

# Review: Molecules

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Start with the full Hamiltonian

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Use the Born-Oppenheimer approximation

$$H_{elec} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Neglect the electron-electron interactions.  $H_{elec}$  is then a sum of  $H_{MO}$ .

$$H_{MO} = \frac{-\hbar^2}{2m_e} \nabla_1^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 |r_1 - r_A|}$$

The molecular orbital Hamiltonian can be solved numerically or by the Linear Combinations of Atomic Orbitals (LCAO)

# Linear combination of atomic orbitals


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Guess that the solution to  $H_{mo}$  can be written as a linear combination of atomic orbitals.

$$\Psi_{mo} = c_1 \phi_{1s,A}^H + c_2 \phi_{1s,B}^H + c_3 \phi_{2s,A}^H + c_4 \phi_{2s,B}^H + \dots$$

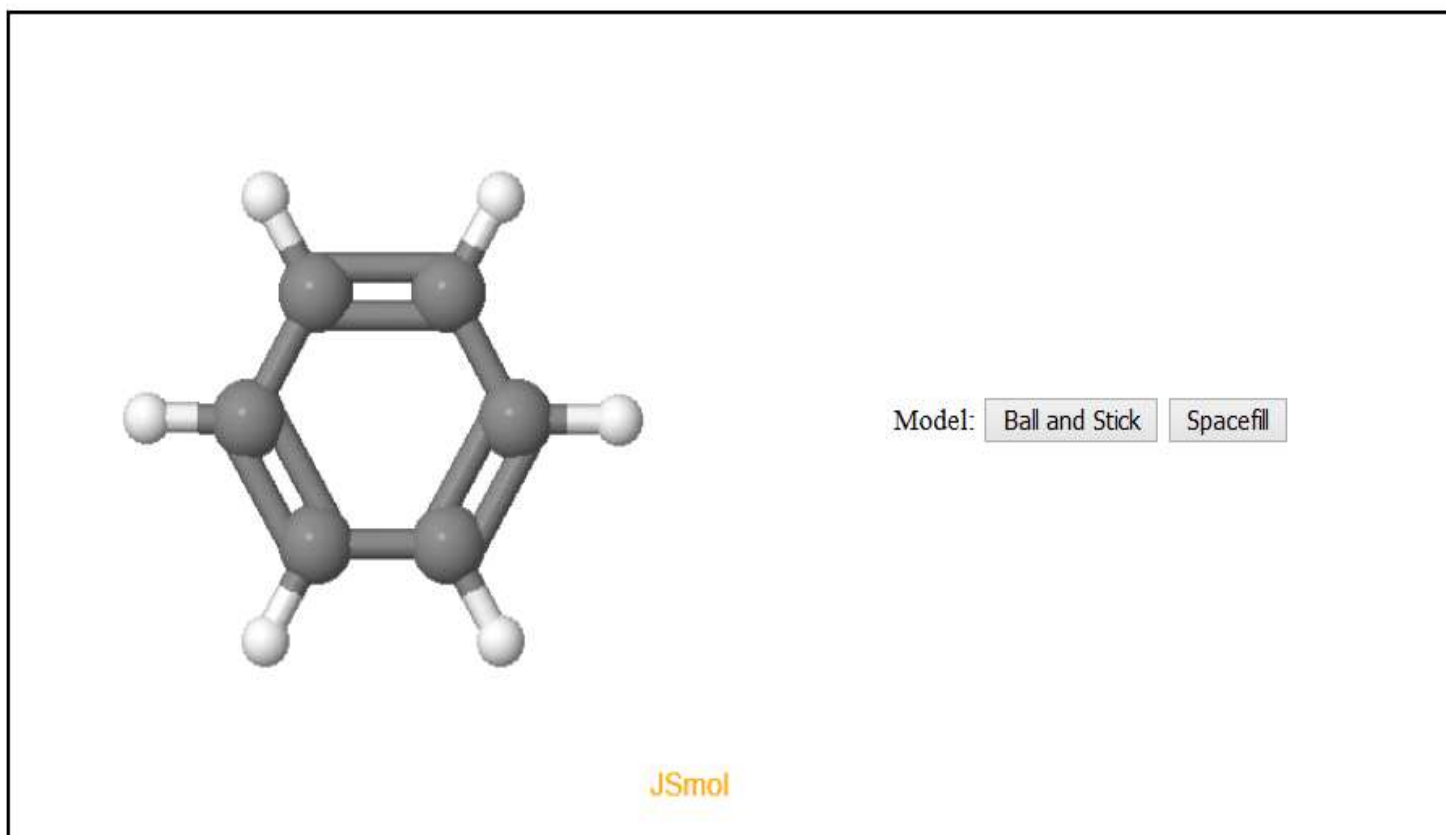
Construct the Hamiltonian matrix.

$$\begin{bmatrix} \langle \phi_{1s,A}^H | H_{mo} | \phi_{1s,A}^H \rangle & \langle \phi_{1s,A}^H | H_{mo} | \phi_{1s,B}^H \rangle \\ \langle \phi_{1s,B}^H | H_{mo} | \phi_{1s,A}^H \rangle & \langle \phi_{1s,B}^H | H_{mo} | \phi_{1s,B}^H \rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} \langle \phi_{1s,A}^H | \phi_{1s,A}^H \rangle & \langle \phi_{1s,A}^H | \phi_{1s,B}^H \rangle \\ \langle \phi_{1s,B}^H | \phi_{1s,A}^H \rangle & \langle \phi_{1s,B}^H | \phi_{1s,B}^H \rangle \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$


$$S \approx \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

## Molecular orbitals of benzene

Benzene ( $C_6H_6$ ) consists of 6 carbon atoms in a ring. A hydrogen atom is attached to each carbon atom. The carbon-carbon bond length is 1.40 Å and the carbon-hydrogen bond length is 1.10 Å.



