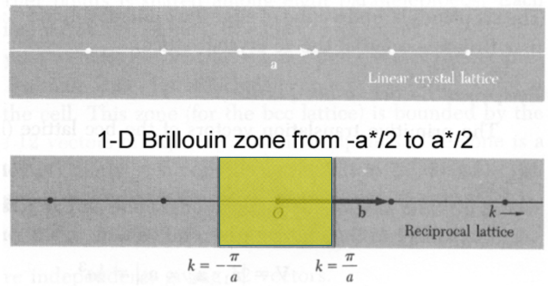
Elementary Band Theory for Extended Solids

$\psi_k = \sum_n \{(\cos kna + i\sin kna)\phi_n\}$

$$\psi(k) = \sum_n e^{inka}\phi_n$$

1-dimensional case



$a^* = 2\pi/a$

$\mathbf{-\pi/a \le k \le \pi/a}$

Consider k = 0: **zone center Γ**

$\cos(kna) = \cos(0) = 1$

$\sin(kna) = \sin(0) = 0$

$\psi = \Sigma\, \phi_n = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \ldots$

Consider k = π/a: **zone border X**

$\cos(kna) = \cos(\pi n) = (-1)^n$

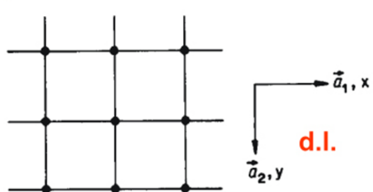
$\sin(kna) = \sin(\pi n) = 0$

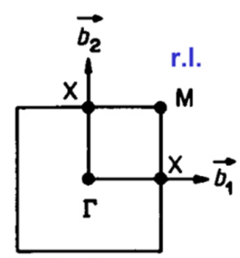
$\psi = \Sigma\, (-1)^n\phi_n = \phi_0 - \phi_1 + \phi_2 - \phi_3 + \ldots$

Elementary Band Theory for Extended Solids

More dimensions: a two-dimensional square net [**s** orbitals only (or $\mathbf{p_z}$)]

Simple Hückel





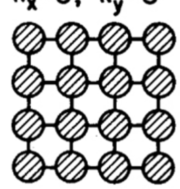
Brillouin zone

$$\psi(k) = \sum_{m,n} e^{ik_x ma + ik_y na} \cdot \phi_{m,n}$$

Consider the **crystal orbitals** at **special k points** (high symmetry)

Γ

$k_x = 0,\ k_y = 0$



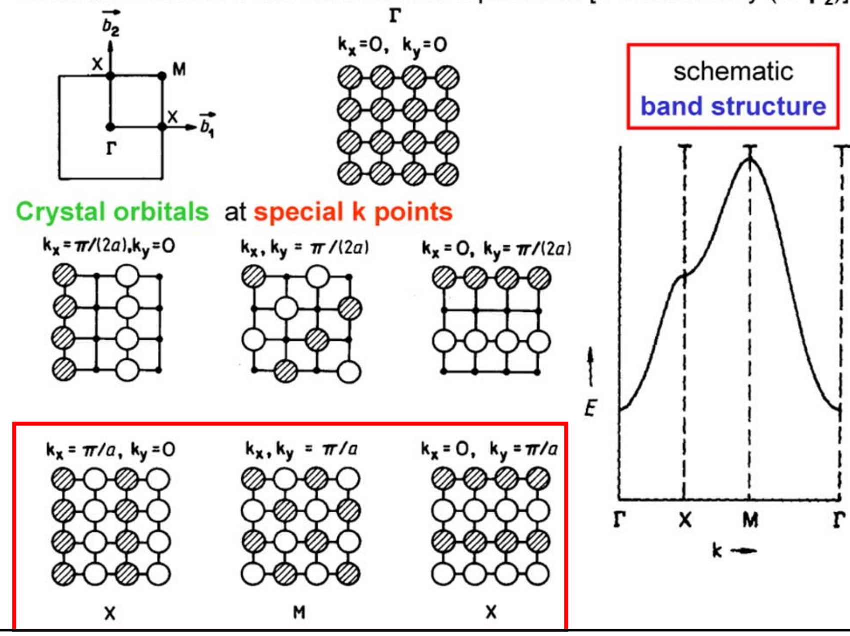
$\Gamma = (k_x=0, k_y=0, k_z=0)$ X = (π/a, 0, 0)
M = (π/a, π/a, 0) Y = (0, π/a, 0)
R = (π/a, π/a, π/a) Z = (0, 0, π/a)

zone center Γ

all a.o. in phase

Elementary Band Theory for Extended Solids

More dimensions: a two-dimensional square net [**s** orbitals only (or $\mathbf{p_z}$)]



