

# Lecture contents

- A few concepts from Quantum Mechanics
  - Particle in a well
  - Two wells: QM perturbation theory
  - Many wells (atoms) → **BAND** formation
  - Tight-binding model
- Solid state physics review
  - Approximations

# Few concepts from Quantum Mechanics

Electrons are waves:

- Psi-function ( $\Psi, \psi$ )
- Schrödinger equation
- Hamiltonian

General (time dependent) Schrödinger equation:

$$i\hbar \frac{\partial \Psi(r, t)}{\partial t} = \hat{H} \Psi(r, t)$$

If  $\hat{H}$  does not depend on time  $\Psi(r, t) = \psi(r) e^{-i\frac{Et}{\hbar}}$ ;  $\xrightarrow{\text{plane\_wave}}$   $\frac{E}{\hbar} = \omega$

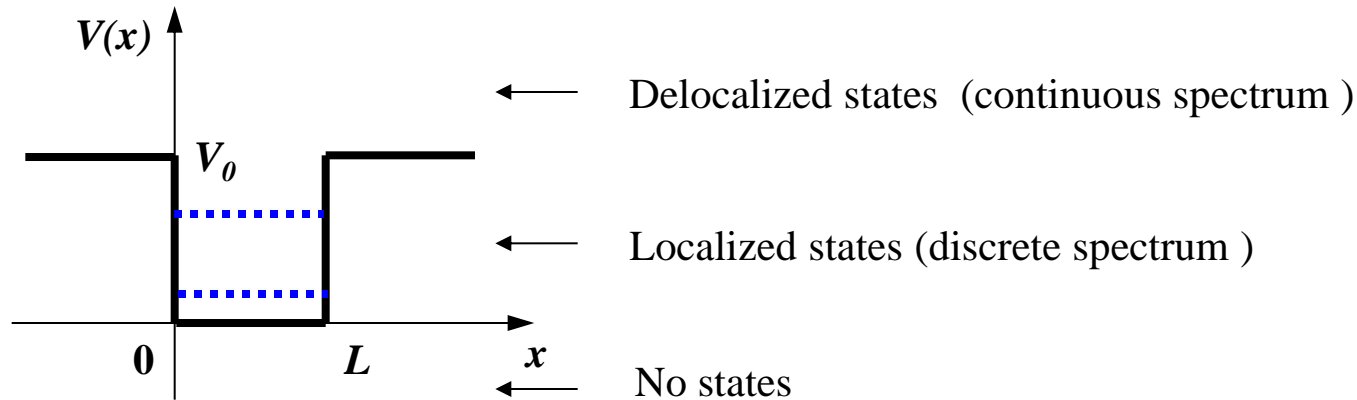
Time-independent Schrödinger equation:  $\hat{H}\psi(r) = E\psi(r)$

$$\hat{H}\psi(r) \equiv \left[ -\frac{\hbar^2}{2m} \Delta + V(r) \right] \psi(r) = E\psi(r)$$

Uncertainty principle (Fourier theorem + w.-p. dualism)  $\Delta p \Delta x \sim \hbar$

Compare to wave packet  $\Delta k$ :  $\Delta k \Delta x \sim 2\pi$

# Quantum Mechanics: particle in a single-dimensional well



$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x) \psi(x) = E \psi(x)$$

$$\begin{aligned}
 V(x) &= V_0 & \text{for } x < 0 \\
 V(x) &= 0 & \text{for } 0 \leq x \leq L \\
 V(x) &= V_0 & \text{for } x > L
 \end{aligned}$$

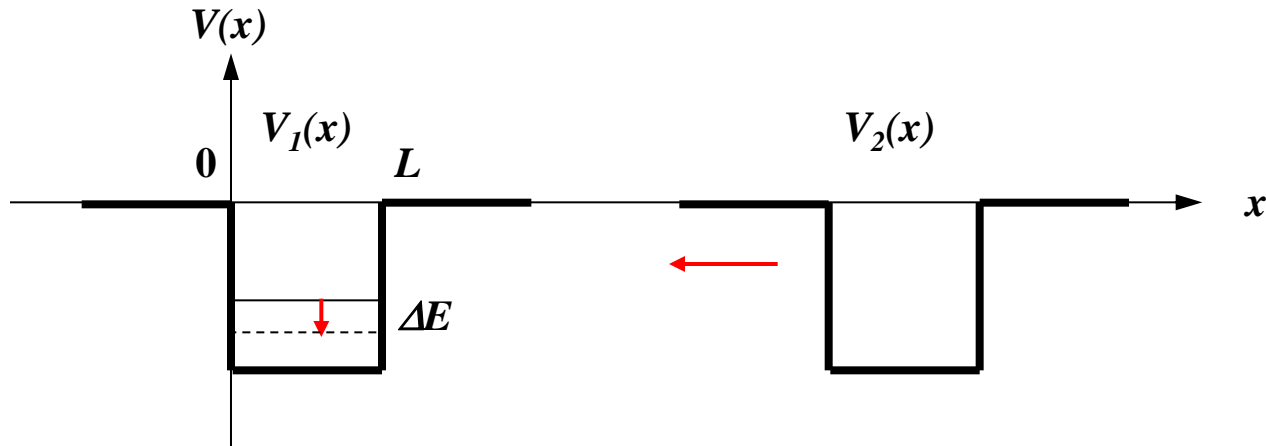
For infinite barrier,  $V_0 \rightarrow \infty$

$$k_n = \frac{\pi n}{L}$$

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} n^2$$

$$\psi_n = \sqrt{\frac{2}{L}} \sin \frac{\pi n x}{L}$$

## Two wells



First approximation of [perturbation theory](#):

$$\Delta E \approx \int_{-\infty}^{+\infty} \psi_1^* V_2(x) \psi_1 dx \equiv \langle \psi_1 | V_2 | \psi_1 \rangle$$

