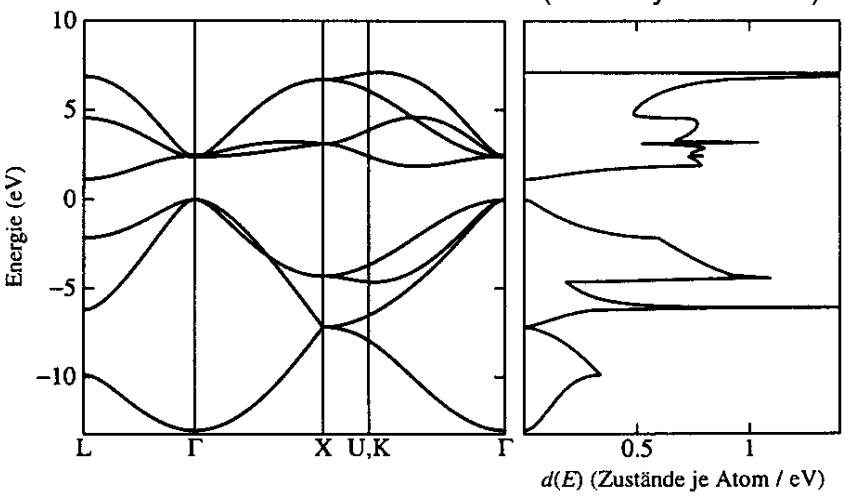
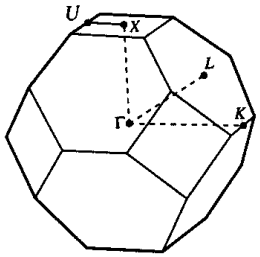
Festkörper - Was wollen wir verstehen ?

Bandstruktur

Zustandsdichte
(Density of states)





Brillouin-Zone

Literatur:

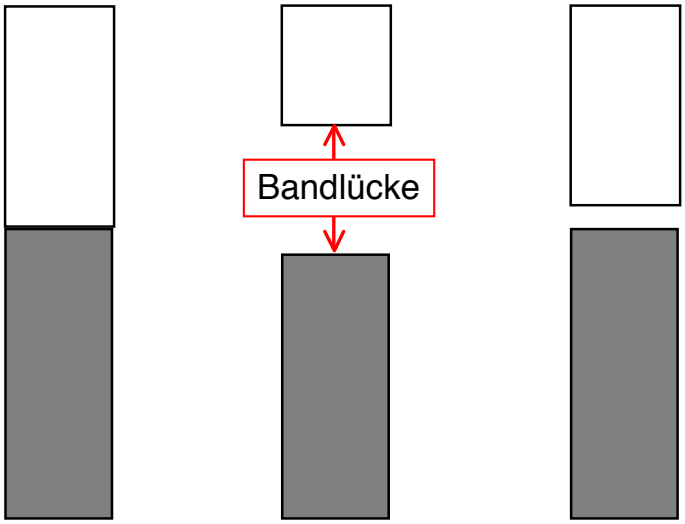
[1] R. Hoffmann, Solids and surfaces, VCH, Weinheim, 1988.
ISBN 3-527-26905-3 VCH Verlagsgesellschaft

[5] A. P. Sutton, The electronic structure of materials, Oxford University Press, 1993.

