A chemist‘s view on the electronic structure of solids

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Literature

(1) **R. Hoffmann**, "Solids and surfaces", VCH, Weinheim, 1988.

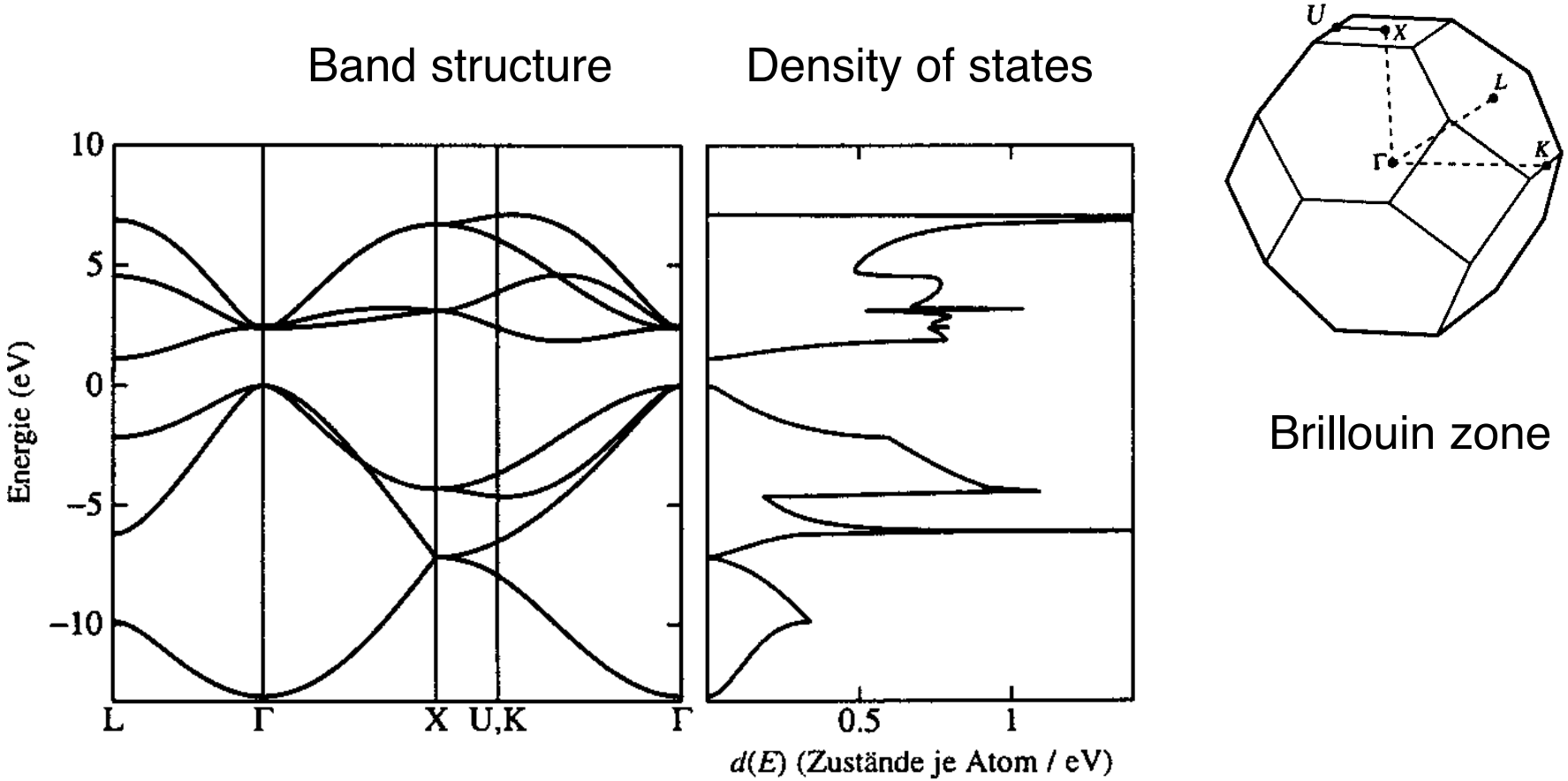
ISBN 3-527-26905-3 VCH Verlagsgesellschaft

(2) **A. P. Sutton**,"The electronic structure of materials, Oxford University Press, 1993.

German edition: VCH, 1966 ISBN 3-527-29395-7

(3) **R. A. van Santen**, "Theoretical Heterogeneous Catalysis", World Scientific, Singapore 1991.

What we would like to understand



Brillouin zone

Abb. 6.11: Die Bandstruktur (links) und die Zustandsdichte (rechts) von Silizium mit kubischer Diamantstruktur, abgeleitet mit den Parametern für den Hamilton-Operator aus den Gl. (6.6.1-6.6.2). Die Rechnungen stammen von Dr. A. T. Paxton (1994), private Mitteilung.

N-membered Polyene Chain

$$E_k = \alpha + 2\beta \cdot \cos 2\pi \frac{k}{N} \qquad k = 0, \pm 1, \pm 2, \ldots \frac{N}{2} \quad n \text{ even}$$

$$k = 0, \pm 1, \pm 2, \ldots \pm \frac{N-1}{2} \quad n \text{ uneven}$$

$$\psi_{\pm|k|} = \sum_{j=1}^{N} c_j \cdot \chi_j = \sum_{j=1}^{N} \exp\left(\pm 2\pi i \frac{|k|}{N} \cdot j \right) \cdot \chi_j$$

Model for 1-dim periodic system
with one orbital and one electron per cell

N-membered Polyene Chain - Real orbitals

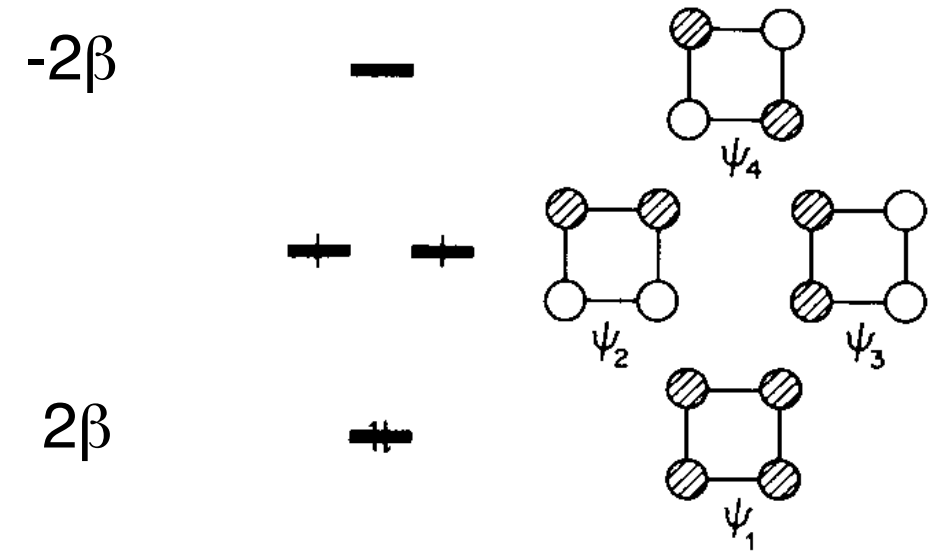
$$\psi_0 = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} 1 \cdot \chi_j$$

$$\psi_{|k|,1} = \sqrt{\frac{2}{N}} \sum_{j=1}^{N} \cos\left(2\pi \frac{|k|}{N} \cdot j\right) \cdot \chi_j$$

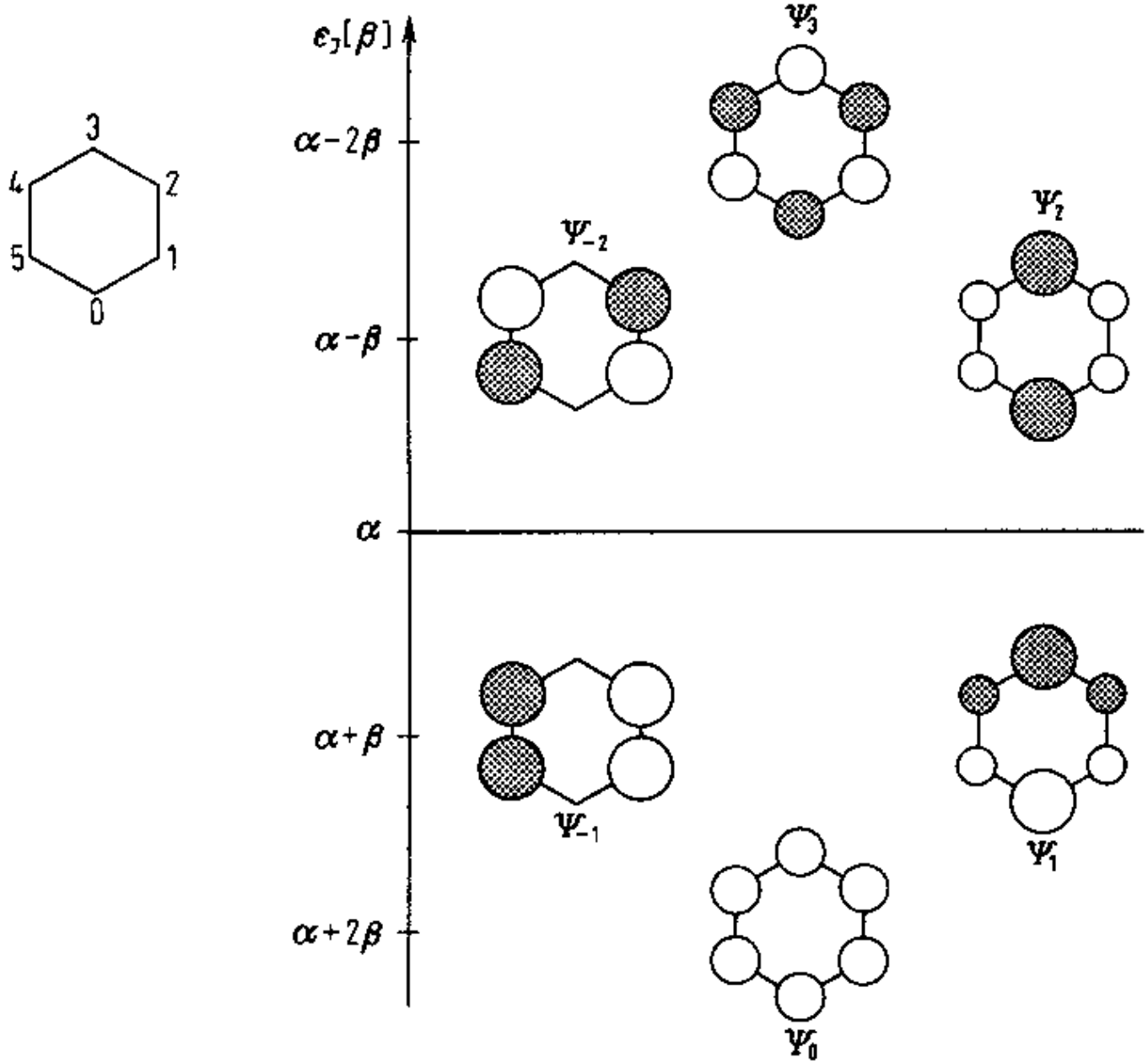
$$\psi_{|k|,2} = \sqrt{\frac{2}{N}} \sum_{j=1}^{N} \sin\left(2\pi \frac{|k|}{N} \cdot j\right) \cdot \chi_j$$

$$\psi_{N/2} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} (-1)^j \cdot \chi_j$$

