

1/1/2018

Lec 2. Homonuclear & Heteronuclear diatomic molecules

Having ignored the e-e repulsion we now need to solve the following eqn.

$$\hat{H}_{IPA} \psi_{\text{IPA}}(\vec{r}) = E_n \psi_n(\vec{r}) \quad \text{--- (1)}$$

$$\text{where } \hat{H}_{IPA} = \sum_{i=1}^N \left\{ -\frac{\nabla_i^2}{2} + V_{\text{ext}}(\vec{r}_i) \right\} \quad \text{--- (2)}$$

This is a separable Hamiltonian which means we can write the solution as a product of wavefn's of individual electrons.

$$\psi_n(\vec{r}) = \prod_{i=1}^N \phi_{k_i}(\vec{r}_i) \quad \text{--- (3)}$$

$$\text{where } \left\{ -\frac{\nabla^2}{2} + V_{\text{ext}}(\vec{r}) \right\} \phi_k = E_k \phi_k \quad \text{--- (4)}$$

$\{\phi_k\} \rightarrow$ orbitals.

Actually, (3) is incorrect as it doesn't satisfy the P. Antisymmetry principle. We'll come back to this point a later lecture. It won't affect us for now.

So it seems that if we solve the 1-electron Schrodinger eqn. (4) that ~~we~~ would also give us the total solutions. Let's take up this problem presently.

H₂ molecule: Let's consider eqn. (4) in Dirac representation.

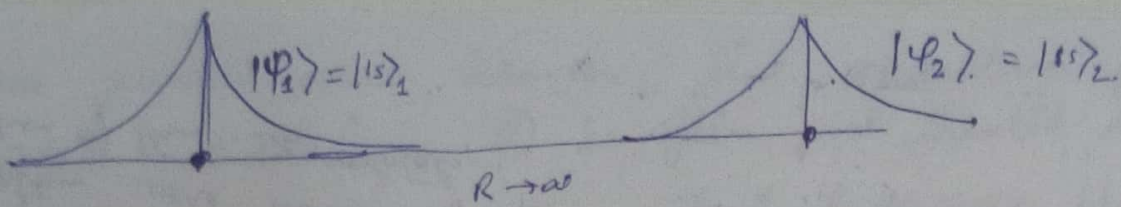
$$\hat{h} |\phi_k\rangle = E_k |\phi_k\rangle \quad \text{--- (5)}$$

~~For the H atom~~ For the H atom we know these solutions.

$$\left\{ |\phi_{nlm}\rangle \equiv |nlm\rangle \right\}; n=1,2,\dots; l=0,1,\dots,n-1; m_l = -l, \dots, l \quad \text{--- (6)}$$

For our purpose we will choose real orbitals: $|\psi_{1s}\rangle, |\psi_{2s}\rangle, |\psi_{2p_x}\rangle, \dots$ which can be obtained a L.C. of the orbitals (6).

Now, consider 2 H atoms separated by a distance R. If the 2 atoms were unaware of each other's existence then the solutions of either of the 1s orbitals.



When we bring them together at "interacting" distance then we can write for the single-electron Hamiltonian:

$$\hat{h} = -\frac{\nabla^2}{2} - \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad \text{--- (7)}$$

when $r_i \rightarrow$ dist. of e^- from atom i .

We need to solve:

$$\hat{h} |\psi\rangle = \epsilon |\psi\rangle \quad \text{--- (8)}$$

We assume that the set of function $\{ |\psi_1^m\rangle, |\psi_2^m\rangle \}$ form a complete set. In particular, we assume that the state $|\psi\rangle$ can be expressed in terms of the 1s orbitals $|\psi_1\rangle, |\psi_2\rangle$.

$$\text{Then } |\psi\rangle = c_1 |\psi_1\rangle + c_2 |\psi_2\rangle \quad \text{--- (9)}$$

This is called the LCAO approximation. This is motivated by the expected nature of the wavefn. close to each atom.

Substituting in (8) we get

$$\hat{h} (c_1 |\psi_1\rangle + c_2 |\psi_2\rangle) = \epsilon (c_1 |\psi_1\rangle + c_2 |\psi_2\rangle)$$

$$c_1 \hat{h} |\psi_1\rangle + c_2 \hat{h} |\psi_2\rangle = \epsilon (c_1 |\psi_1\rangle + c_2 |\psi_2\rangle) \quad \text{--- (10)}$$

Projecting on $|\psi_1\rangle$ & $|\psi_2\rangle$ we get:

$$\left. \begin{aligned} c_1 h_{11} + c_2 h_{12} &= \epsilon (c_1 + c_2 S_{12}) \\ c_1 h_{21} + c_2 h_{22} &= \epsilon (c_1 S_{21} + c_2) \end{aligned} \right\} \quad \text{--- (11)}$$

$$\text{where } h_{ij} = \langle \psi_i | \hat{h} | \psi_j \rangle \quad \& \quad S_{ij} = \langle \psi_i | \psi_j \rangle \quad \text{--- (12)}$$

$S \rightarrow$ overlap matrix, $h \rightarrow$ Hamiltonian matrix.

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$$\begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} s_{11} & s_{12} \\ s_{21} & s_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \quad (13)$$

$$S_{12}(R) = \int d^3r \phi_{1s}^*(\vec{r}-\vec{R}_1) \phi_{1s}(\vec{r}-\vec{R}_2) = S_{21}(R) = \left\{ 1 + R + \frac{1}{2} R^2 \right\} e^{-R} \quad (14)$$

$\Rightarrow S$ is w.r. increasing R .

So as a first approx. we will ignore it. $S_{ij} = \delta_{ij} \quad (15)$

$$\therefore \begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \quad (16)$$

This eqn. has non-trivial solution if

$$\begin{vmatrix} h_{11} - E & h_{12} \\ h_{21} & h_{22} - E \end{vmatrix} = 0$$

$$\Rightarrow E^2 - (h_{11} + h_{22})E + h_{11}h_{22} - |h_{12}|^2 = 0 \quad (17)$$

(h_{ij} are real.)