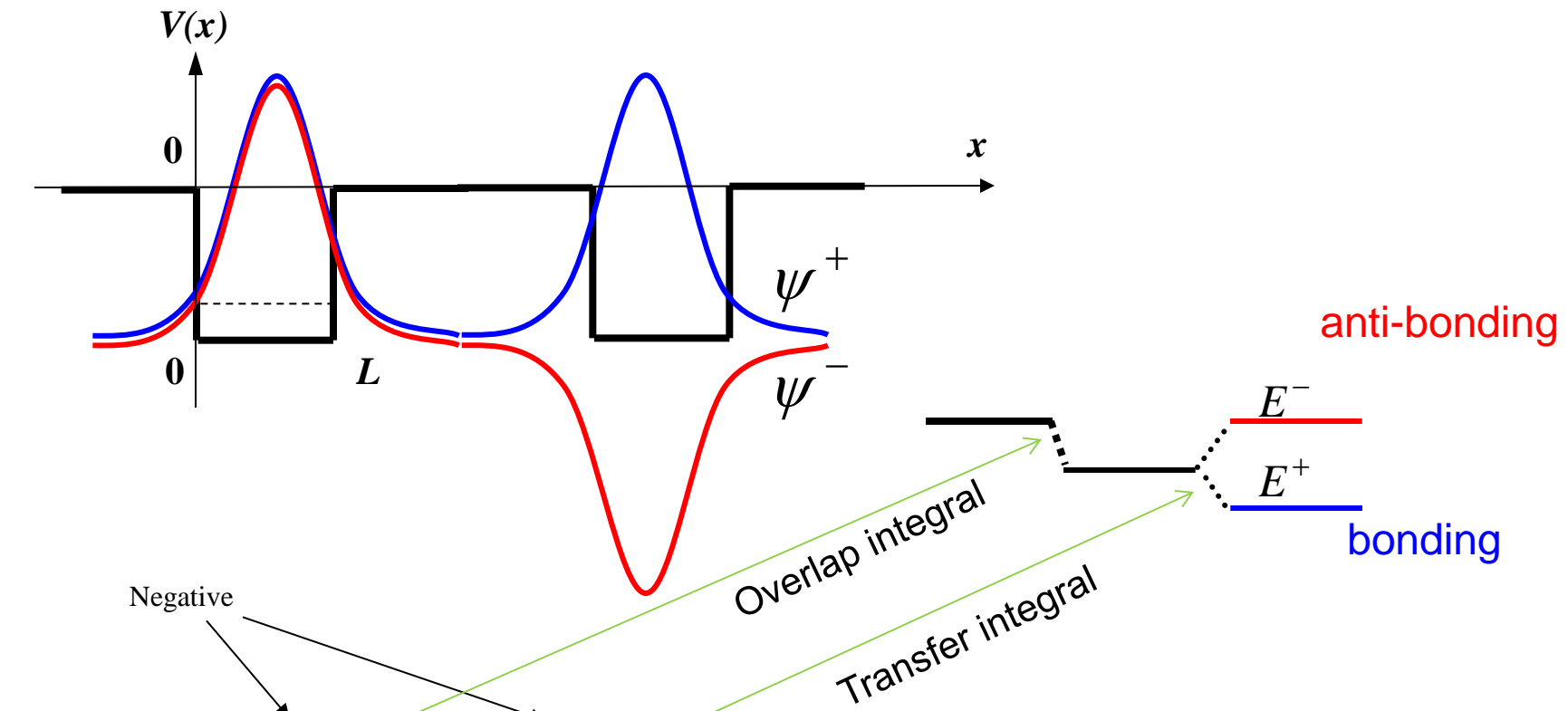
What will happen if the wells are resonant ?