Metall

Isolator

Halbleiter



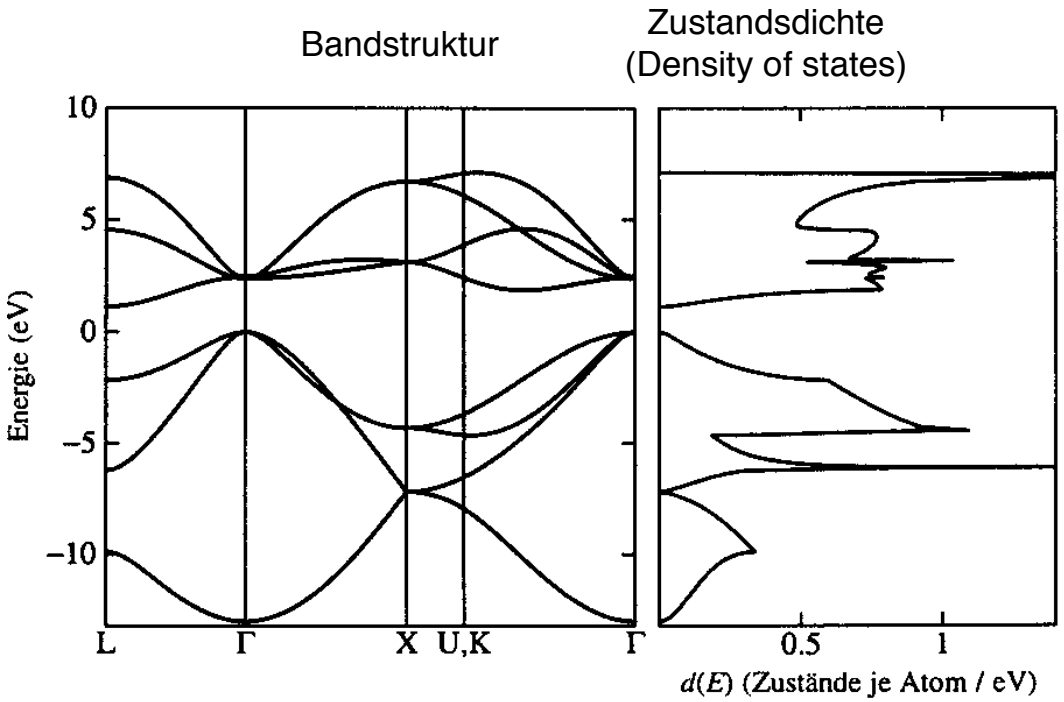
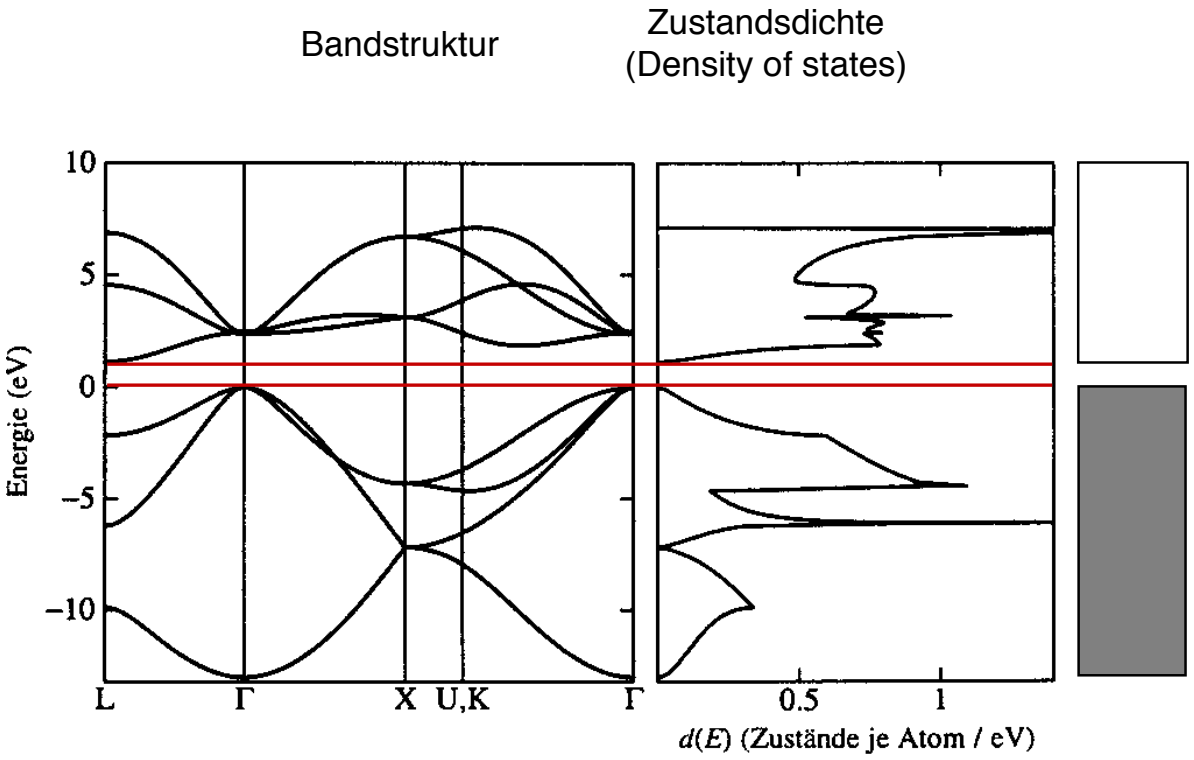


Abb. 6.11: Die Bandstruktur (links) und die Zustandsdichte (rechts) von Silizium mit kubischer Diamantstruktur, abgeleitet mit den Parametern für den Hamilton-Operator aus den Gl. (6.6.1-6.6.2). Die Rechnungen stammen von Dr. A. T. Paxton (1994), private Mitteilung.



N-gliedriger Polyenring

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

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

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

Modell für 1-dim periodisches System
mit einem Orbital und einem Elektron pro Zelle

N-membered Polyene Ring

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

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

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

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

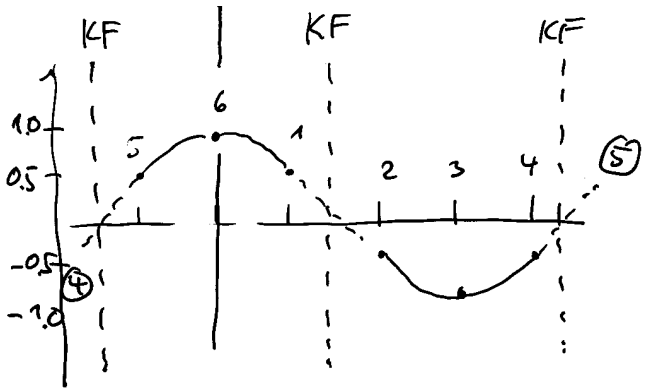
N-membered Polyene Ring - Real orbitals

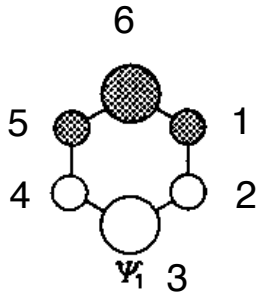
$$\psi_0 = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} 1 \cdot \chi_j$$

$$\left.\begin{aligned} \psi_{|k|,1} &= \sqrt{\frac{2}{N}} \sum_{j=1}^{N} \cos\left(2\pi \frac{|k|}{N} \cdot j\right) \cdot \chi_j \\ \psi_{|k|,2} &= \sqrt{\frac{2}{N}} \sum_{j=1}^{N} \sin\left(2\pi \frac{|k|}{N} \cdot j\right) \cdot \chi_j \end{aligned}\right\} \quad |k| = 1, 2, \ldots \left(\frac{N}{2} - 1\right)$$

