

Electronic structure of solids

Eigenvalue equation:

$$\hat{A}f(x) = af(x)$$

KNOWN: \hat{A} is an operator.

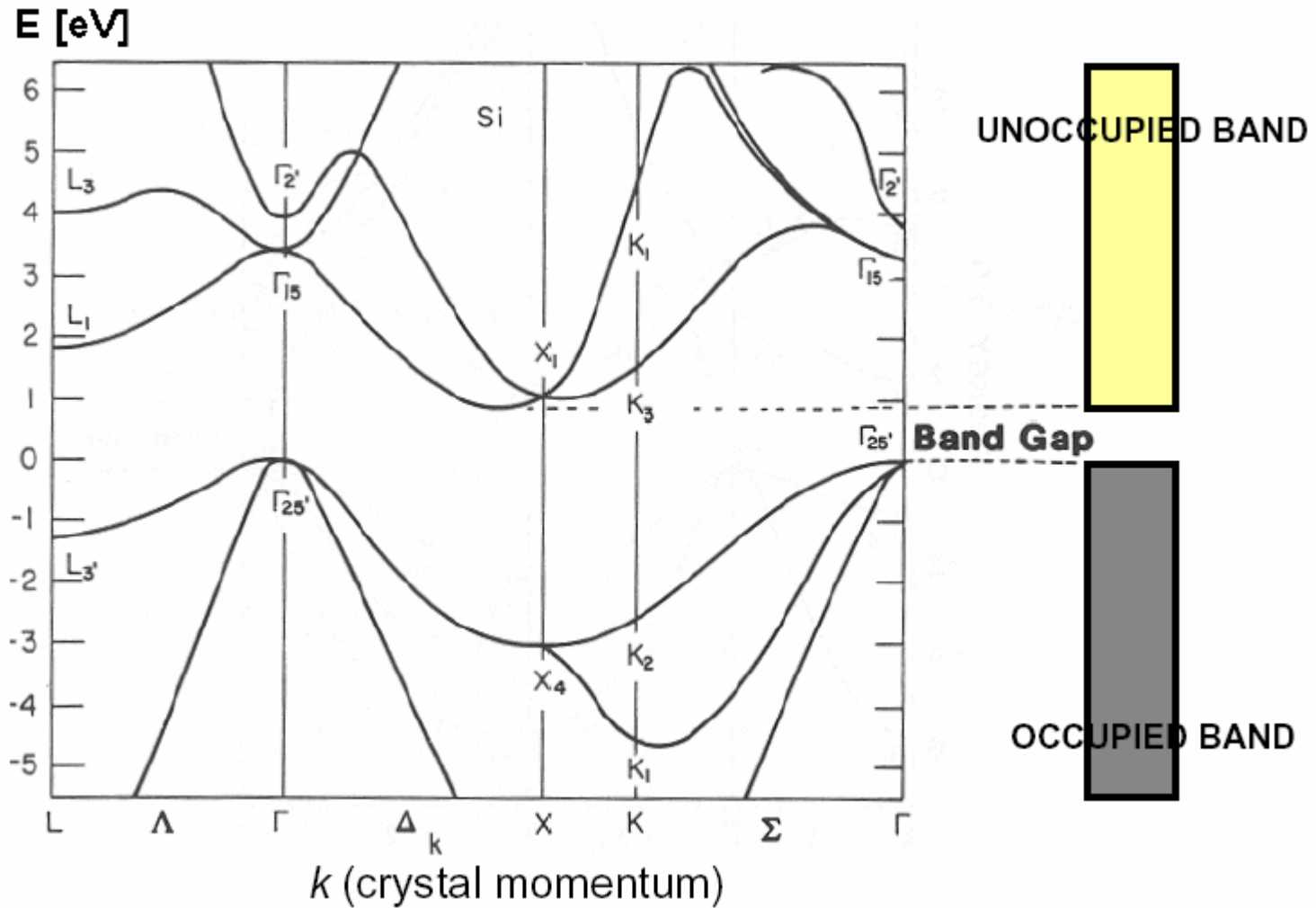
UNKNOWN:

$f(x)$ is a function (and a vector), an 'eigenfunction' of \hat{A} ;

a is a number (scalar), the 'eigenvalue'.

Acknowledgement: These slides have used materials from the following link:
<http://www.tyndall.ie/research/computational-modelling-group/cm4107/>

Problem....



How do we approach the problem?



PE operator $V = ?$ to describe system, boundary conditions

KE operator $T = -(\hbar^2/2m) d^2/dx^2$, where m is mass and $\hbar = h/2\pi$

Hamiltonian $H = T+V$

Time-independent Schrödinger equation, $H\Psi = E \Psi$

Suggest a general solution $\Psi(x)$

Solve for E

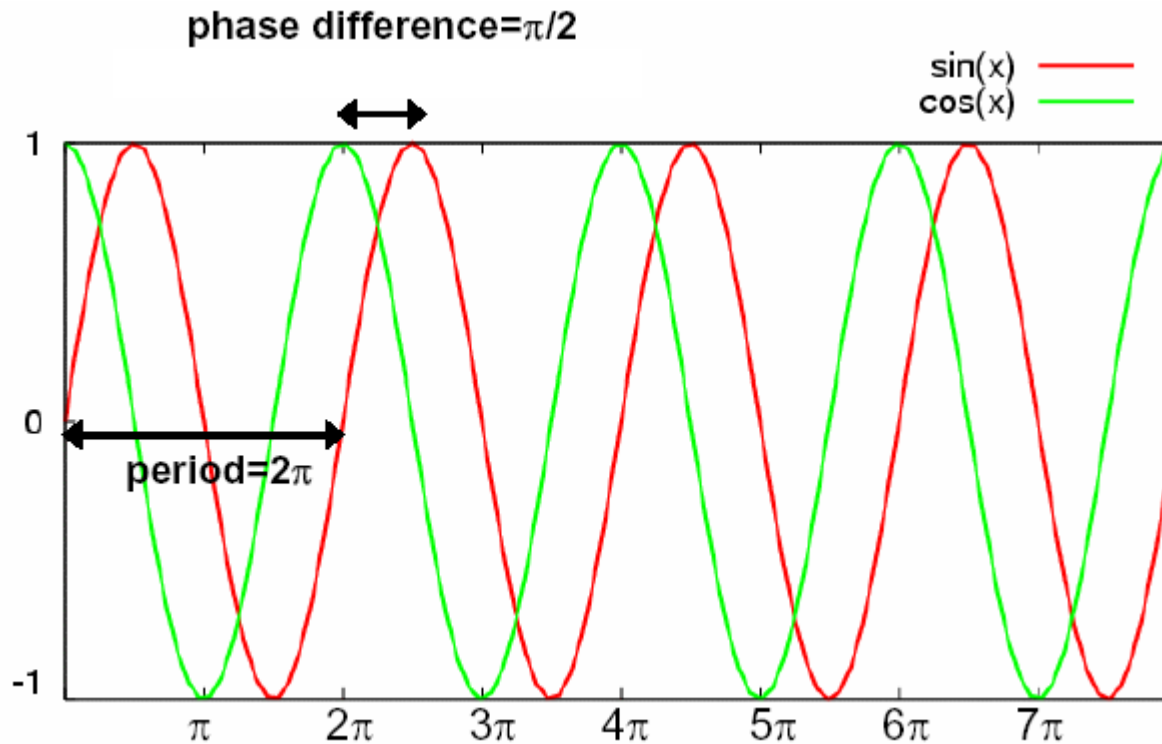
Apply boundary conditions, get quantum number -- n

Specific set of solutions $\Psi_n(x), E_n$

$e^{ix} = \exp(ix) = \cos(x) + i \sin(x) \dots$ wavelength = 2π
phase difference = $\pi/2$ between sin and cos functions

For other functions

$e^{ikx} = \exp(ikx) = \cos(kx) + i \sin(kx) \dots$ Wavelength = $2\pi/k$



Wavefunction for a free electron

Potential energy, $V(x) = 0$ everywhere

Kinetic energy, $T = -(\hbar^2/2m)d^2/dx^2$

$$H = T + V$$

Schrödinger equation, $H\Psi = E\Psi$

Solutions:

$\Psi_k(x) = [1/\sqrt{a}] \cdot \exp(ikx) = [1/\sqrt{a}] [\cos(kx) + i\sin(kx)]$ are plane waves

k is the quantum number; any value of k is possible for the free electron.

$E_k = \hbar^2 k^2 / 2m$ is kinetic, also the total energy, as $V = 0$.

Monochromatic: wavelength = $2\pi/k$

Precisely defined momentum, $p_x = \hbar k$ and $\Delta p_x = 0$

$p_y = p_z = 0$, $\Delta p_y = \Delta p_z = 0$

Totally delocalised position: $\Psi(x)\Psi^*(x) = 1/a = \text{constant over } x$

ie. $\Delta x = \infty$

But Heisenberg uncertainty principle demands, $\Delta p_x \cdot \Delta x \geq \hbar/2$

Real beams of free electrons are somewhat localised ($\Delta x \neq \infty$)

It can be represented as a wave packet, with a distribution of momenta ($\Delta p_x > 0$).

Question:

Is free electron a good approximation for the electrons in a crystalline solid?

Hückel Theory

Aim: A model for π systems such as C_nH_m

1. Hückel theory is wavefunction-based.
MO's are formed by LCAO

Use the $\phi=C:2p_z$ as the atomic orbital 'basis'

n ϕ 's are used

LCAO to form n MOs ψ_j labeled with $j=0..(n-1)$:

$$\Psi_j = N \cdot \sum_m c_{jm} \phi_m$$

sum runs over $m = 1$ to n , c_{jm} are coefficients to be determined and N is a normalization constant.