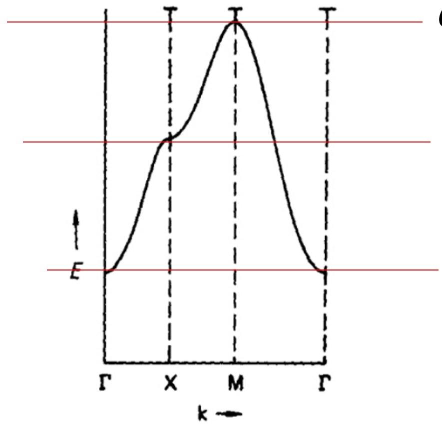
How to calculate E(k)?

$$\psi(k)=\sum_{m,n} e^{ik_x ma+ik_y na}\cdot\phi_{m,n}$$

Crystal Schrodinger Equation: $H\psi(k)=E(k)\psi(k)$

$$E(k)=\frac{<\psi^*(k)|\hat{H}|\psi(k)>}{<\psi^*(k)|\psi(k)>}$$

$$E(k)=\alpha+2\beta(\cos k_x a+\cos k_y a)$$



$\alpha - 4\beta$

$M(\frac{\pi}{a}, \frac{\pi}{a})$

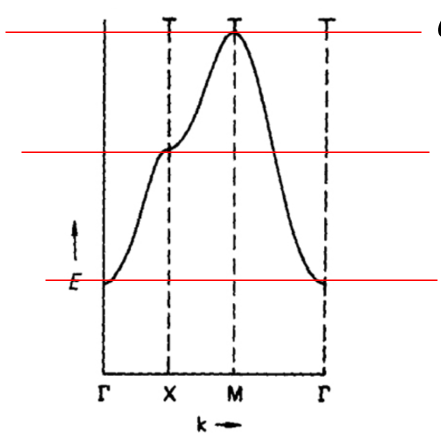
α

$\alpha + 4\beta$

$\Gamma(0,0)$

$$E(k) = \alpha + 2\beta(\cos k_x a + \cos k_y a)$$

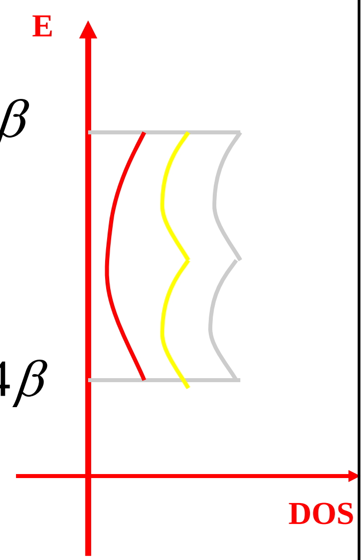
$$W = 4Z\beta$$



$\alpha - 4\beta$

α

$\alpha + 4\beta$

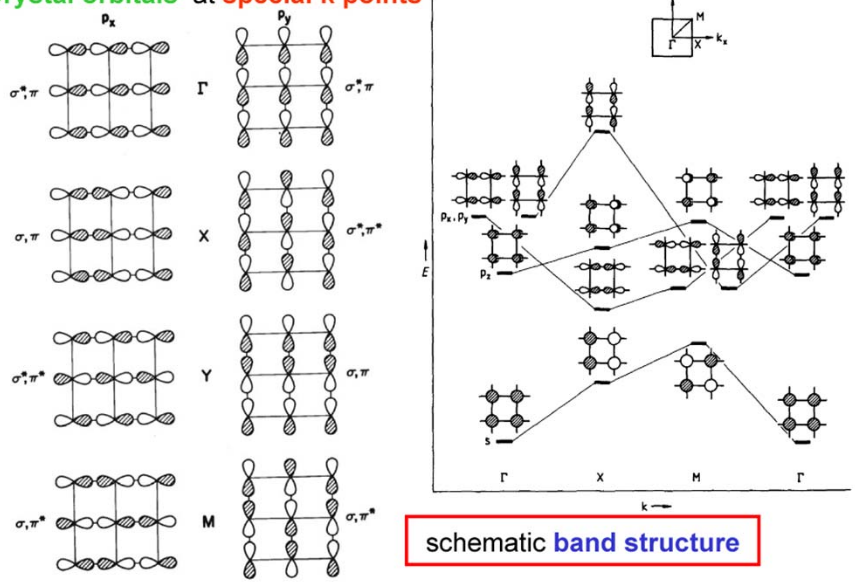


$$E(k) = \alpha + 2\beta(\cos k_x a + \cos k_y a)$$

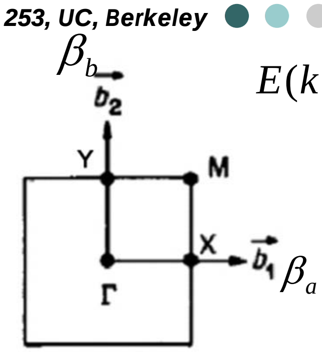
Elementary Band Theory for Extended Solids

More dimensions: a two-dimensional square net [**s** and **p** orbitals]