The molecular orbital Hamiltonian is,

$$H_{\text{mo}} = -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_{a=1}^A \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_a|}$$

# Tight binding

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Tight binding does not include electron-electron interactions

$$H_{MO} = \frac{-\hbar^2}{2m_e} \nabla^2 - \sum_A \frac{Z_A e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_A|}$$

$$\psi_k = \frac{1}{\sqrt{N}} \sum_{l,m,n} \exp\left(i\left(l\vec{k} \cdot \vec{a}_1 + m\vec{k} \cdot \vec{a}_2 + n\vec{k} \cdot \vec{a}_3\right)\right) \psi_{\text{unit\_cell}}(\vec{r} - l\vec{a}_1 - m\vec{a}_2 - n\vec{a}_3)$$

$$\psi_{\text{unit\_cell}}(\vec{r}) = \sum_i c_i \phi_i(\vec{r} - \vec{r}_i)$$

Atomic wave functions

This is the tight-binding wave function.

$$T_{pqS} \psi_k = \exp\left(i\left(p\vec{k} \cdot \vec{a}_1 + q\vec{k} \cdot \vec{a}_2 + s\vec{k} \cdot \vec{a}_3\right)\right) \psi_k$$

# Tight binding

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$$\psi_k = \sum_{l,m,n} \exp\left(i\left(l\vec{k} \cdot \vec{a}_1 + m\vec{k} \cdot \vec{a}_2 + n\vec{k} \cdot \vec{a}_3\right)\right) \sum_a c_a \phi_a(\vec{r} - l\vec{a}_1 - m\vec{a}_2 - n\vec{a}_3)$$

Substitute the tight-binding wave function into the time independent Schrödinger equation.

$$H_{MO}\psi_k = E_k\psi_k$$

Multiply from the left by one of the atomic orbitals.

$$\langle \phi_a | H_{MO} | \psi_k \rangle = E_k \langle \phi_a | \psi_k \rangle$$

$$\begin{aligned} & c_a \langle \phi_a | H_{MO} | \phi_a \rangle + \sum_{\text{nearest neighbors } m} c_m \langle \phi_a | H_{MO} | \phi_m \rangle \exp(i(h\vec{k} \cdot \vec{a}_1 + j\vec{k} \cdot \vec{a}_2 + l\vec{k} \cdot \vec{a}_3)) + \text{small terms} \\ & = E_k c_a \langle \phi_a | \phi_a \rangle + \text{small terms} \end{aligned}$$

There is one equation for each atomic orbital

# Tight binding, one atomic orbital

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$$c_a \langle \phi_a | H_{MO} | \phi_a \rangle + \sum_{\text{nearest neighbors } m} c_m \langle \phi_a | H_{MO} | \phi_m \rangle \exp(i(h\vec{k} \cdot \vec{a}_1 + j\vec{k} \cdot \vec{a}_2 + l\vec{k} \cdot \vec{a}_3)) + \text{small terms}$$
$$= E_k c_a \langle \phi_a | \phi_a \rangle + \text{small terms}$$

For only one atomic orbital in the sum over valence orbitals

$$E_k c_a \langle \phi_a | \phi_a \rangle = c_a \langle \phi_a | H_{MO} | \phi_a \rangle + \sum_{\text{nearest neighbors } m} c_a \langle \phi_a | H_{MO} | \phi_m \rangle \exp(i(h\vec{k} \cdot \vec{a}_1 + j\vec{k} \cdot \vec{a}_2 + l\vec{k} \cdot \vec{a}_3))$$

$$E_k = \varepsilon - t \sum_m e^{i\vec{k} \cdot \vec{\rho}_m}$$

$$\varepsilon = \langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r}) \rangle$$

On-site energy

$$t = -\langle \phi_a(\vec{r}) | H_{MO} | \phi_a(\vec{r} - \vec{\rho}_m) \rangle$$

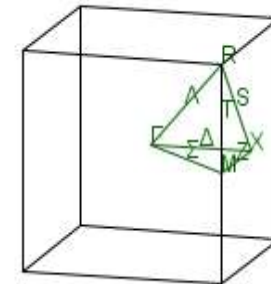
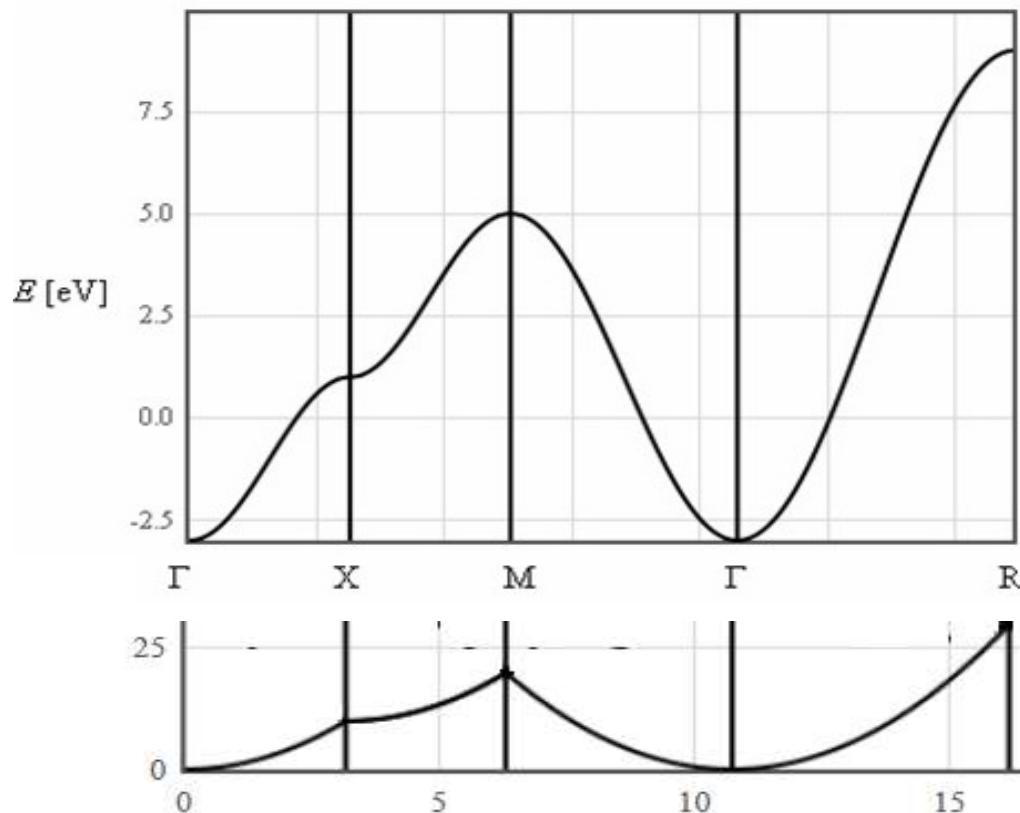
Overlap integral