2. Hückel theory is semi-empirical.

We evaluate the electronic energy of a system in terms of two integrals.

$$H_{ii} = \int \varphi_i H \varphi_i d\tau$$

$$H_{ij} = \int \varphi_i H \varphi_j d\tau$$

The values of these integrals are used by fitting. Use experimental data or use higher levels of theory ("semi-empirical" method).

For $\varphi = \text{C:}2p_z$ we use the AO energy:

$$\alpha = E(\text{C:}2p_z) = H_{ii} = \text{coulomb integral} = \int \varphi_1 H \varphi_1 d\tau = 1050 \text{ kJ/mol} > 0$$

Interaction between two AOs:

$$\beta = H_{ij} = \text{exchange or overlap integral} = \int \varphi_1 H \varphi_2 d\tau = E(p_z\text{-}p_z \text{ overlap}) < 0$$

Secular determinant

$$\Phi = \sum_{n=1 \dots N} c_n f_n$$

H is known

Apply variational principle to get energy

$$\Phi = c_1 f_1 + c_2 f_2$$

$$\begin{aligned} \int \Phi H \Phi d\tau &= \int (c_1 f_1 + c_2 f_2) H (c_1 f_1 + c_2 f_2) d\tau \\ &= c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22} \end{aligned}$$

$$H_{ij} = H_{ji}$$

$$\int \Phi^* \Phi d\tau = c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}$$

$$S_{ij} = S_{ji}$$

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22}}{c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}}$$

Rewrite the eq.

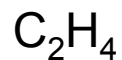
Differentiate w.r.t c_1 and c_2

$$\partial E / \partial c_1 = 0$$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

Secular determinant.

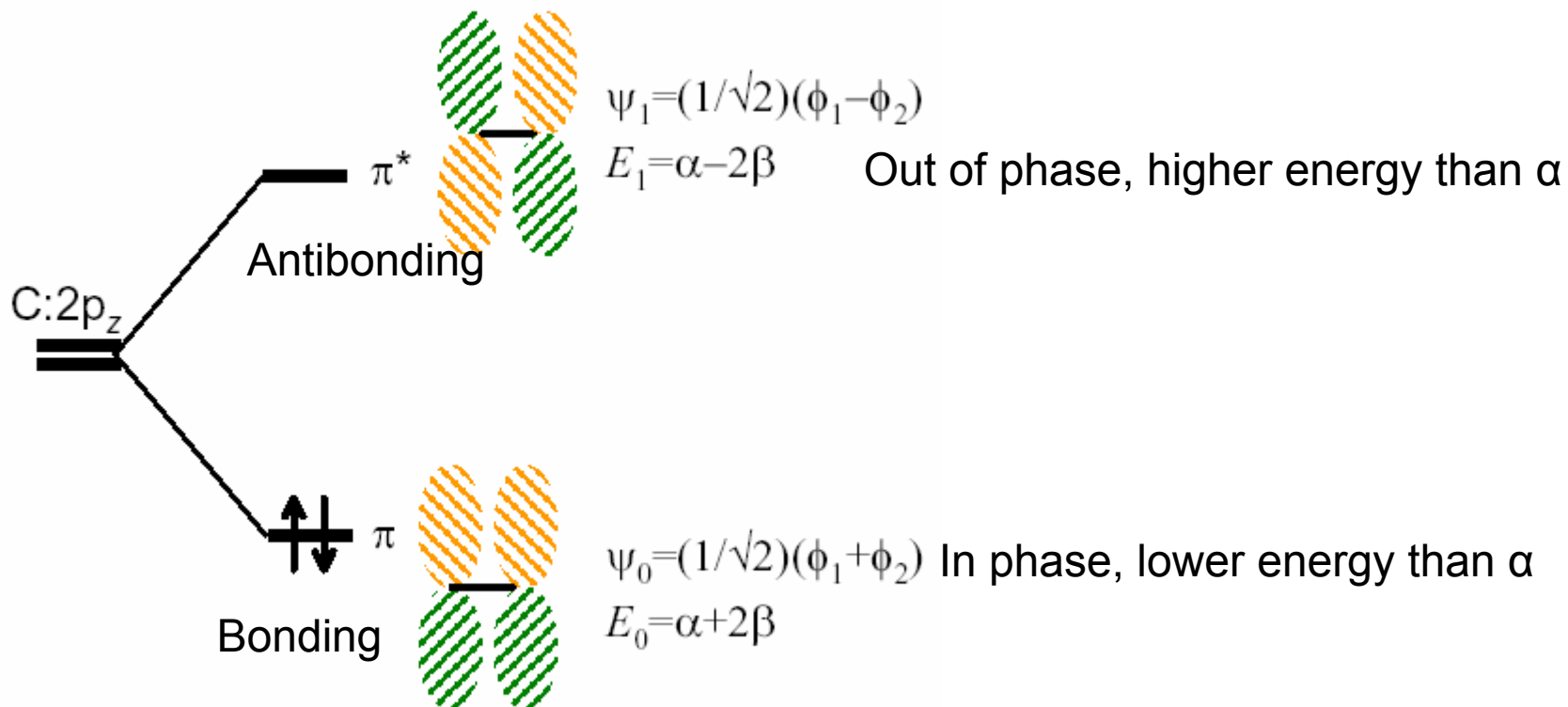
$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$



C: $2s+2p_x+2p_y = sp^2 \rightarrow$ forms σ skeleton for C-C and C-H

C: $2p_z \rightarrow$ form C-C π

2 'free' electrons occupy the π system.



We have two atoms, two AOs (m) labeled 1 and 2
 Two MOs (j) labeled 0,1.

$$\psi_j = (1/\sqrt{2}) \sum_m \exp[i\pi j(m-1)] \cdot \varphi_m$$

$$E_j = \alpha + 2\beta \cos(\pi j)$$

Consider $j = 0$, in-phase

$$\psi_0 = (1/\sqrt{2})(\exp[0] \cdot \varphi_1 + \exp[0] \cdot \varphi_2)$$

$$= (1/\sqrt{2})(\cos[0] \cdot \varphi_1 + i\sin[0] \cdot \varphi_1 + \cos[0] \cdot \varphi_2 + i\sin[0] \cdot \varphi_2)$$

$$= (1/\sqrt{2})([1] \cdot \varphi_1 + i[0] \cdot \varphi_1 + [1] \cdot \varphi_2 + i[0] \cdot \varphi_2)$$

$$= (1/\sqrt{2})(\varphi_1 + \varphi_2)$$

$$E_0 = \alpha + 2\beta \cos(\pi j)$$

$$= \alpha + 2\beta \text{ and}$$

Consider $j=1$, out of phase

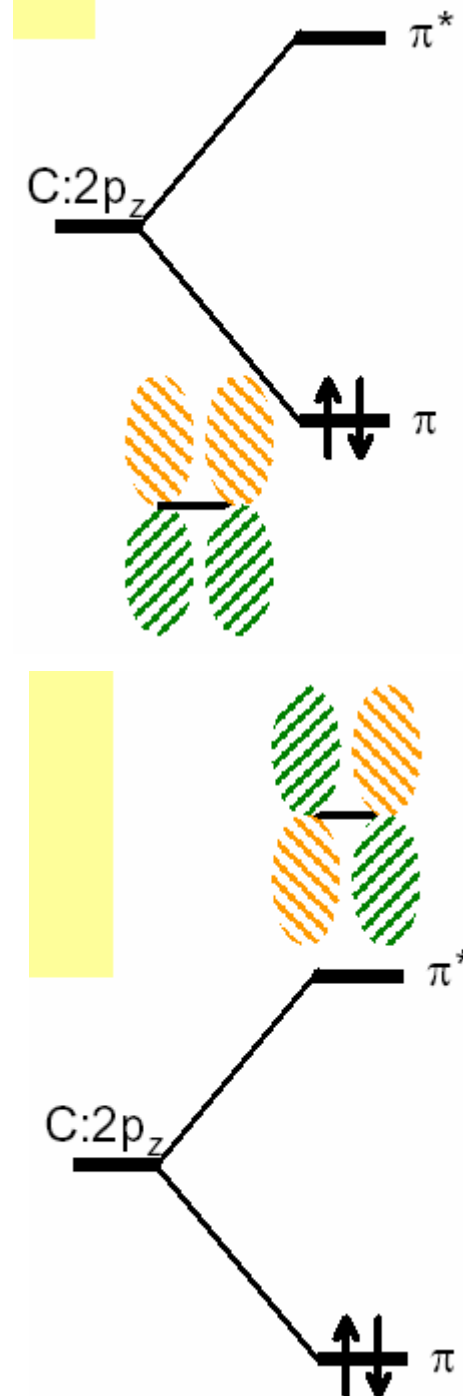
$$\psi_1 = (1/\sqrt{2})(\exp[0] \cdot \varphi_1 + \exp[i\pi] \cdot \varphi_2)$$

$$= (1/\sqrt{2})(\cos[0] \cdot \varphi_1 + i\sin[0] \cdot \varphi_1 + \cos[\pi] \cdot \varphi_2 + i\sin[\pi] \cdot \varphi_2)$$

$$= (1/\sqrt{2})([1] \cdot \varphi_1 + i[0] \cdot \varphi_1 + [-1] \cdot \varphi_2 + i[0] \cdot \varphi_2)$$