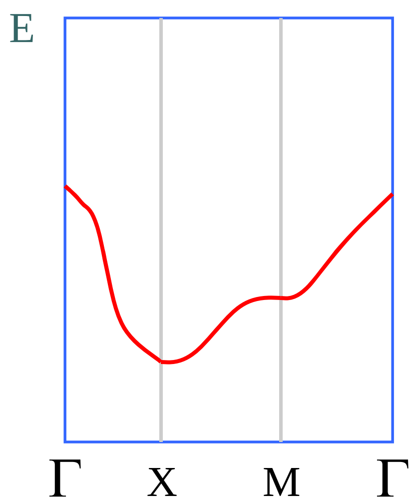
Crystal orbitals at **special k points**

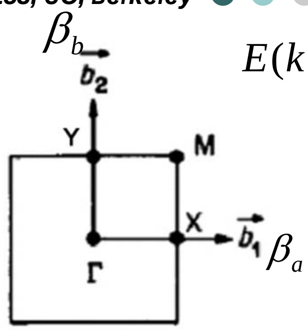


schematic **band structure**

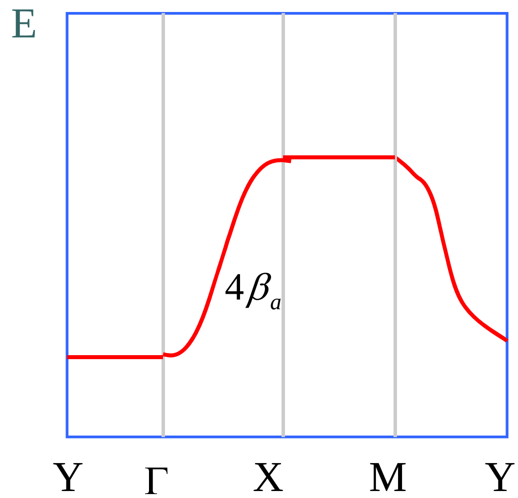


$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$

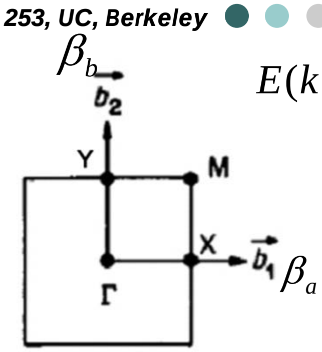




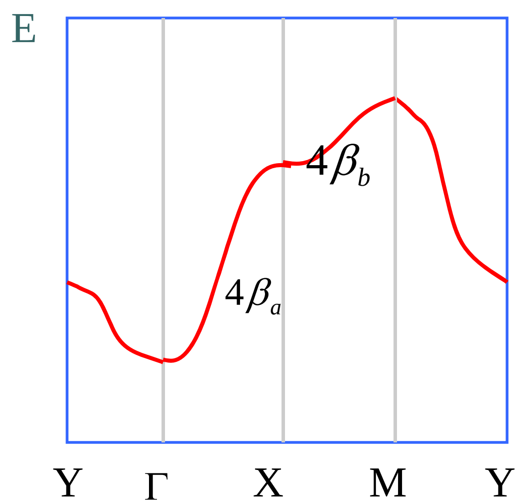
$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$



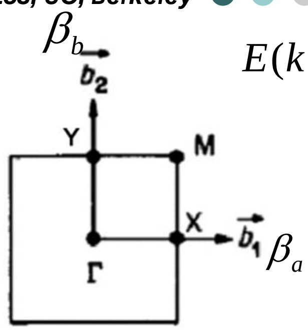
$$\beta_a < \beta_b = 0$$



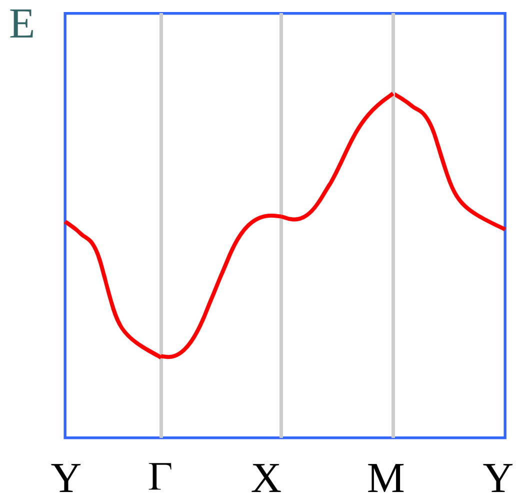
$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$



$$\beta_a < \beta_b < 0$$



$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$

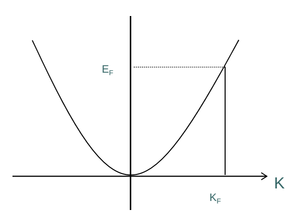


$$\beta_a = \beta_b < 0$$

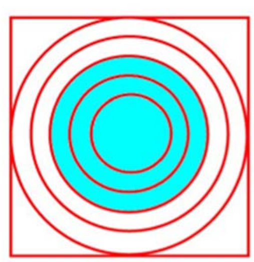
Fermi Surface

For free electrons, the constant energy surfaces are circular.