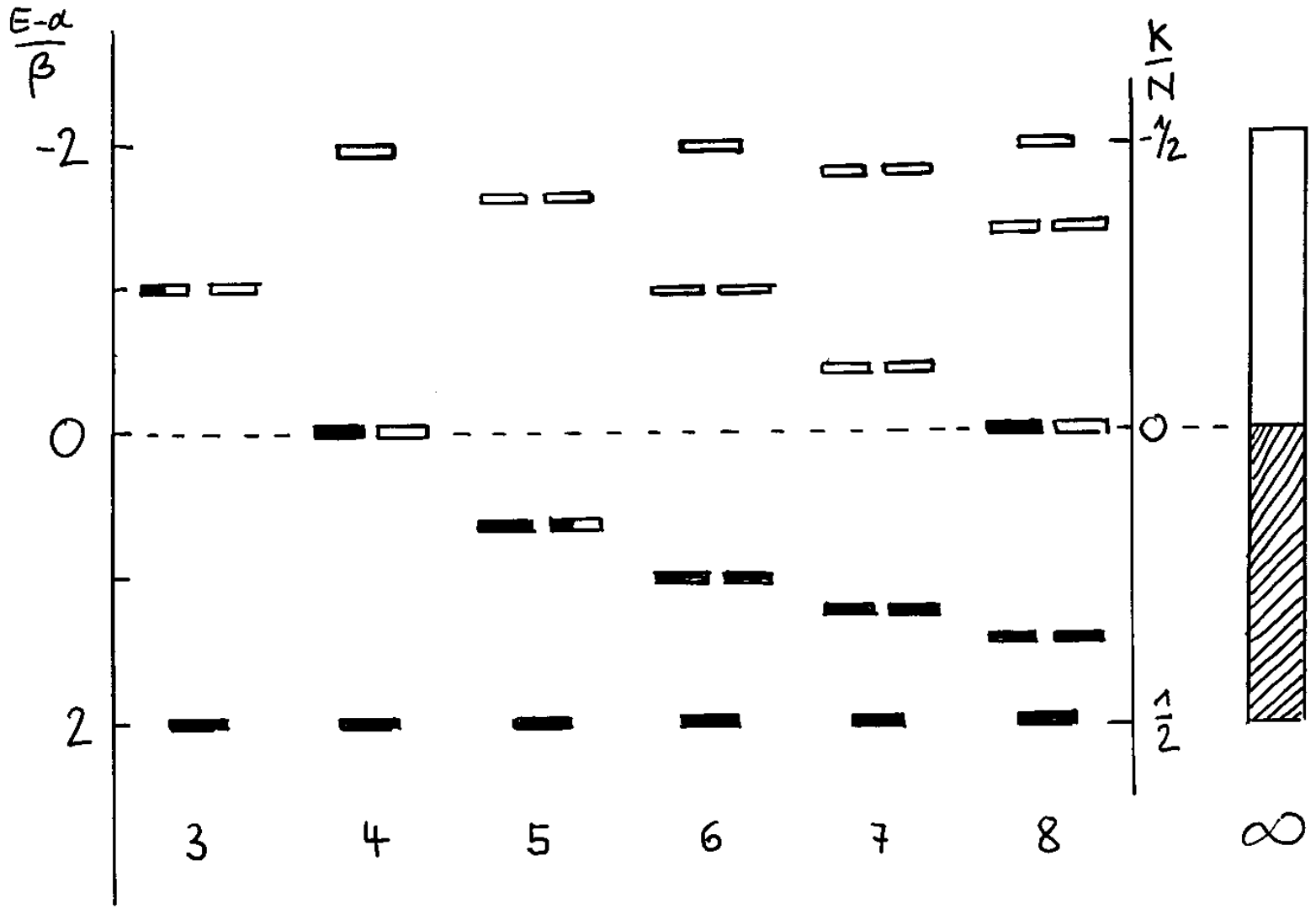
HMO solution for cyclobutadiene (N=4)



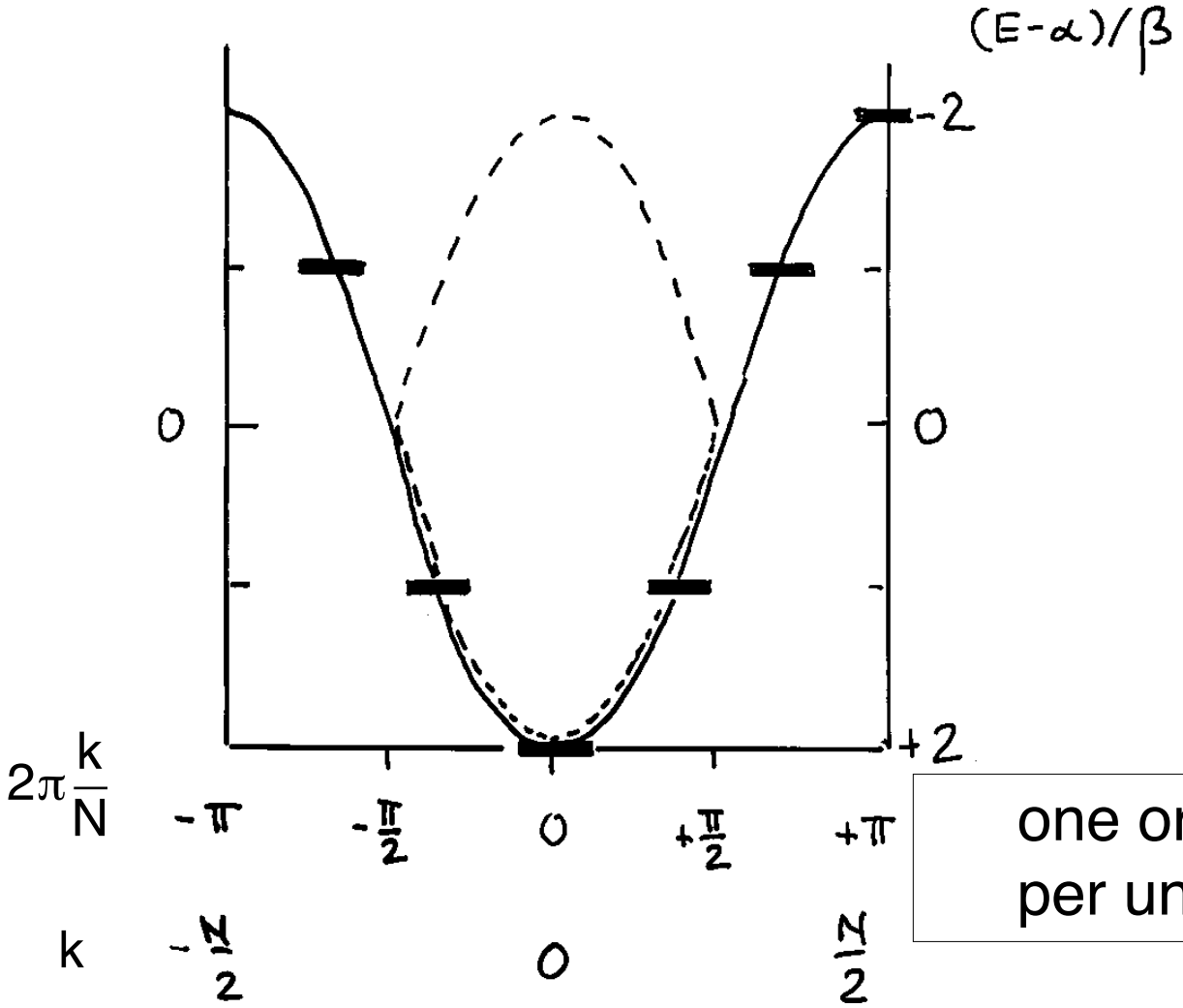
HMO solution for benzene (N=6)



Orbital energies for cyclic systems as a function of N



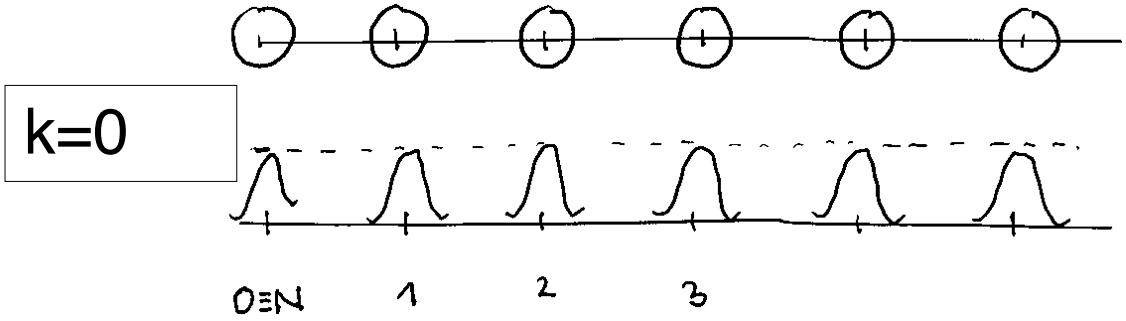
Orbital energy as a function of parameter k - band structure



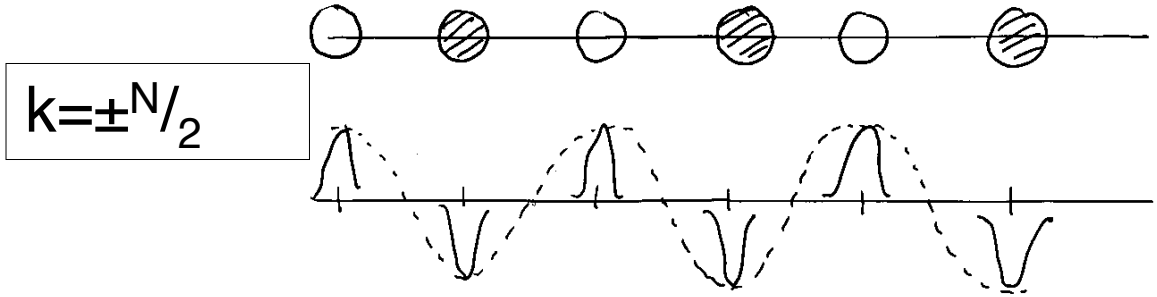
one orbital
per unit cell

$$E_k = \alpha + 2\beta \cdot \cos 2\pi \frac{k}{N} \qquad k = 0, \pm 1, \pm 2, \ldots \frac{N}{2} \qquad n \text{ even}$$

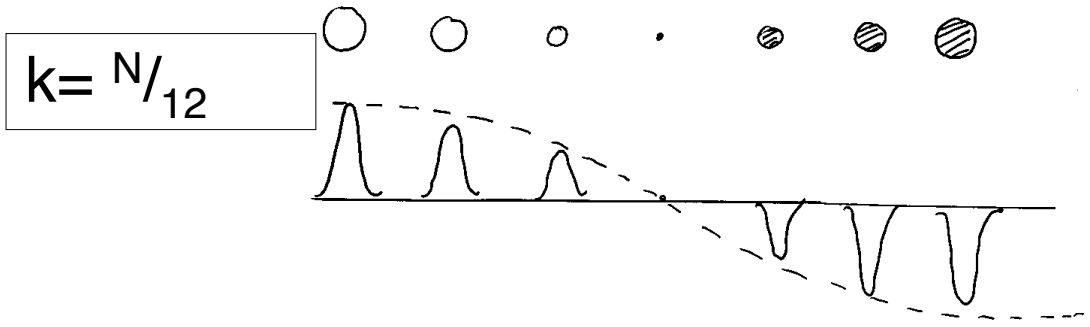
Illustration of c_j along infinite structure for orbitals with different k