Now $h_{11} = \langle \psi_1 | -\frac{D^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} | \psi_1 \rangle = E_{1s} - \langle \psi_1 | \frac{1}{r_2} | \psi_1 \rangle \quad (18)$

Why $h_{22} = \langle \psi_2 | -\frac{D^2}{2} - \frac{1}{r_2} - \frac{1}{r_1} | \psi_2 \rangle = E_{1s} - \langle \psi_2 | \frac{1}{r_1} | \psi_2 \rangle$

Note that $\langle \psi_1 | \frac{1}{r_2} | \psi_1 \rangle = \langle \psi_2 | \frac{1}{r_1} | \psi_2 \rangle$ (inversion symmetry) (show)

$$\int d^3r \phi_{1s}(\vec{r}-\vec{R}_1) \frac{1}{|\vec{r}-\vec{R}_2|} \phi_{1s}(\vec{r}-\vec{R}_1) = \int d^3r \phi_{1s}(\vec{r}-\vec{R}_2) \frac{1}{|\vec{r}-\vec{R}_1|} \phi_{1s}(\vec{r}-\vec{R}_2)$$

(show)

$\vec{r}-\vec{R}_1 = \vec{r}'$
 $\vec{r}-\vec{R}_2 = \vec{r}' + \vec{R}_1 - \vec{R}_2$
 let $\vec{r}' = \vec{r} - \vec{R}_2$

$\Rightarrow h_{11} = h_{22} = \alpha$ site energy

$$h_{12} = \langle \psi_1 | -\frac{\nabla^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} | \psi_2 \rangle = \alpha E_{1s} \langle \psi_1 | \psi_2 \rangle - \langle \psi_1 | \frac{1}{r_2} | \psi_2 \rangle$$

$$= - \langle \psi_1 | \frac{1}{r_2} | \psi_2 \rangle = - \int d^3r \frac{\psi_1^*(r) \psi_2(r)}{|r - R_2|} \quad \text{--- } \beta < 0$$

$h_{21} = h_{12}$ (by symmetry & hermiticity)

$\beta \rightarrow$ hopping integral or transfer integral

\therefore (17) becomes $\epsilon^2 - 2\alpha\epsilon + \alpha^2 - \beta^2 = 0$

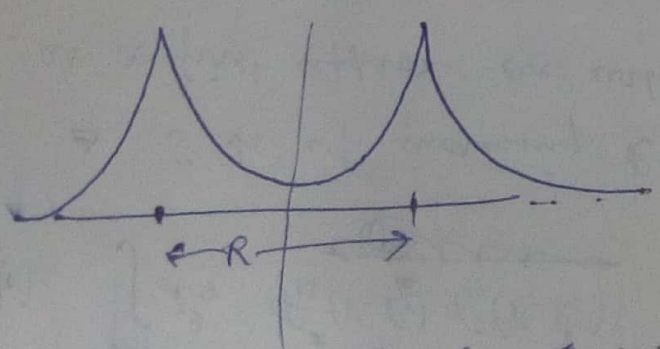
$\therefore \epsilon = \alpha \pm \sqrt{\beta^2} = \alpha \pm \beta$ --- (19)

Thus, we get the levels $\left. \begin{aligned} \epsilon_0 &= \alpha + \beta \\ \epsilon_1 &= \alpha - \beta \end{aligned} \right\}$ w/ $\epsilon_0 < \epsilon_1$ --- (20)

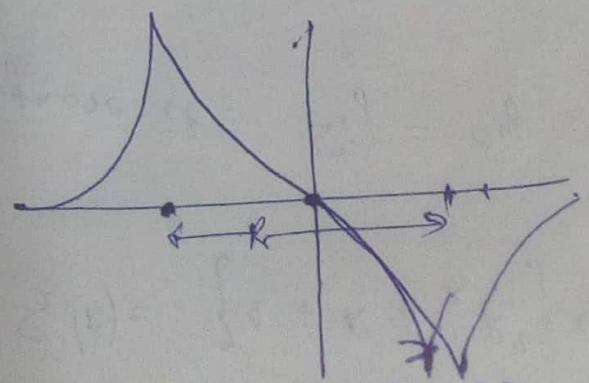
Solving for the coefficients we get

$|\psi_0\rangle = \frac{1}{\sqrt{2}} (|\psi_1\rangle + |\psi_2\rangle)$

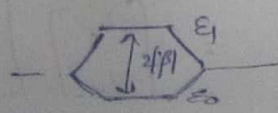
$|\psi_1\rangle = \frac{1}{\sqrt{2}} (|\psi_1\rangle - |\psi_2\rangle)$



Bonding Molecular Orbital



Anti Bonding MO



Charge density

Since we have 2 electrons we can accommodate both of them in ~~orbital~~ $|\psi_0\rangle$ states but with opposite spins. Thus we get the total energy of the system to be:

$$E_0 = 2\epsilon_0 = 2(\alpha + \beta) \quad (21)$$

Charge density = $\rho(\mathbf{r}) = 2 \times |\psi_0(\mathbf{r})|^2$
 $= \{ n_1(\mathbf{r}) + n_2(\mathbf{r}) + n_{\text{bond}}(\mathbf{r}) \}$ (22)

where $n_i(\mathbf{r}) = 2|\psi_i(\mathbf{r})|^2$ (23)

& $n_{\text{bond}}(\mathbf{r}) = 4\psi_1(\mathbf{r})\psi_2(\mathbf{r})$

The $n_{\text{bond}}(\mathbf{r})$ pushes e^- density between the nuclei and is responsible for the bonding. This is a purely QM result.

Heteronuclear Diatomic Molecule: Same analysis could be done for a heteronuclear molecule AB. Let's take one atomic orbital per site once again.

$|\psi_A\rangle$ & $|\psi_B\rangle$. Let $h_{11} = h_{22} = \beta_{AB}$, $h_{11} = \alpha_A$, $h_{22} = \alpha_B$. We assume, that $\alpha_A > \alpha_B$. If we assume $|\psi\rangle = c_A|\psi_A\rangle + c_B|\psi_B\rangle$, then we get ($S_{AB} = 0$):

$$\begin{vmatrix} \alpha_A - \epsilon & \beta_{AB} \\ \beta_{AB} & \alpha_B - \epsilon \end{vmatrix} = 0 \quad (24)$$

$$\epsilon^2 - (\alpha_A + \alpha_B)\epsilon + \alpha_A\alpha_B - \beta_{AB}^2 \quad (25)$$

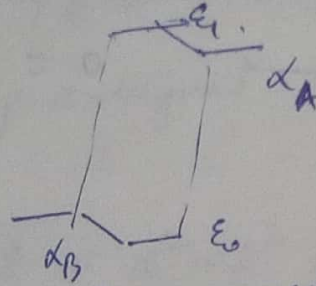
$$\Rightarrow \epsilon = \frac{(\alpha_A + \alpha_B)}{2} \pm \frac{1}{2} \sqrt{(\alpha_A - \alpha_B)^2 + 4\beta_{AB}^2} \quad (26)$$

Let $\Delta = \frac{(\alpha_A - \alpha_B)}{2}$ & $\alpha = \frac{\alpha_A + \alpha_B}{2}$ (average site energy)

Then we have
$$\left. \begin{aligned} E_0 &= \alpha + \sqrt{\Delta^2 + \beta^2} \\ &\& E_1 &= \alpha - \sqrt{\Delta^2 + \beta^2} \end{aligned} \right\} (27)$$

again $E_0 < E_1$.