# Tight binding, simple cubic

$$E = \varepsilon - t \sum_{lmn} e^{i\vec{k} \cdot \vec{\rho}_{lmn}}$$

$$E = \varepsilon - t \left( e^{ik_x a} + e^{-ik_x a} + e^{ik_y a} + e^{-ik_y a} + e^{ik_z a} + e^{-ik_z a} \right)$$

$$= \varepsilon - 2t \left( \cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right)$$

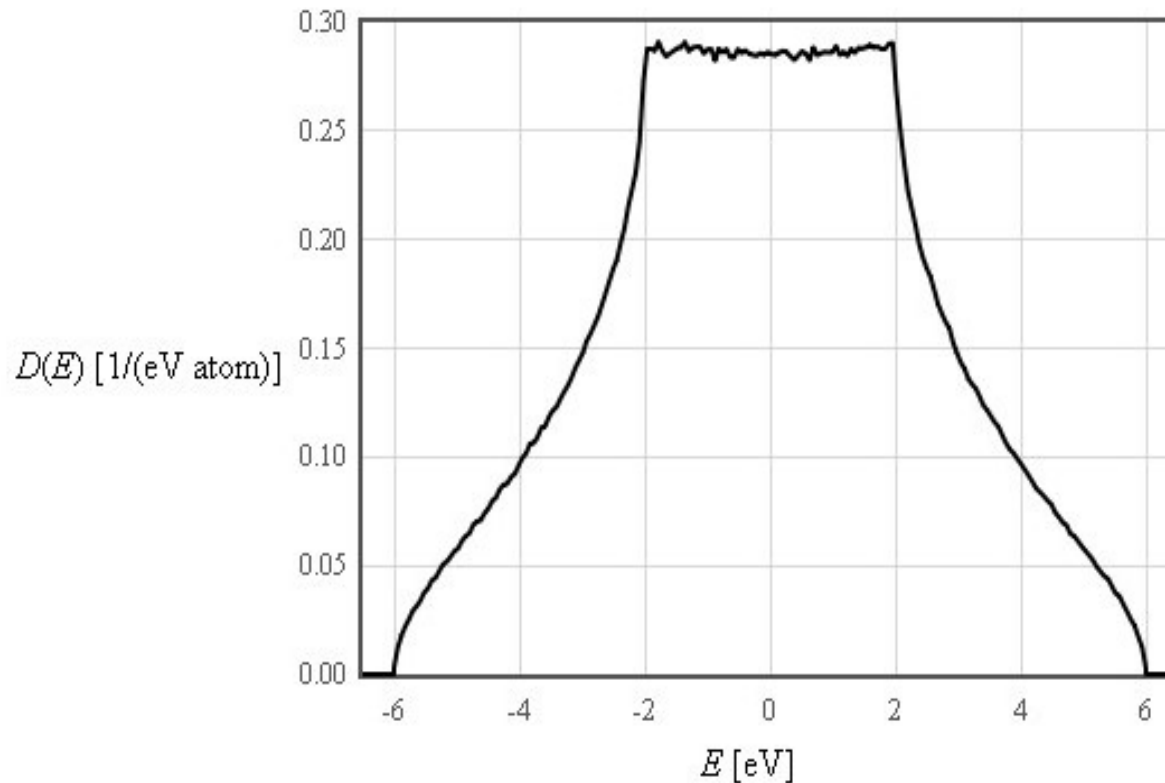


Effective mass  $m^* = \frac{\hbar^2}{\frac{d^2 E}{dk^2}} = \frac{\hbar^2}{2t a^2}$

Narrow bands  $\rightarrow$  high effective mass

# Density of states (simple cubic)

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Calculate the energy for every allowed  $k$  in the Brillouin zone

