y | + \langle p_z |) \hat{U}' (-|s\rangle + |p_x\rangle + |p_y\rangle + |p_z\rangle) \\
 &= \frac{1}{4} (V_{ss\sigma} - \sqrt{3} V_{sp\sigma} - 3V_{pp\sigma})
 \end{aligned}$$

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$|V_2| \rightarrow$  covalent energy



The coupling between the ~~atom~~ 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:

$$V_2 = -\frac{1}{4} (V_{ssp} - \frac{2\sqrt{3}}{3} V_{sp\sigma} + V_{pp\sigma}) \quad (173)$$

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

where  $E_{h\pm}$  refers to the cation/anion site.  
 e.g. GaAs.  $V_3 = 2.16 \text{ eV}$ .  
 $+ \rightarrow$  higher energy hybrid (less electronegative)  
 $- \rightarrow$  lower energy hybrid (more electronegative)

Another coupling is between hybrids on the same site.

This is called the metallic energy.  $-V_1 = \frac{\bar{\epsilon}_p - \bar{\epsilon}_s}{4}$  (176)

Both  $V_1$  &  $V_2'$  are inter-bond couplings. They result in broadening of the valence and conduction bands.

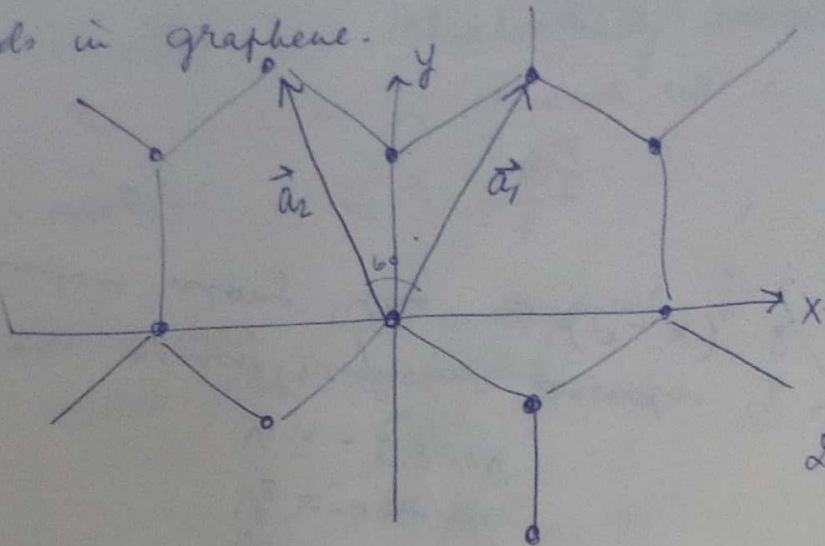
H.W.  
 A simple model for Si is the Weaire-Thorpe model (Phys. Rev. B 13, 2508 (1971)) where only  $V_2$  &  $V_1$  are taken to be non-zero. Reasonable values for these are (Elementary Electronic Structure, W. Harrison)

$$V_2 = -4.44 \text{ eV}$$

$$V_1 = -1.80 \text{ eV}$$

Given the nearest neighbour vectors of Si, ~~and~~ derive the bandstructure along the  $\Delta$  ( $\Gamma-X$ ) &  $\Lambda$  ( $L-\Gamma$ ) lines.

(2)  $\pi$ -bands in graphene.



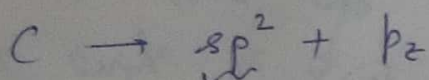
primitive translation vectors

$$\vec{a}_1 = a \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right)$$

$$\vec{a}_2 = a \left( -\frac{1}{2}, \frac{\sqrt{3}}{2} \right)$$

$$a = 2.45 \text{ \AA}$$

2 atoms in the primitive cell (conventional hexagonal cell)



3 hybrid bands well separated from the  $\pi$ -bands formed by  $p_z$ .

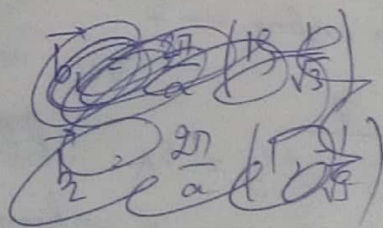
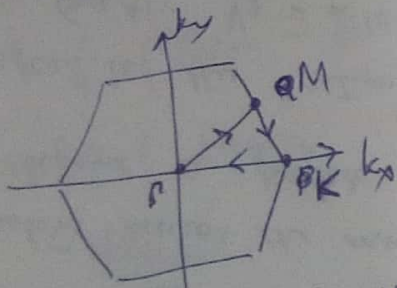
These two sets do not interact with each other

$\therefore$  Hamiltonian at every  $k$ -point factors into a  $(6 \times 6)$  block and a  $(2 \times 2)$  block.