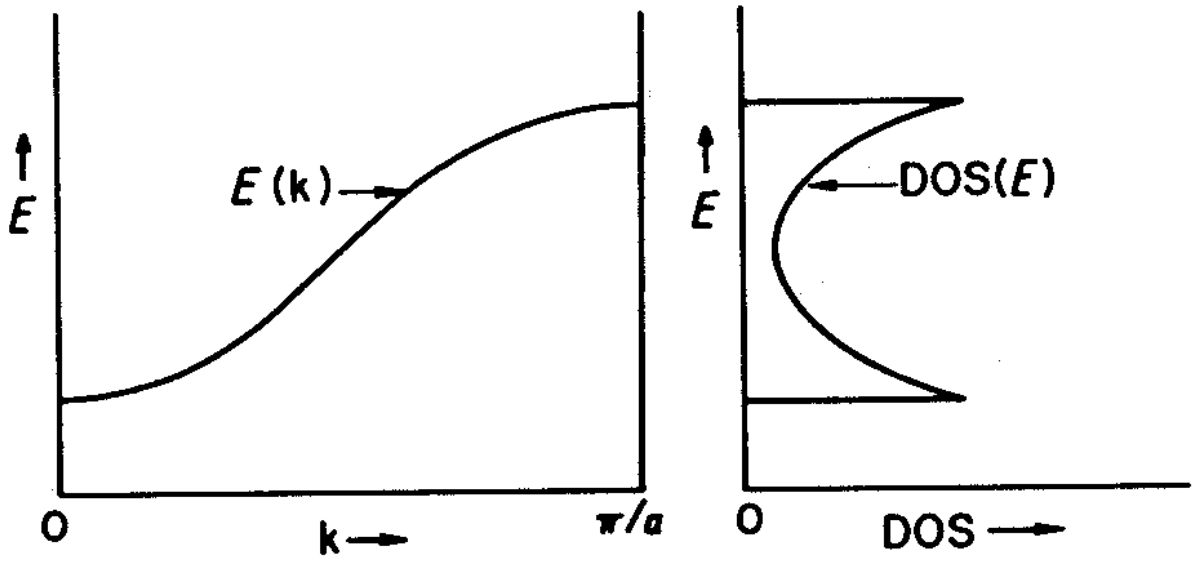
lowest energy



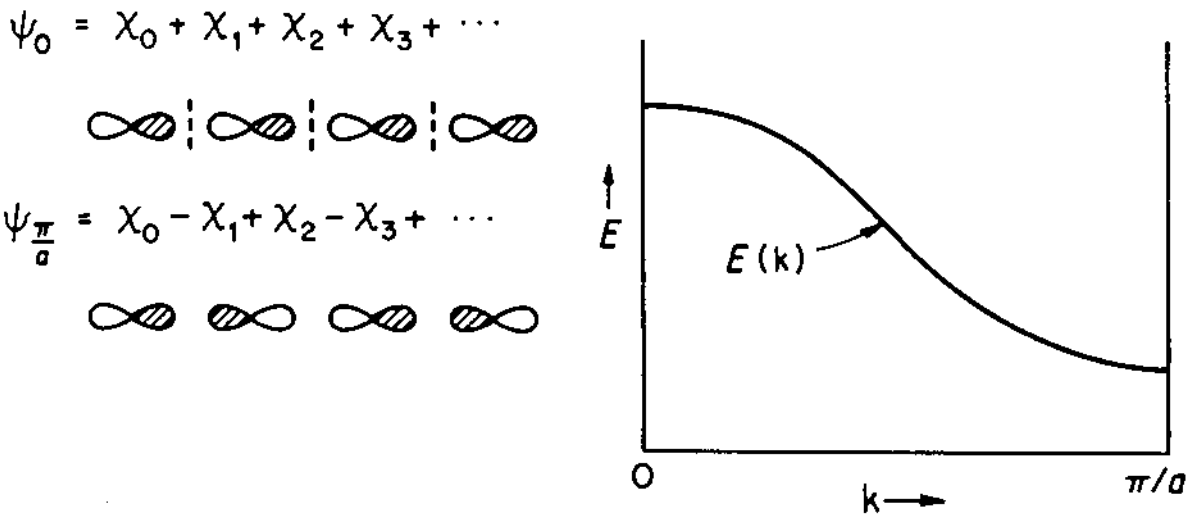
highest energy



Density of states



How do the bands run ?



For chains of p orbitals along the periodic direction the crystal orbital for k=0 has the maximum number of nodal planes

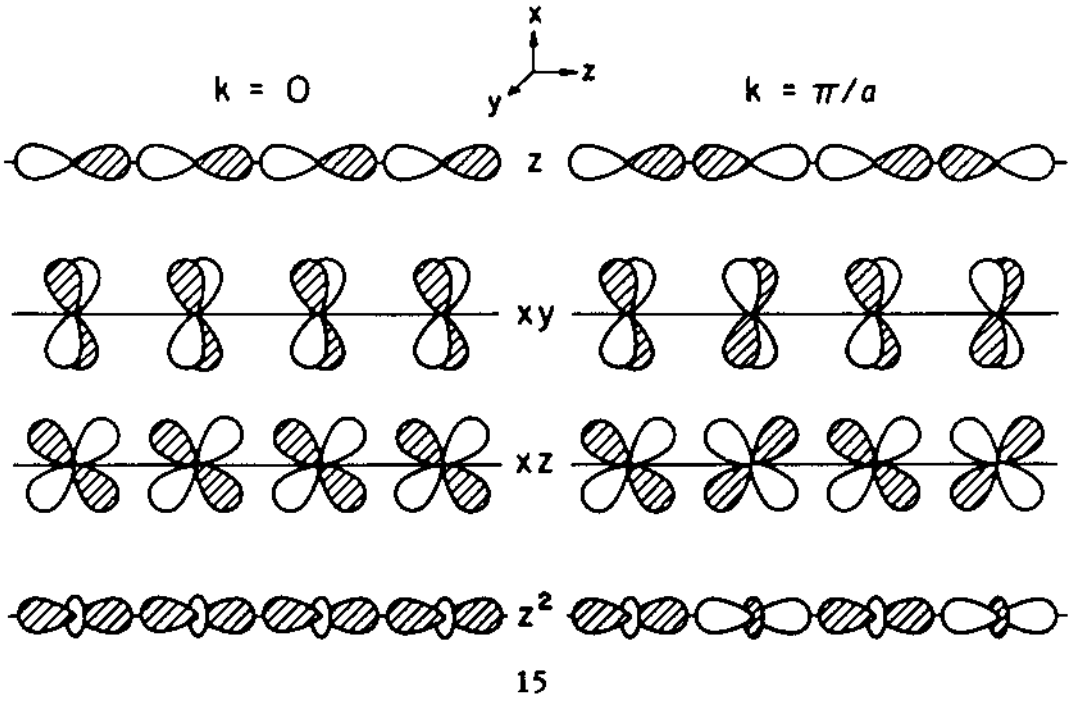
is therefore highest in energy

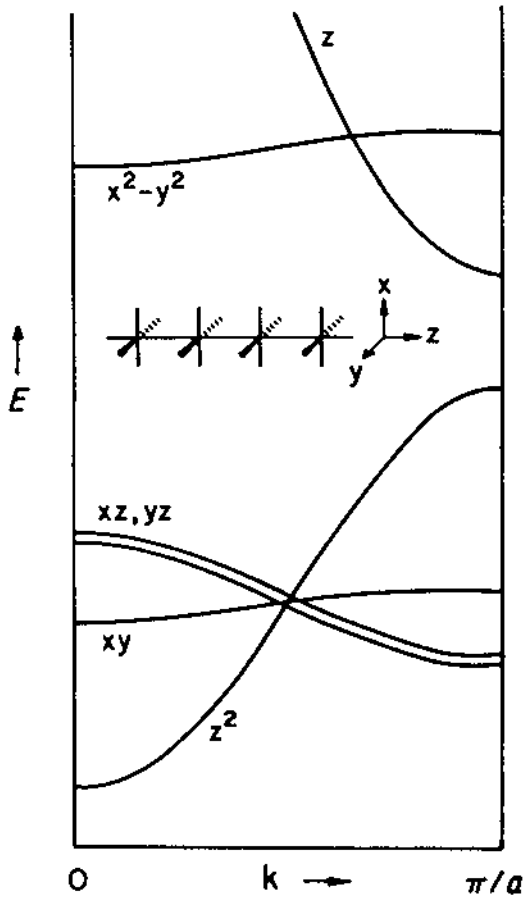
forms the top of the band

The orbital for k=N/2 has no nodal planes across the bonds (only within the atom)

forms therefore the bottom of the band

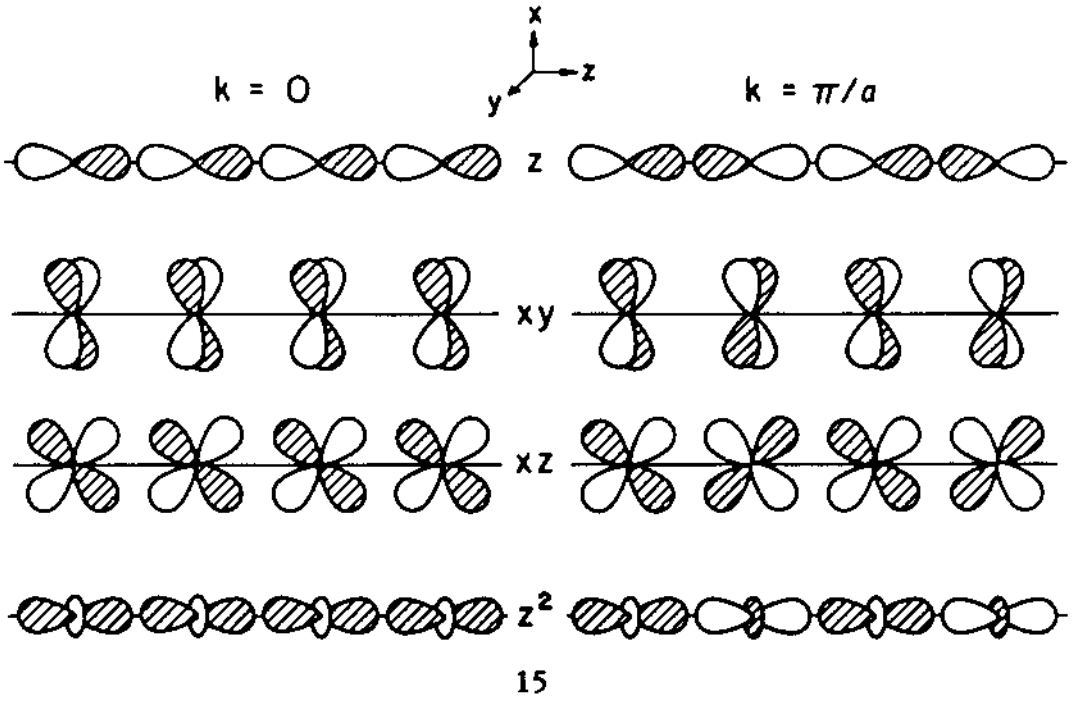
p and d bands





Note:
Increase or decrease with increasing k is determined by nodal behaviour
Band width is determined by strength of interaction (magnitude of β)

Band dispersion (band width)



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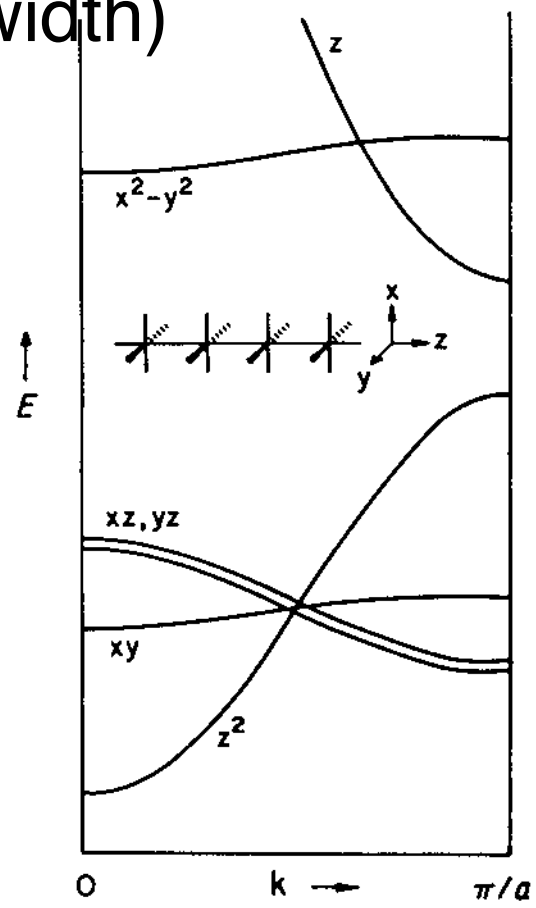