$$= (1/\sqrt{2})(\varphi_1 - \varphi_2)$$

$$E_1 = \alpha + 2\beta \cos(\pi) = \alpha - 2\beta$$



Cyclic polyenes

For a general π system of cyclic C_nH_n

There are n atomic orbitals $\varphi=C:2p_z$

n MO ψ_j labeled with $j=0..(n-1)$ formed by LCAO:

$$\psi_j = N \sum_m c_{jm} \varphi_m$$
$$\psi_j = (1/\sqrt{n}) \sum_{m=1..n} \exp[i(m-1) \cdot \mathbf{phase-angle}] \cdot \varphi_m$$

$$E_j = \alpha + 2\beta \cos(\mathbf{phase-angle})$$

where $\mathbf{phase-angle} = 2\pi j/n$

Huckel theory: waverfunctions

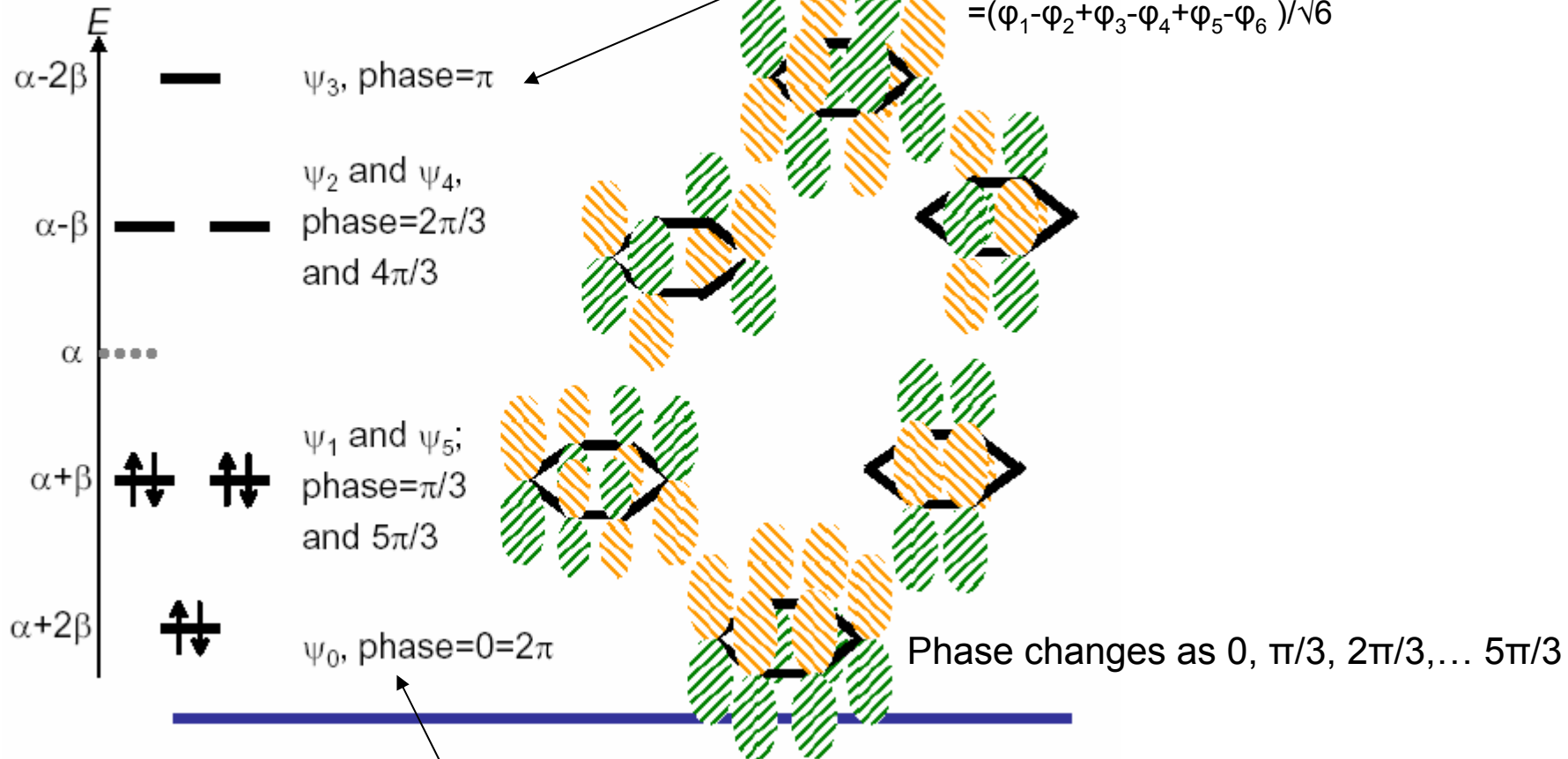
$$j=3, \psi_3, \text{ phase} = \pi$$

$$\psi_j = (1/\sqrt{6}) \sum_{m=1..6} \exp[i \cdot j(m-1) \cdot \pi/3] \cdot \phi_m, \quad j=0..5$$

$$\psi_3 = 1/\sqrt{6} \sum_{m=1..6} \exp[i\pi(m-1)] \cdot \phi_m$$

$$= 1/\sqrt{6} \sum_{m=1..6} (-1)^{m-1} \cdot \phi_m$$

$$= (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) / \sqrt{6}$$



$$\psi_j = (1/\sqrt{6}) \sum_{m=1..6} \exp[ij(m-1) \cdot \pi/3] \cdot \phi_m, \quad j = 0..5$$

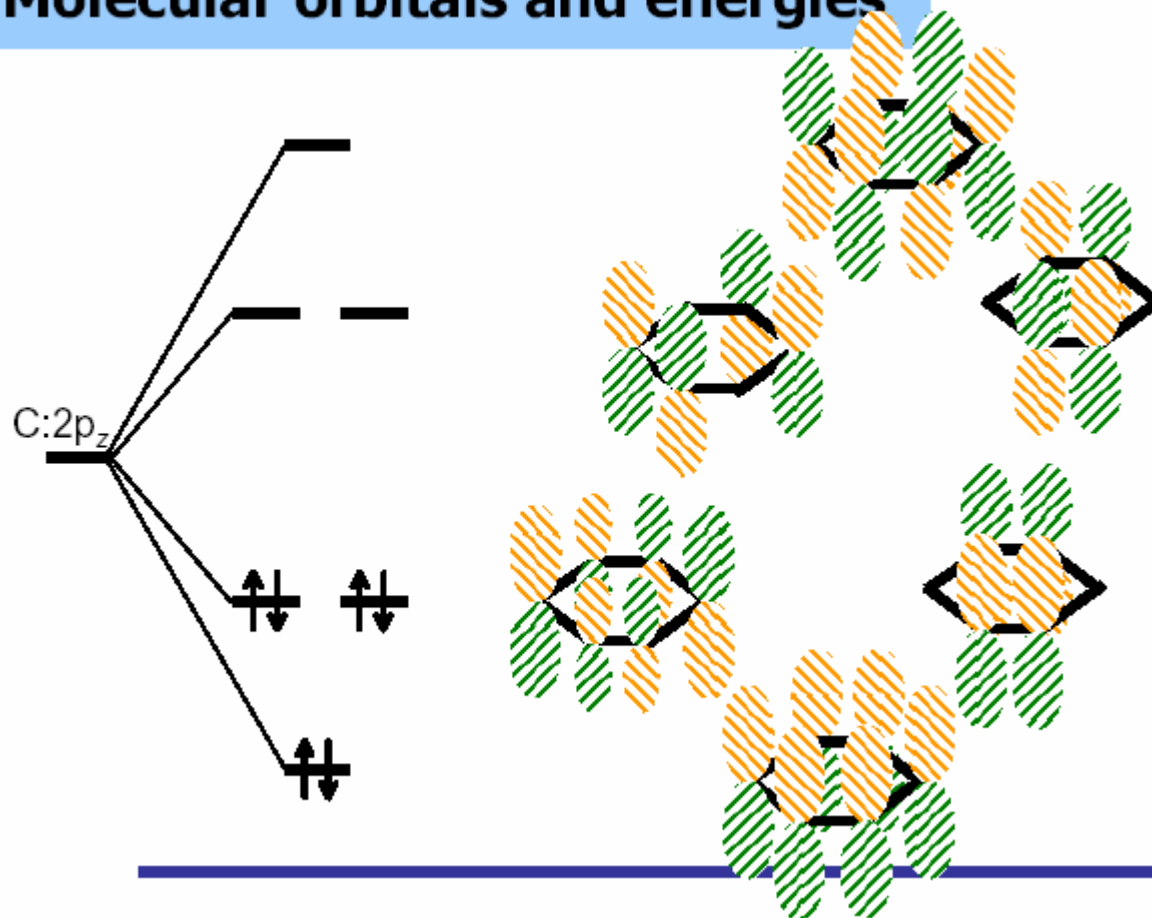
e.g. $\psi_0 = (1/\sqrt{6}) \sum_{m=1..6} \exp[i0(m-1)] \cdot \phi_m$

