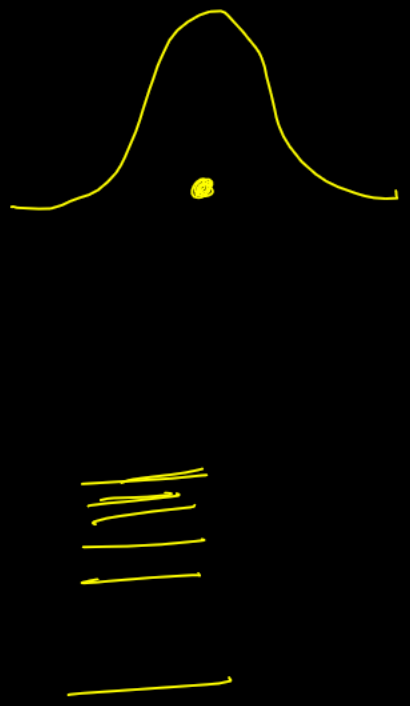
Lecture 23

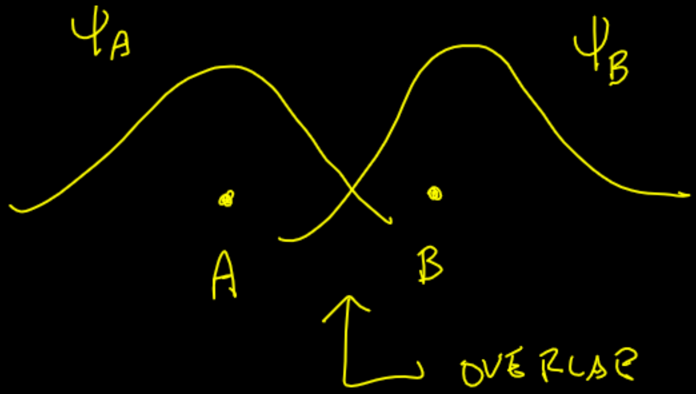
Monday, March 8, 2013

TIGHT BINDING METHOD

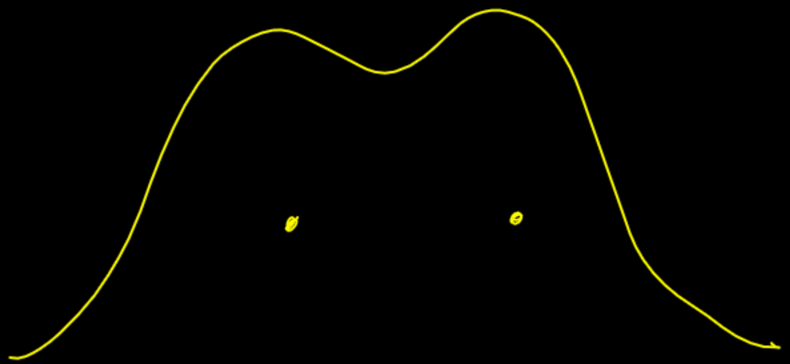
$$H\Psi = \epsilon\Psi \qquad H = -\frac{\hbar^2\nabla^2}{2m} + \underbrace{U(\vec{r})}_{\text{XTAL (PERIODIC)}}$$



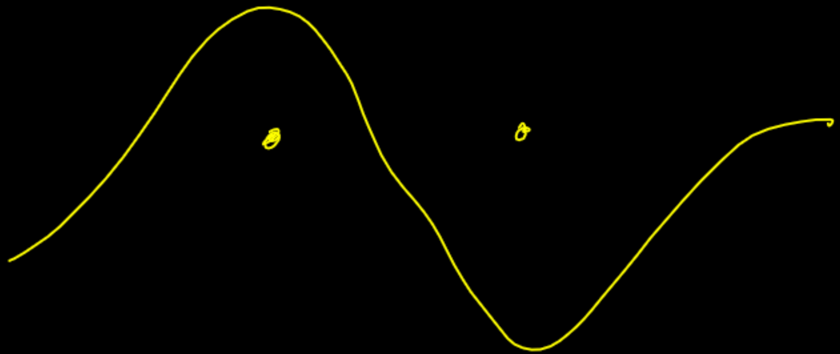
SPATIAL EXTENT OF WAVE FUNCTIONS IS SMALL