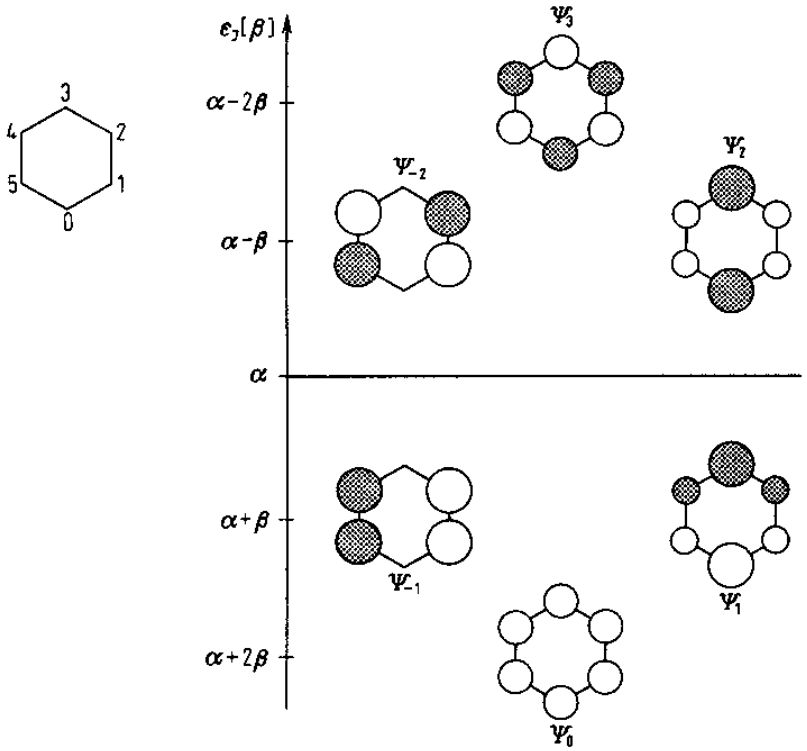
$$\psi_{N/2} = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} (-1)^j \cdot \chi_j$$