$sp^2 \rightarrow \sigma$ -bands. ~~with~~ gap of  $\sim 10\text{eV}$  between valence & conduction bands

Band structure around F.L is due to the  $\pi$ -bands

B-7.



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~~ <sup>dispersion</sup> along the path  $K\Gamma M K$ . Use the orthogonal TBM with  $V_{pp\pi} = -2.38\text{eV}$

Comment on the gap structure you find.



24/11/2019

Lec 10. Systems with band gap: Recrystallization of 1-d Binary Alloy

Show Si band-structure (from A.P. Sutton).

- 4 valence bands completely occupied
- VB maximum at  $\Gamma$  and CB minimum at X (in actuality)
- Band gap (smallest range of forbidden energies) is 1.1 eV and of indirect nature ( $\Gamma \rightarrow X$ ).

$$\langle \vec{r} | \psi_{\vec{k}} \rangle = \psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r})$$

$$\hat{p} \psi_{\vec{k}}(\vec{r}) = \frac{\hbar}{i} \vec{\nabla} \psi_{\vec{k}}(\vec{r}) = (\hbar \vec{k} + \frac{\hbar}{i} \vec{\nabla}) \psi_{\vec{k}}(\vec{r})$$

$\vec{k}$  = crystal momentum

In scattering process in the crystal total momentum is conserved. Any change in  $\vec{k}$  should be compensated by appropriate change in the scatterer.

~~Indirect excitations require lattice momentum change in the scattering process (phonon emission/absorption) caused by the presence of indirect band gap.~~  
 Optical properties of Si are affected by the presence of indirect band gap.

→ Inclusion of d orbitals in the AO basis improves the description of conduction band.

Band gaps can be realized with more than 1 orbital per atom as in  $\text{Bi}_2$ , or even by more than one atom in the unit cell,

e.g. a binary (AB) alloy in 1-d, with 1 orbital on each site.

$E_A, E_B \rightarrow$  site energies



$$\text{Let } \Delta = \frac{(\epsilon_A - \epsilon_B)}{2}$$

$$\epsilon_A > \epsilon_B \text{ (say)}$$

$$\epsilon = \frac{(\epsilon_A + \epsilon_B)}{2}$$

hopping integral:

$$-t = \langle \psi_A | \hat{H} | \psi_B \rangle$$

177

- H.W. =
- ① Calculate the band structure and determine the gap in terms of  $t, \Delta, \epsilon$ .
  - ② Plot ~~Calculate~~ the total density of states  $D(E)$ .
  - ③ Plot the local density of states  $D_A(E)$  &  $D_B(E)$ .
  - ④ ~~For a given~~ Given that each site A/B contributes  $1 e^-$ , determine the average charge difference between A & B sublattice per unit cell.
  - ⑤ How would the above charge difference depend on the Fermi energy?

Density of states: When the system becomes very large, many energy levels result and they are distributed in a dense fashion. ~~with~~ In a given energy range many energy state can be packed. ~~and their number~~ To see this let's just consider the infinite linear chain of Li atoms as before.

The number of <sup>distinct</sup>  $k$  quantum numbers allowed =  $\frac{\text{length of B.Z.}}{\text{spacing of } k\text{-pts.}} = \text{No. of unit cells}$

$$\therefore \text{number of states per unit length of B.Z.} = \frac{N}{2\pi/a} = \frac{Na}{2\pi} \equiv d(k) \quad \text{--- (78)}$$

What is the number of states per unit energy interval  $dE$  placed around a certain energy  $E$ ?



Let  $N(E) \rightarrow$  number of states upto energy  $E$  from the bottom most part of the band

Then the density of states ~~is~~ <sup>per atom</sup> is defined ~~through~~ <sup>as</sup>:

$$D(E) = \frac{1}{N} \frac{dN}{dE} = \frac{2}{N} \frac{dN}{dk} \left| \frac{dk}{dE} \right| = \frac{\frac{dN}{dk}}{\left| \frac{dE}{dk} \right|} \quad \text{--- (179)}$$

For the 1d chain the modulus of  $\frac{dE}{dk}$  is taken because  $D(E)$  cannot be negative. The factor of 2 accounts for the  $\pm k$  degeneracy of  $E(k)$ .

For a 1-d linear chain of  $N$  atoms, we can evaluate this by noting that  $\frac{dN}{dk} = d(k) = \frac{Na}{2\pi}$