If β is 0 then we get back the α_B & α_A for bonding & antibonding states



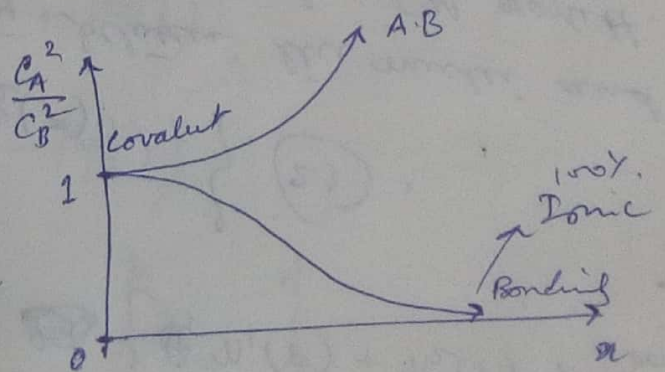
We can determine coefficients from eigenvalues as:

$$\frac{C_A^2}{C_B^2} = \frac{1}{1 + 2x^2 + 2x(1+x^2)^{1/2}} \quad \text{for bonding} \quad \left. \vphantom{\frac{C_A^2}{C_B^2}} \right\} (28)$$

$$\frac{C_A^2}{C_B^2} = \frac{1}{1 + 2x^2 - 2x(1+x^2)^{1/2}} \quad \text{for antibonding}$$

where $x = \frac{\Delta}{|\beta|}$

C_A^2 \propto charge density at site A
 $\therefore \langle \psi_A | \psi \rangle^2 = C_A^2$



We see that as the Δ is electron tends to localize on B site in the bonding MO \Rightarrow Ionic config A^+B^- whereas it's the opposite (A^-B^+) in the antibonding MO.
 \Rightarrow Bond is, in general, partially ionic

We can define the terms ~~delta~~ polarity & covalency of a bond as follows:

$$\left. \begin{aligned} \chi_p &= \frac{x}{(1+x^2)^{1/2}} \\ \chi_c &= \frac{1}{(1+x^2)^{1/2}} \end{aligned} \right\} (29)$$

Note that $\chi_p^2 + \chi_c^2 = 1$

These ideas can be generalized to crystal as well,

Spin function: \because H doesn't depend on spin - we can write states as $|\psi\rangle \otimes |\chi\rangle$ where

$$\left. \begin{aligned} |\chi\rangle &= \begin{cases} |\chi_+\rangle \\ |\chi_-\rangle \end{cases} \\ \hat{S}_z |\chi_{\pm}\rangle &= \pm \frac{1}{2} |\chi_{\pm}\rangle \end{aligned} \right\} (30)$$

Overlap is not 0 in the H_2 problem

A symmetry based approach for H_2^+ molecule:

$$\text{Let } |\psi_{1,1s}\rangle \equiv |1\rangle \quad |\psi_{2,1s}\rangle \equiv |2\rangle \quad \text{--- (31)}$$

$$\hat{H} = \hat{T} + \hat{V}_1 + \hat{V}_2$$

Consider the Parity/inversion operator \hat{P} : $\hat{P}|1\rangle = |2\rangle$ & $\hat{P}|2\rangle = |1\rangle$ --- (32)

\hat{P} is a symmetry operator that leaves the Hamiltonian invariant --- (33)

$$\hat{P}^\dagger \hat{H} \hat{P} = \hat{H}$$

or $[\hat{P}, \hat{H}] = 0$ since \hat{P} is unitary --- (34)

$$\hat{P}\hat{P}^\dagger = \hat{P}^\dagger\hat{P} = \hat{1} \quad \text{--- (35) (Show)}$$

Since \hat{P} & \hat{H} commute they have common eigenstates. Let's solve the eigenvalue eqn for \hat{P} .

$$\hat{P}|\psi\rangle = \pi|\psi\rangle \quad \text{--- (36)}$$

$$\hat{P}^2|\psi\rangle = \pi^2|\psi\rangle = |\psi\rangle \Rightarrow \pi^2 = 1 \Rightarrow \pi = \pm 1 \quad \text{--- (37)}$$

P is also Hermitian. $\Rightarrow P|2\rangle = |2\rangle \Rightarrow \langle 2|P|1\rangle = 1$
 $\Rightarrow \langle 1|P^\dagger = \langle 2| \Rightarrow \langle 2|P^\dagger|2\rangle = 1$
 $\Rightarrow \langle 2|P|1\rangle = \langle 1|P^\dagger|2\rangle \Rightarrow P$ is Hermitian

Note that P is also Hermitian.

$$P^\dagger P|01\rangle = P^\dagger|2\rangle = |1\rangle = P|2\rangle \Rightarrow P = P^\dagger \Rightarrow \text{Hermitian}$$

Thus the eigenvalues are real $\pi_\pm = \pm 1$

Eigenfun are odd & even.

$$|\psi_+\rangle = c_1^+ |1\rangle + c_2^+ |2\rangle$$

$$P|\psi_+\rangle = |\psi_+\rangle = c_1^+ |2\rangle + c_2^+ |1\rangle$$

Comparing eqn 2 we get $c_1^+ = c_2^+ = \frac{1}{\sqrt{2}}$ (normalized)

$$\text{Similarly } |\psi_-\rangle = c_1^- |1\rangle + c_2^- |2\rangle$$

$$P|\psi_-\rangle = c_1^- |2\rangle + c_2^- |1\rangle = -|\psi_-\rangle$$

Comparing we get $c_1^- = -c_2^- = \frac{1}{\sqrt{2}}$

$$\Rightarrow |\psi_\pm\rangle = \frac{1}{\sqrt{2}} (|1\rangle \pm |2\rangle)$$

These are also eigenfun of \hat{H} .

$$\hat{H}|\psi_+\rangle = \frac{1}{\sqrt{2}} \hat{H} (|1\rangle + |2\rangle)$$

$$= \frac{1}{\sqrt{2}} (|1\rangle \langle 0| + |2\rangle \langle 0|) \hat{H} (|1\rangle + |2\rangle)$$

$$= \frac{1}{\sqrt{2}} (|1\rangle (H_{11} + H_{12}) + |2\rangle (H_{21} + H_{22}))$$

$$= (H_{11} + H_{12}) |\psi_+\rangle \quad \text{--- (40)}$$

where $H_{11} = H_{22}$ & $H_{12} = H_{21}$ (Hermitian & real)

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 conjugates.

Thus $E_+ = \langle H_{11} + H_{12} \rangle$

$= \alpha + \beta$

Why $E_- = H_{11} - H_{12}$.