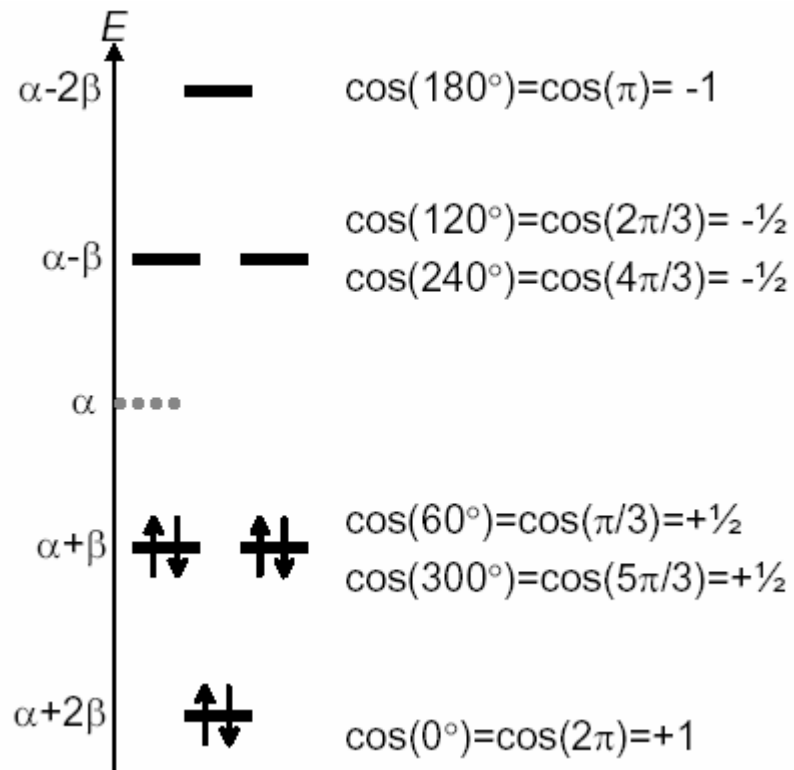
$$= (1/\sqrt{6}) \sum_{m=1..6} (+1)^{m-1} \cdot \phi_m$$

$$= (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) / \sqrt{6}$$

phase = 0

Molecular orbitals and energies





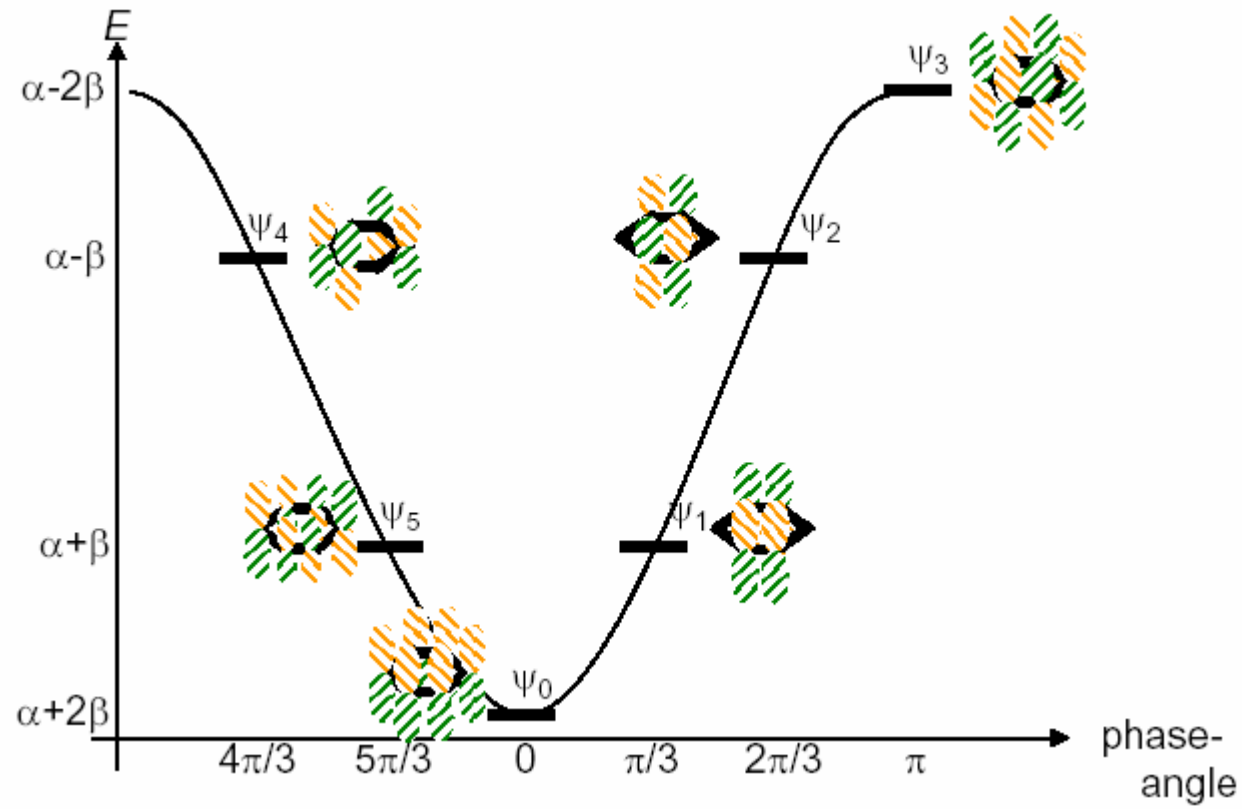
For benzene:

$$E_j = \alpha + 2\beta \cos(\text{phase-angle})$$

$$\text{phase-angle} = 2\pi j/n$$

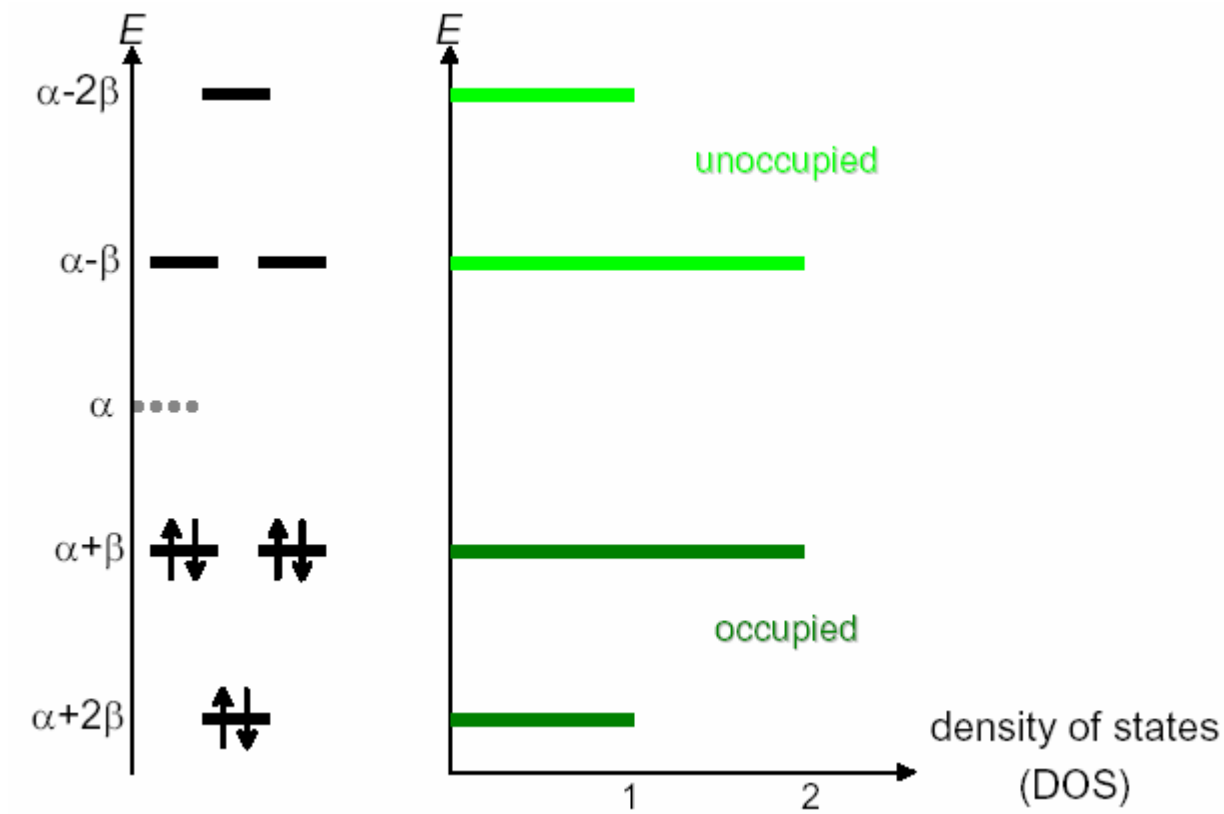
$$n = 6, j = 0..5$$

Energy as a function of phase angle



Dispersion diagram

Density of states



Total MO ψ is formed by combining

atomic wavefunctions ϕ . phase factor $\exp(i\theta)$.

Because of periodic/cyclic boundary conditions, ψ can be labeled according to phase.

MO energies depend on phase. Because phase is limited ($0..2\pi$), the energies are bounded: in the Hückel case, $\alpha+2\beta \leq E \leq \alpha-2\beta$.

α is the contribution to the energy from an individual unit ϕ .

β is due to (i) geometrical arrangement in space; (ii) closeness in energy; (iii) shape, parity of ϕ .

Why are cyclic polyenes relevant for crystalline solids?

Periodicity = cyclic symmetry or **translational symmetry**.

Consider each C atom as a 1-D unit cell of length a .

Define 'crystal momentum' $k = \text{phase}/a$.

Wavefunctions ψ_k are obtained by combining the wavefunction for a single cell with the phase factor k for the interactions between cells.

Combining energy for single cell energy (\sim Hückel α) with interaction between cells (β and phase factor k) gives a 'band' of energies $E(k)$.