$$\hat{H}\psi(r) \equiv (T + V_1 + V_2)\psi = E\psi$$

Solution in the form:  $\psi = C_1\psi_1 + C_2\psi_2$

↗  
Negative

## Two wells: energy level splitting



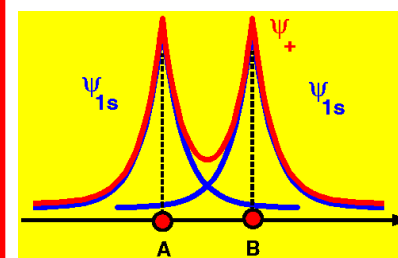
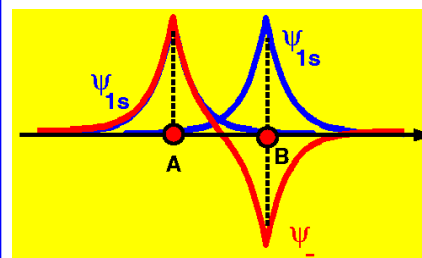
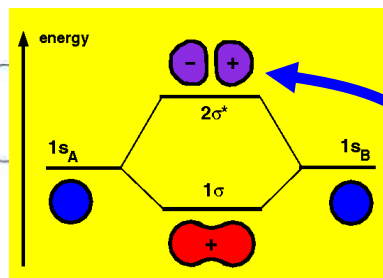
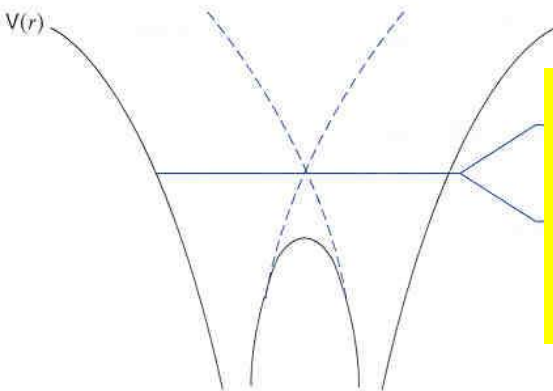
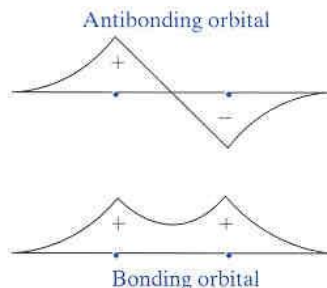
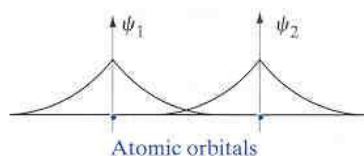
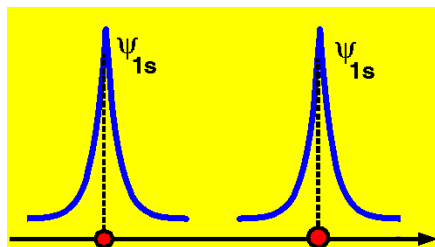
$$\Delta E^\pm \approx \langle \psi_1 | V_2 | \psi_1 \rangle \pm \langle \psi_1 | V_1 | \psi_2 \rangle$$

$$\psi^\pm \approx \frac{1}{\sqrt{2}} (\psi_1 \pm \psi_2)$$

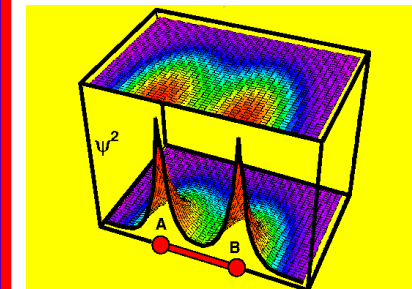
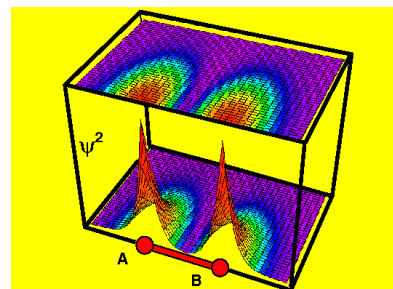
- Resonant levels split
- Splitting increases at small distances

# Bonding and antibonding

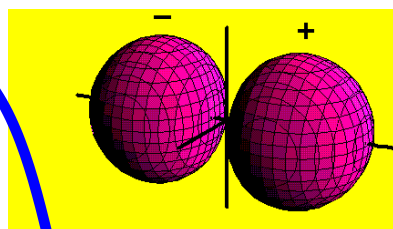
When two atoms brought together, wave functions interact each other and energy levels split.



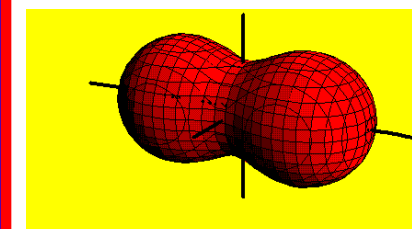
Wave function



Probability density function

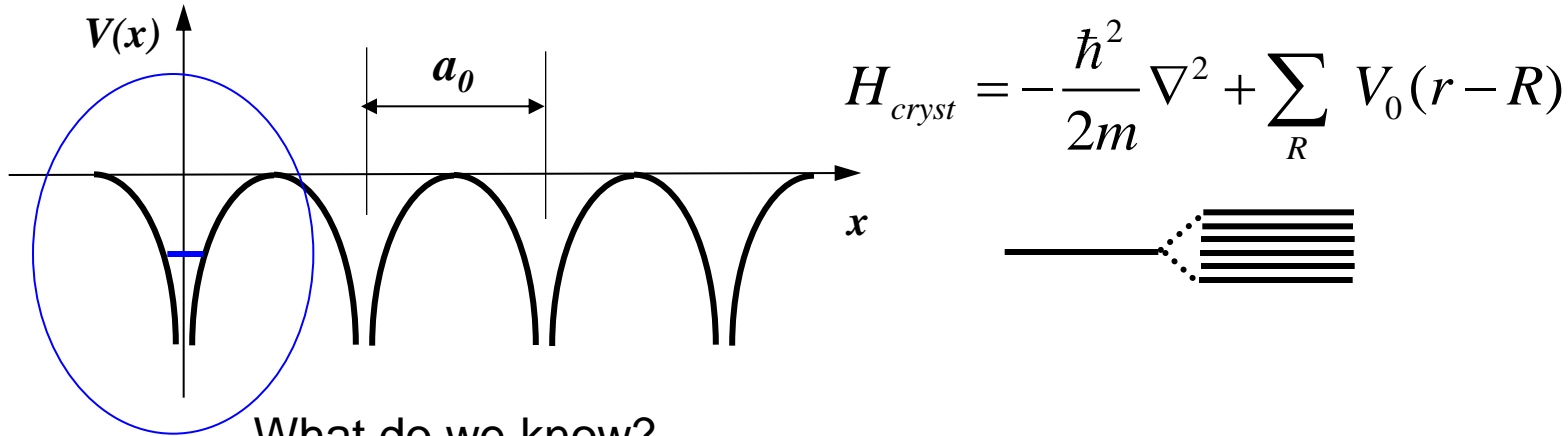


Antibonding



Bonding

# Tight-binding model: periodic array of atoms



What do we know?