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

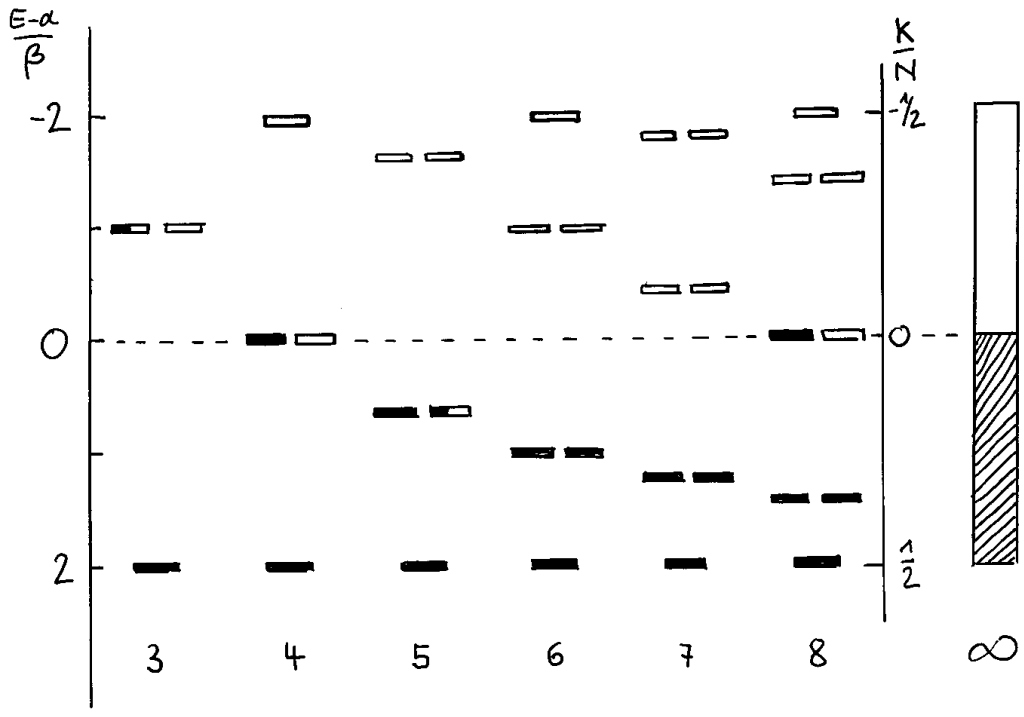




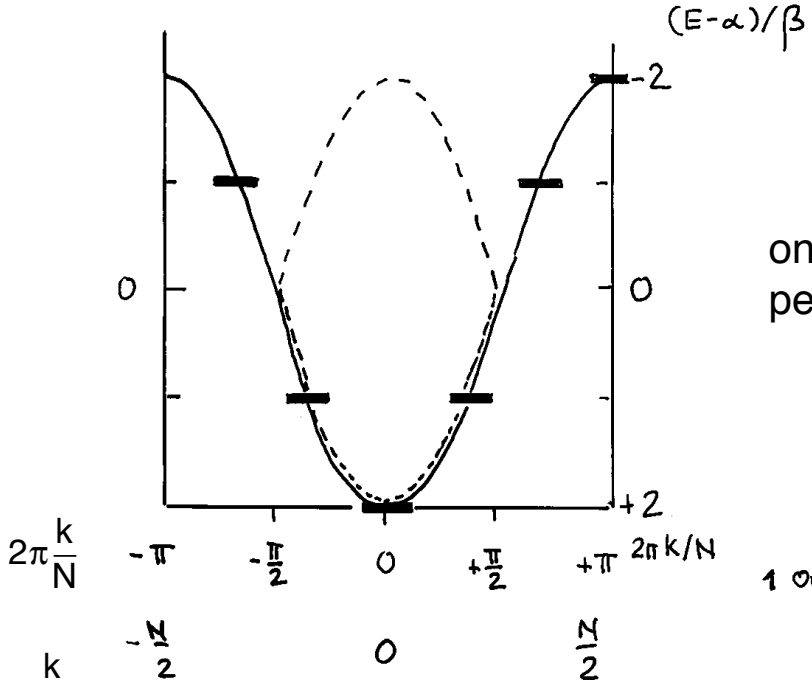
HMO solution for benzene (N=6)



Orbital energies for cyclic systems as a function of N



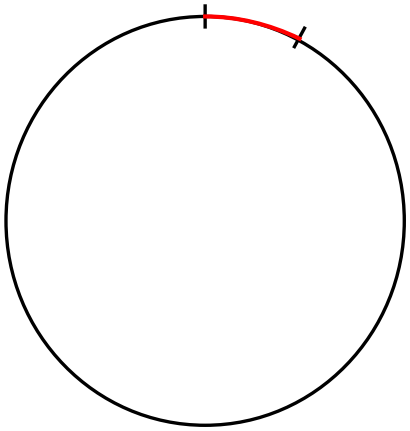
Orbital energy as a function of parameter k - band structure



one orbital per unit cell

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

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

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

k is vector of reciprocal space
k-space

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

defines reciprocal cell
BRILLOIN zone

$b = 2\pi / a = N$

includes permitted k values
0 ... N ;- $^N/_2$ ....+ $^N/_2$
0.... $^{2\pi}/_a$; $^{\pi}/_a$ .... + $^{\pi}/_a$

Density of states

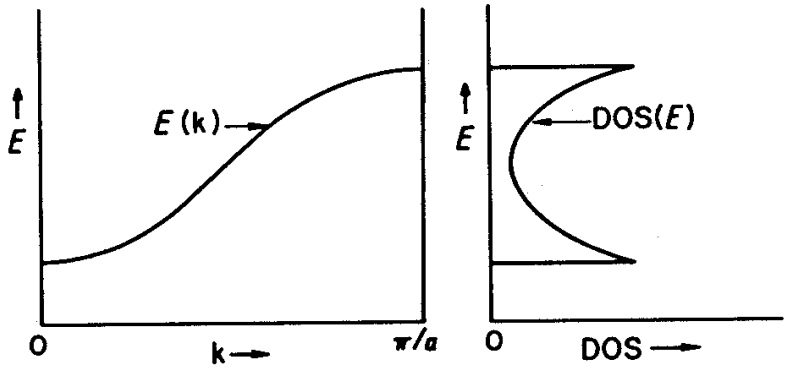
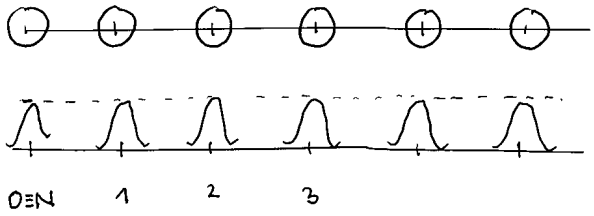