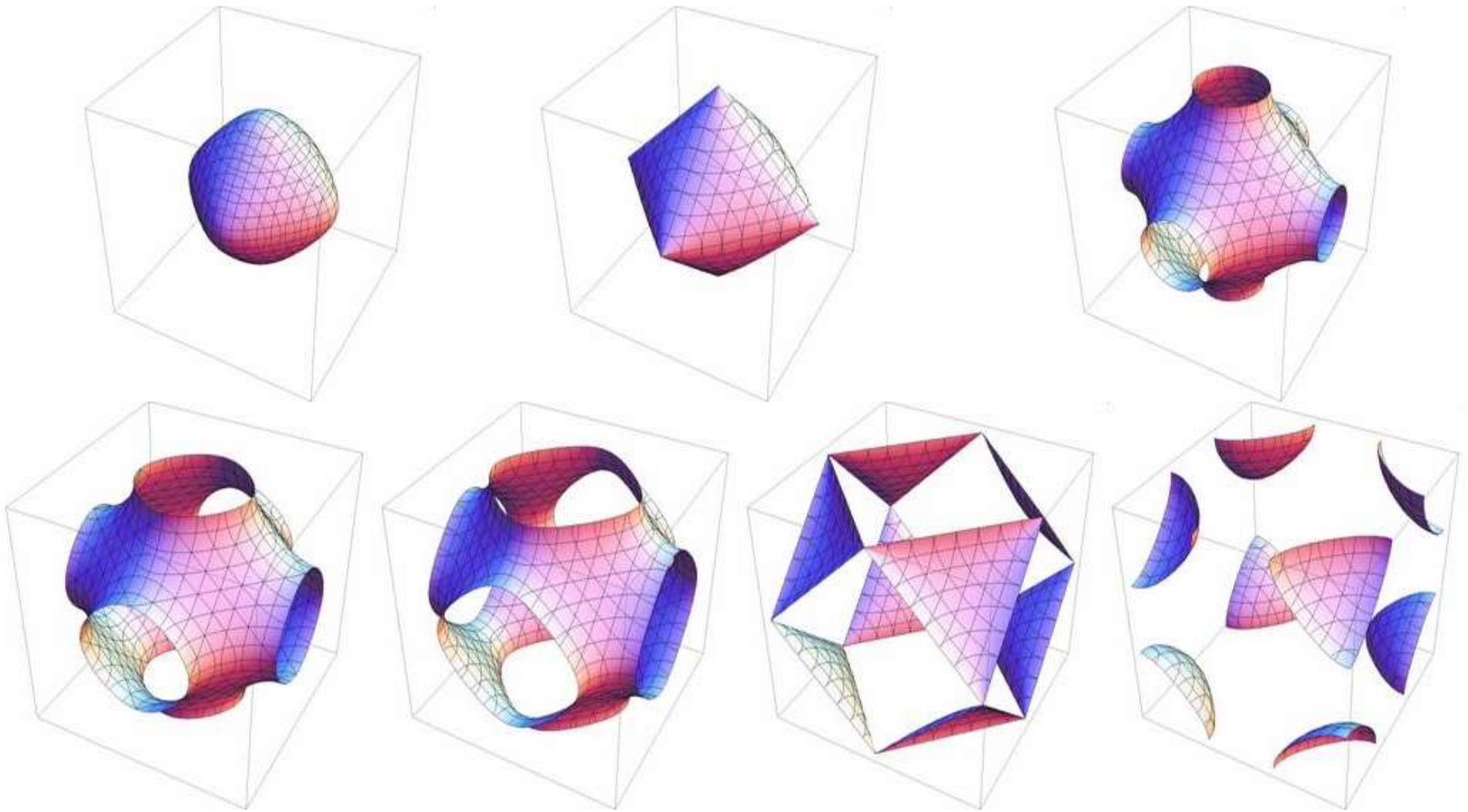
$$E = \varepsilon - 2t \left( \cos(k_x a) + \cos(k_y a) + \cos(k_z a) \right)$$

<http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/tbtable.html>



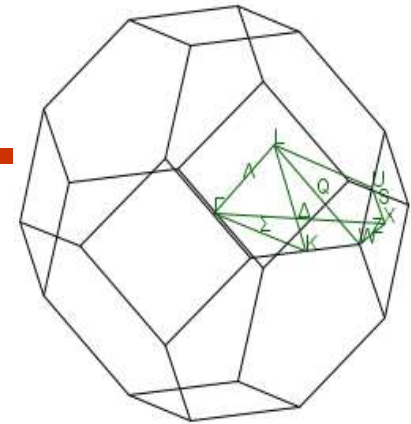
# Tight binding, simple cubic

$$E = \varepsilon - 2t(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))$$



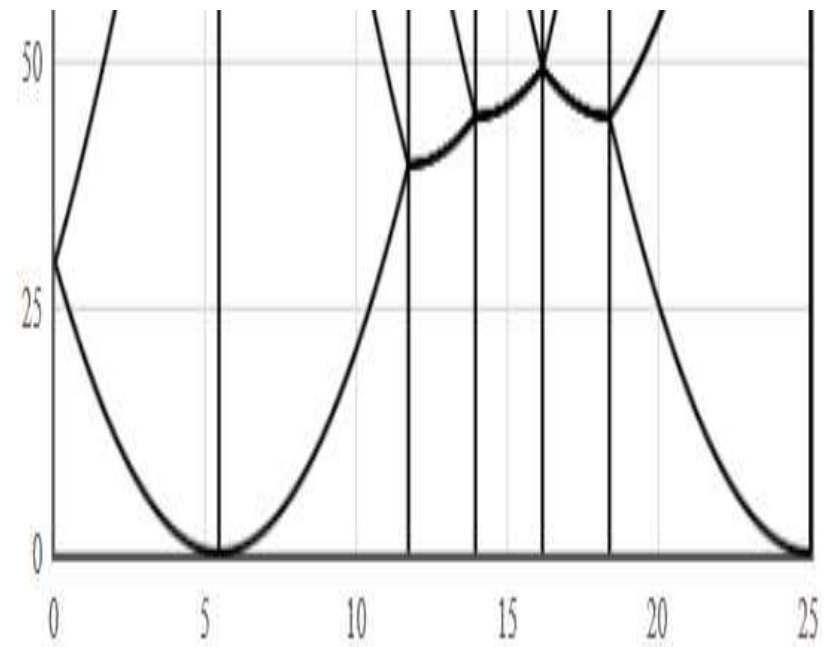
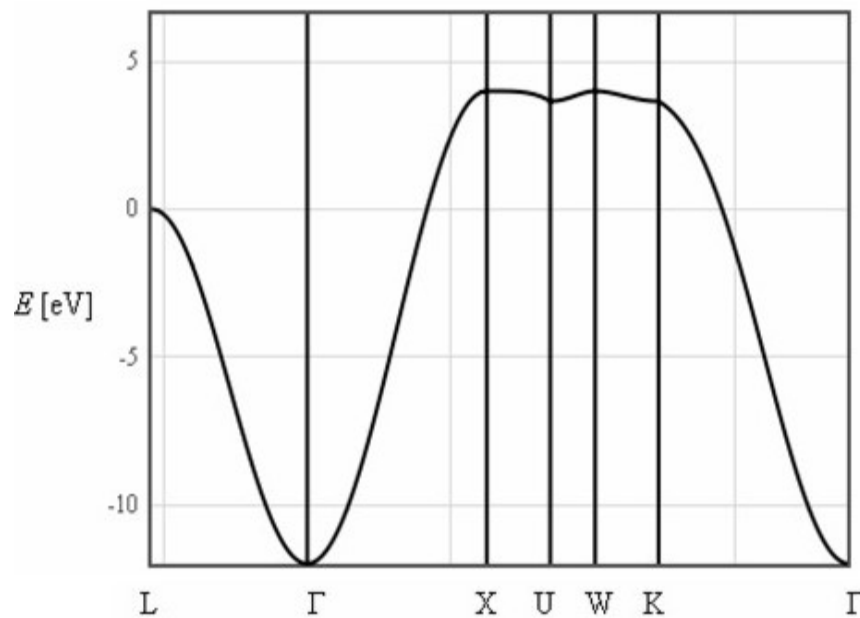
Christian Gruber, 2008