- Formation of energy band
- Width depends mainly on interaction of the closest neighbors
- Wavefunctions are renormalized

Start with valence state: 
$$H_{at} \psi_0(r) = E_0 \psi_0(r)$$

Consider crystal Hamiltonian as atomic + perturbation :

$$H_{cryst} = H_{at} + \Delta V$$

Solution in the form :

$$\psi = \sum_R C_R \psi_0(r-R); \quad R = ma_0; \quad m = 0, \pm 1, \dots$$

## Tight-binding model: solution

$$\psi = \sum_R C_R \psi_0(r-R) \quad , \quad R - \text{translation vector}$$

$$\psi(r) = \sum_R C_R \psi_0(r-R) [E_0 - E + \Delta V] = 0$$

$$\int dr \sum_R C_R \left\{ (E_0 - E) \underbrace{\langle \psi_0(r) | \psi(r-R) \rangle}_{\alpha(R)} + \underbrace{\langle \psi_0(r) | \Delta V | \psi_0(r-R) \rangle}_{-\gamma(R)} \right\} = 0$$

$$C_R = N^{-1/2} e^{ikR}$$

Applying (periodic)  
boundary conditions

$|C_R|^2$  - probability to find  
electron on  $R^{\text{th}}$  site

$$\psi = \sum_R N e^{ikR} \psi_0(r-R) = e^{ikr} \cdot \underbrace{\sum_R N e^{-ik(r-R)} \psi_0(r-R)}_{\text{periodic Bloch function}}$$

$$N \sum_R \left\{ (E_0 - E) \alpha(R) - \gamma(R) \right\} e^{ikR} = 0$$

$$E_k = E_0 - \frac{\sum_R \gamma(R) e^{ikR}}{\sum_R \alpha(R) e^{ikR}}$$

$k$  - quasi wavevector is a quantum number  
to innumerate the electron states



## Tight-binding model: solution

Solution for band constructed from a single atomic orbital (s-band):

$$E_k = E_0 + \frac{\sum \langle \psi_0(r) | \Delta V | \psi_0(r-R) \rangle e^{ikR}}{\sum_R \langle \psi_0(r) | \psi_0(r-R) \rangle e^{ikR}}$$

When overlap is negligible:

$$\langle \psi_0(r) | \psi_0(r-R) \rangle = \delta(R)$$

Transfer integrals :

$$\langle \psi_0(r) | \Delta V | \psi_0(r-R) \rangle = -\gamma$$

Diagonal element:

$$\langle \psi_0(r) | \Delta V | \psi_0(r) \rangle = -\beta$$

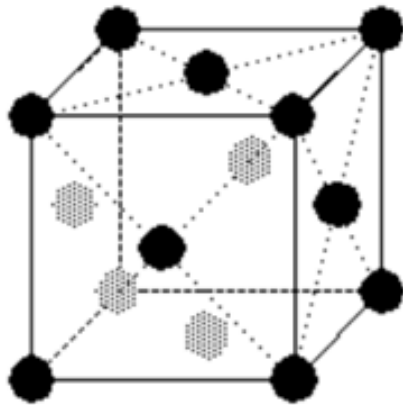
S-band:

$$E_k = E_0 - \beta - \sum_R \gamma(R) e^{ikR}$$

← Over nearest neighbors

Width of a 1D S-band =  $2\gamma$

# Tight-binding model: s-band in FCC crystal



$$E_{\mathbf{k}} = E_0 - \beta - \sum_{\mathbf{R}} \gamma(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}}$$

For FCC: 12 closest neighbors:

$$\frac{a_0}{2} (\pm 1, \pm 1, 0) \dots$$

Along  $\Delta$ -direction:  $\vec{k} = \frac{2\pi}{a_0} (1, 1, 1) \cdot \alpha$

$$\sum_{\mathbf{R}} \gamma(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} = \gamma\left(\frac{a_0}{\sqrt{2}}\right) \left\{ \begin{array}{l} e^{i\alpha\pi\sqrt{2}} + e^{-i\alpha\pi\sqrt{2}} + e^{i\alpha\pi} + e^{-i\alpha\pi} \\ + \text{SAME} + \text{SAME} \end{array} \right\}$$