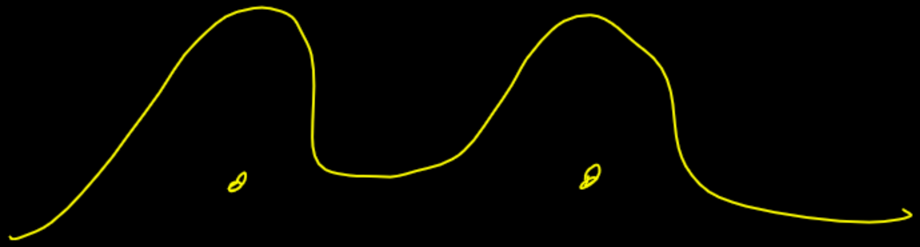


$\psi_A + \psi_B$



$\psi_A - \psi_B$



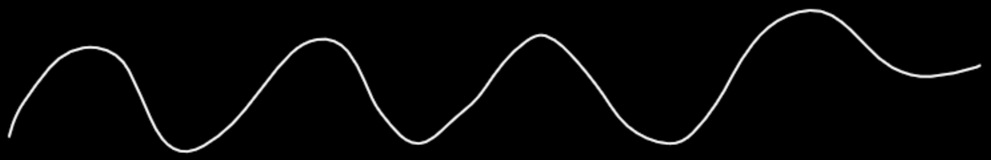


$|\psi_A + \psi_B|^2$

LOWER ENERGY STATE

$|\psi_A - \psi_B|^2$

HIGHER ENERGY

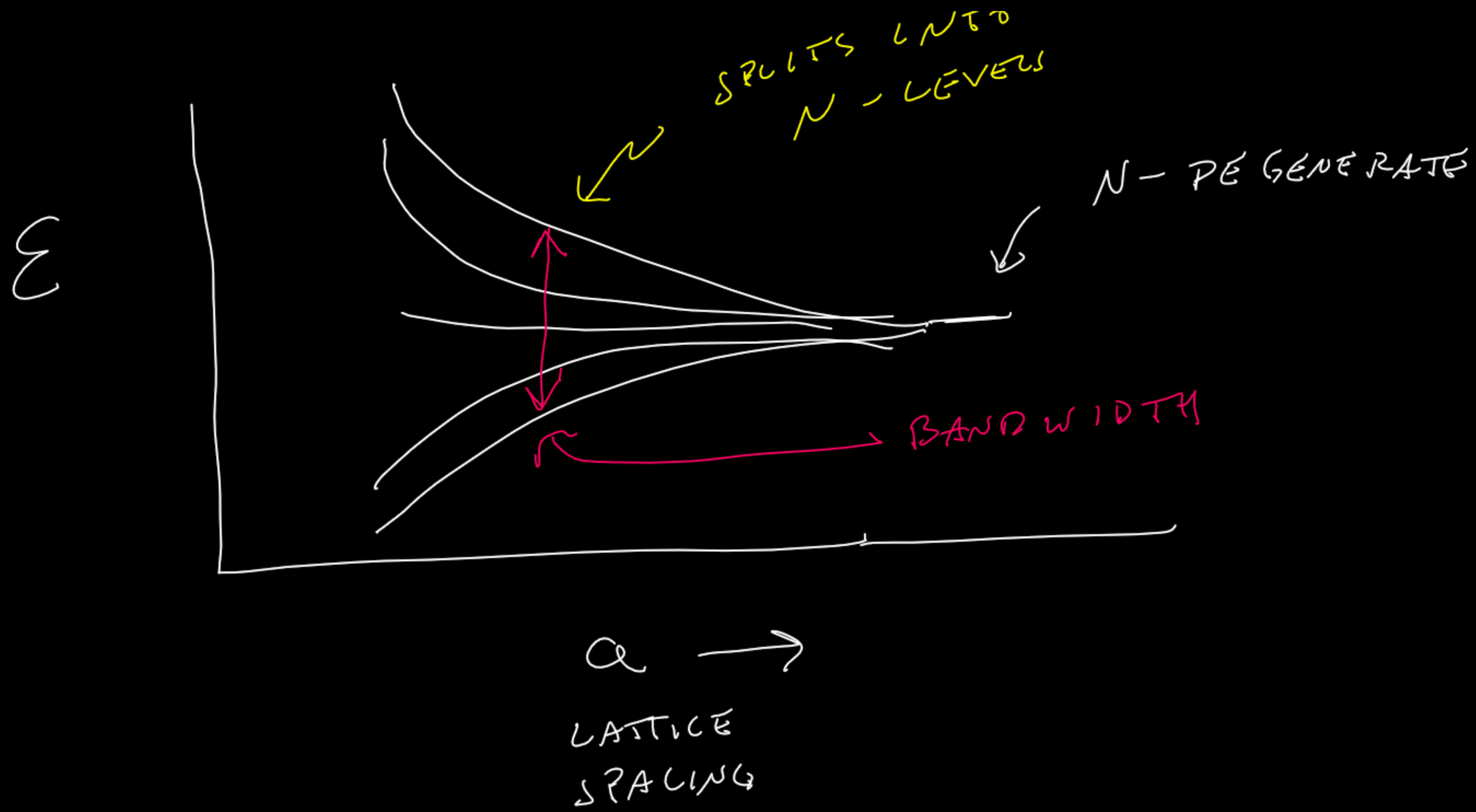


← LOWER ENERGY

$$K.E. = -\frac{\hbar^2 \nabla^2}{2m}$$

← HIGHER ENERGY

IF N ATOMS & BRING CLOSE TOGETHER (N - ORBITALS)



BANDWIDTH ~ OVERLAP OF WAVE FUNCTIONS **

TIGHT BINDING IS VALID WHEN OVERLAP IS WEAK!