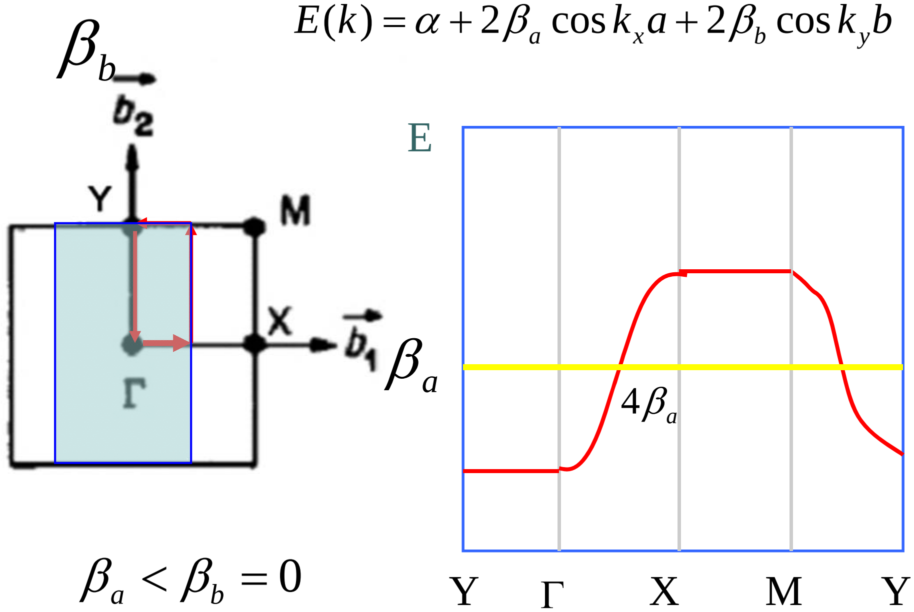
$$E(k) = \frac{\hbar^2 k_x^2}{2m}$$



For a monovalent element, the volume of the Fermi surface is half that of the Brillouin zone:



$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$



$\beta_a < \beta_b = 0$

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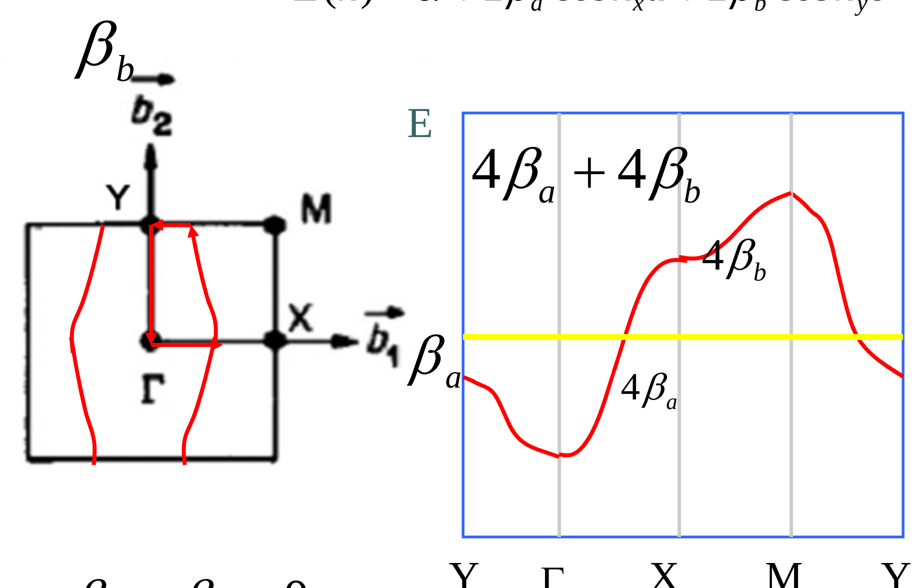
$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$



$\beta_a < \beta_b < 0$

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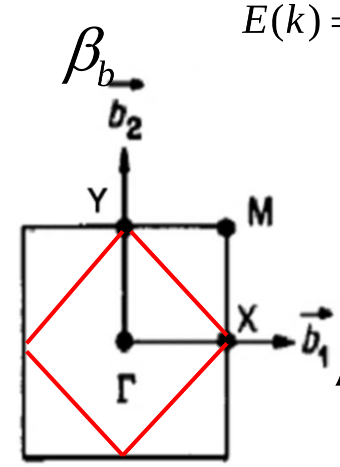
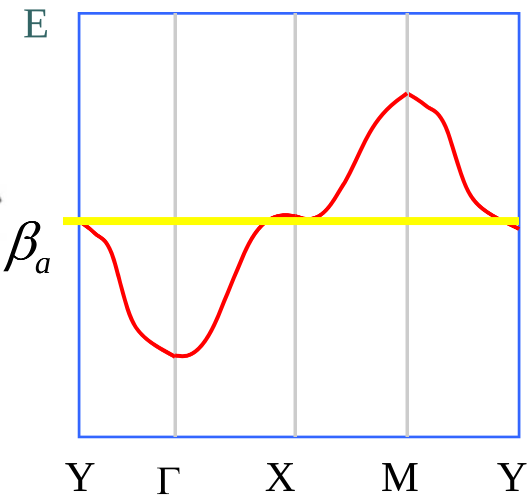
$$E(k) = \alpha + 2\beta_a \cos k_x a + 2\beta_b \cos k_y b$$