Difference between the highest point and the lowest point of a band
For our model: 4 β
Magnitude of β depends on strength of interaction

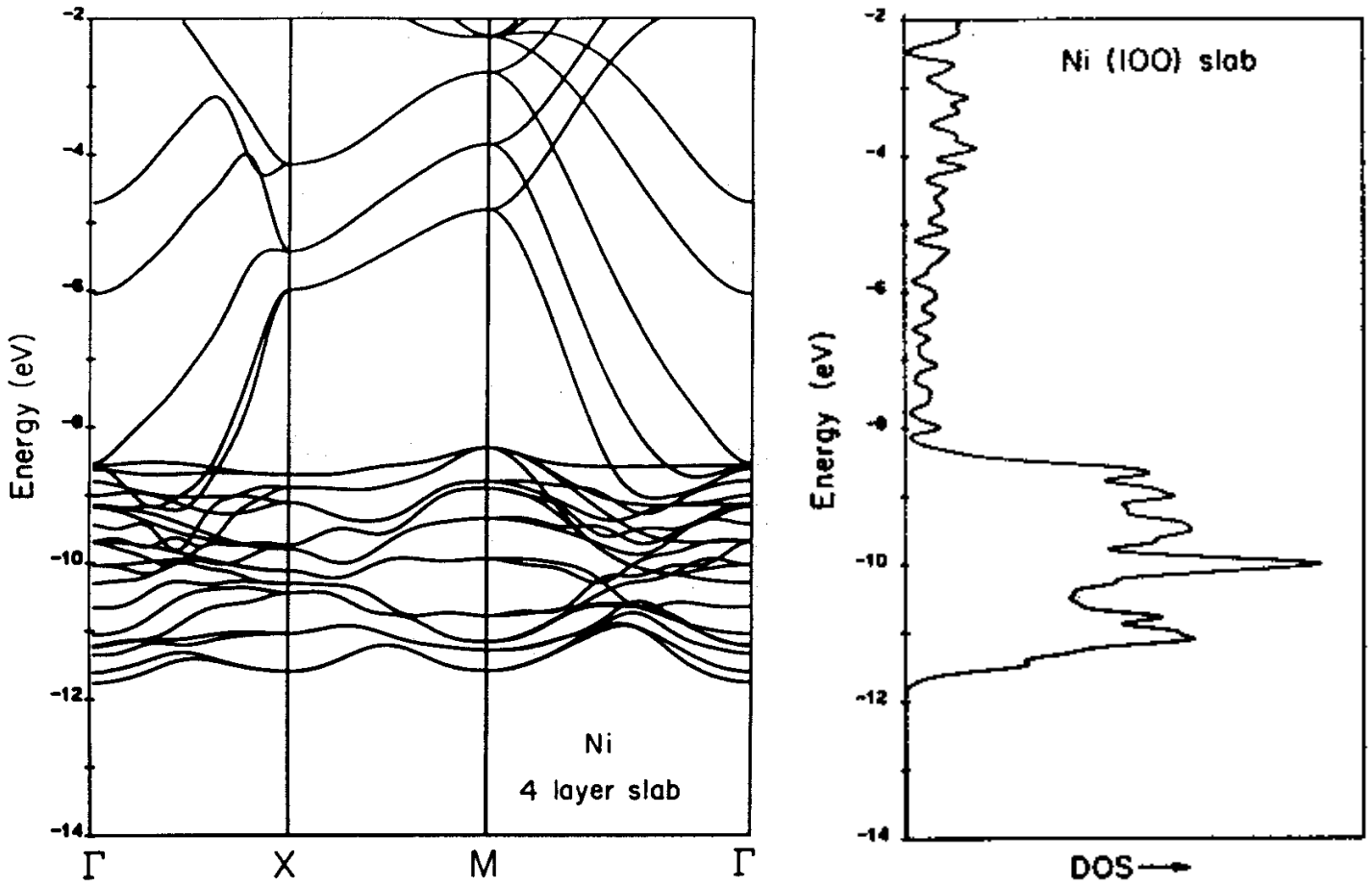
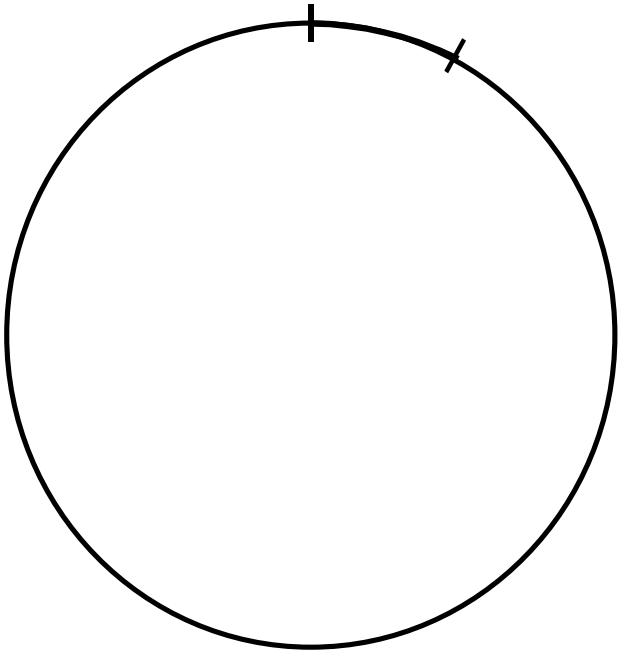


Figure 7 The band structure of a four-layer Ni slab that serves as a model for a Ni(100) surface. The flat bands are derived from Ni 3d; the more highly dispersed ones above these are 4s, 4p.

Reciprocal space



lattice vector (cell size)

$a = \frac{2\pi}{N}$ shifts by one cell

$a_j = \frac{2\pi}{N} \cdot j = a \cdot j$ shifts by j cells

$a \cdot b = 2\pi \qquad (a_i \cdot b_j = 2\pi \cdot \delta_{ij})$

defines reciprocal cell
BRILLOIN zone

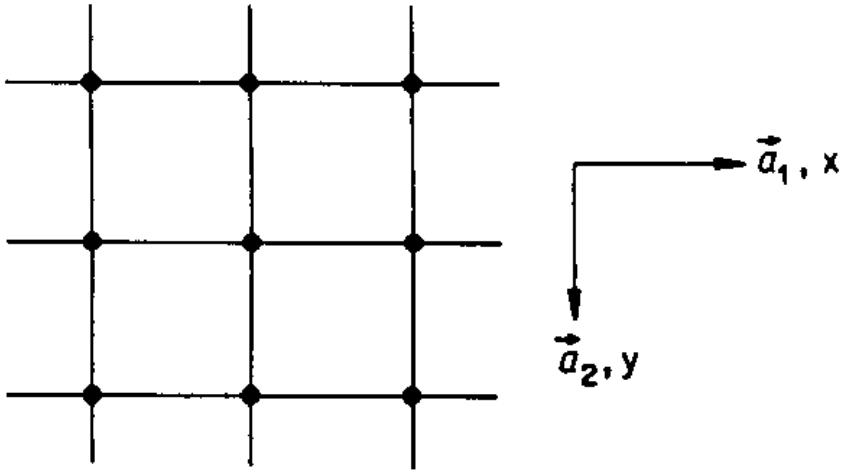
$b = 2\pi / a = N$

k is vector of reciprocal space
k-space

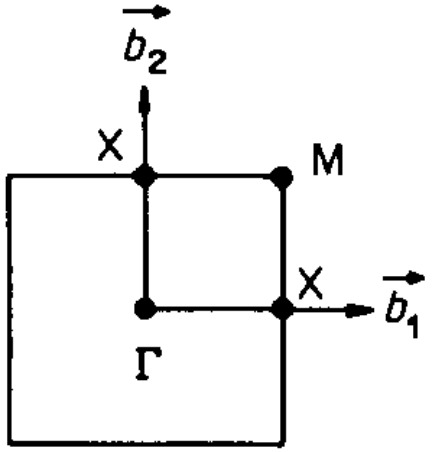
$$\psi_k = \sum_{j=1}^{N} e^{-i \cdot 2\pi \frac{k}{N} j} \chi_j = \sum_{j=1}^{N} e^{-i \cdot a_j \cdot k} \chi_j$$

includes permitted k values
0 ... N; $-\,{}^{N}/_{2}$ ....+ ${}^{N}/_{2}$

Two dimensions



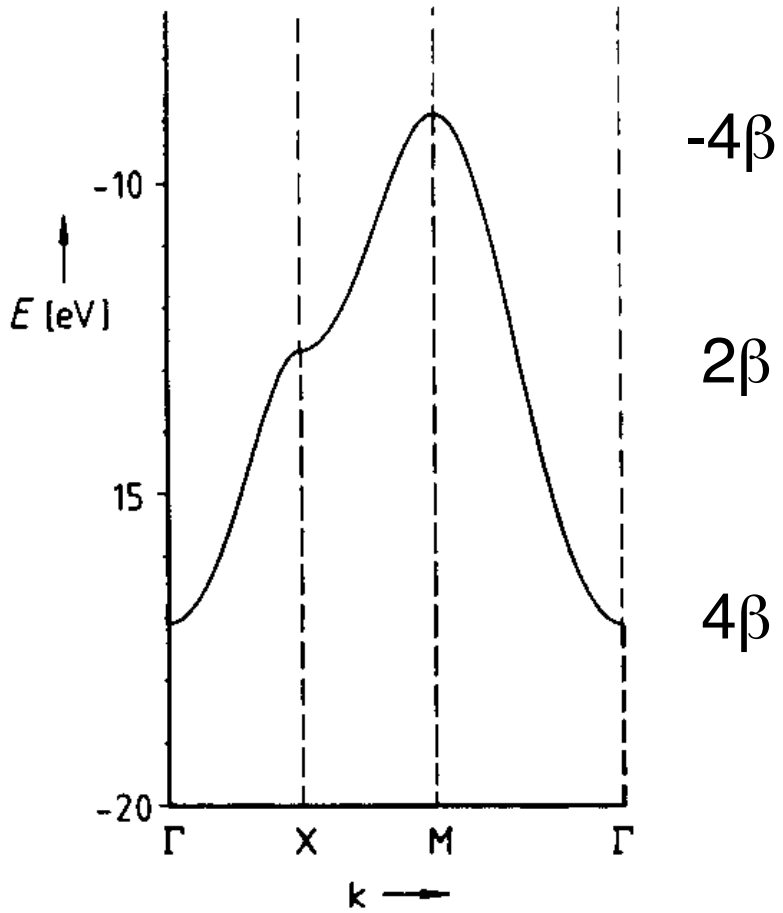
crystal lattice
(direct space)