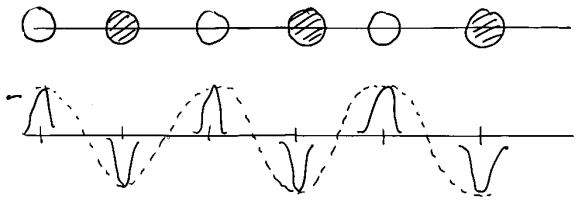
Illustration of c_j along infinite structure for orbitals with different k

k=0



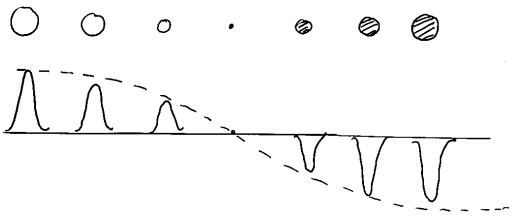
lowest energy

$k=\pm N/2$

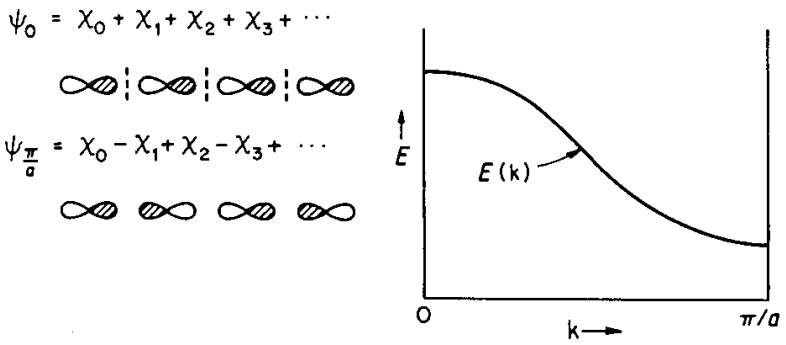


highest energy

$k=N/12$



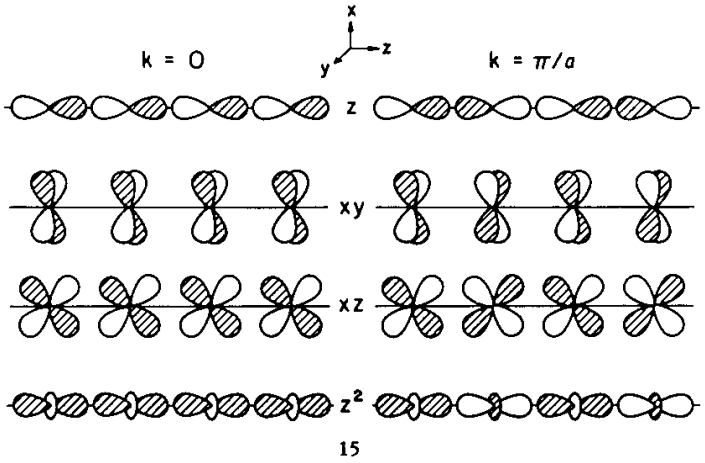
How do the bands run ?



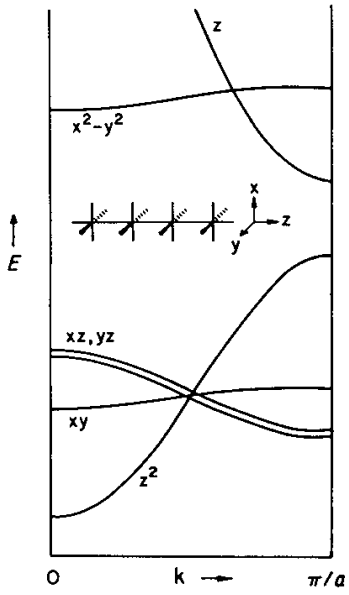
For chains of p orbitals along the periodic direction the crystal orbital for k=0 has the maximum number of nodal planes
- is therefore highest in energy
- forms the top of the band

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

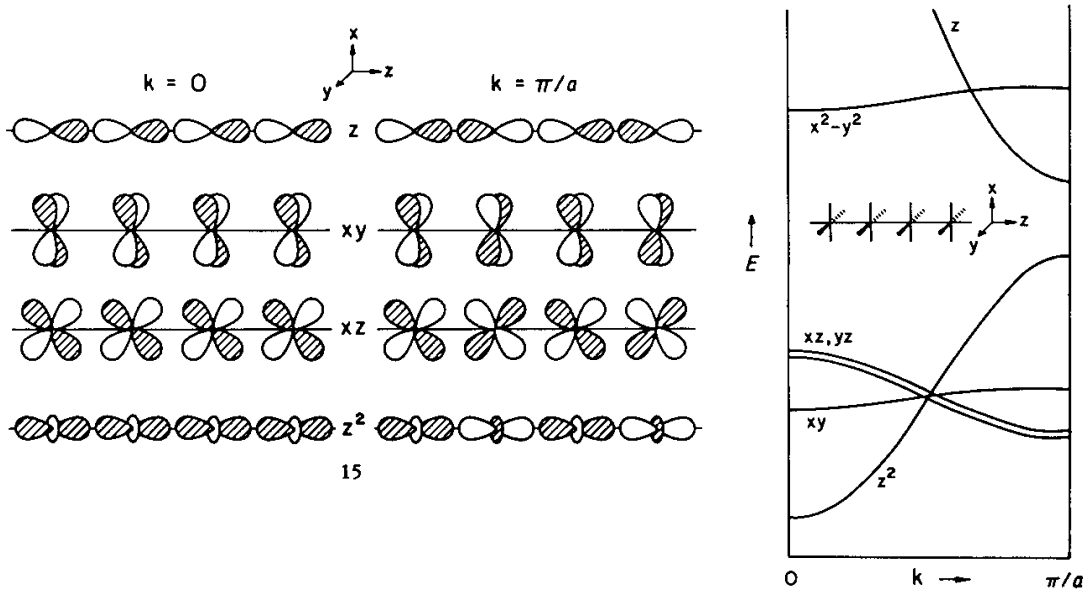


15



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)