$$\beta_a = \beta_b < 0$$

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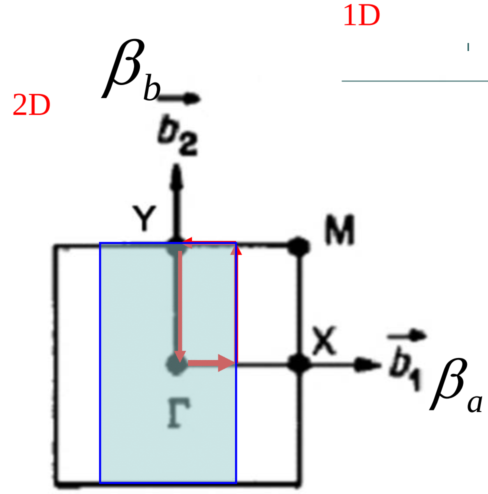
1D

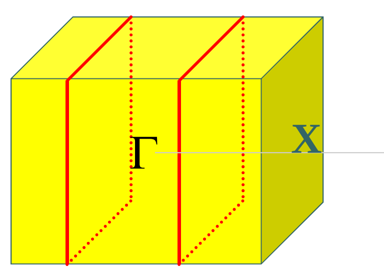
2D



$$\beta_a < \beta_b = 0$$

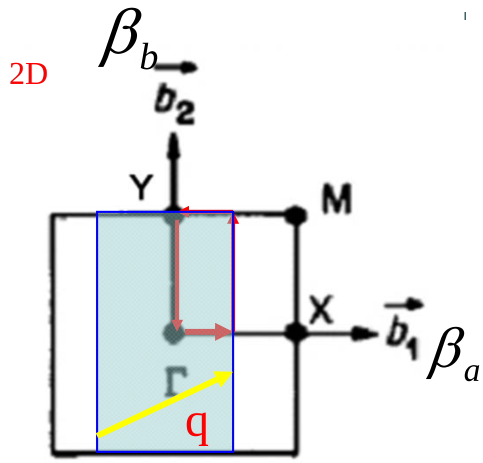
3D

$$\beta_a < \beta_b = \beta_c = 0$$



Fermi surface nesting

When a piece of a Fermi surface can be translated by a vector q and superimposed on another piece of the Fermi surface, the Fermi Surface is said to be nested by the vector q.



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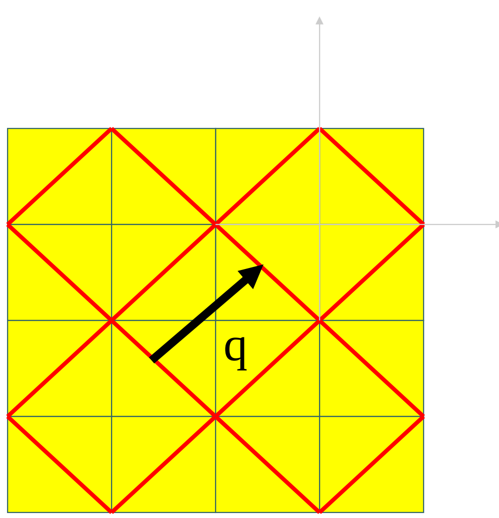
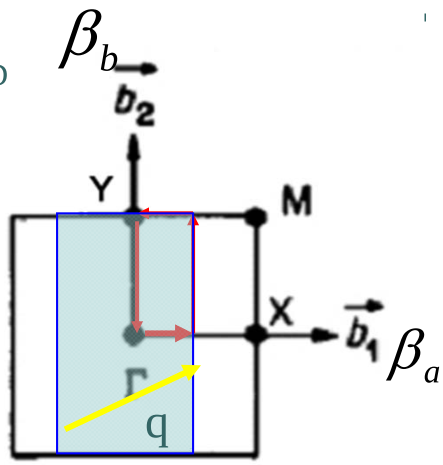


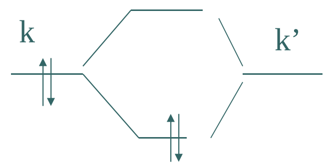
Important consequence of Fermi Level nesting:

A metallic system with a nested Fermi surface possesses electronic Instability and is likely to undergo a metal-insulator transition.