$H_{11} = \langle 1 | \hat{T} + \hat{V}_1 | 1 \rangle + \langle 1 | V_2 | 1 \rangle \equiv \alpha$ (on-site energy)
 $H_{21} = \langle 1 | \hat{T} + \hat{V}_1 + \hat{V}_2 | 2 \rangle \approx \langle 1 | V_2 | 2 \rangle \rightarrow$ hopping integral

118
 Now, if we ~~assume~~ do not assume the overlaps to be 0, then
 $\langle \psi_1 | \psi_2 \rangle \neq 0$. The states $|\psi_{\pm}\rangle$ are not normalized but are orthogonal
 The energies change as follows:

$E_+ = \frac{\langle \psi_+ | \hat{H} | \psi_+ \rangle}{\langle \psi_+ | \psi_+ \rangle} = \frac{\alpha + \beta H_{12}}{1 + \langle \psi_1 | \psi_2 \rangle} = \frac{\alpha + \beta H_{12}}{1 + S_{12}}$

$= \frac{(\alpha + H_{12})(1 - S_{12})}{1 - S_{12}^2}$

$= \frac{\alpha(1 - S_{12}^2) + \alpha' + H_{12} - \alpha S_{12} - H_{12} S_{12} - \alpha S_{12}^2}{1 - S_{12}^2}$

$= \alpha + \frac{H_{12} - \alpha S_{12}}{1 - S_{12}^2} - S_{12} \frac{H_{12} - \alpha S_{12}}{1 - S_{12}^2}$

$\equiv \alpha + V_{SSO} - S_{12} V_{SSO}$ (41)

Why

$E_- \equiv \alpha - V_{SSO} - S_{12} V_{SSO}$

where $V_{SSO} = \frac{H_{12} - \alpha S_{12}}{1 - S_{12}^2}$ (42)

$$H_{12} = \epsilon_{1s} S_{12} + \langle \psi_1 | V_2 | \psi_2 \rangle < 0 \quad (42)$$

For an attractive potential $V_{SSO} < 0$.

$$\Rightarrow V_{SSO} = \frac{\epsilon_{1s} S_{12} + \langle \psi_1 | V_2 | \psi_2 \rangle - \epsilon_{1s} S_{12} + \langle \psi_1 | V_2 | \psi_1 \rangle S_{12}}{1 - S_{12}^2}$$

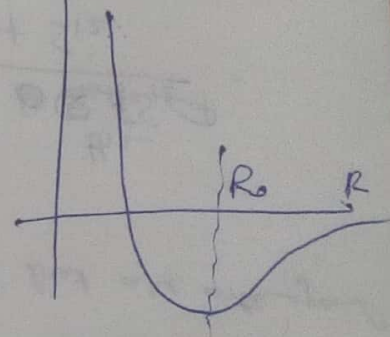
$$= \frac{\langle \psi_1 | V_2 | \psi_2 \rangle + \langle \psi_1 | V_2 | \psi_1 \rangle S_{12}}{1 - S_{12}^2} < 0 \quad (43)$$

for attractive potential

$$E_+ = \underbrace{\epsilon_{1s}^0}_{\text{effective orbital energy}} + \underbrace{V_{SSO}}_{\text{binding}} - S_{12} \underbrace{V_{SSO}}_{\text{repulsion at small } R} \quad (44)$$

$$V_{SSO} = \langle \psi_1 | V_2 | \psi_1 \rangle$$

Binding energy curve $E_+ - \epsilon_{1s}$



Renormalized

Repulsion term is significant only at $d \ll d_0$.
But it only yields a rigid shift in both levels
So we'll ignore it.

We can continue with the orthogonal TB.

model: $E_+ = \epsilon_{1s} + V_{SSO}$

We can use the H atom wavefn to analytically compute these integrals. We get $d_0 = 2.5 \text{ a.u.}$ & a corresponding binding energy $E_b = \epsilon_{1s}^0 - E_+(d_0) = 170 \text{ kJ/mol}$ ($\sim 40 \text{ kcal/mol} \sim 1.8 \text{ eV}$)

Expts $E_b = 268 \text{ kJ/mol}$ ($\sim 2.8 \text{ eV}$) & $d_0 = 2.0 \text{ a.u.}$

This is not too bad considering the simplification done

In operator form we can write:

$$\hat{h} = \sum_{i,j} \tilde{\epsilon}_{ij}^0 (|\psi_i\rangle\langle\psi_j| + |\psi_j\rangle\langle\psi_i|) + V_{SSO} (|\psi_1\rangle\langle\psi_2| + |\psi_2\rangle\langle\psi_1|) \quad (46)$$

where

Let's extend this to site energies

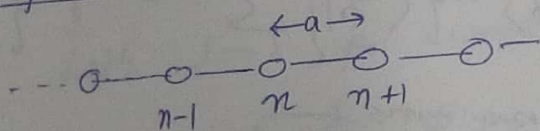
This can readily be generalized to:

$$h = \sum_{i,j} |\psi_i\rangle h_{ij} \langle\psi_j| \quad (47)$$

where $h_{ii} = \tilde{\epsilon}_i^0$ (on-site) } for 2 sites
 $\Delta h_{12} = h_{21} = V_{SSO}$

Let's extend this orthogonal TBM to N-site problem.

Tight-binding model for a linear chain:



Lattice spacing = a
 eg. linear chain of Li atoms

We assume periodic boundary condition: $n \leftrightarrow n+N$.
 This has the topology of a ring. But for $N \rightarrow \infty$ it is indistinguishable from an open chain (we shall see).

Let $|\psi_n\rangle \equiv$ An atomic orbital state located at site n.
 eg. $2s$ state of Li.

Note that we are applying a core-valence separation here. i.e. we are assuming that the core levels ($1s^2$) do not participate in bonding and only contribute an overall shift in energies.

In the orthogonal TBM we have:

$$\hat{h} = \sum_{i,j} -\frac{V_{ij}}{r_{ij}} + \sum_{i=1}^N V_{\sigma}(\vec{r}-\vec{R}_i) \quad (48)$$

We choose the orbitals $\{|\psi_m\rangle\}$ as a basis and write,

$$\hat{h} = \sum_{m,n} |\psi_m\rangle \langle \psi_m | \hat{h} | \psi_n \rangle \langle \psi_n| \quad \text{--- (49)}$$

We further make the assumption that h_{mn}

$$h_{mn} = \begin{cases} \tilde{\epsilon}_0 & \text{if } m=n \\ -t & \text{if } |m-n|=1, t > 0. \\ 0 & \text{if } |m-n| > 1 \end{cases} \quad \text{--- (50)}$$

This is called the nearest-neighbour TBB.

$$\hat{h} = \sum_{\langle mn \rangle} |\psi_m\rangle h_{mn} \langle \psi_n| \quad \text{--- (51)}$$

→ sum over nearest neighbours only.

or the 1d becomes $\left. \begin{aligned} \hat{h} &= \sum_n \left[|\psi_n\rangle h_{nn} \langle \psi_n| + |\psi_n\rangle h_{n,n+1} \langle \psi_{n+1}| + |\psi_n\rangle h_{n,n-1} \langle \psi_{n-1}| \right] \end{aligned} \right\} \quad \text{--- (52)}$

By symmetry $h_{n,n+1}, h_{n+1,n}$ do not depend on n and are both equal.

$$\therefore \hat{h} = \tilde{\epsilon}_0 \left(\sum_n |\psi_n\rangle \langle \psi_n| \right) - t \left(\sum_n \left(|\psi_n\rangle \langle \psi_{n+1}| + |\psi_n\rangle \langle \psi_{n-1}| \right) \right) \quad \text{--- (53)}$$

$$= \tilde{\epsilon}_0 \left(\sum_n |\psi_n\rangle \langle \psi_n| \right) - t \sum_n \left(|\psi_n\rangle \langle \psi_{n+1}| + |\psi_{n+1}\rangle \langle \psi_n| \right) \quad \text{--- (54)}$$

h is represented by a tridiagonal matrix,

$$h = \begin{pmatrix} \tilde{\epsilon}_0 & t & 0 & \dots & t \\ -t & \tilde{\epsilon}_0 & t & & \\ 0 & -t & \tilde{\epsilon}_0 & t & \\ & & & \ddots & \\ t & & & & \tilde{\epsilon}_0 \end{pmatrix} \quad \text{--- (55)}$$

we again exploit symmetry to diagonalize this.