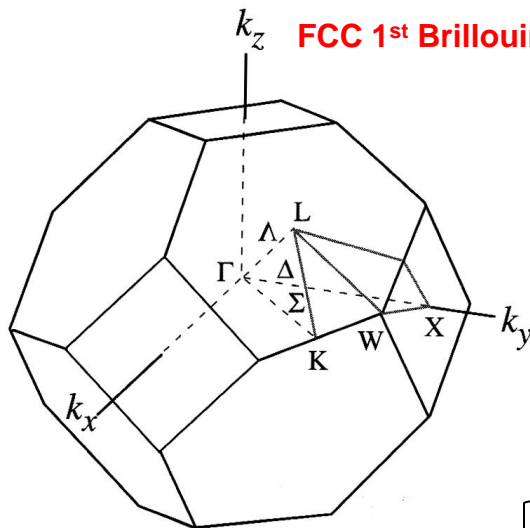
$\alpha = 0 \dots 0.5$

$$= \gamma \left\{ 2 + 2 \frac{e^{i\alpha\pi\sqrt{2}} + e^{-i\alpha\pi\sqrt{2}}}{2 \cos 2\pi\alpha} \right\} = 6\gamma (1 + \cos 2\pi\alpha)$$

$$= 12\gamma \cos^2 \pi\alpha$$

$$E_{\mathbf{k}} = E_0 - \beta - 12\gamma \cos^2 \pi\alpha \quad (\text{along } (111))$$

FCC 1st Brillouin zone



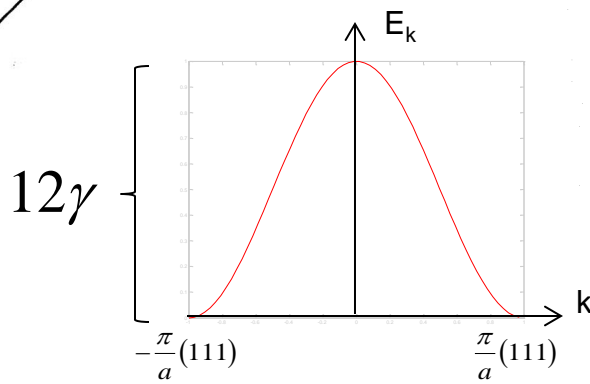
$\Gamma$ - point: (0,0,0)

X- point:  $\frac{2\pi}{a} (1,0,0)$

L- point:  $\frac{\pi}{a} (1,1,1)$

K- point:  $\frac{2\pi}{a} \left(\frac{3}{4}, \frac{3}{4}, 0\right)$

W- point:  $\frac{2\pi}{a} \left(1, \frac{1}{2}, 0\right)$



## Tight-binding model: effective mass

Close to the  $\Gamma$ -point in the  $\Delta$ -direction

$$\begin{aligned}
 E_{\mathbf{k}} &= E_0 - \beta - 12\gamma \cos^2 \pi \alpha = \\
 &= E_0 - \beta - 12\gamma \left(1 - \frac{(\pi \alpha)^2}{2}\right)^2 = \\
 &= E_0 - \beta - 12\gamma \left(1 - (\pi \alpha)^2\right) = \\
 &= E_0 - \beta - 12\gamma + \gamma a_0^2 k^2
 \end{aligned}$$

$$\left\{ \begin{aligned} |\mathbf{k}| &= \frac{\pi}{a_0} \sqrt{3} \alpha \\ \alpha &= \frac{a_0 k}{2\pi\sqrt{3}} \end{aligned} \right.$$

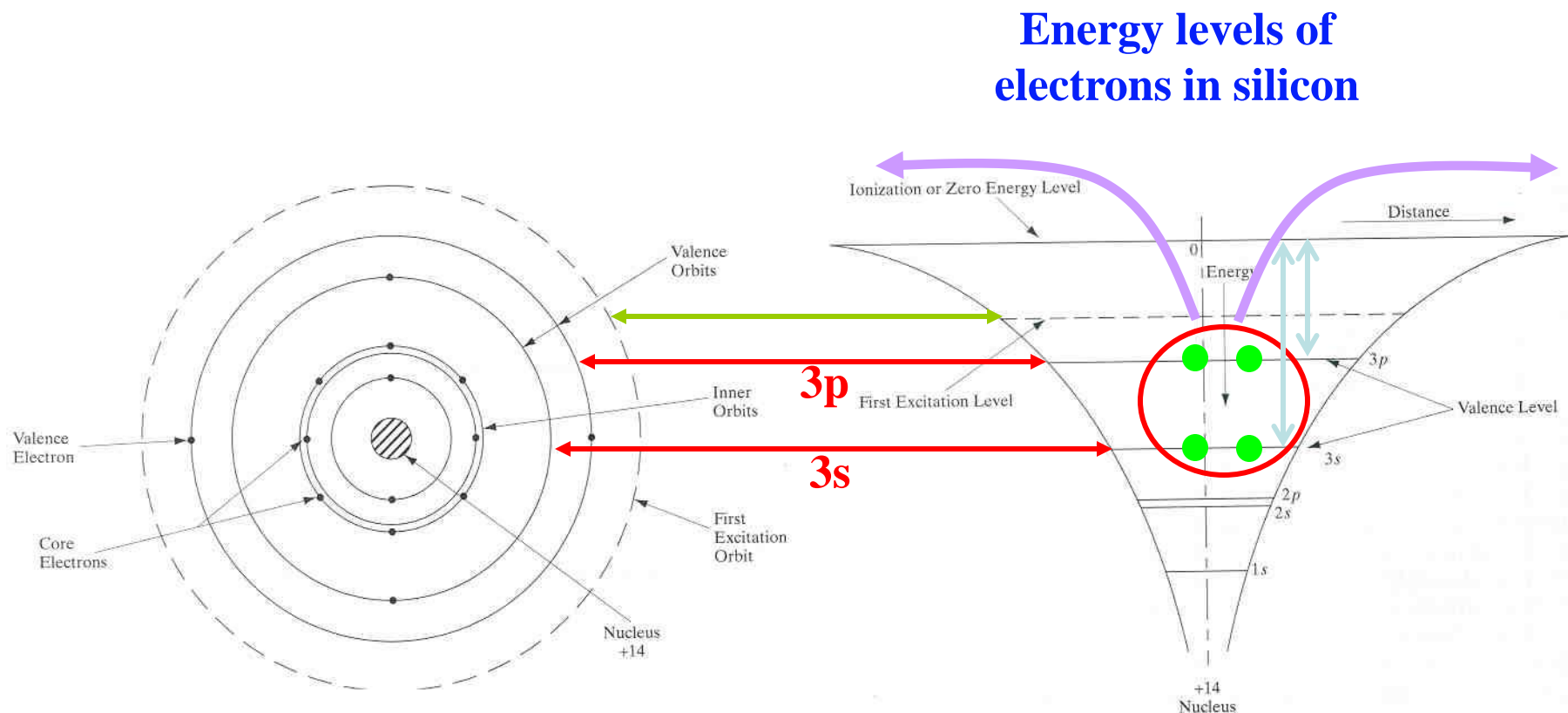
Compare: Parabolic band dispersion (e.g. free electron)