Block Theorem

Solution of the Schrodinger equation for a periodic potential will be of the type,
 $\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}) \exp(\mathbf{i}\mathbf{k}\cdot\mathbf{r})$

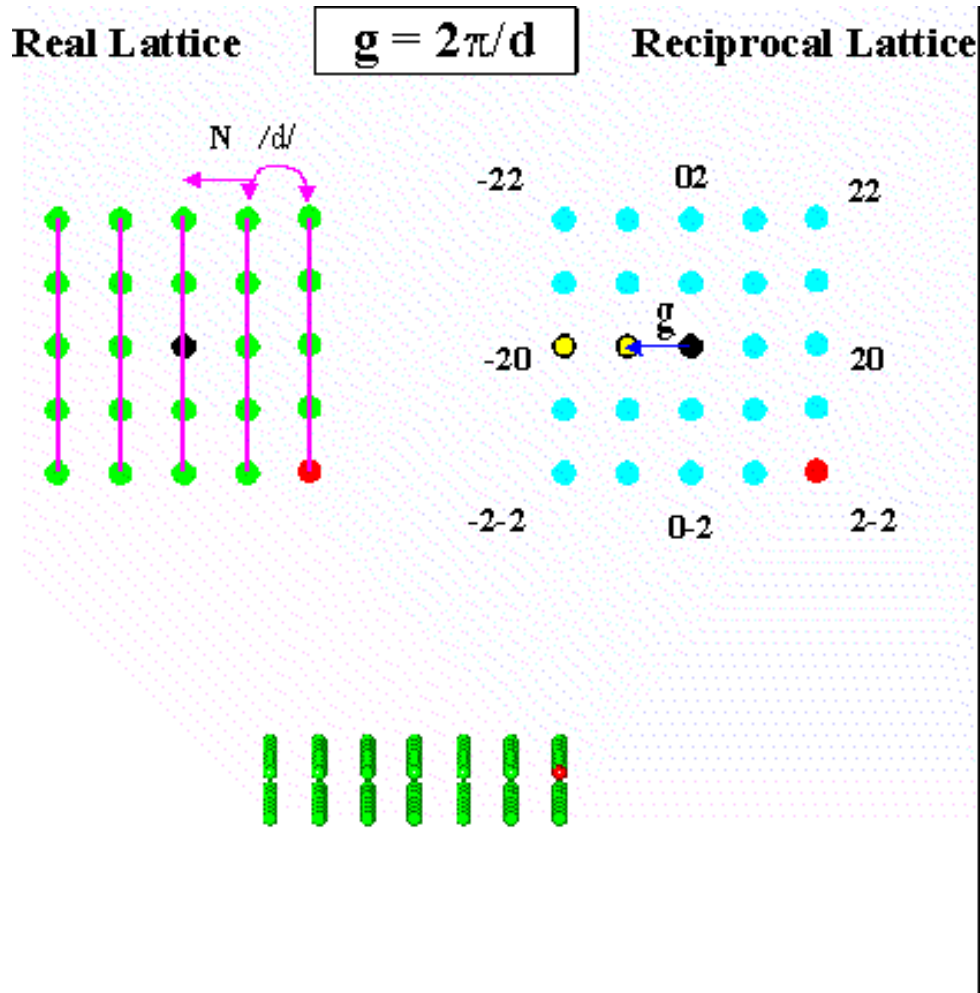
Where $u_{\mathbf{k}}(\mathbf{r})$ has the period of the crystal lattice.

$\exp(\mathbf{i}\mathbf{k}\cdot\mathbf{r})$ introduces correct phase, where $\mathbf{k}\cdot\mathbf{r} = k_x\mathbf{x}+k_y\mathbf{y}+k_z\mathbf{z}$

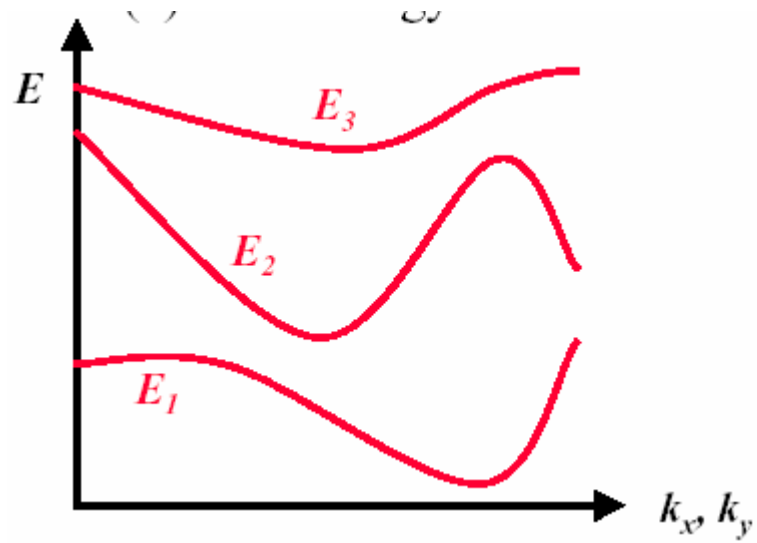
Solutions continuous at cell boundaries will be chosen.

$\Psi_{n,k}(x)$ and $E_n(k)$ in the range of $-\pi/a \leq k \leq \pi/a$ (first Brillouin zone) will be of significance

The energies spanned for each n will form a band.



- a) from this origin, lay out the normal to every family of parallel planes in the direct lattice
- b) set the length of each normal equal to 2π times the reciprocal of the interplanar spacing for its particular set of planes
- c) place a point at the end of each normal.



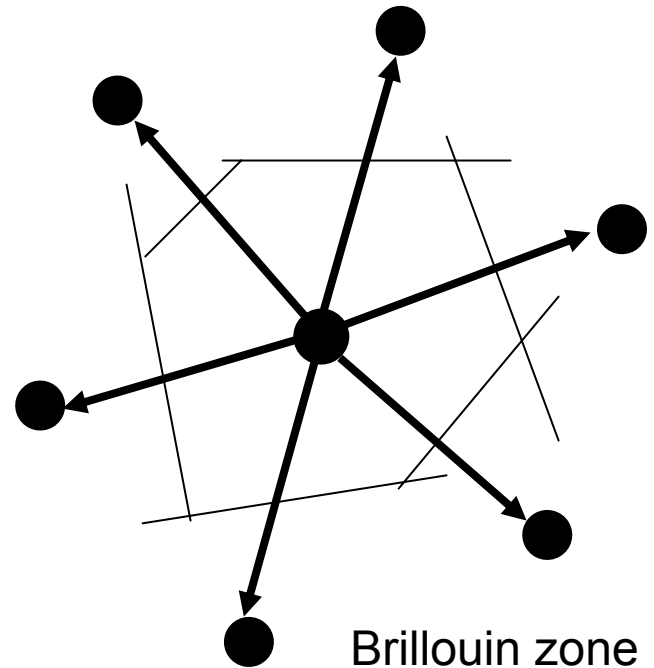
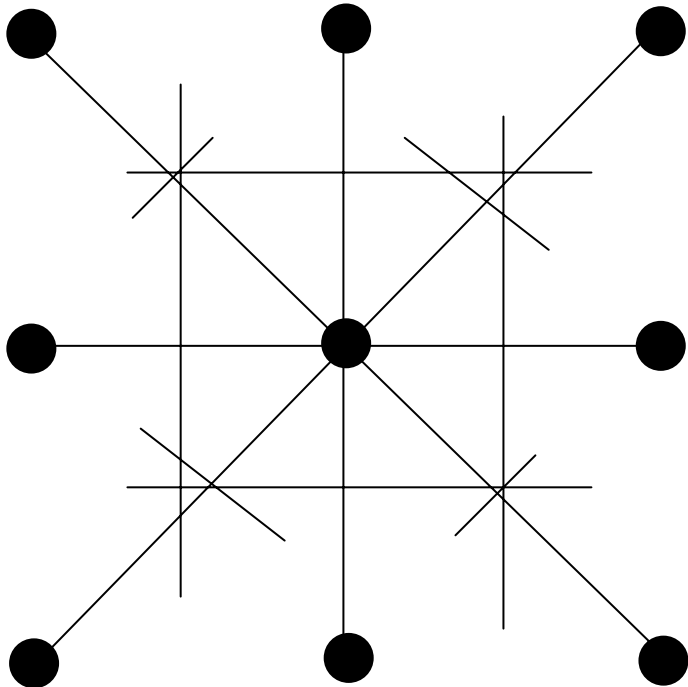
Energy bands in one dimension

Brillouin zone

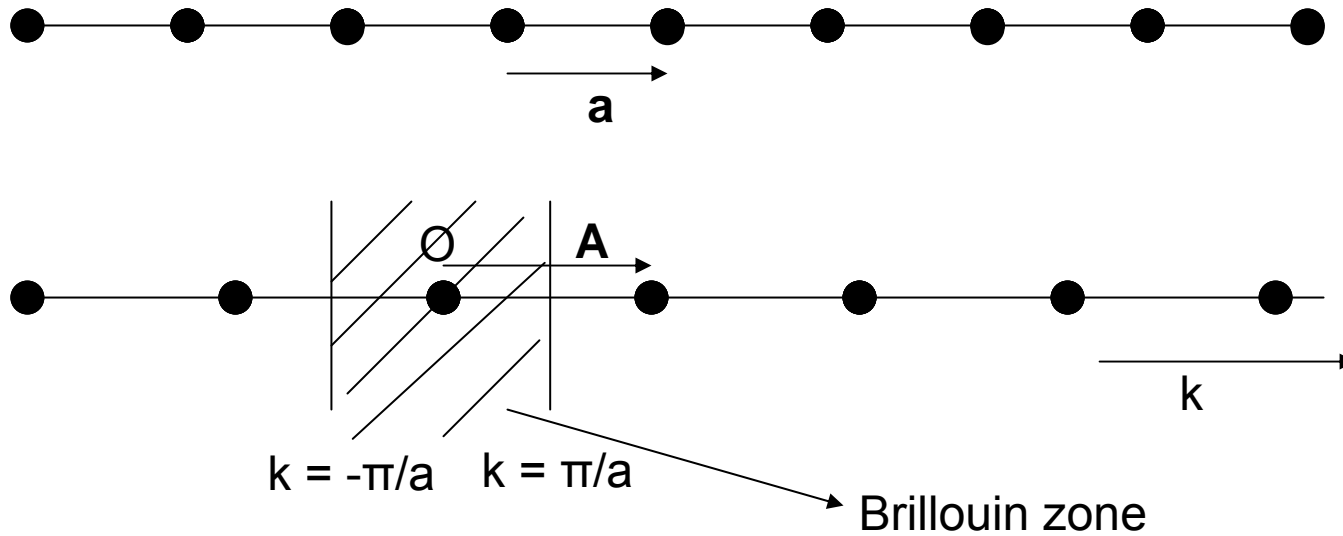
A Brillouin zone is a Wigner-Seitz cell in the reciprocal lattice.