We'll again exploit symmetry to diagonalize this.

Let \hat{T}_a indicate a finite translation along the chain by a .

$$\hat{T}_a |\psi_n\rangle = |\psi_{n+1}\rangle \quad \forall n$$

Note: \rightarrow if $b = ma$, then $\hat{T}_b = (\hat{T}_a)^m$ — (56)

\rightarrow Any 2 translations commute $[\hat{T}_b, \hat{T}_c] = 0$. — (57)
(Abelian group.)

$\Rightarrow \hat{T}_a$ is unitary $(\hat{T}_a^\dagger \hat{T}_a = \hat{T}_a \hat{T}_a^\dagger = \mathbb{1})$ — (58)

$\rightarrow \hat{T}_a^N |\psi_n\rangle = |\psi_{n+N}\rangle = |\psi_n\rangle$ cyclic PBC.

$\Rightarrow \hat{T}_a^N = \mathbb{1}$ — (59)

Also, $[\hat{T}_a, \hat{H}] = 0$ — (60) (show why?)

$\Rightarrow \hat{T}_a$ & \hat{H} share eigenstates.

Let's look for eigenstates of \hat{T}_a .

Let $\hat{T}_a |\psi\rangle = \tau |\psi\rangle$ — (69)

Here, $|\psi\rangle = \sum_n c_n |\psi_n\rangle$ — (70)

Clearly, $\hat{T}_a^\dagger \hat{T}_a = \mathbb{1} \Rightarrow |\tau|^2 = 1$. — (71)

& $\tau^N = 1$. — (72)

Thus, τ is one of the N roots of unity.

$\tau_k = \exp(-ika)$ — (73)

where $k = \frac{2\pi l}{N}$, $l \in \mathbb{Z}$; $0 \leq l \leq N$ — (74)

Note that the choice of the interval is arbitrary; any interval such that $j < l \leq j+N$ w/ j an arbitrary integer w/d work just as well.

1/1/2018 Lec 5. Tight Binding: 1d lattice (cont.)

Conventionally one chooses:

$$-\frac{N}{2} < l \leq \frac{eN}{2} \quad (25)$$

(assuming N is even
wh/ is irrelevant
as $N \rightarrow \infty$)

For the wave-vector k this ~~amount~~ amount is

$$-\frac{\pi}{a} < k \leq \frac{\pi}{a} \quad (26) \quad \text{w/ } k = \frac{2\pi l}{Na}$$

This constitutes the (first) Brillouin zone.

Thus the eigenstates of \hat{T}_a (and hence of any \hat{T}_b) are labelled by an index k belonging to the B.Z.

$$\hat{T}_a |\psi_k\rangle = e^{-ika} |\psi_k\rangle \quad (27)$$

On the other hand using (20) we have:

$$\begin{aligned} \hat{T}_a |\psi_k\rangle &= \sum_n c_n^k |\psi_{n+1}\rangle = \sum_n c_{n-1}^k |\psi_n\rangle \\ &= e^{-ika} \sum_n c_n^k |\psi_n\rangle \quad (28) \end{aligned}$$

Comparing coefficients we get

$$c_n^k = e^{ika} c_{n-1}^k$$

$$\text{or } \boxed{c_{n+1}^k = e^{ika} c_n^k} \quad (29)$$

$$\Rightarrow \boxed{c_n^k \propto e^{ikna}} \quad (30)$$

Let $x_n = na$. Then,

$$\boxed{|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikx_n} |\psi_n\rangle} \quad (31)$$

Normalisation.

Block sums.

Eq. (31) is an equivalent statement of the Bloch's theorem.

Because $(\hat{T}_a)^\infty |\psi_k\rangle$ is also an eigenstate of H .

Now, $\langle x | \hat{T}_a | \psi_k \rangle = e^{-ika} \langle x | \psi_k \rangle \equiv e^{-ika} \psi_k(x)$ — (82)

But $\hat{T}_a |x\rangle = |x+a\rangle$ — (83)

\therefore (82) $\Rightarrow \langle x+a | \psi_k \rangle = e^{-ika} \psi_k(x)$

or $\psi_k(x+a) = e^{-ika} \psi_k(x)$ — (84)

This is only satisfied if $\psi_k(x) = e^{ikx} u_k(x)$ — (85)

where $u_k(x+ma) = u_k(x) \forall m \in I$.
 u a periodic fn.

(85) constitutes an alternative statement of Bloch's theorem.

$$\hat{H} |\psi_k\rangle = \sum_n \frac{e^{ikx_n}}{\sqrt{N}} \left[\tilde{E}^0 \sum_m |\psi_m\rangle \langle \psi_m | \psi_n \rangle - t \left(\sum_{m \neq n} |\psi_m\rangle \langle \psi_{m+1} | \psi_n \rangle + |\psi_{n+1}\rangle \langle \psi_n | \psi_n \rangle \right) \right]$$

$$= \sum_n \frac{e^{ikx_n}}{\sqrt{N}} \left[\tilde{E}^0 |\psi_n\rangle - t (|\psi_{n-1}\rangle + |\psi_{n+1}\rangle) \right]$$

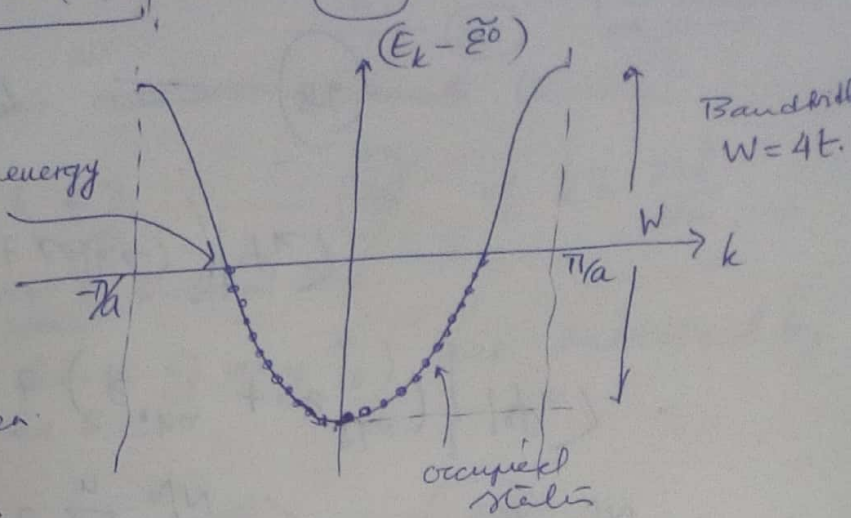
$$= \tilde{E}^0 |\psi_k\rangle - t \sum_n \frac{e^{ikx_n}}{\sqrt{N}} |\psi_{n-1}\rangle - t \sum_n \frac{e^{ikx_n}}{\sqrt{N}} |\psi_{n+1}\rangle$$