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

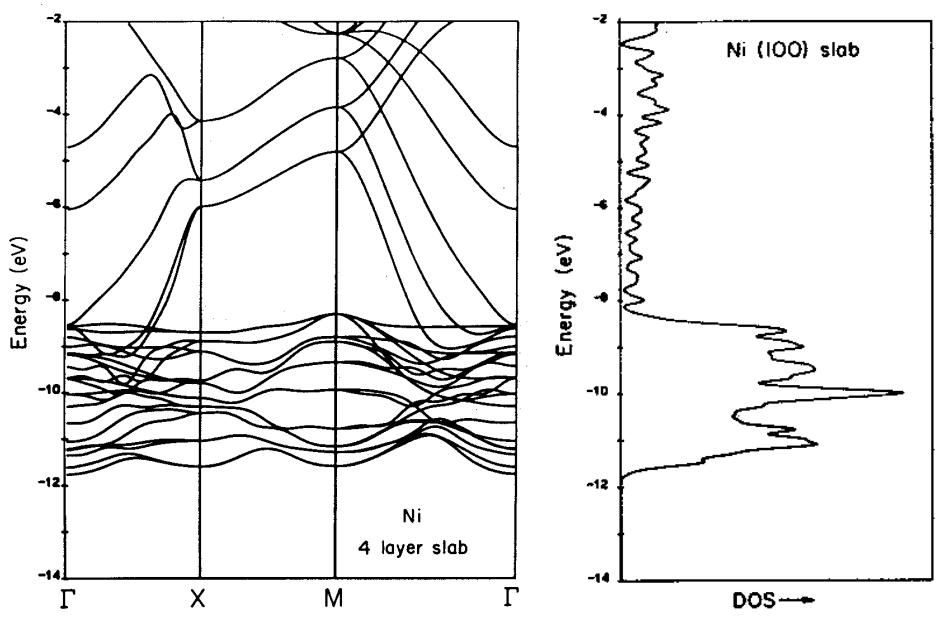
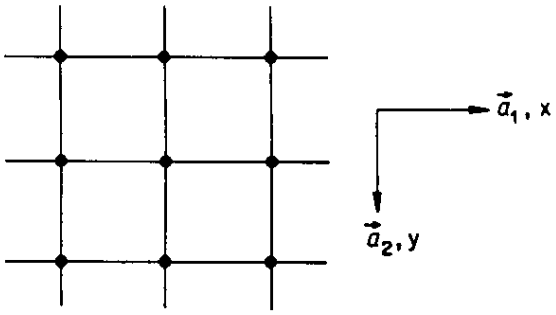
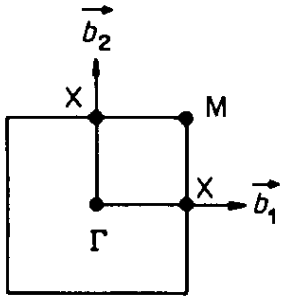


Figure 7 The band structure of a four-layer Ni slab that serves as a model for a Ni(100) surface. The flat bands are derived from Ni 3d; the more highly dispersed ones above these are 4s, 4p.

Two dimensions



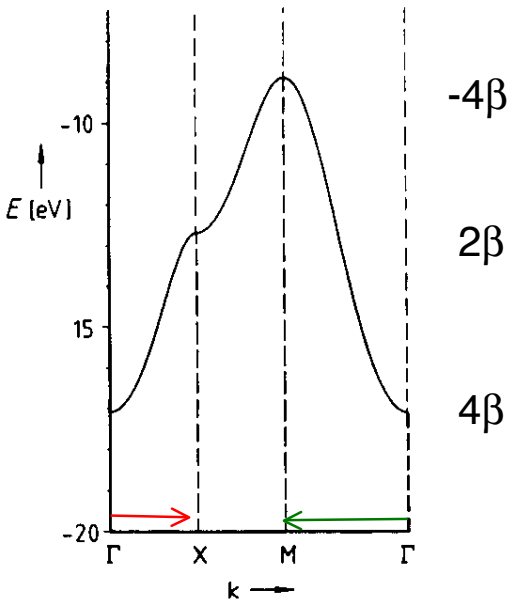
crystal lattice
(direct space)



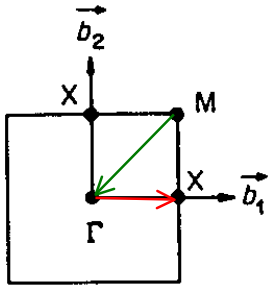
reciprocal lattice
(k space)