$$\& E(k) = \tilde{E}_0 - 2t \cos(ka)$$

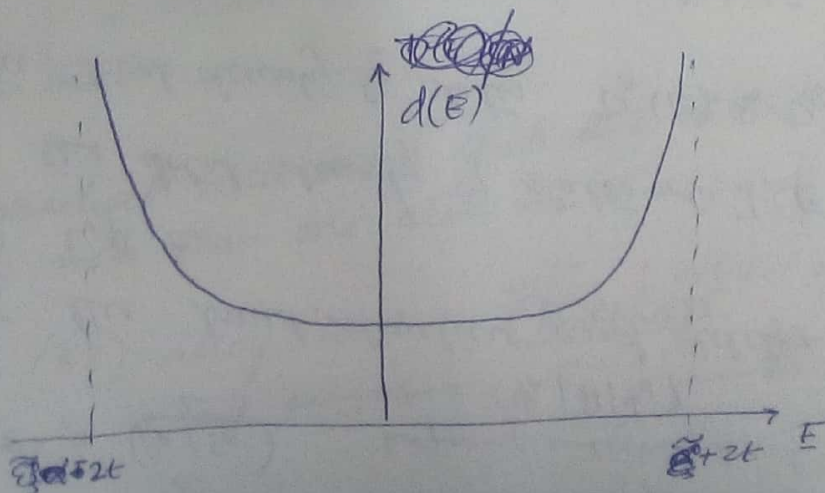
$$\Rightarrow \left| \frac{dE}{dk} \right| = 2ta \sin(ka) \quad \text{--- (181)}$$

$$\therefore D(E) = \frac{2Na}{2\pi} \times \frac{1}{2ta \sin(ka)} \quad \text{--- (182)}$$

The factor of 2 is

$$= \frac{2}{2\pi} \frac{1}{\sqrt{4t^2 - (E - \tilde{E}_0)^2}} \quad \text{--- (183)}$$

~~$2 \frac{dk(E)}{dE}$~~   
The den



If we integrate over all the energies in the band we get 1.

$$\int_{\tilde{E}_0 - 2t}^{\tilde{E}_0 + 2t} \frac{D(E) dE}{N} = 1 \quad (184)$$

This basically means that there is 1 state per atom.

Often the d.o.s is used to mean the density of occupied states. In this case it is customary to multiply (183) by a factor of 2 for double occupancy of each level and by the occupation function  $f(E)$ . E.g. for a system at  $0 K$ ,  $f(E) = 2\theta(E - E_f)$  — (185).

And a d.o.s per atom (or per unit volume) is defined as:

$$d(E) \equiv \frac{1}{N} D(E) = \frac{1}{\pi} \frac{1}{\sqrt{4t^2 - (E - \tilde{E}_0)^2}} \quad (186)$$

For an infinite chain since all sites are equivalent  $Nd(E) = D(E)$ . But for systems with defects or edges or inequivalent atoms (AB alloy) this relation is not true. To distinguish "bulk" and "surface" or between sublattices we can define a local density of states (LDOS).

$$N\langle \Psi_E | \Psi_E \rangle = \sum_n |\Psi_n\rangle \langle \Psi_n | \Psi_E \rangle \quad (187)$$

for this eigenstate probability of finding an electron on the atom site  $n$  is:

$$P_n(E) = |\langle \Psi_n | \Psi_E \rangle|^2 \quad (188)$$

the energy we can use  $P_n(E)$  to weight the DOS. to determine the d.o.s arising from the atomic state  $|\Psi_n\rangle$ . If there are other eigenstates with energy  $E = E(E)$  then we must sum over these as well to get the total weight.

$$\text{Contribution of } |\Psi_E\rangle \text{ to } D(E) \rightarrow \int \delta(E - E(E)) \quad (189)$$



Actually,  $D(E)$  is just a way to count energies in a range.  
 So we can write,

$$D(E) = 2 \sum_{\vec{k} \in BZ} \delta(E(\vec{k}) - E) \quad (189)$$

including the spin degeneracy

But,  $\sum_{\vec{k} \in BZ} = \frac{Na}{2\pi} \int_{BZ} dk$  (190)

in the limit of  $N \rightarrow \infty$ .

$$\therefore D(E) = \frac{2Na}{2\pi} \int d\vec{k} \delta(E(\vec{k}) - E) \quad (191)$$

$$= \frac{Na}{\pi}$$

As we'll show in the next lecture the contribution to the D.O.S. from each localized state  $|\psi_n\rangle$  is:

$$d_n(E) = \sum_{\text{all } \vec{k}} |\langle \psi_n | \psi_{\vec{k}} \rangle|^2 \delta(E - E_{\vec{k}}) = \sum_{\vec{k} \in BZ} P_n(\vec{k}) \delta(E - E(\vec{k})) \quad (190)$$

As  $N \rightarrow \infty$ ,  $\sum_{\vec{k} \in BZ} \rightarrow \frac{Na}{2\pi} \int_{BZ} d\vec{k}$  (191)

$$\therefore d_n(E) \rightarrow \frac{Na}{2\pi} \int_{BZ} d\vec{k} P_n(\vec{k}) \delta(E - E(\vec{k})) \quad (192)$$

$\rightarrow$  LDOs.

Note that

$$D(E) = \sum_n d_n(E) = \sum_{\substack{\text{all } \vec{k} \\ \vec{k} \in BZ}} \delta(E - E(\vec{k})) \quad (193)$$