$$E = V_0 + \frac{\hbar^2 k^2}{2m}$$

$$\frac{1}{m^*} = \frac{d^2 E}{\hbar^2 dk^2} = \frac{2\gamma a_0^2}{\hbar^2}$$

effective mass  $m^* = \frac{\hbar^2}{2\gamma a_0^2}$

# Orbital structure and energy levels of Si atom

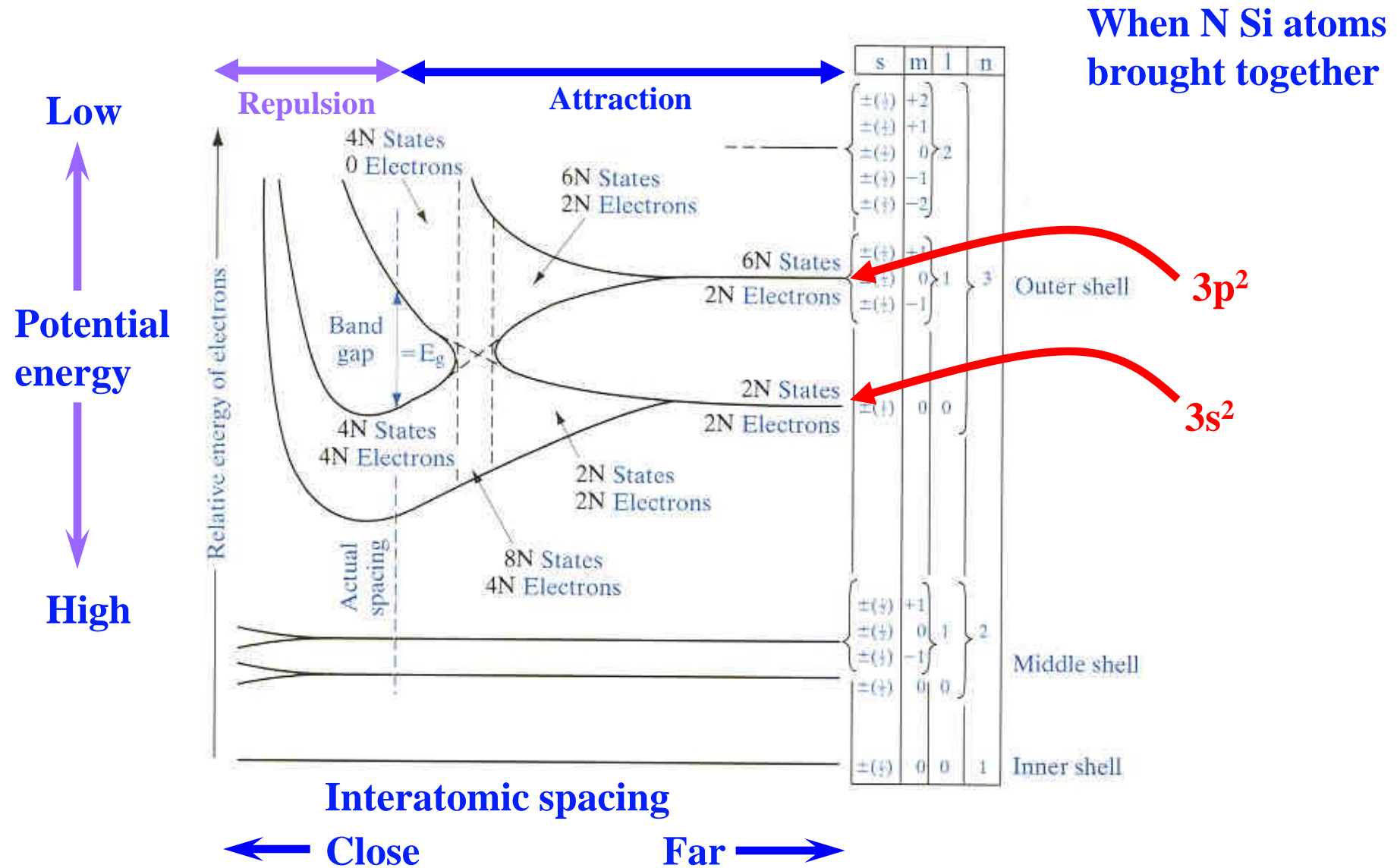


**Orbital structure**

**Silicon:  $1s^2 2s^2 2p^6 3s^2 3p^2$**

**Energy levels are filled according to Pauli principle**

# Energy levels of Si as a function of interatomic spacing



# Few concepts from Solid State Physics

## 1. Adiabatic approximation

When valence and core electrons are separated, general Schrödinger equation for a condensed medium without spin