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

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



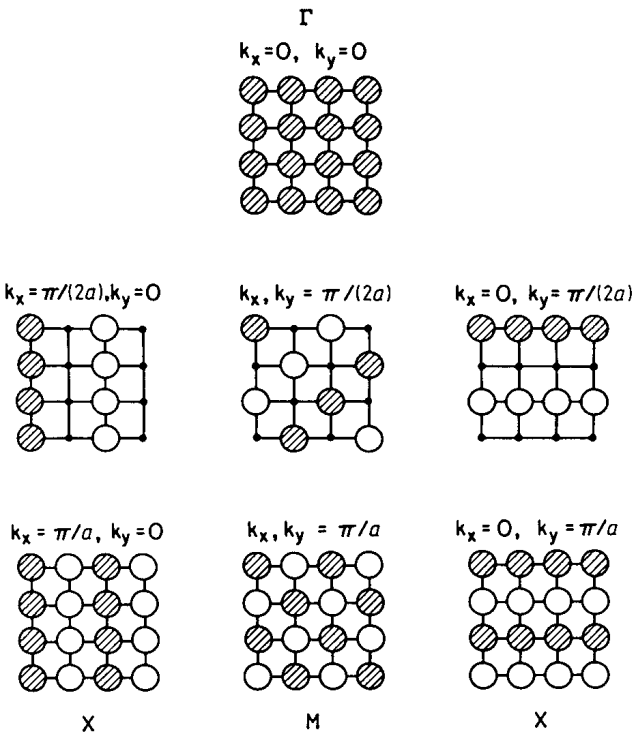
band structure corresponds to different planes through k space



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

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

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



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

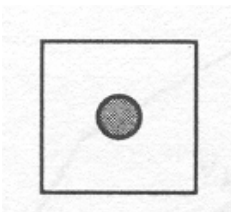
FERMI surface

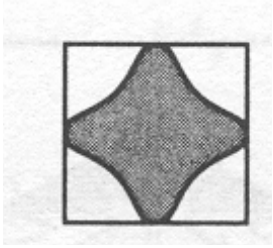
includes all k values in the Brillouin zone which belong to occupied states

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

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

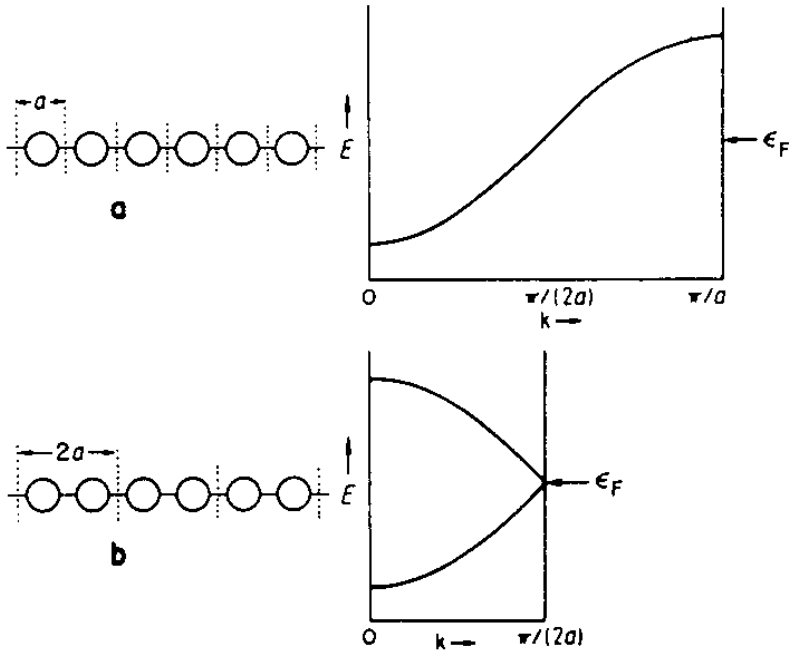
half of the states occupied
$E_{Fermi}(k)= \alpha$
$\cos k_x a+\cos k_y a=0$





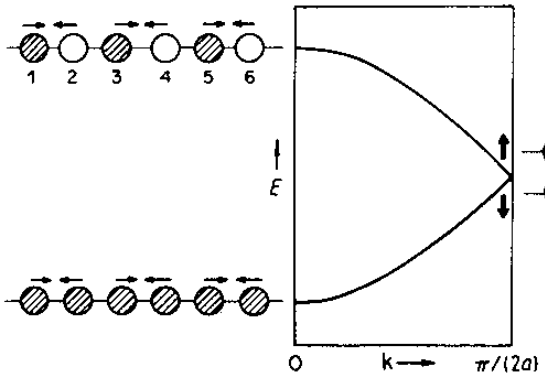
$$k_x, k_y = \pm\frac{\pi}{a}$$

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
(bond alternation)

86

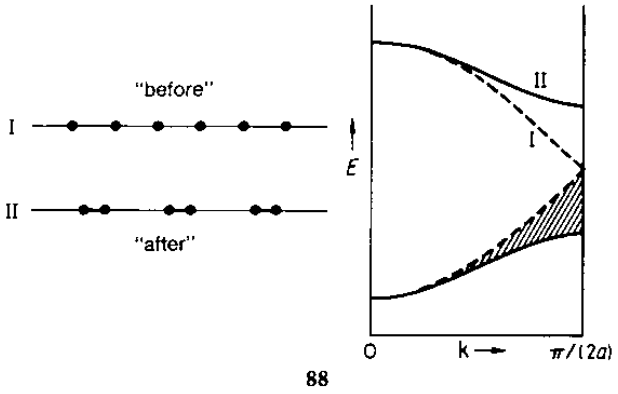


87

antibonding interaction becomes stronger - destabilization

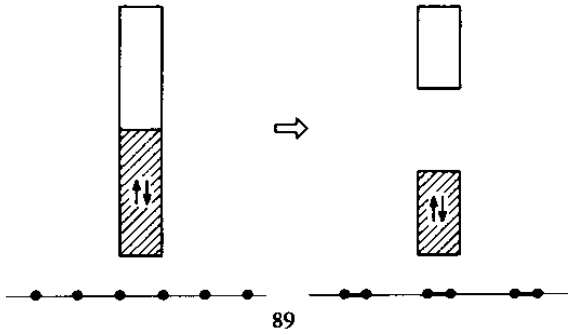
bonding interaction becomes stronger - stabilization