(GOOD FOR "CORE" STATES
d - BANDS IN TRANSITION METALS)

(NOT GREATEST FOR
CONDUCTION BANDS)

METHOD:

$$\underbrace{\psi_{\vec{k}}(\vec{r})}_{\text{BLOCH WAVE FUNCTION}} = \underbrace{\sum_{j}}_{\text{(LATTICE SITES)}} C_{\vec{k}j} \, \underbrace{\varphi(\vec{r}-\vec{r}_j)}_{\text{ATOMIC LIKE ORBITAL}}$$

"LINEAR COMBINATION OF ATOMIC ORBITALS"

LCAO

"S" STATE (NON-DEGENERATE)

ψ_k MUST HAVE "BLOCH" FORM $\Rightarrow$ $\boxed{C_{k,j} = \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{r}_j}}$

PROOF:

$$\psi_k(\vec{r}+\vec{R}) = \frac{1}{\sqrt{N}} \sum_j e^{i\vec{k}\cdot\vec{r}_j} \varphi(\vec{r}+\vec{R}-\vec{r}_j)$$

$$\vec{r}_j' = \vec{r}_j - \vec{R}$$

$$= \frac{1}{\sqrt{N}} e^{i\vec{k}\cdot\vec{R}} \sum_j e^{i\vec{k}\cdot\vec{r}_j'} \varphi(\vec{r}-\vec{r}_j')$$

$$= e^{i\vec{k}\cdot\vec{R}} \psi_k(\vec{r})$$

$$\langle k | H | k' \rangle$$ (DIAGONALIZE $\Rightarrow$ ENERGY LEVELS)

$$\langle k | H | k \rangle$$ GIVE ENERGY

$$= \frac{1}{N} \sum_{l} \sum_{m} e^{i \vec{k} \cdot (\vec{r}_l - \vec{r}_m)} \langle \varphi_l | H | \varphi_m \rangle$$

$$= \frac{1}{N} \sum_{l} \sum_{m} e^{i \vec{k} \cdot (\vec{r}_l - \vec{r}_m)} \int d^3\vec{r} \; \varphi^*(\vec{r} - \vec{r}_l) \, H \, \varphi(\vec{r} - \vec{r}_m)$$

$$= \sum_{m} e^{i \vec{k} \cdot \vec{\rho}_m} \int d^3\vec{r} \; \varphi^*(\vec{r} - \vec{\rho}_m) \, H \, \varphi(\vec{r})$$

$$\vec{\rho}_m = -(\vec{r}_m - \vec{r}_e)$$

$$\int d^3\vec{r}\ \varphi^*(r)\ H\varphi(r) \equiv -\alpha \quad \left(\begin{array}{c}\text{SAME SITE} \\ \text{"ON SITE"}\end{array}\right)$$

$$\int d^3\vec{r}\ \varphi^*(\vec{r}-\vec{\rho})\ H\varphi(\vec{r}) \equiv -\gamma \quad (\text{OVERLAP TERM})$$

$$\varepsilon_{\vec{k}} \equiv \langle k|H|k\rangle = -\alpha - \gamma \sum_{n.n.} e^{(-i\vec{k}\cdot\vec{\rho})}$$

NEAREST NEIGHBOR LATTICE POINTS

2 HYDROGEN, "1s" STATE ($n=1 \Rightarrow \varepsilon = -13.6\,eV$)

$$\gamma = 2\left(1 + \frac{\rho}{a_0}\right) \mathrm{EXP}\left(-\rho/a_0\right)$$

EXPONENTIALLY DECAYS WITH DISTANCE

SIMPLE CUBIC

$$\vec{\rho}_m = (\pm a, 0, 0), \quad (0, \pm a, 0), \quad (0, 0, \pm a) \qquad 6 \text{ n.n.}$$

$$\varepsilon_k = -\alpha - 2\gamma\left(\cos k_x a + \cos k_y a + \cos k_z a\right)$$

ε

$$\varepsilon_k = -\alpha - 2\gamma\left(\cos k_x a + \cos k_y a + \cos k_z a\right)$$

"COSINE BANDS"