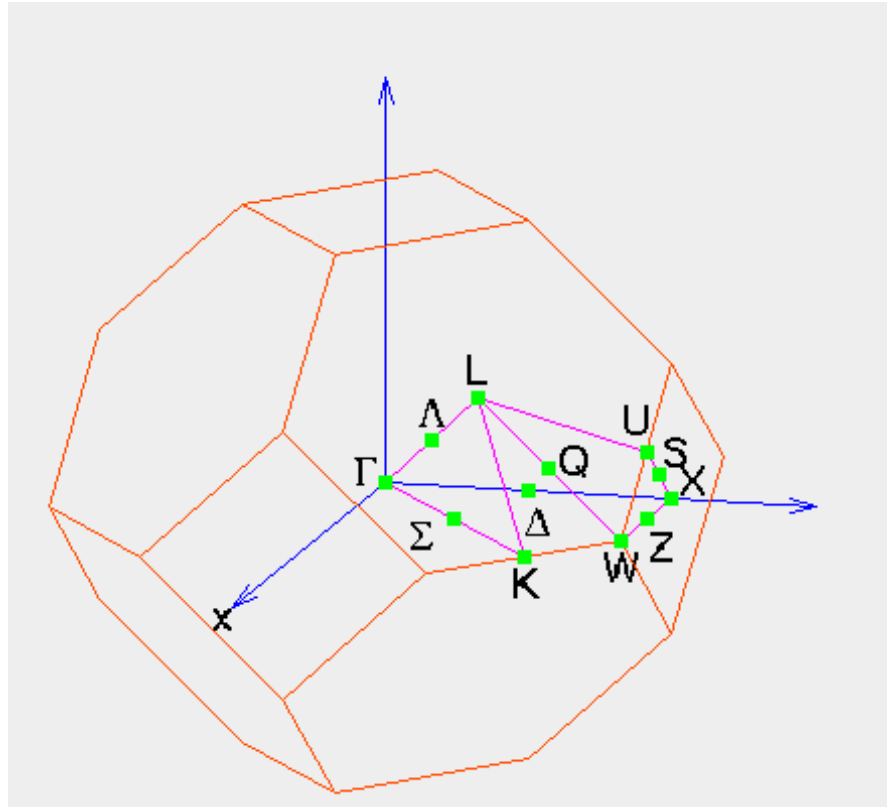
Wigner-Seitz cell

1. Draw lines to connect a lattice point to all the nearby points
2. At the midpoint of these lines draw new lines, normal to these lines
3. Smallest volume occupied this way is the Wigner-Seitz primitive cell. All available space of the crystal can be filled with this.