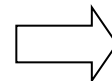
$$H = \sum_l \frac{\mathbf{p}_l^2}{2M_l} + \sum_{l,m} U(\mathbf{R}_l - \mathbf{R}_m) + \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i,l} V(\mathbf{r}_i - \mathbf{R}_l) + \sum_{i,j} \frac{e^2/4\pi\epsilon_0}{|\mathbf{r}_i - \mathbf{r}_j|} = H_L + H_e$$

$$H\Psi(R, r) = E\Psi(R, r)$$

- Mass of ions >1000 times greater than mass of electrons
- Ion velocities >1000 times slower
- Electrons adjust ‘instantaneously’ to the positions of atoms

$$\Rightarrow \Psi(R, r) \approx \psi(r, R)\Phi(R)$$

- Separate ion and electron motion (accuracy  $\sim m/M$ )



$$H_L \Phi(R) = E_L \Phi(R)$$

$$H_e \psi(r, R) = E_e \psi(r, R)$$

# Few concepts from Solid State Physics

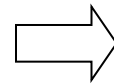
## 2. Phonons

Hamiltonian for lattice motion (harmonic oscillations) :

$$H_L = \sum_l \frac{p_l^2}{2M_l} + \sum_{l,m} U_0 (R_l^0 - R_m^0) + \sum_{l,m} \frac{1}{2} C_{l,m} (u_l - u_m)^2 + U_{anhar}$$

Displacements show up as plane waves with weak interaction via anharmonicity:

$$u_{k,\omega} = u_0 e^{ikr - i\omega t}$$



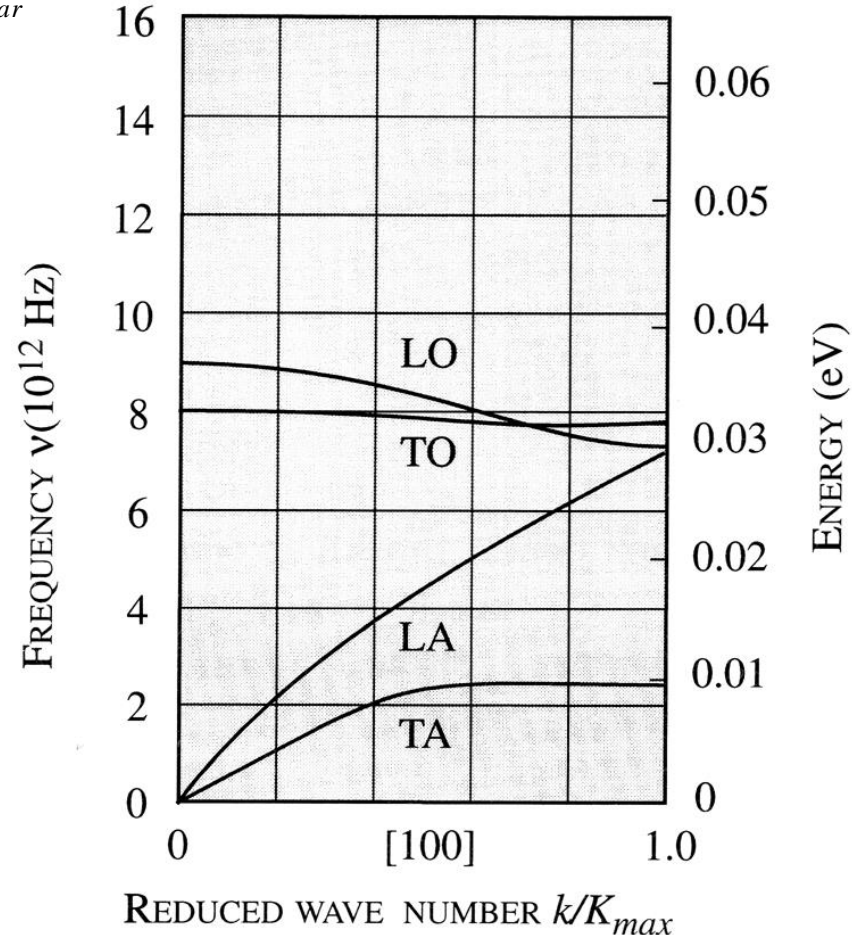
Energy in a mode:

$$E(k, \omega) = \left( n(k, \omega) + \frac{1}{2} \right) \hbar \omega$$

Equilibrium distribution (Bose Einstein):