$$= \left\{ \tilde{E}^0 - t (e^{ika} + e^{-ika}) \right\} |\psi_k\rangle$$

$$= (\tilde{E}^0 - 2t \cos(ka)) |\psi_k\rangle$$

$$\equiv E_k |\psi_k\rangle \text{ — (86)}$$

$$E_k = \tilde{E}^0 - 2t \cos(ka) \quad (82)$$

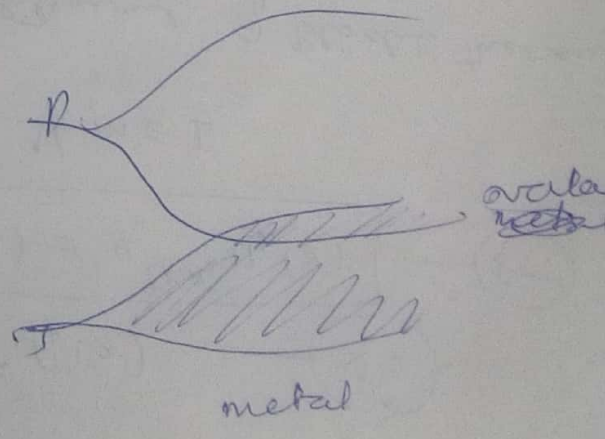
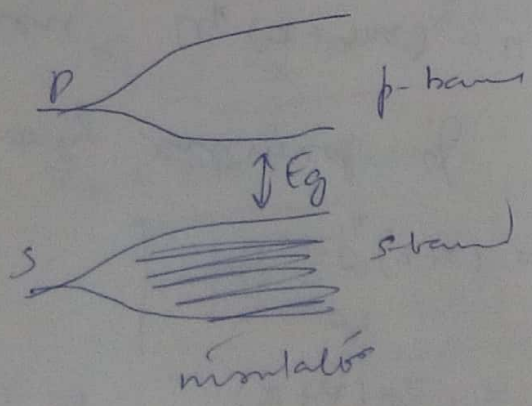


- $|\psi_{k=0}\rangle \rightarrow$ Fully symmetric
- $|\psi_{k=\pi/a}\rangle \rightarrow$ Fully antisymmetric

All other states are in between.
The band contains N states.

If there for Li chain, each site gives $1e^-$ & $2e^-$ can occupy a state (2 spin) \Rightarrow Only half the available states occupied. Hence, the band is half-filled.
The system is metallic, meaning that an infinitesimal amount of energy is sufficient to excite the system into a excited eigenstate. This is always so for a partially filled band.

More than one band can be derived from multiple atomic states on a site, when they interact among themselves.



Note: Bloch theorem holds generally w/o assuming TBMs.
For instance if we change to next-nearest neighbours hopping
B.T. still holds. But $E_k = E^0 - 2t_{NN} \cos(ka) - 2t_{NNN} \cos(3ka)$ (85)

→ E_k is generally periodic function of k w/ periodicity $\frac{2\pi}{a}$.

→ Note here that $E_k = E_{-k}$ — (89). This results from TR symmetry (real H)

∴ H is real, its eigenstates can always be chosen to be real. Then the time propagated state eigenstate will have the form $\Psi_E(\vec{r}) e^{-iEt/\hbar}$ where $\Psi_E(\vec{r})$ is real. Conjugate of this state is $\Psi_E(\vec{r}) e^{iEt/\hbar}$, which can also result by setting $t \rightarrow -t$ (TR). Since the H is invariant under TR, the eigen cannot change under TR.

On the other hand, TR acting on $|\Psi_k\rangle$ transforms it into $|\Psi_{-k}\rangle$ as can be easily seen. Let K be the complex conjugation operator

$$K \Psi_k(x) = K(e^{ikx} u_k(x)) = e^{-ikx} u_k^*(x) \quad \text{--- (90)}$$

$u_k^*(x)$ is still a periodic in \mathbb{R} . $K \Psi_k(x)$ must be an eigen of H (TR invariance) $u_k^*(x)$ must be equal to $u_{-k}(x)$ (apart from a constant phase factor)

$$u_k^*(x) = u_{-k}(x) \quad \text{--- (91)}$$

Note that the above analysis will be slightly different if we include also spin into the picture.

As a consequence of TR symmetry,

Suppose we have found the state $\psi_k(x)$. It satisfies

$$\hat{H} \psi_k(x) = E_k(x) \psi_k(x) \quad \text{--- (90)}$$

Taking c.c. $\hat{H} \psi_k^*(x) = E_k(x) \psi_k^*(x) \quad \text{--- (91)}$

$\Rightarrow \psi_k^*(x)$ is also an eigenstate of the same eigenvalue $E_k(x)$. But is it distinct? First what is it?

$$i\hbar \frac{\partial \psi_k(x,t)}{\partial t} = \hat{H} \psi_k(x,t) \quad \text{--- (92)}$$

T.R. $t \rightarrow -t \Rightarrow -i\hbar \frac{\partial \psi_k(x,-t)}{\partial t} = \hat{H} \psi_k(x,-t)$

$$\Rightarrow i\hbar \frac{\partial \psi_k^*(x,-t)}{\partial t} = \hat{H} \psi_k^*(x,-t) \quad \text{--- (93)}$$

$$\psi_k^*(x,t) = (\psi_k(x,-t))^* = \psi_k^*(x) e^{-iE_k(x)t} \quad \text{--- (94)}$$

$\Rightarrow \psi_k^*(x)$ is just the T.R. ^{block} state ^{conjugate} of $\psi_k(x)$.

Now, we know that, $\psi_k(x+a) = e^{ika} \psi_k(x) \quad \text{--- (95)}$

$$\Rightarrow \psi_k^*(x+a) = e^{-ika} \psi_k^*(x)$$

$$\Rightarrow \psi_k^*(x) = \psi_{-k}(x) \quad \& \therefore \underline{\underline{E(k) = E(-k)}} \quad \text{--- (96)}$$

Thus, as a result of TR symmetry each eigenvalue $E = E_k = E_{-k}$ is (in 1D) 2-fold degenerate. $\psi_k(x)$ & $\psi_{-k}(x)$ are in general complex functions.

However one can always revert to real eigenfn. by taking real combinations

$$\psi_E^1 = \frac{1}{\sqrt{2}} (\psi_k(x) + \psi_{-k}(x)), \quad \psi_E^2 = \frac{i}{\sqrt{2}} (\psi_k(x) - \psi_{-k}(x)) \quad \text{--- (97)}$$

However, these are not eigenfn of the translation operator

$k=0$ & $k=\pi/a$ only give singly degenerate fr.

11/2018

Sec. 6. Tight binding in 3D

Let's consider the case of a simple cubic lattice first.