Crystal and reciprocal lattice in 1D





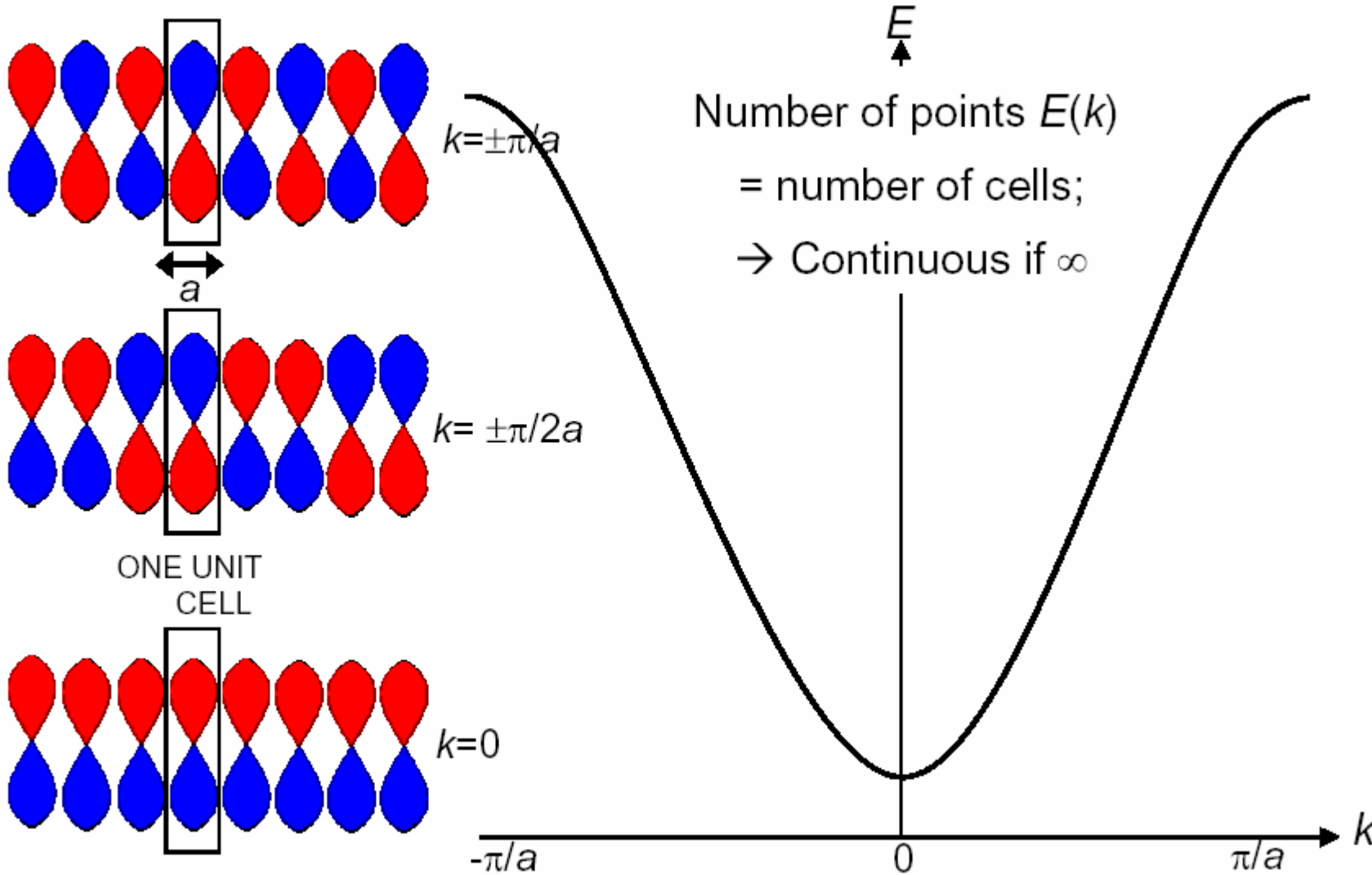
First Brillouin zone for fcc

Dispersion

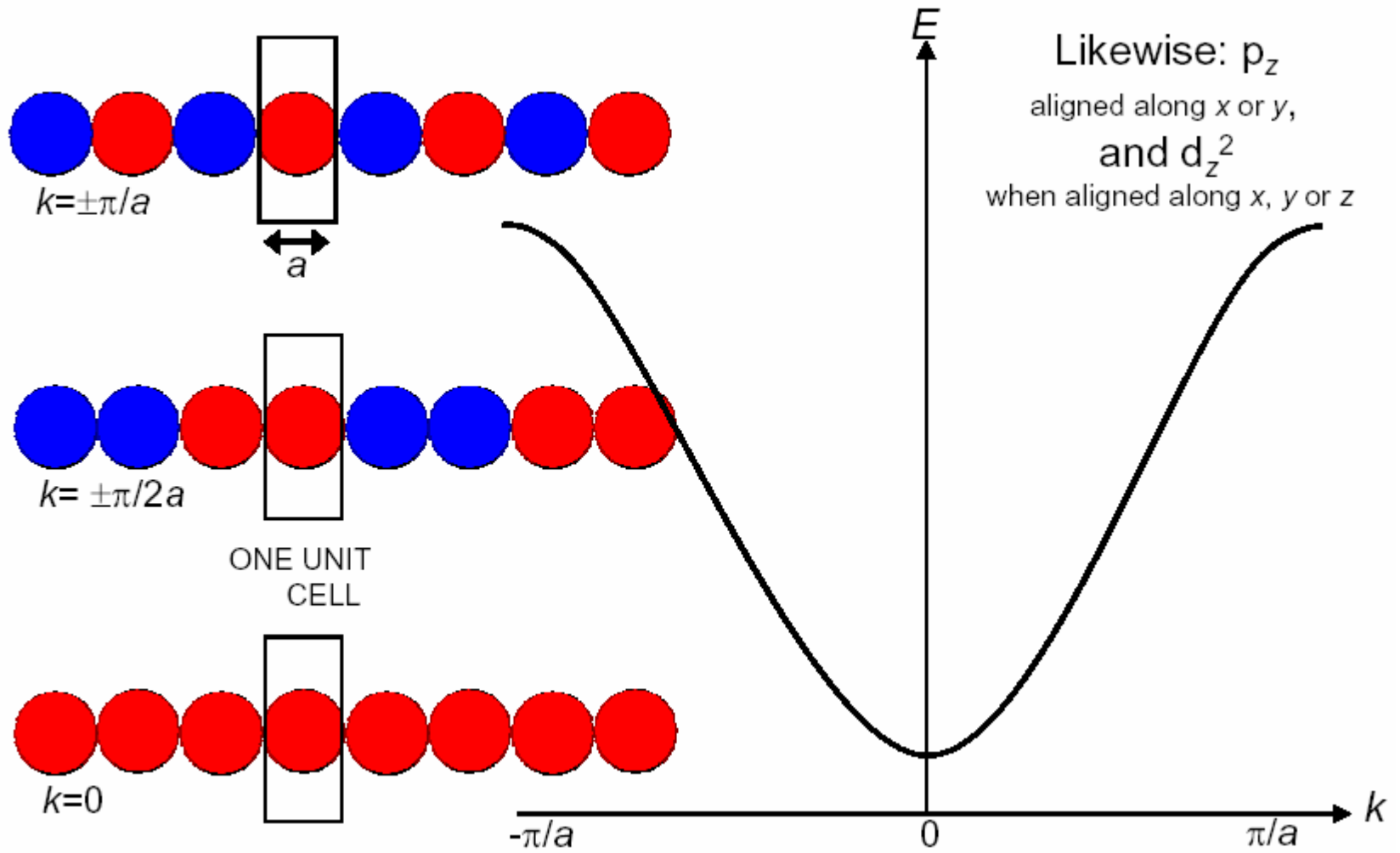
Each solution $u_n(x)$ leads to a band of energies $E_n(k)$. There exist forbidden regions of E where boundary conditions can not be fulfilled at any k ; these are 'band gaps'.

$E_n(k)$ is called the dispersion of the band.

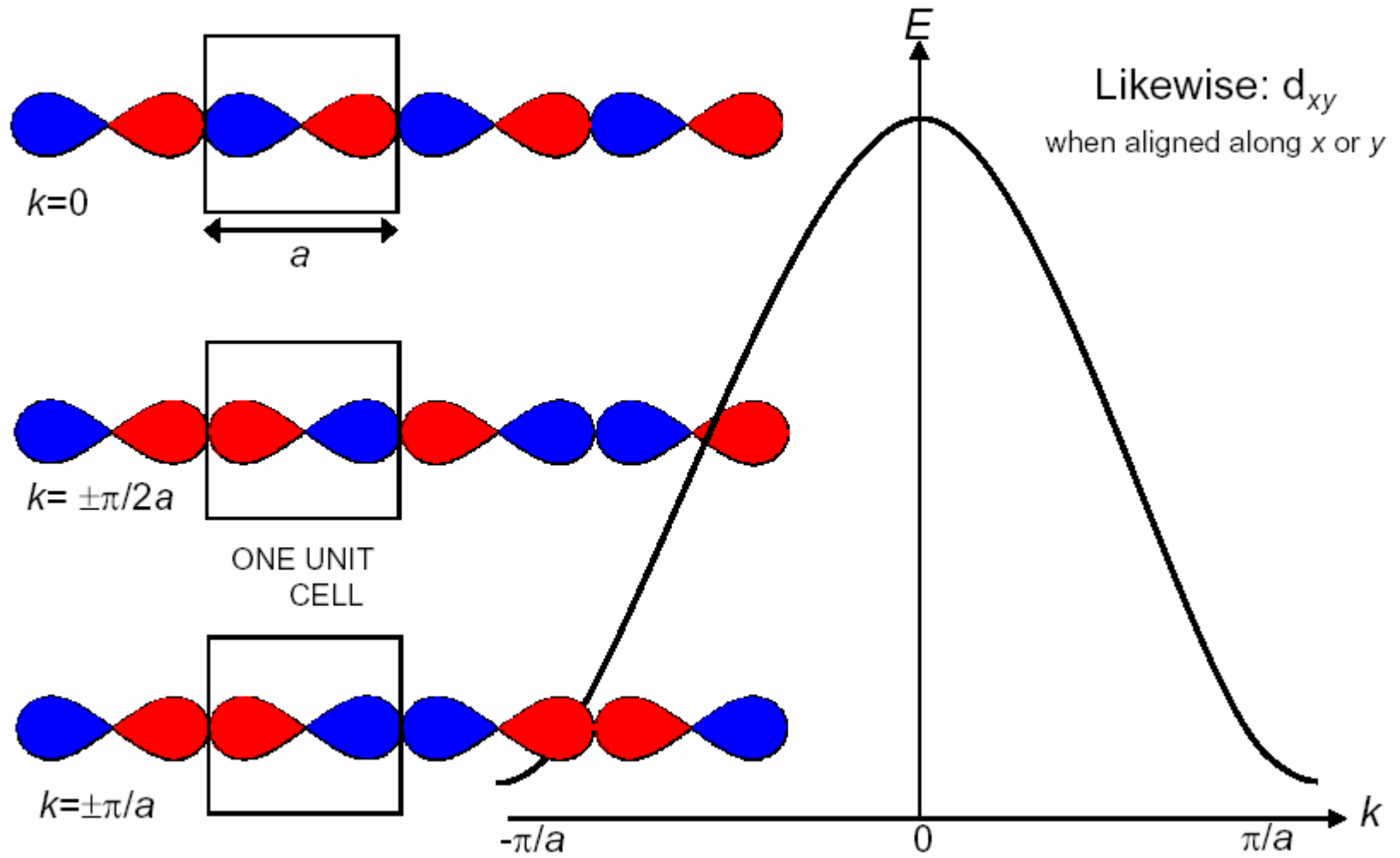
Dispersion diagram of p_z orbitals for infinite atoms arranged on x or y direction