$$n(\omega) = \frac{1}{\exp\left(\frac{\hbar \omega}{kT}\right) - 1}$$

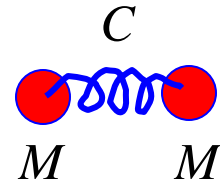
Phonon dispersion relation in GaAs



# Quantum harmonic oscillator

Quantum harmonic oscillator: Hamiltonian

$$H = \frac{p^2}{2M} + \frac{1}{2}Cx^2$$

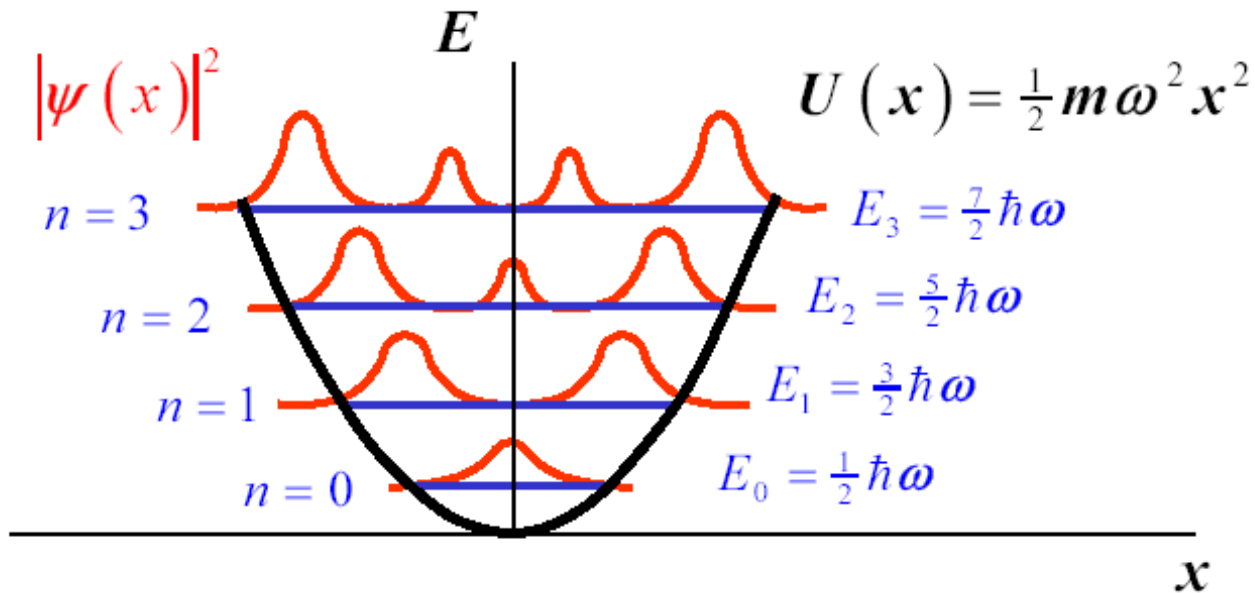
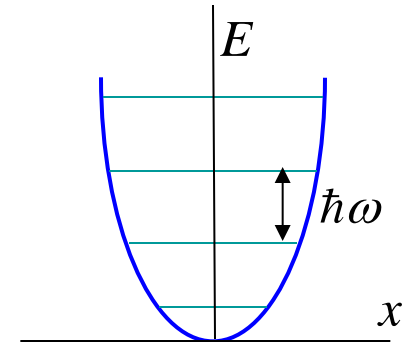


Solution gives resonance frequency (as in classical mechanics)

$$\omega^2 = \frac{C}{M}$$

And quantum oscillation spectrum:  
( $n$  may be considered as number of “quasiparticles”)

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$





# Quantization of lattice vibrations: phonons

For a single oscillator the frequency is fixed, but when many oscillators interact we have a number of modes (normal modes)

$$\omega_k$$

Each mode is occupied by  $n_k$  phonons

$$E_k = \left( n_k + \frac{1}{2} \right) \hbar \omega_k$$

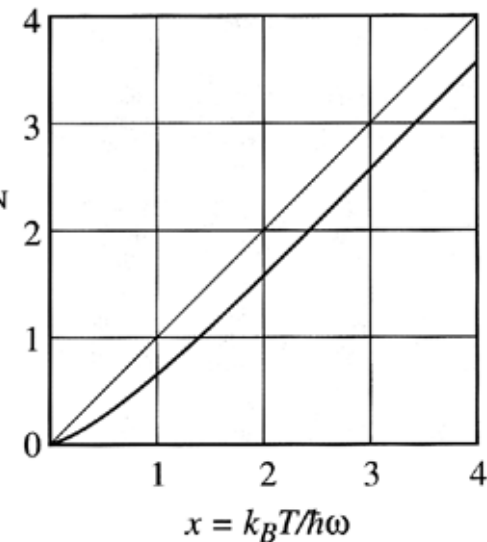
For a 1D chain states are determined as:  $k = \frac{2\pi n}{Na}$ ; for  $n = 0, \pm 1, \dots, \pm \frac{N}{2}$

Occupancy of modes is given by Bose-statistics:

$$n(\omega) = \frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}$$

PHONON  
OCCUPATION  
 $\langle n \rangle$

Bose-Einstein distribution  
function



# Few concepts from Solid State Physics

## 3. One-electron (mean-field) approximation

Schrödinger equation for the electrons (no spin):

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i,l} V(\mathbf{r}_i - \mathbf{R}_l) + \sum_{i,j} \frac{e^2/4\pi\epsilon_0}{|\mathbf{r}_i - \mathbf{r}_j|}$$

$\sum_i V_e(r_i) + V_{e-e}$

Introduce one-electron states,  $\psi_j$  :

$$\psi(r, R) = \prod_i \psi_i(r_i, R)$$

$$H_{ei} = \frac{p_i^2}{2m} + \sum_l V(r_i - R_l^0) + V_{e-ph} + V_{e-e}$$

Small perturbation

One-electron Schrödinger equation (each state can accommodate up to 2 electrons):

$$\left[ \frac{p^2}{2m} + V(r) \right] \psi(r) = E \psi(r)$$

$\mathbf{V}(\mathbf{r})$  has periodicity of the crystal