# Tight binding, fcc



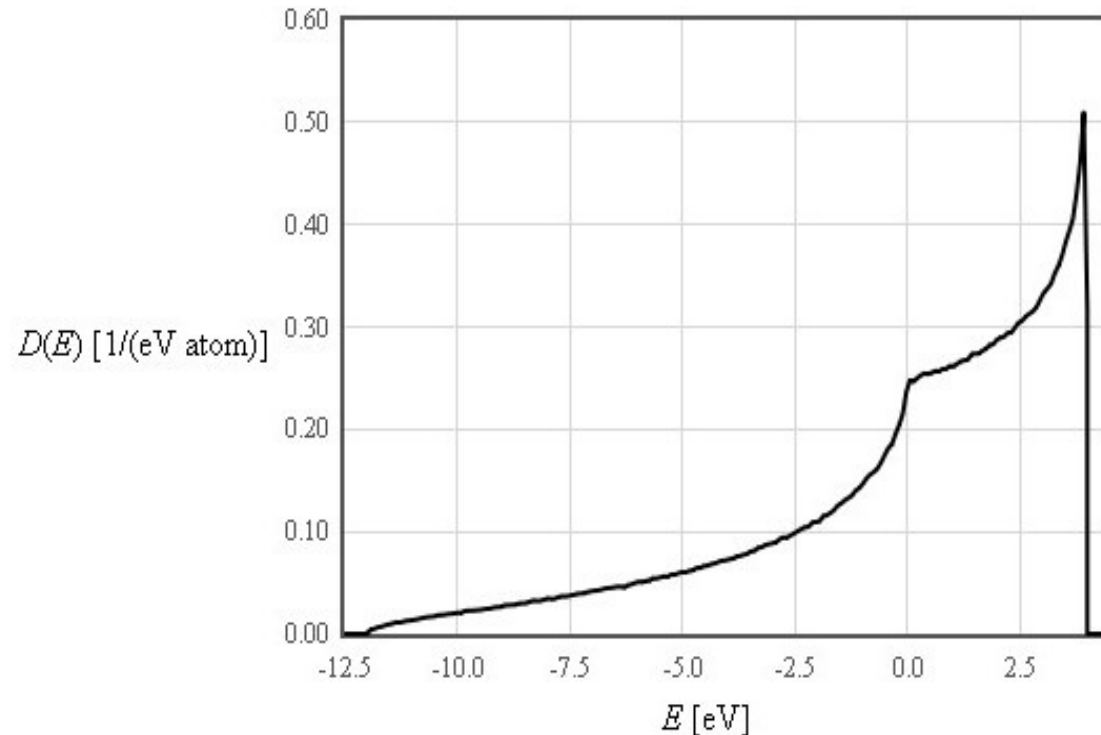
$$E = \varepsilon - t \sum_{lmn} e^{i\vec{k} \cdot \vec{\rho}_{lmn}}$$

$$E = \varepsilon - 4t \left( \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \right)$$