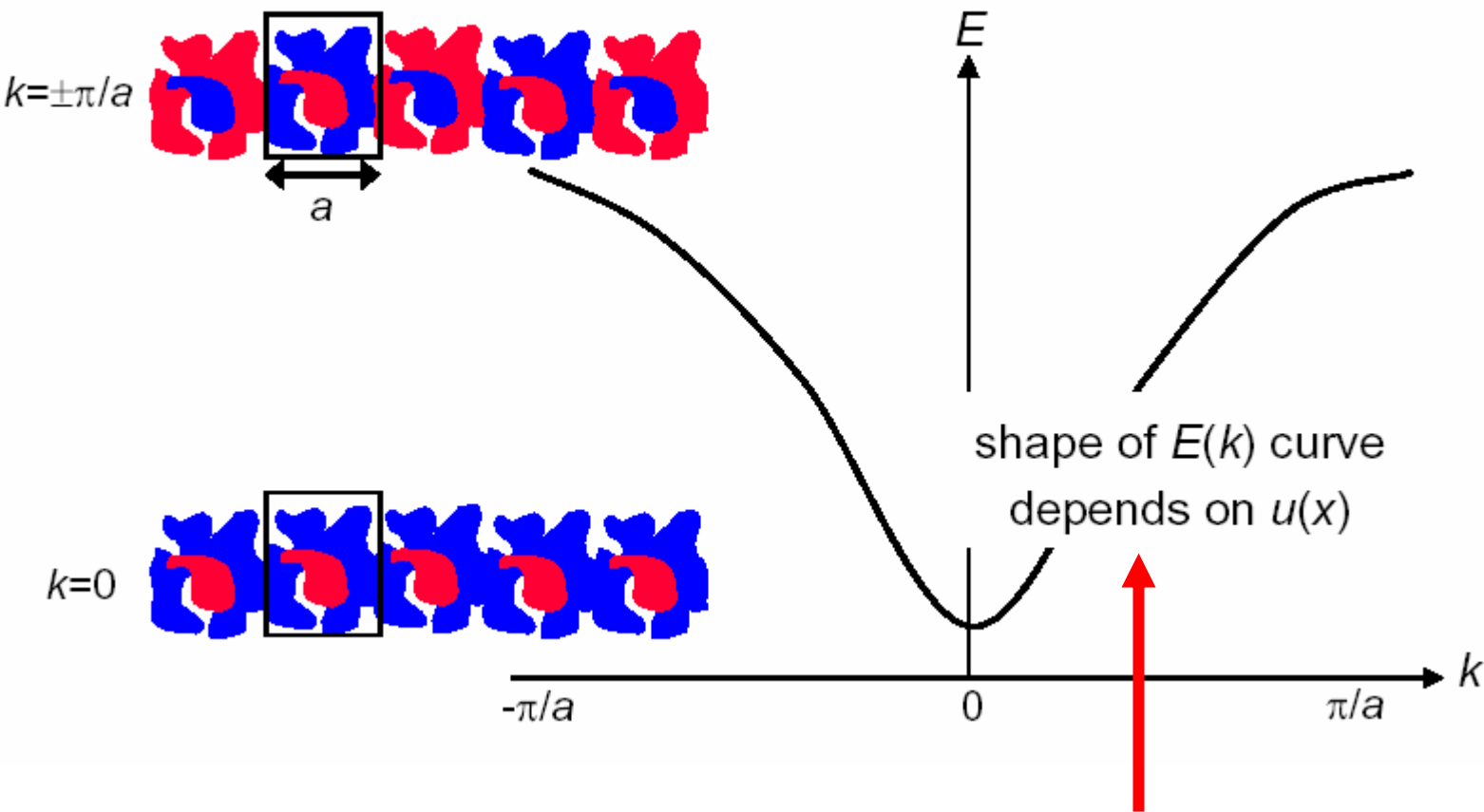
s orbitals



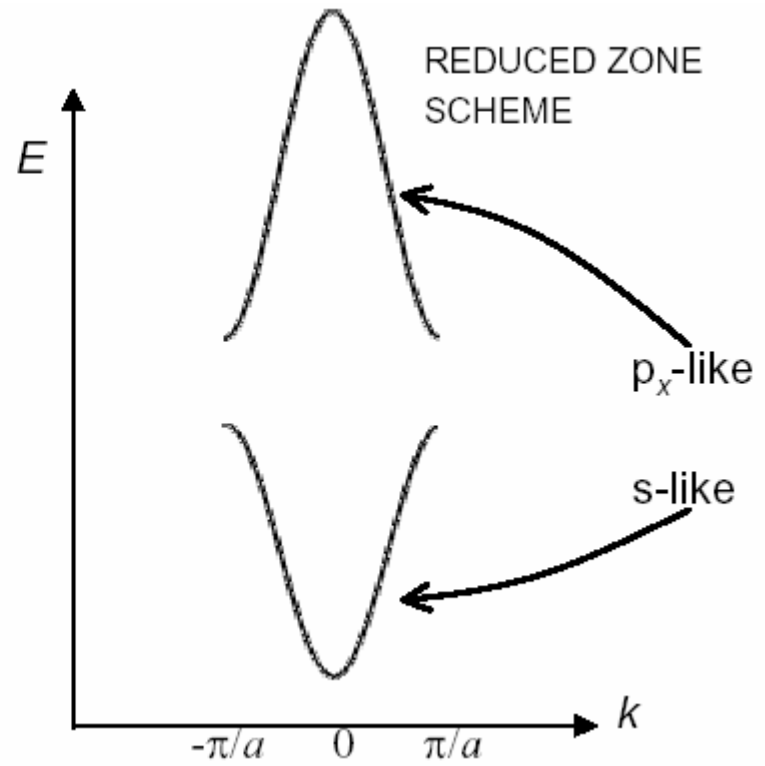
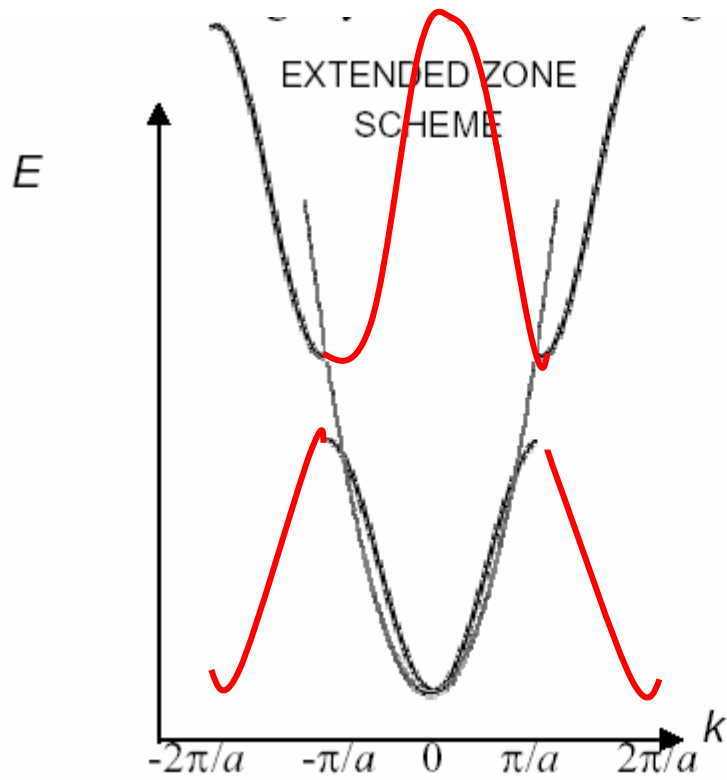
p_x orbitals

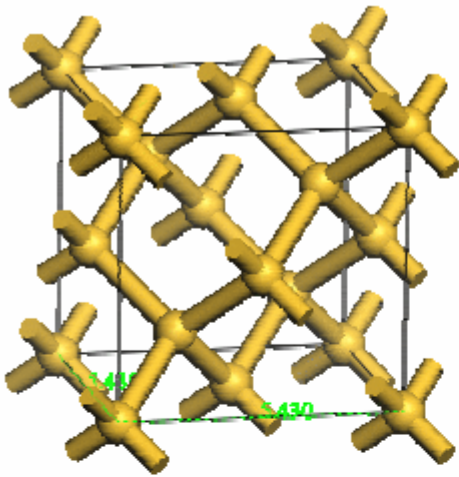


An arbitrary system



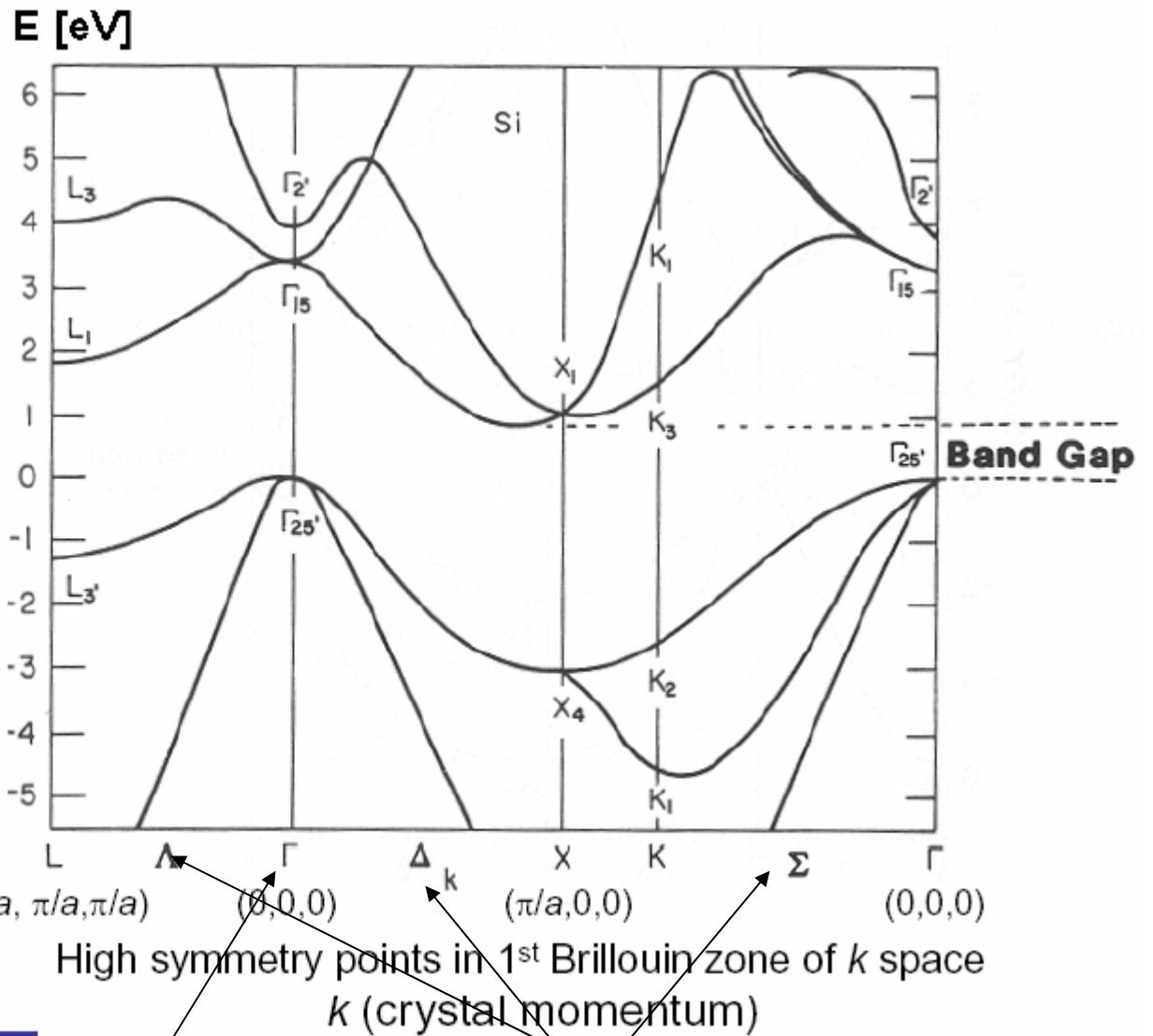
Crystal potential splits E_k





Si unit cell
(cubic $a=543$ pm,
diamond struct).

Bands can overlap
in 2-D and 3-D
(not in 1-D).



origin

Symmetry points in the Brillouin zone

References:

C. Kittel, Introduction to Solid State Physics, Wiley Eastern Ltd., New Delhi, 1993.

D.A. McQuarrie and J. D. Simon, Physical Chemistry A Molecular Approach, Viva Books Pvt. Ltd. New Delhi, 1998.