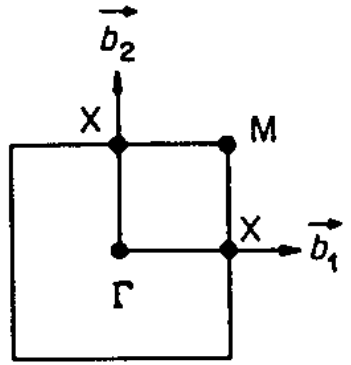
reciprocal lattice
(k space)

$$a_1 \cdot b_1 = 2\pi; \quad a_2 \cdot b_2 = 2\pi$$

$$-\frac{\pi}{a_{1/2}} \leq k_{x/y} \leq +\frac{\pi}{a_{1/2}}$$



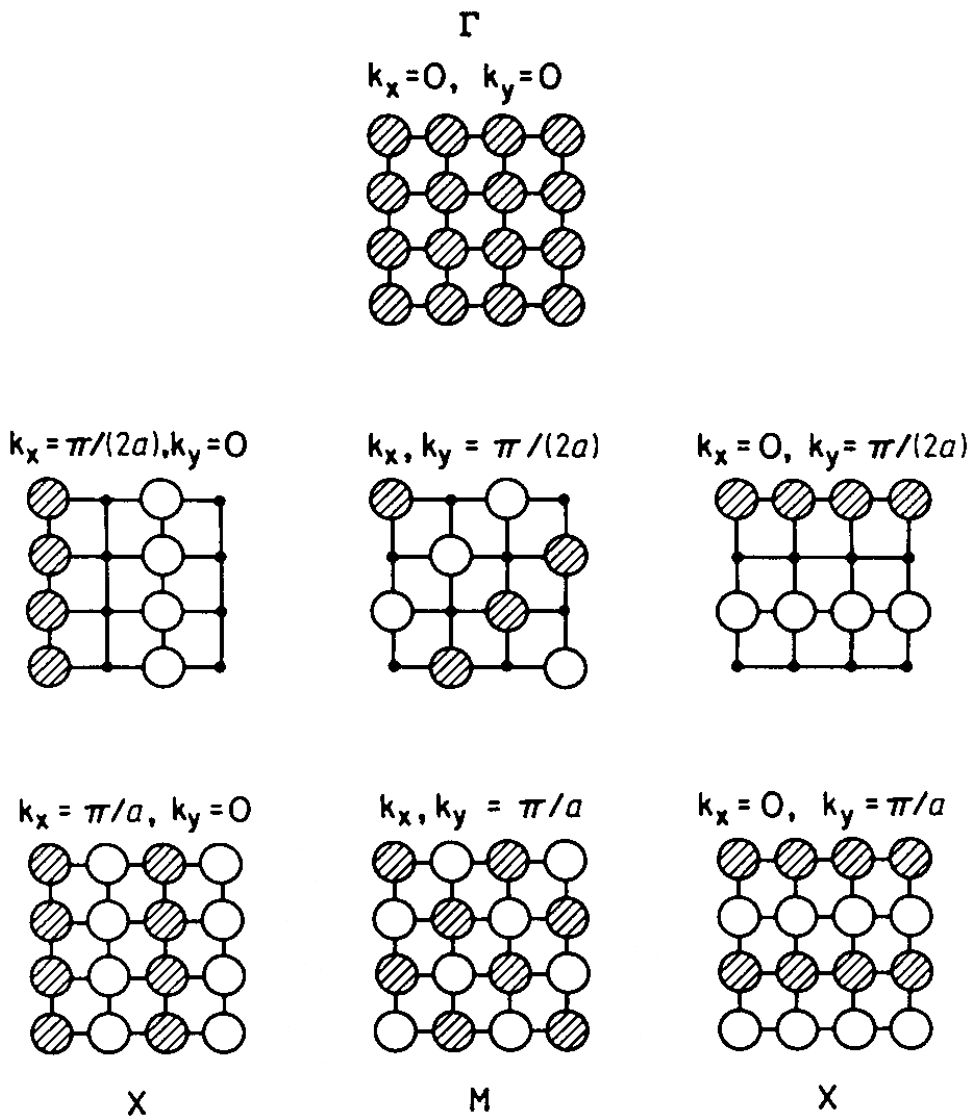
band structure corresponds to different planes through k space



$$-\frac{\pi}{a} \le k_x, k_y \le +\frac{\pi}{a}$$

The band structure of a square lattice of H atoms, H–H separation 2.0

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



Different nodal behaviour depending on minimum/maximum k value in one, the other, two directions

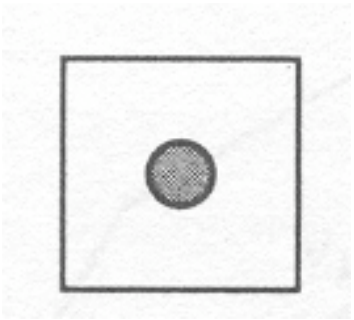
FERMI surface

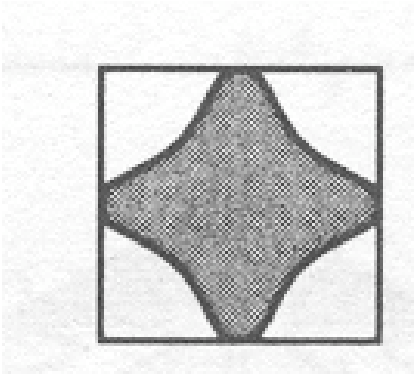
includes all k values in the Brillouin zone which belong to occupied states

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

only a few states occupied
(lowest energy for k=0)

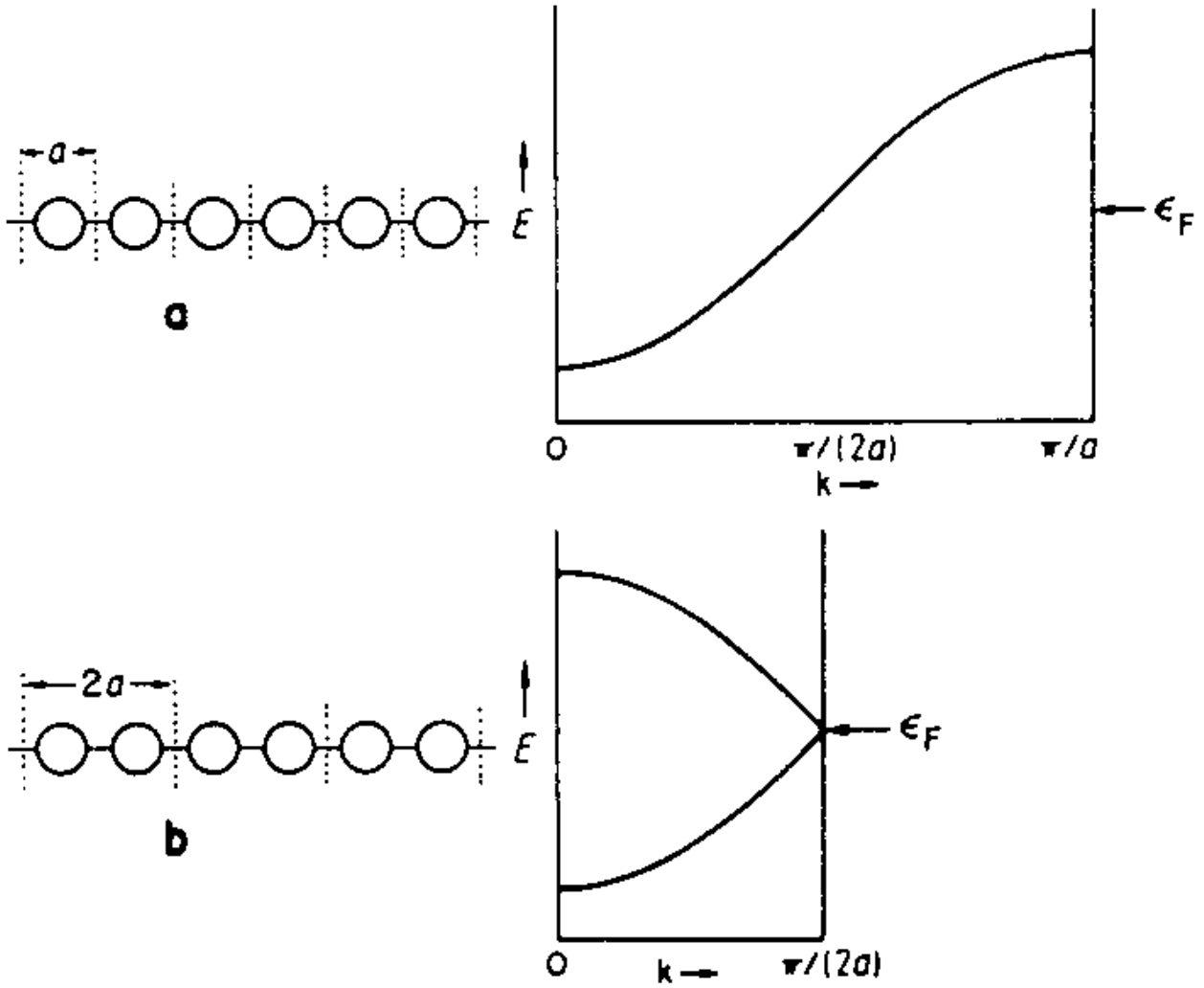
half of the states occupied
$E_{Fermi}(k)= \alpha$
$\cos k_x a+\cos k_y a=0$



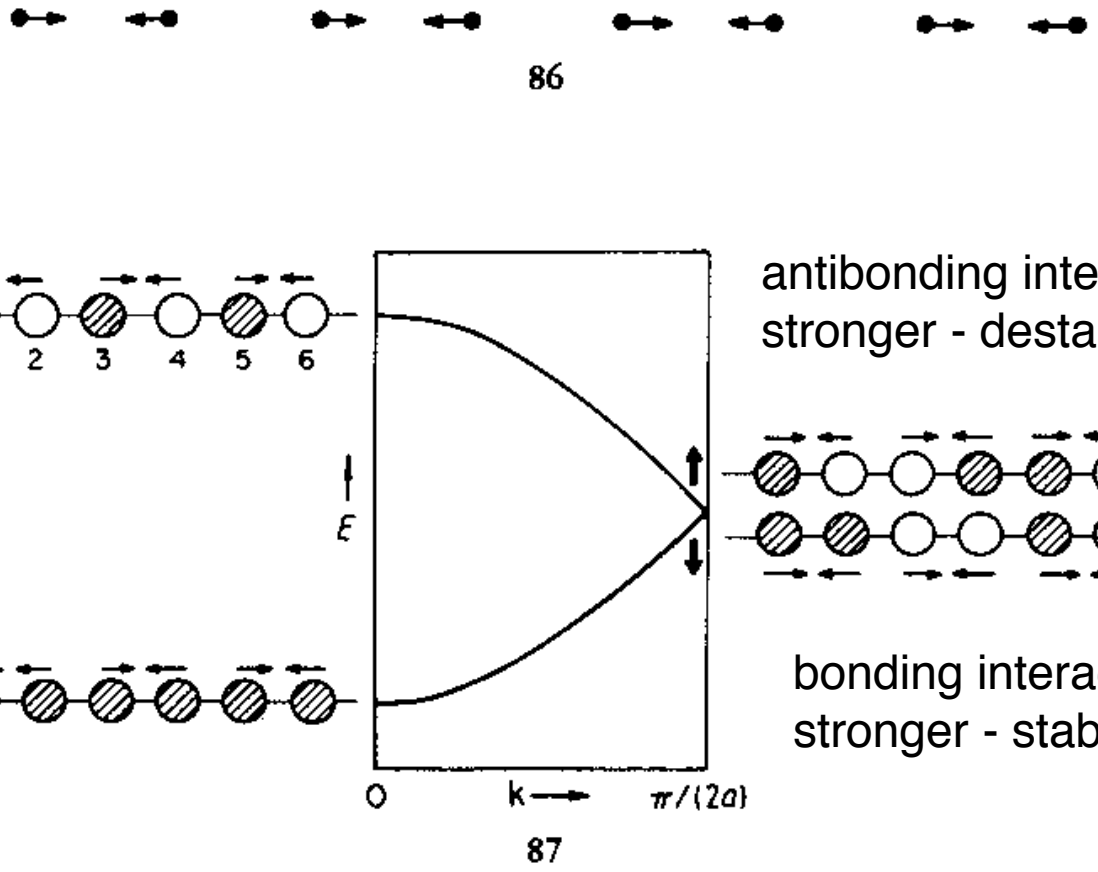


$$k_x, k_y = \pm \frac{\pi}{a}$$

Double unit cell - two solutions per k value
only half of the k values - "folding" of band structure