# Density of states (fcc)

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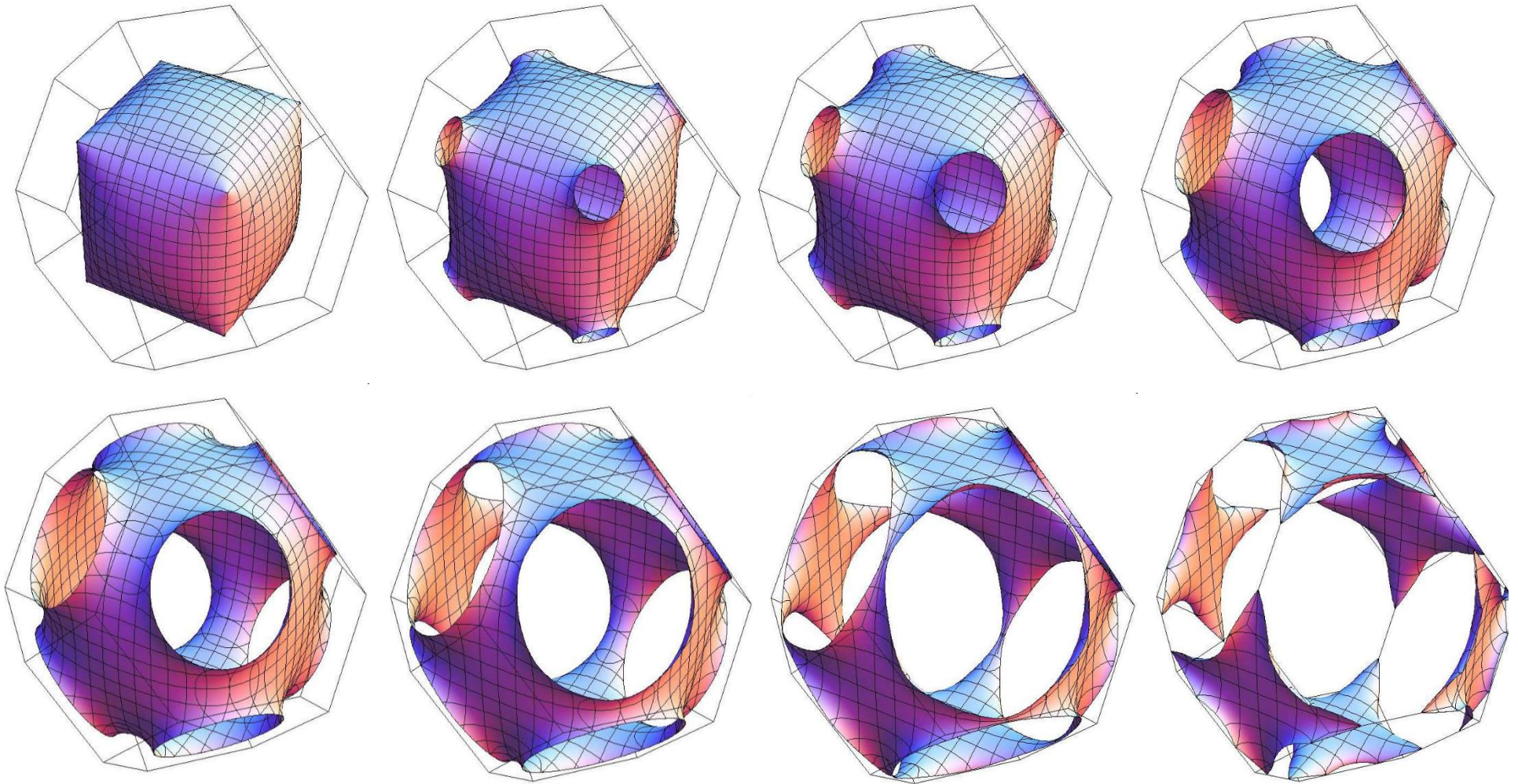


Calculate the energy for every allowed  $k$  in the Brillouin zone

$$E = \varepsilon - 4t \left( \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{k_z a}{2}\right) + \cos\left(\frac{k_y a}{2}\right) \cos\left(\frac{k_z a}{2}\right) \right)$$

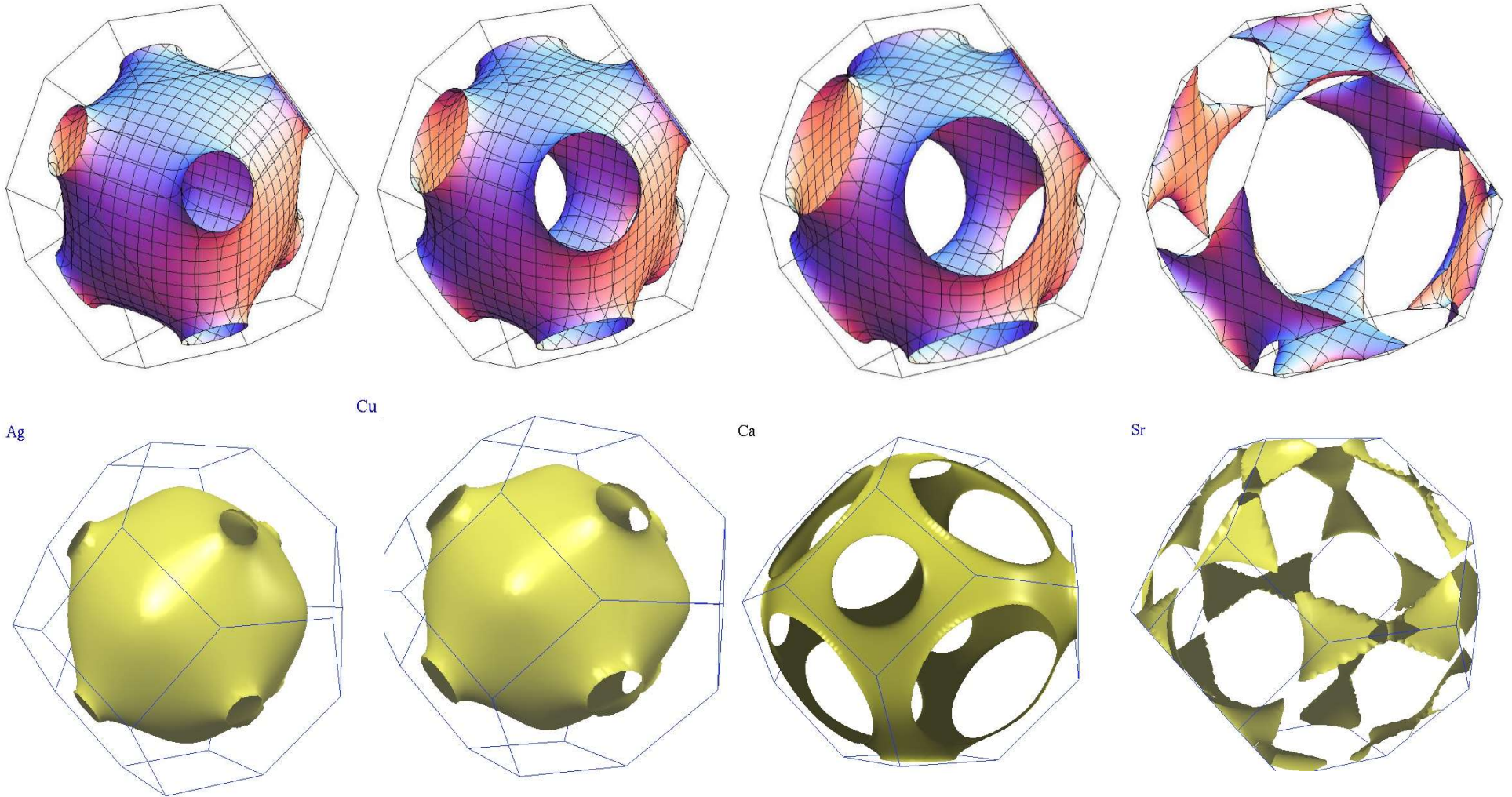
<http://lamp.tu-graz.ac.at/~hadley/ss1/bands/tbtable/tbtable.html>