2D



Orbital mixing



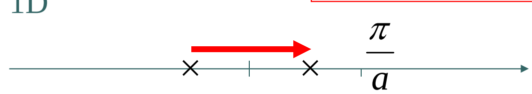
Vector q: defines the way the structure changes/distorts

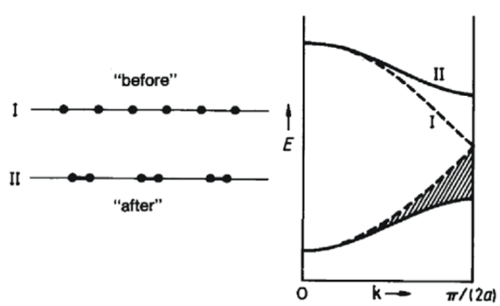
1D: q=b/2 → doubling of unit cell

$$k_F = \frac{\pi}{2a} = \frac{2\pi}{a}\frac{1}{4} = \frac{b}{4}$$

$$b = \frac{2\pi}{a}$$

1D





Peierls Distortion

In general, for 1D (unit cell a) if $k_F = b/m$

$$b = \frac{2\pi}{a}$$

Then, the new (electronically stabilized) unit cell will be

m/2 times the old one.

Example: H2

polyacetylene

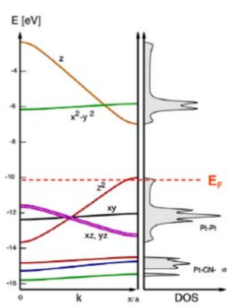
$$k_F = \frac{\pi}{2a} = \frac{1}{4}\frac{2\pi}{a} = b/m$$

Distortion does not necessary commensurate with the lattice.

$$K_2Pt(CN)_4Cl_{0.3}$$

Metal > 150K

$$d_{z^2} = \frac{1.7}{2.0} full = 0.85 full$$



$$k_F = 0.425b = \frac{b}{2.35}$$

$k_F = b/m$

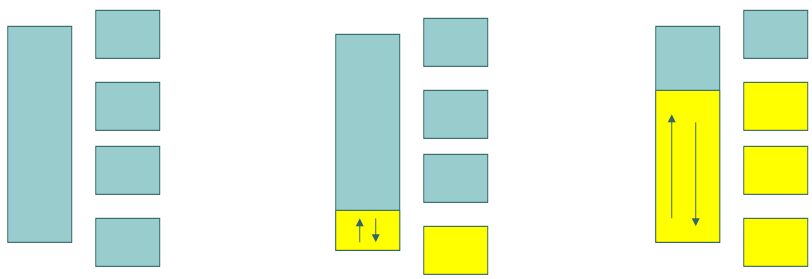
$b = \frac{2\pi}{a}$

1D

Stabilized Cell:

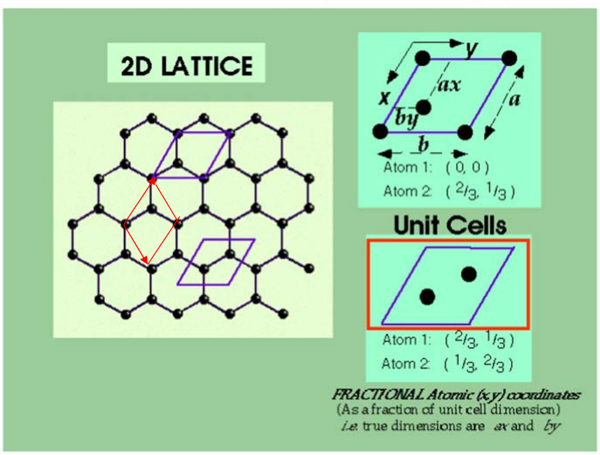
$$\frac{2.35}{2} = 1.175$$

In general, when a unit cell size is increased n-fold by a distortion,
The band is split into n subbands.
Consequently, a 1D system having a partially filled band of occupancy 1/n or (n-1)/n is likely to undergo a distortion which increase the unit cell **n** times.

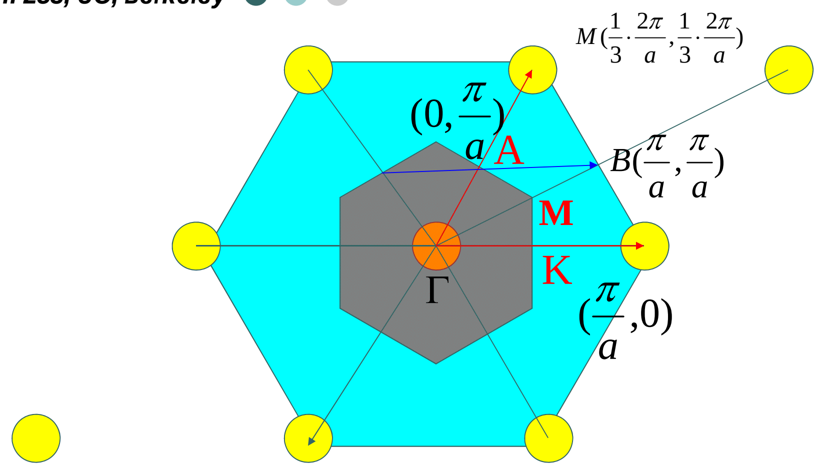


Elementary Band Theory for Extended Solids

More dimensions: the 2D hexagonal net of graphite



π orbitals: p_z, viewed from the top.
2 per cell.