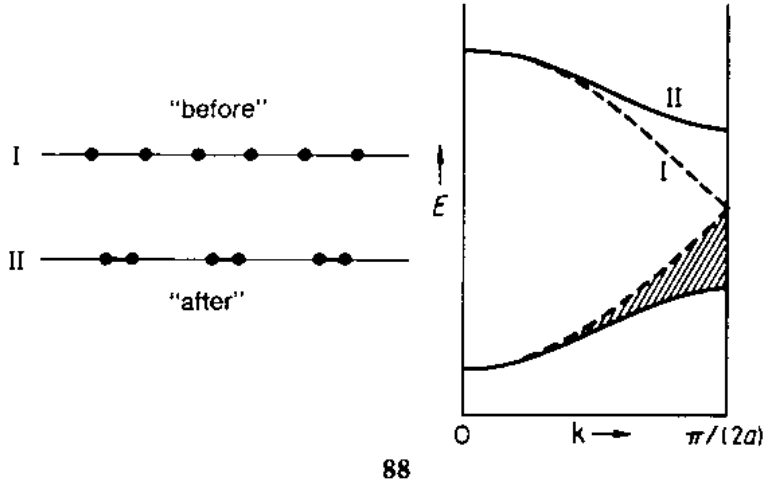
We use the double cell to study the effect of distortion



antibonding interaction becomes stronger - destabilization

bonding interaction becomes stronger - stabilization

Peierls Distortion



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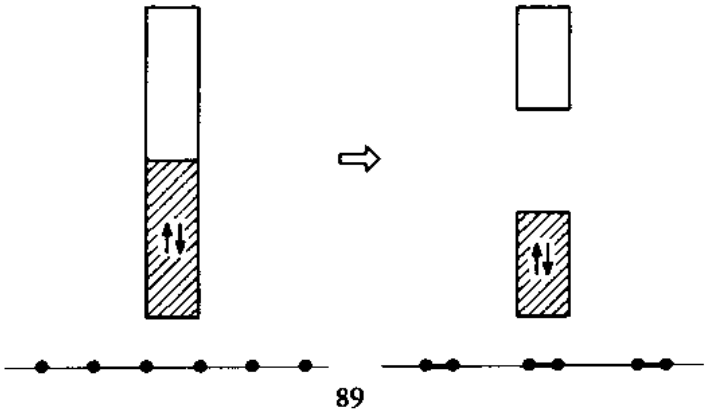
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Alternation of long (weak - small b) and short (strong - large b) bonds leads to a splitting for large k values


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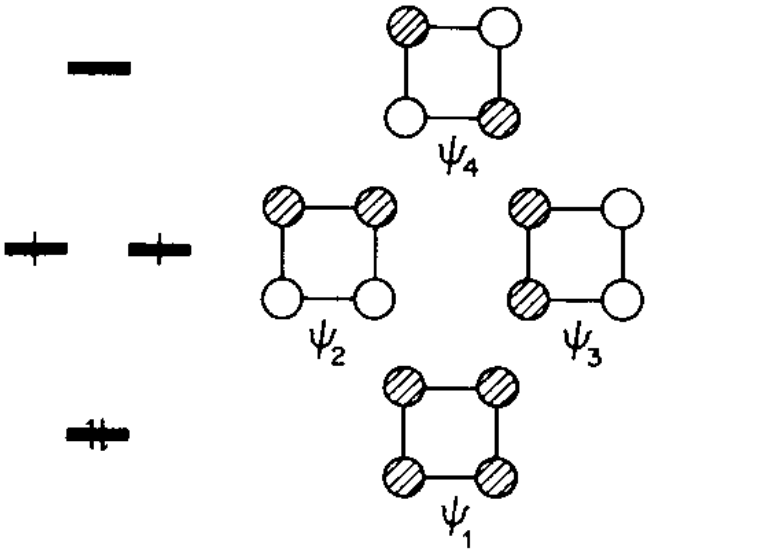
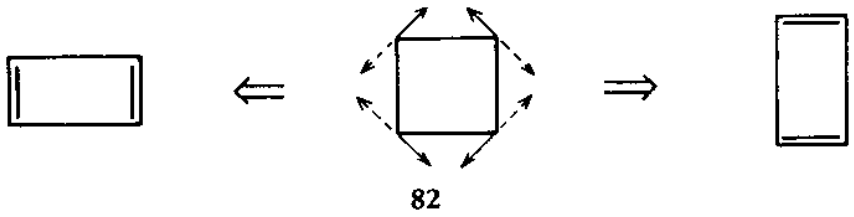


2 of the 4 electrons are in degenerate orbitals. Distortion of symmetry lifts degeneracy. The 2 electrons occupy the stabilized orbital while the destabilized orbital remains empty - this is the driving force for the distortion.



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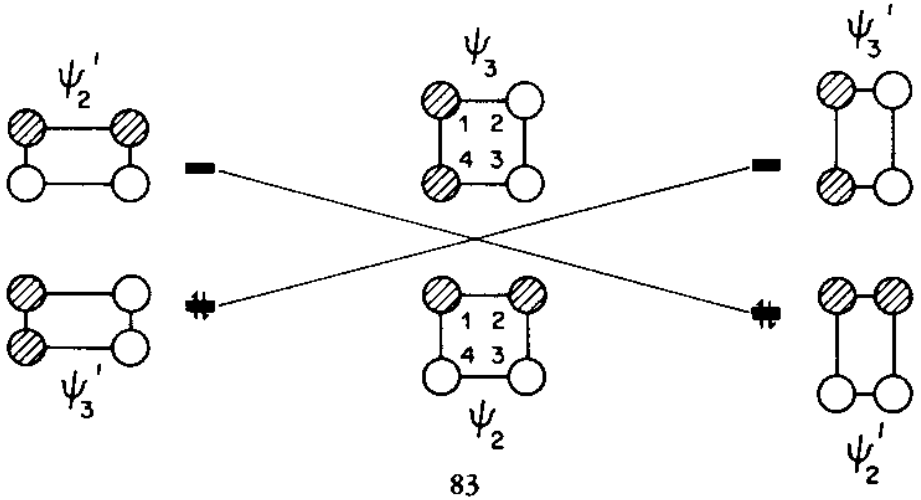
Cf. Jahn-Teller Effect



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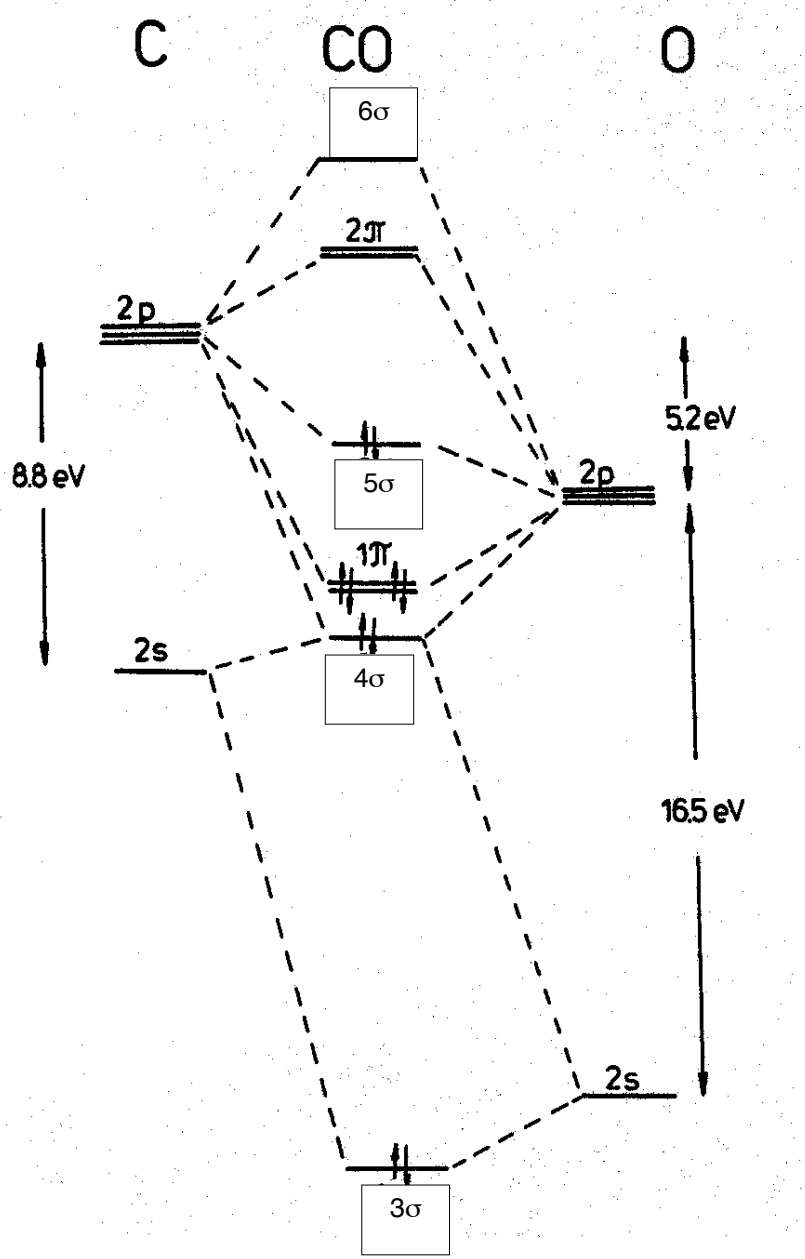
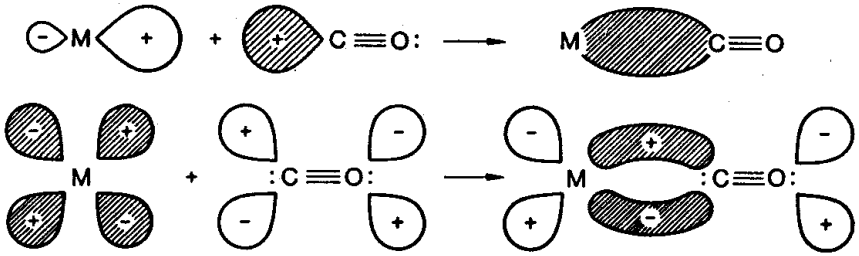
Orbitalschema - CO





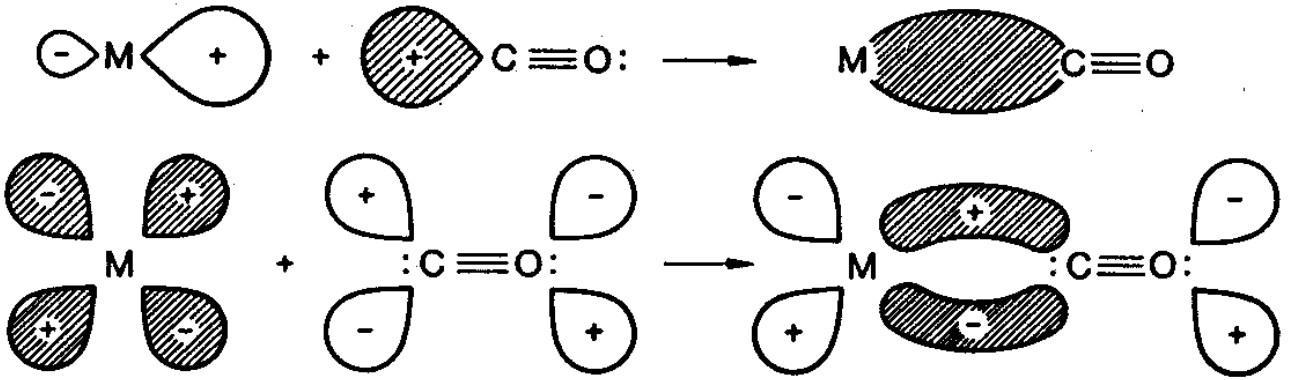
Dewar-Chatt-Duncanson-Modell*
(Oberflächen: Blyholder-Modell)

bes. 5σ-Orbital: CO → M donation
unbes. 2π*-Orb. CO ← M back don.