# Tight binding, fcc



Christian Gruber, 2008

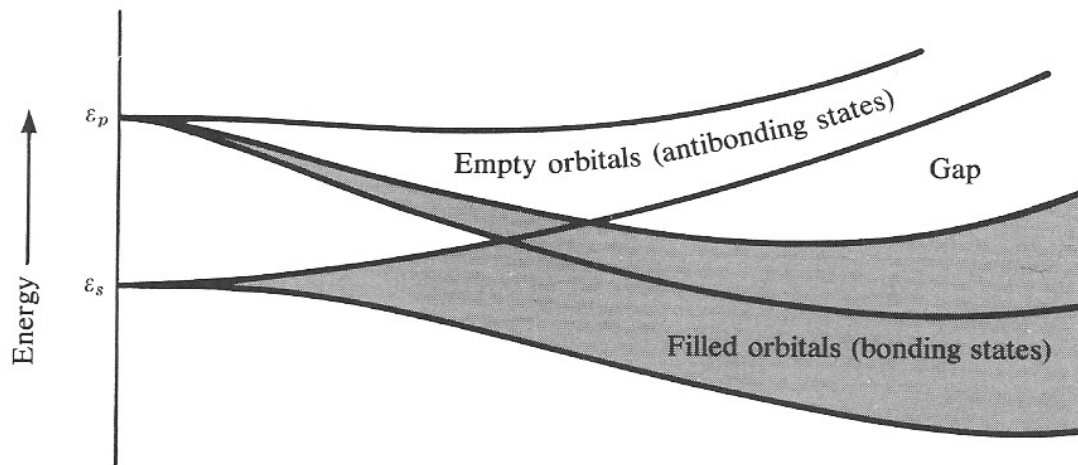
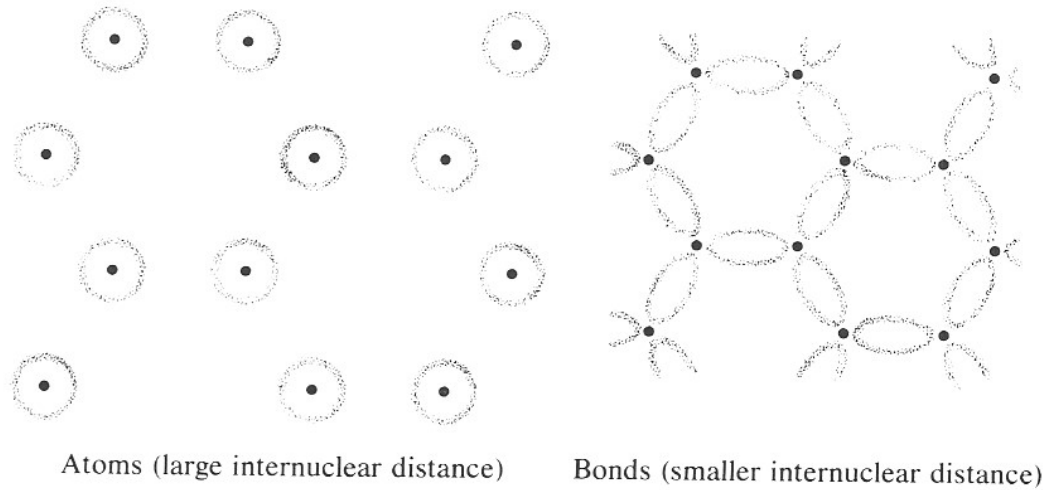
# Tight binding, fcc



<http://www.phys.ufl.edu/fermisurface/>

	Linear Chain	2-D square lattice	
relation	$E = \varepsilon - 2t \cos(k_x a)$ <p>Calculate E(k)</p>	$E = \varepsilon - 2t (\cos(k_x a) + \cos(k_y a))$ <p>Calculate E(k)</p>	$E = \varepsilon - 2t$ <p>Gamma</p>
of states	$D(k) = \frac{2}{\pi}$	$D(k) = \frac{k}{\pi} \text{ m}^{-1}$	
of states	$D(E) = \frac{1}{at \sqrt{1 - \left(\frac{\varepsilon - E}{2t}\right)^2}} \text{ J}^{-1} \text{ m}^{-1}$		

# Tight binding

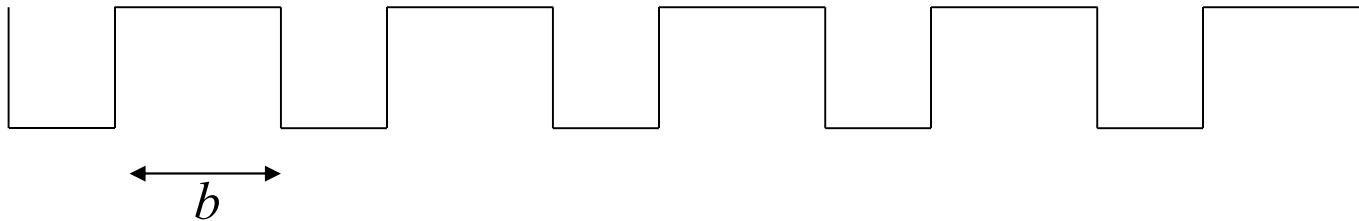
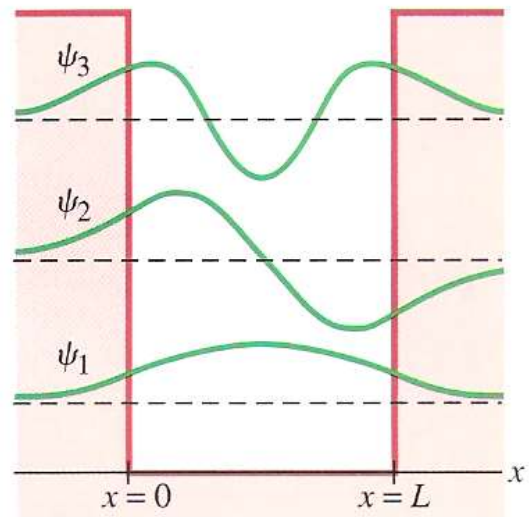