Primitive translation vectors: $\vec{a}_1 = (a, 0, 0)$; $\vec{a}_2 = (0, a, 0)$; $\vec{a}_3 = (0, 0, a)$ — (98)

A general ^{lattice} translation vector is: $\vec{a}_n = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$ — (99)
 $n = (n_1, n_2, n_3)$

A general translation operators is given by:

$$\hat{T}_{\vec{a}_n} = \hat{T}_{n_1 \vec{a}_1} \hat{T}_{n_2 \vec{a}_2} \hat{T}_{n_3 \vec{a}_3} \quad \text{--- (100)}$$

⊗ The order is irrelevant since the operators mutually commute.

Note: $\hat{T}_{N \vec{a}_1} = \hat{T}_{N \vec{a}_2} = \hat{T}_{N \vec{a}_3} = \hat{1}$ — (101)

The primitive reciprocal lattice vectors are defined as:

$$\vec{b}_1 = \left(\frac{2\pi}{a}, 0, 0\right), \vec{b}_2 = \left(0, \frac{2\pi}{a}, 0\right), \vec{b}_3 = \left(0, 0, \frac{2\pi}{a}\right) \quad \text{--- (102)}$$

From (98) & (102) we see that $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$ — (103)

A general reciprocal lattice vector:

$$\vec{G}_n = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3 \quad n = (n_1, n_2, n_3) \in I \quad \text{--- (104)}$$

Since each $\{\hat{T}_{n_i \vec{a}_i}\}$ for $n_i = 1, 2, \dots, N_i$ is a 1-d translation group of operators one can use the same arguments as in the 1-d lattice case to get.

$$\hat{T}_{\vec{a}_n} = \hat{T}_{n_1 \vec{a}_1} \hat{T}_{n_2 \vec{a}_2} \hat{T}_{n_3 \vec{a}_3} |\psi_{\vec{k}}\rangle = \exp(-i \vec{k} \cdot \vec{a}_n) |\psi_{\vec{k}}\rangle \quad \text{--- (105)}$$

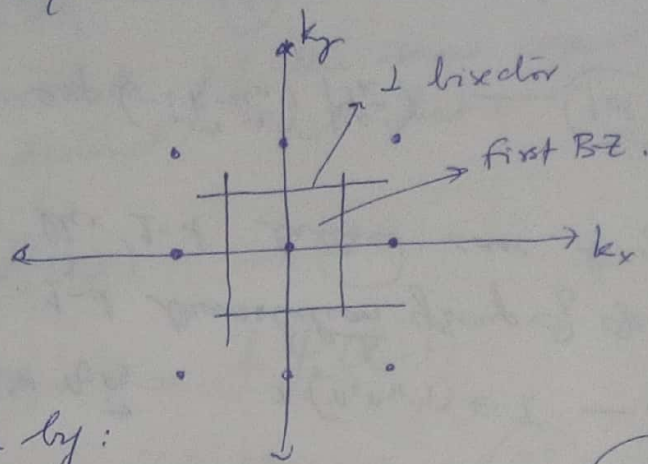
where $\vec{a}_n = \sum_{i=1}^3 n_i \vec{a}_i$ and

$$\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3 \quad \text{--- (106)}$$

w/ $k_i = \frac{l_i}{N_i}$ and $-\frac{N_i}{2} < l_i \leq \frac{N_i}{2}$ — (107)

Given a reciprocal lattice we can construct the first BZ by the Wigner Seitz construction. This is done by drawing \perp bisector planes to the translation vectors from the chosen center to the nearest equivalent lattice sites. e.g. 2D square lattice.

The domain of the reciprocal space defined by (107) is a simple cubic unit cell, which constitutes the BZ in our simple cubic case.



The volume of the BZ is given by:

$$\Omega_{BZ} = \left(\frac{2\pi}{a}\right)^3 = \frac{(2\pi)^3}{\Omega} \rightarrow \text{vol. of direct primitive unit cell} \quad (108)$$

Note: $\Omega = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| \quad (109)$

$$\Omega_{BZ} = |\vec{b}_1 \cdot \vec{b}_2 \times \vec{b}_3| = \frac{(2\pi)^3}{\Omega} \quad (110)$$

The orthogonal TBM of 1-d lattice can be easily extended to a 3-d lattice.

We write:

$$|\psi_{\vec{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{n}=(n_1, n_2, n_3)} e^{i\vec{k} \cdot \vec{a}_n} |\psi_n\rangle \quad (111)$$

or in spatial representation of Bloch Theorem.

$$\psi_{\vec{k}}(\vec{r}) \equiv \langle \vec{r} | \psi_{\vec{k}} \rangle = e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) \quad (112)$$

where $u_{\vec{k}}(\vec{r} + \vec{a}_n) = u_{\vec{k}}(\vec{r}) \quad (113)$

is a 3-D periodic function.

The Hamiltonian of the TBM is still given by:

$$\hat{h} = \sum_{\langle nn' \rangle} |\psi_n\rangle h_{nn'} \langle \psi_{n'}| \quad \text{--- (114)}$$

$$\text{w/ } h_{nn} = \tilde{\epsilon}^0 \quad \& \quad \langle \psi_{nn'} \rangle = -t \quad \text{--- (115)}$$

Since each site has 6 n.n (each pair in a given orthogonal direction) one obtains for the eigenvalues of energy:

$$E_{\vec{k}} = \tilde{\epsilon}^0 - 2t [\cos(2\pi k_1) + \cos(2\pi k_2) + \cos(2\pi k_3)] \quad \text{--- (116)}$$

$$\text{where } \vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3$$

$$\text{or } E_{\vec{k}} = \tilde{\epsilon}^0 - 2t \sum_{i=1}^3 \cos(\vec{k} \cdot \vec{a}_i) \quad \text{--- (117)}$$

$E_{\vec{k}}$ is now a function of a 3-d vector \vec{k} , hence it is a surface in 4-D space. We can represent it by giving its ~~cut~~ ^{cut} along a generic \vec{k} direction.

In general, the primitive translation vectors do not have the simple form (98) nor the corresponding reciprocal lattice vectors have the form (102). However, our formulation of Bloch's theorem, (112) & (111) remain valid.

eg. BCC lattice. primitive lattice vectors are
 $\vec{a}_1 = \frac{a}{2}(-1, 1, 1)$; $\vec{a}_2 = \frac{a}{2}(1, -1, 1)$; $\vec{a}_3 = \frac{a}{2}(1, 1, -1)$ --- (118)
 primitive reciprocal lattice vectors: $\vec{b}_1 = \frac{2\pi}{a}(0, 1, 1)$; $\vec{b}_2 = \frac{2\pi}{a}(1, 0, 1)$; $\vec{b}_3 = \frac{2\pi}{a}(1, 1, 0)$ --- (119)

Translation operators are still valid and all expressions for eigenvalues & eigenvectors of these operators are still valid. However, since the directions corresponding to the reciprocal triad are no longer mutually orthogonal, the BZ is no longer a simple cubic cell: indeed it is regular rhombic dodecahedron.

Ω_1, Ω_2 are still given by the same formula.