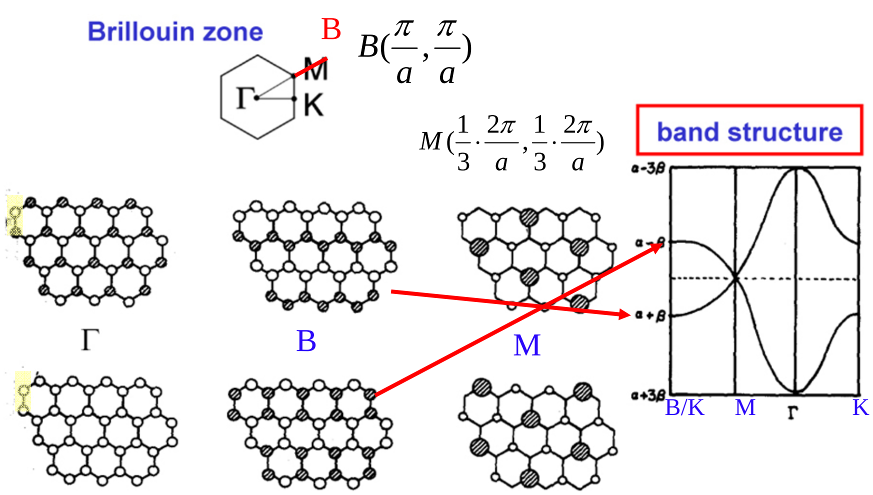


$$E(A) = E(B) = E(K)$$

Rotational/translational symmetry

Elementary Band Theory for Extended Solids

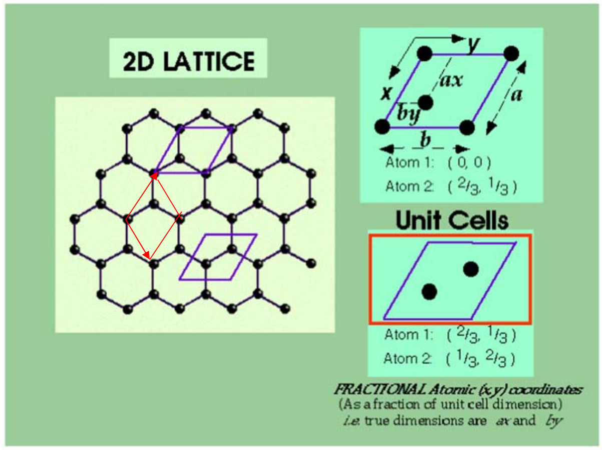
More dimensions: the 2D hexagonal net of graphite



$$\psi(k) = \sum_{m,n} e^{ik_x ma + ik_y na} \cdot \phi_{m,n}$$

Elementary Band Theory for Extended Solids

More dimensions: the 2D hexagonal net of graphite

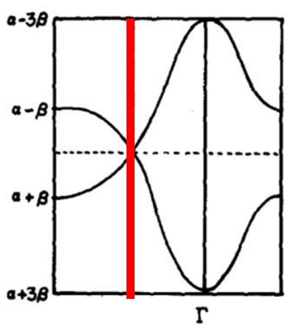


π orbitals: p_z, viewed from the top.
2 per cell.

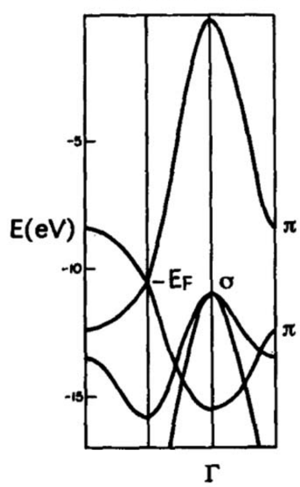
Elementary Band Theory for Extended Solids

More dimensions: the 2D hexagonal net of graphite

Simple Hückel;
only π interactions (p_z orbital)