*Chatt-Duncanson, JCS 1953, 2929:
C_2H_4-$PtCl_2$

Orbitalmischung

M - d_{z^2} 5σ - CO



M - d_{xz} d_{yz} $2\pi^*$ - CO

Festkörper: Bänder von Orbitalenergien ersetzen die diskreten Orbitalenergien von Molekülen
d-Bänder sind schmal - geringe Überlappung

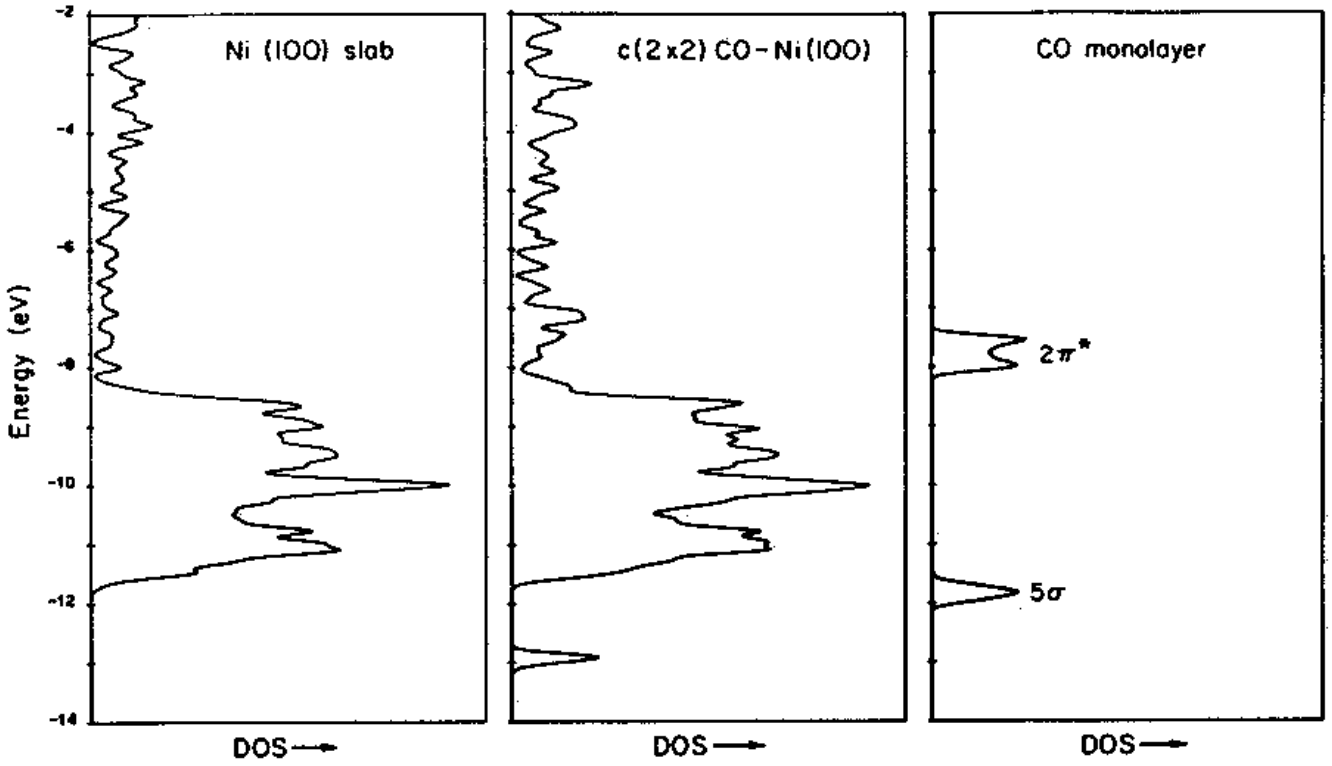


Figure 14 The total density of states of a model $c(2 \times 2)$CO–Ni(100) system (center), compared to its isolated four-layer Ni slab (left) and CO monolayer components.

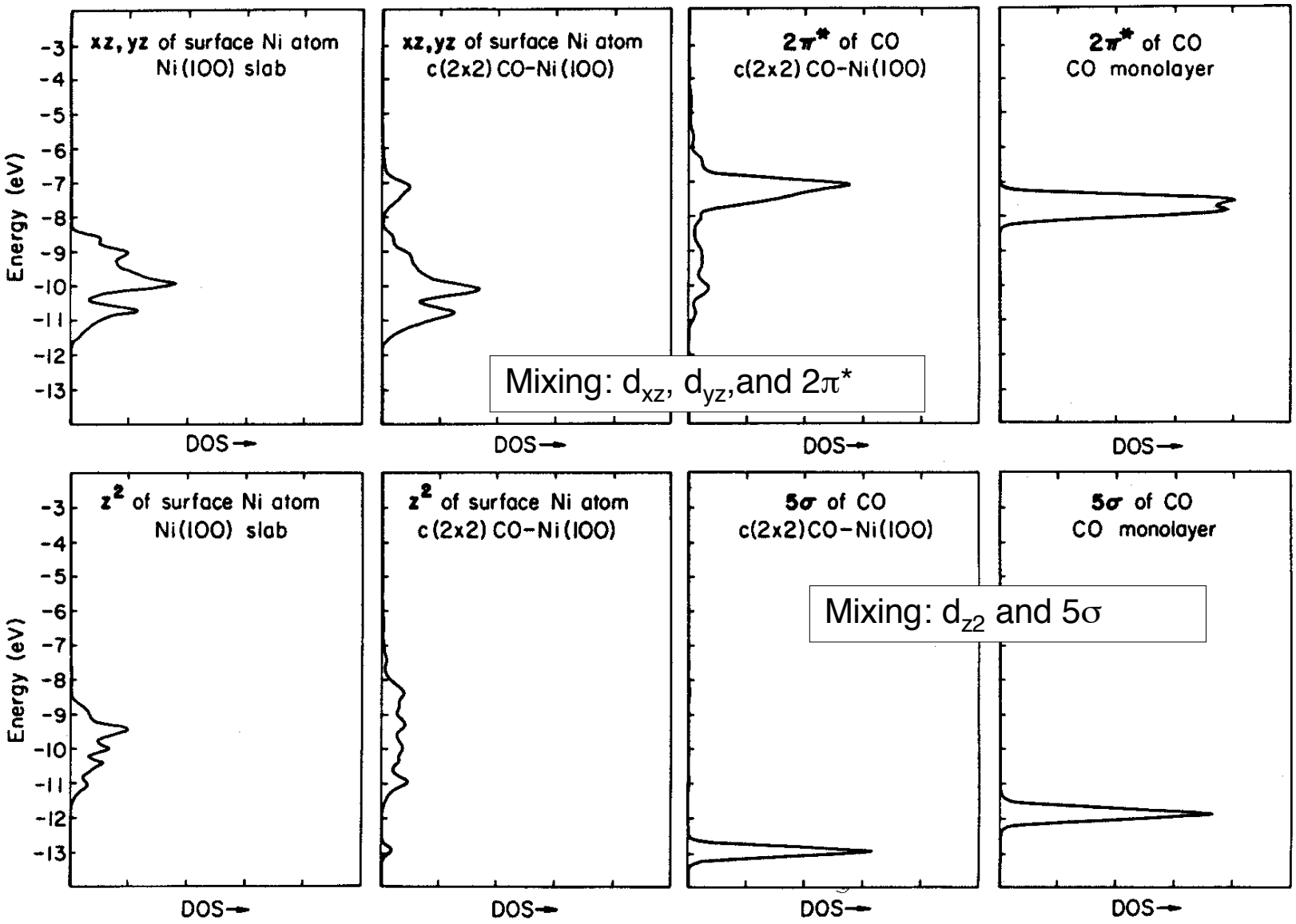
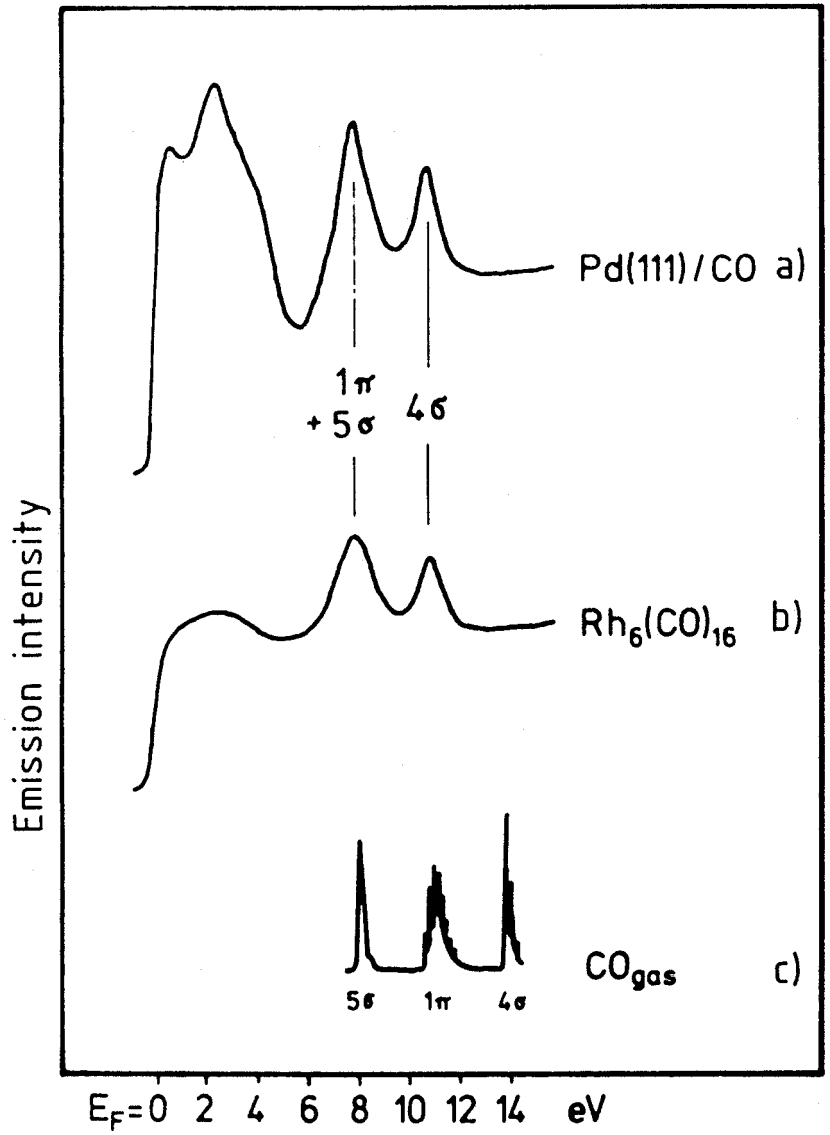


Figure 16 Interaction diagrams for 5σ and $2\pi^*$ of $c(2 \times 2)$C)–Ni(100). The extreme left and right panels in each case show the contributions of the appropriate orbitals (z^2 for 5σ, xz, yz for $2\pi^*$) of a surface metal atom (left) and of the corresponding isolated CO monolayer MO. The middle two panels then show the contributions of the same fragment MOs to the DOS of the composite chemisorption system.