IIIly for FCC lattice $\vec{a}_1 = \frac{a}{2} (0, 1, 1)$, $\vec{a}_2 = \frac{a}{2} (1, 0, 1)$; $\vec{a}_3 = \frac{a}{2} (1, 1, 0)$ (120)

& $\vec{b}_1 = \frac{2\pi}{a} (-1, 1, 1)$; $\vec{b}_2 = \frac{2\pi}{a} (1, -1, 1)$; $\vec{b}_3 = \frac{2\pi}{a} (1, 1, -1)$ (121)

We see that the reciprocal lattice of BCC is FCC & vice versa.
BZ of FCC is a truncated octahedron.

We can write the energy eigenvalues generally as:

$$E_{\vec{k}} = \bar{E}^0 - t \sum_{\vec{a}_n} e^{i\vec{k} \cdot \vec{a}_n} \quad (122)$$

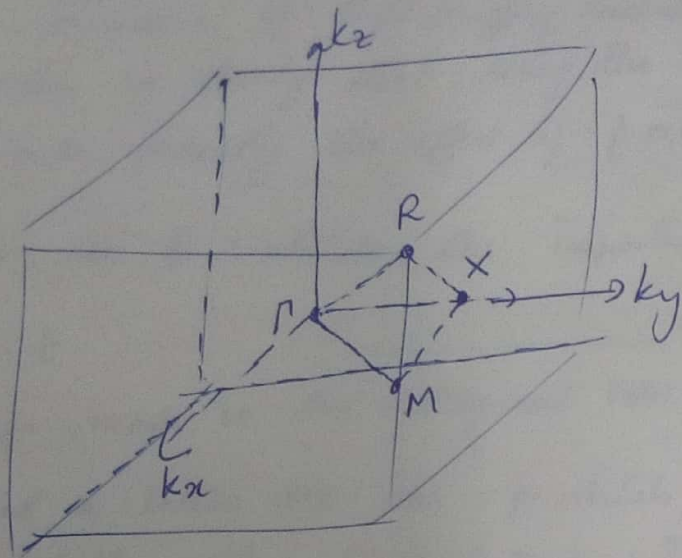
where \vec{a}_n are the nearest-neighbour vectors.
there are 6 nn in the sc lattice, 12 in the FCC.

FCC $\rightarrow \frac{a}{2} (0, \pm 1, \pm 1)$, $\frac{a}{2} (\pm 1, 0, \pm 1)$, $\frac{a}{2} (\pm 1, \pm 1, 0)$ (123)

$$\Rightarrow \sum_{\vec{a}_n} e^{i\vec{k} \cdot \vec{a}_n} = 4 \left(\cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \right) \quad (124)$$

(Show.)

Energies plotted for SC lattice: Each cut along $\vec{b}_1, \vec{b}_2, \vec{b}_3$ will look the same as the 1-d plot before.

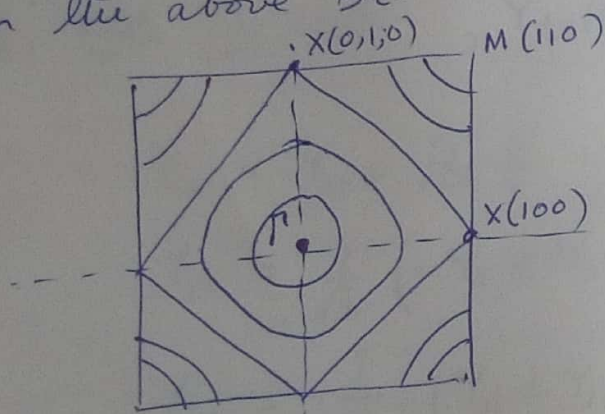


Some special points in the SC BZ.

$E_{\vec{k}}$ is also a periodic function.

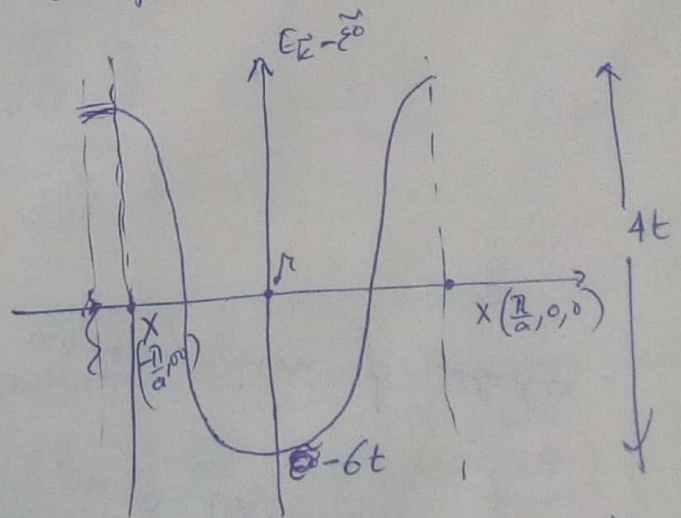
$$E_{\vec{k} + \vec{G}_n} = E_{\vec{k}} \quad \text{--- } (125)$$

We can also draw contours for energies. Imagine a plane sliced from the above BZ.



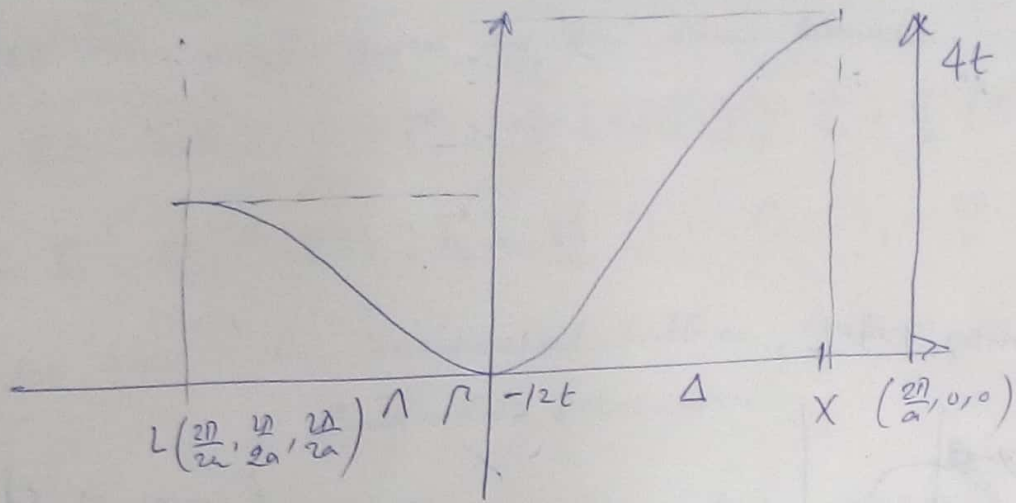
$N = N_1 N_2 N_3$ states of which only ~~one~~ half are completely occupied doubly by e_s .

Energy contour in the (001) plane. The FS is clearly not spherical.



Total band width is ^{now} $W = 12t$

FCC.



s-like band
in the BZ
of the FCC.

Next we'll consider d -bands arising from p -states.