Extended Hückel;
all interactions



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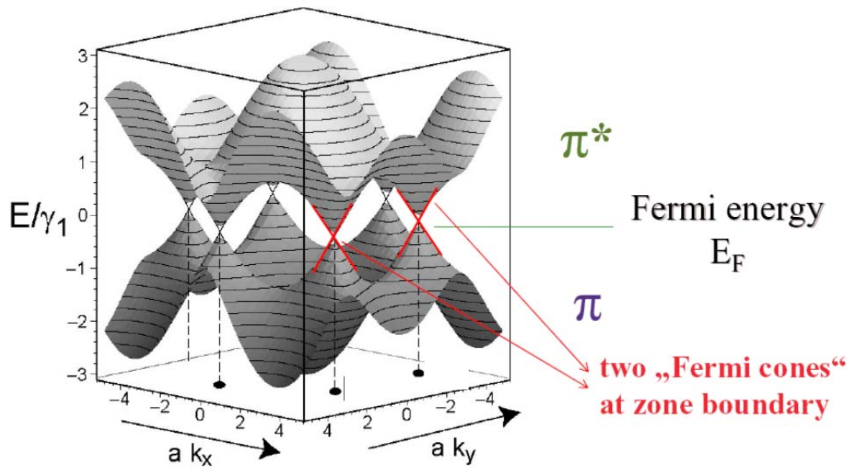
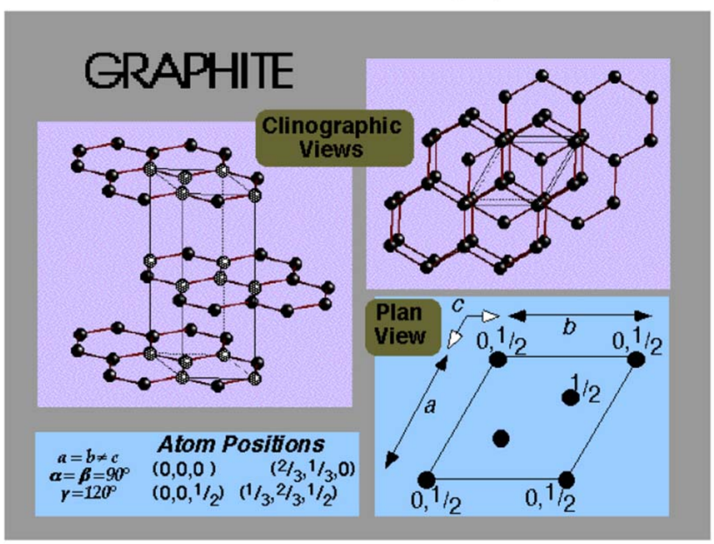


Elementary Band Theory for Extended Solids

More dimensions: the 3D structure of graphite

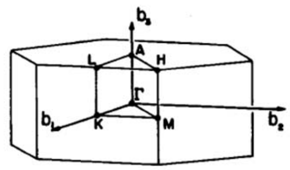


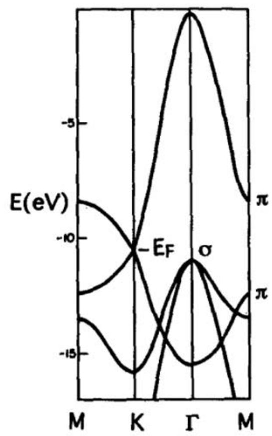
π orbitals: 4 per cell.

Elementary Band Theory for Extended Solids

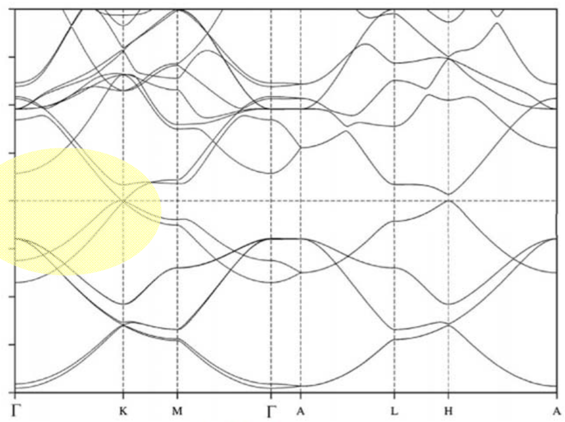
More dimensions: the 3D structure of graphite

Brillouin zone





Extended Hückel;
2D



"*ab initio*"; 3D

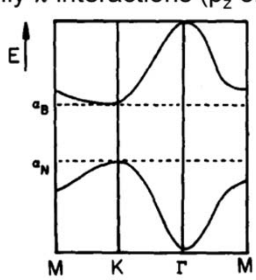
Elementary Band Theory for Extended Solids

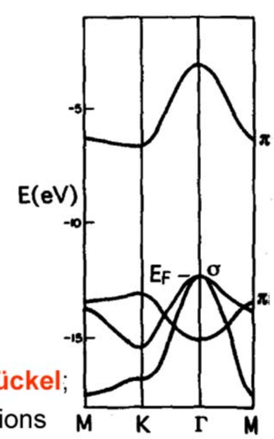
More dimensions: the 2D hexagonal net of BN

π orbitals: p_z,
viewed from the top.
1 B + 1 N per cell.

N is larger and more electronegative, compared to B.

Simple Hückel;
only π interactions (p_z orbitals)





Extended Hückel;
all interactions