R. Hoffmann, Solids & Surfaces, VCH 1988.



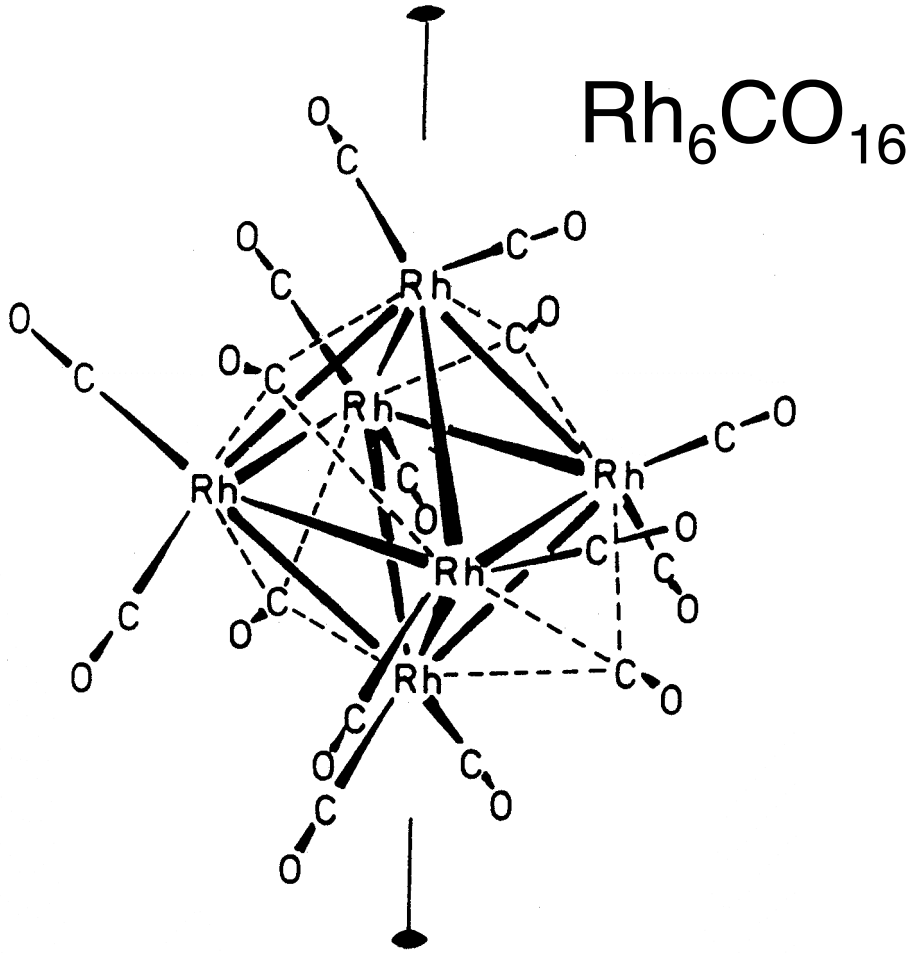


Fig. 4.34. UP spectra (He II radiation) from a) CO adsorbed on a Pd(111) surface; b) $Rh_6(CO)_{16}$; c) Gaseous CO [88a]. The energy scale is referred to the Fermi level of the metallic sample. The onset of emission in spectrum b) is lined up with E_F from spectrum a). Spectrum c) is displaced by the metallic work function, φ = 6 eV. From Conrad et al. [87].

Diamond structure Si and C

- Tetrahedral coordination
- localized bonds built from sp^3 hybrid orbitals
- model: one-dimensional chain of sp-hybrid orbitals

One-dimensional chain of sp-hybrid orbitals

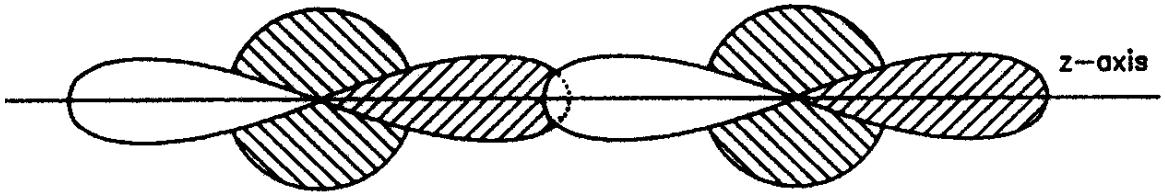


Figure 2.32. p_z- and s-atomic orbitals orientated along the z axis.

$\beta = \beta_{ss}$ α_s

$\beta' = \beta_{sp}$

$\beta'' = \beta_{pp}$ α_p

Hückel equation for one s and one p orbital per cell

$$(2\beta \cos L + \alpha_s - E)c_s(L) \quad - i2\beta' \sin L \; c_p(L) \quad = 0$$

$$i2\beta' \sin L \; c_s(L) \qquad (-2\beta'' \cos L + \alpha_p - E)c_p(L) = 0$$

$$L = 2k\pi / N$$

No interaction between s and p at neighboring sites:
2 separate bands, s and p, as we know already

$$(2\beta \cos L + \alpha_s - E)c_s(L) = 0$$
$$(-2\beta'' \cos L + \alpha_s - E)c_p(L) = 0$$

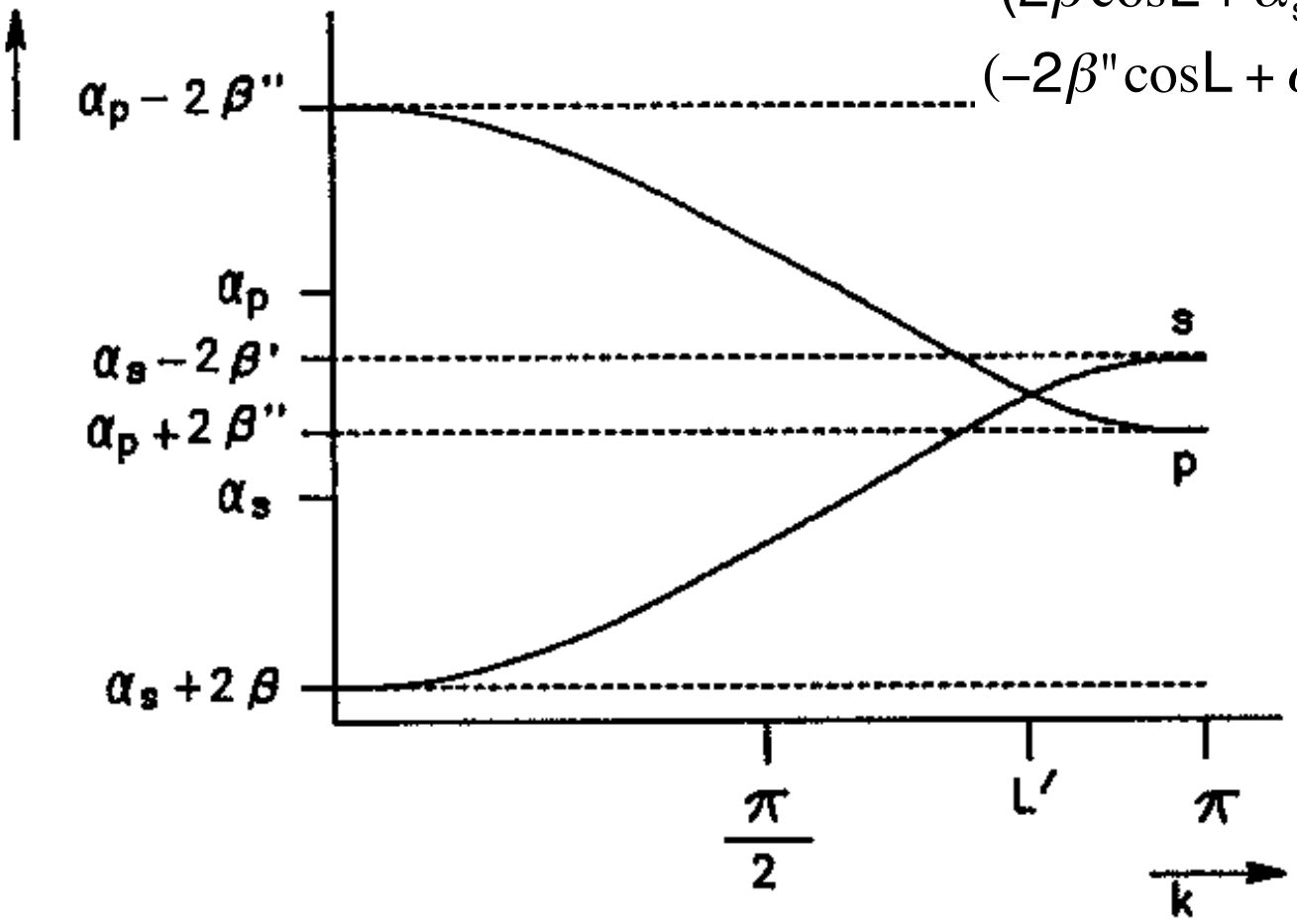


Figure 2.33. Overlapping non interacting *s* and *p* atomic valence electron bands

General solution for s-p-interaction

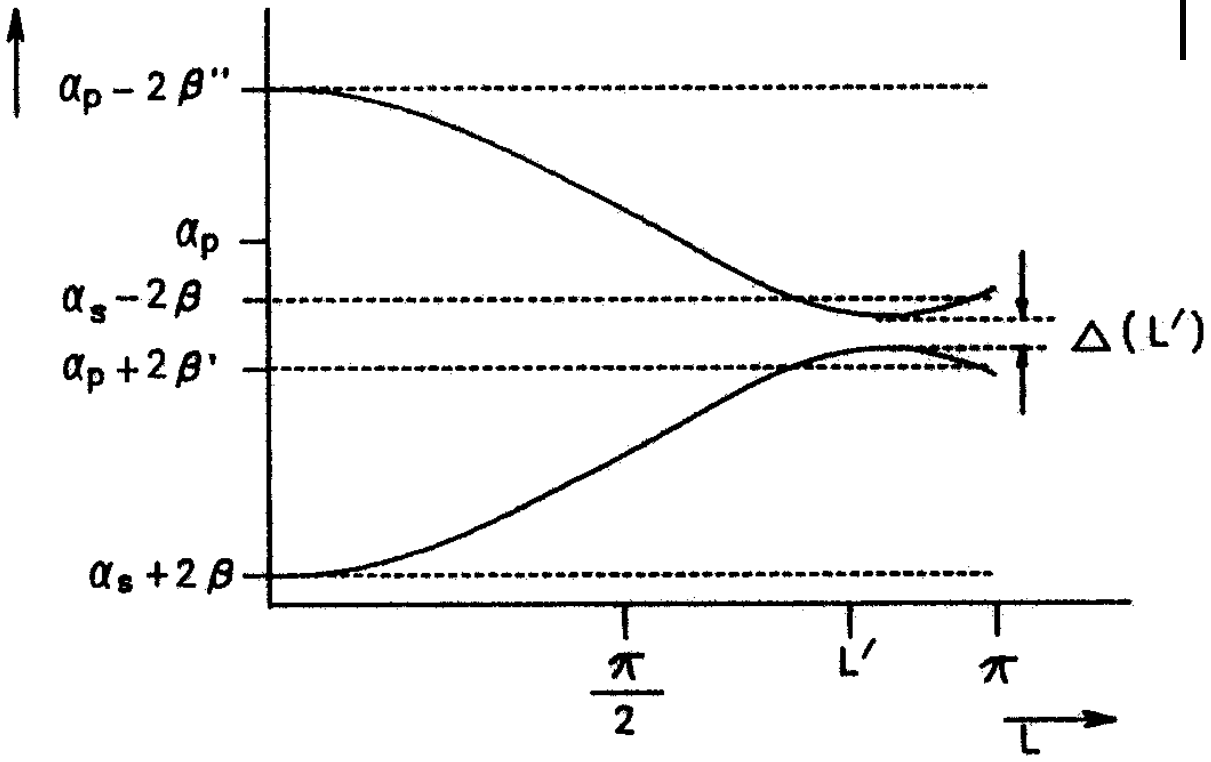
$$E_{1/2} = \tfrac{1}{2}(\alpha_s + \alpha_p) + 2(\beta - \beta'')\cos L$$

$$\pm \tfrac{1}{2}\sqrt{\left[\alpha_s - \alpha_p + 2(\beta + \beta'')\cos L\right]^2 + 16\beta'^2 \sin^2 L}$$

$$E_{1/2} = \alpha \pm 2\beta$$

Ideal hybridisation

$$\beta = \beta' = \beta'' \quad \alpha_s = \alpha_p$$



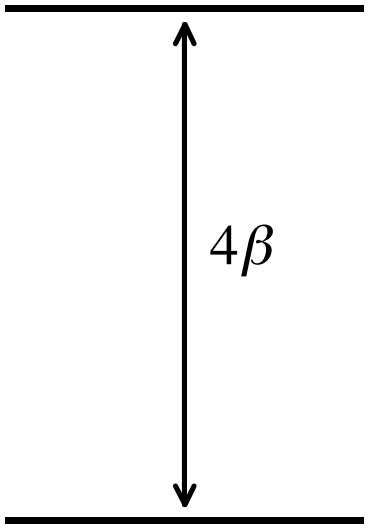


Figure 2.34. Overlapping crossing *s*- and *p*-atomic valence electron bands.