Harrison, Electronic Structure, Freeman 1980

# Tight binding 1-d

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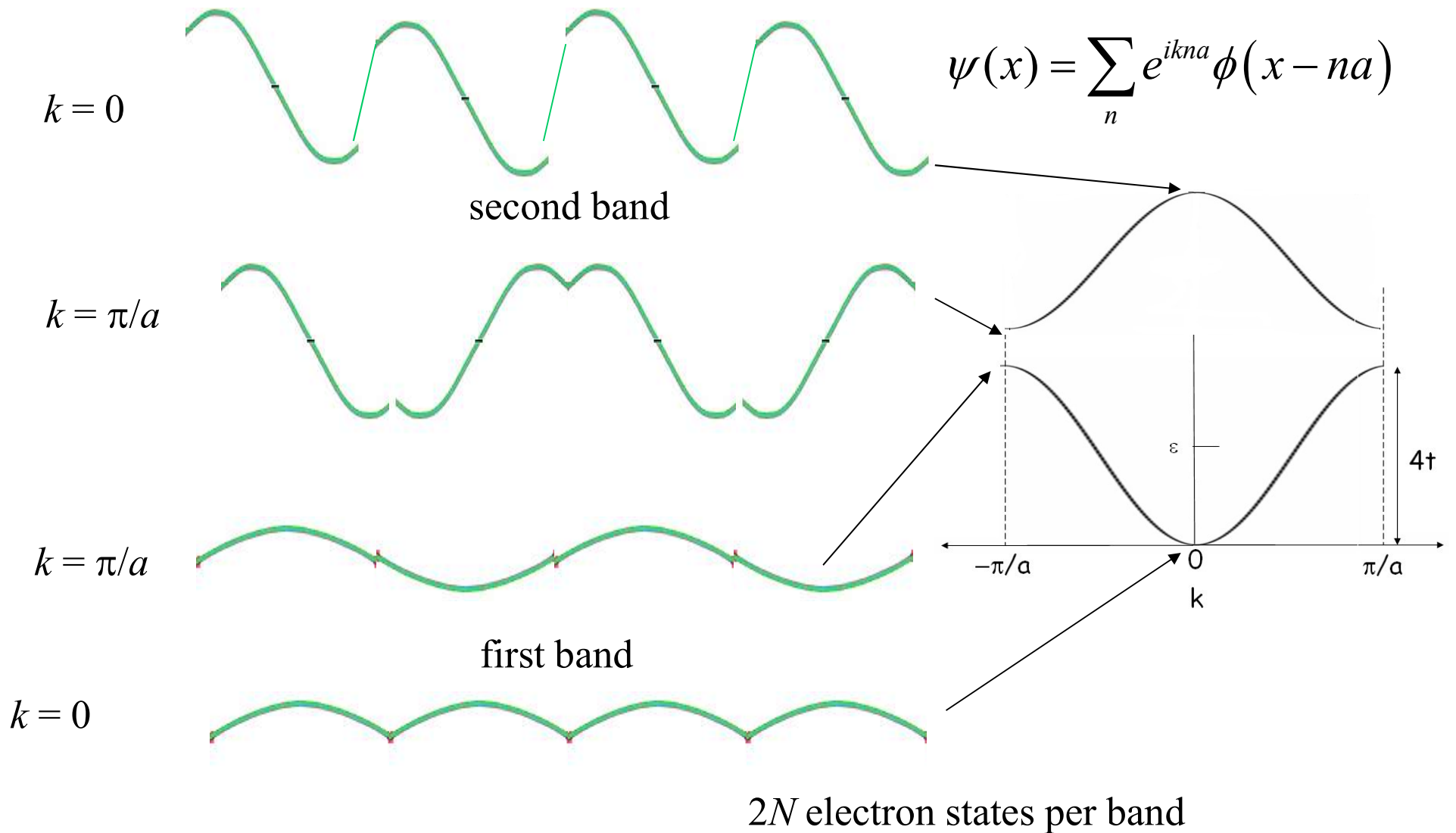
Finite potential well



Tight binding fails when the electrons aren't mostly localized.



# Tight binding 1-d



# 2 electron states/band

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The  $N$  atomic orbitals in the tight binding wave function can hold  $2N$  electrons

$N$  atoms in the crystal

$N$  translational symmetries

$N$  allowed  $k$  states in the first Brillouin zone

these  $k$ 's can be put in one-to-one correspondence with the eigenvalues of the translation operator

$N$  solutions to the Schrödinger equation of Bloch form labeled by  $k$

$2N$  electron states in the first Brillouin zone

$2N$  electrons per band

# 2N states per Brillouin zone

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A crystal  $L \times L \times L$  has  $N = \frac{L^3}{a^3}$  unit cells.

The first Brillouin zone contains  $N = \frac{\left(\frac{2\pi}{a}\right)^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{L^3}{a^3}$   $k$  points.

There are  $N$  translational symmetries.

Each  $k$  state can hold 2 electrons (spin).

There are  $2N$  per Brillouin zone.