Peierls Distortion

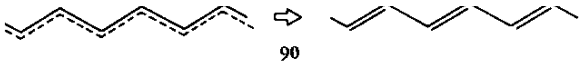


88

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

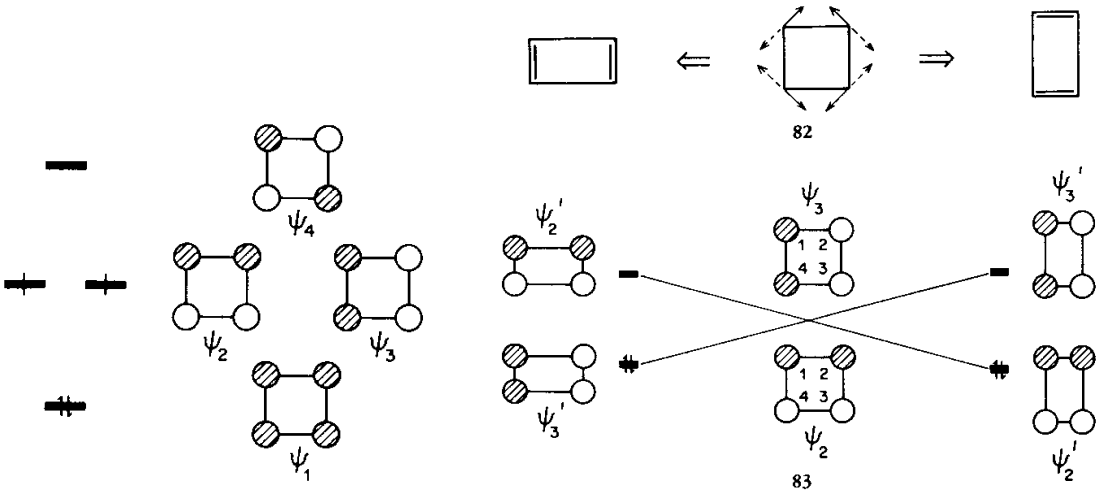


89



90

Jahn-Teller Effect



82

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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.

One-dimensional chain of sp-hybrid orbitals

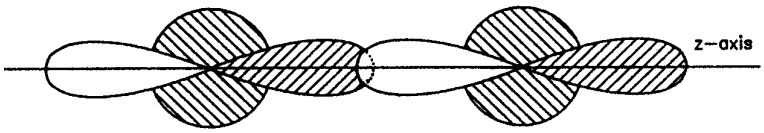


Figure 2.32. p_z- and s-atomic orbitals orientated along the z axis.

$\beta = \beta_{ss}$ 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, that we know already

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

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

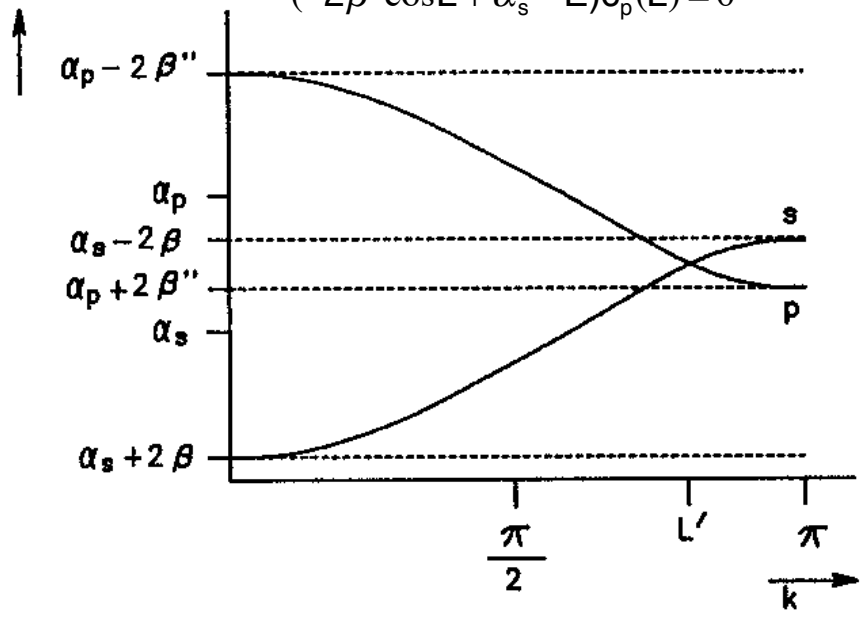


Figure 2.33. Overlapping non interacting s and p atomic valence electron bands

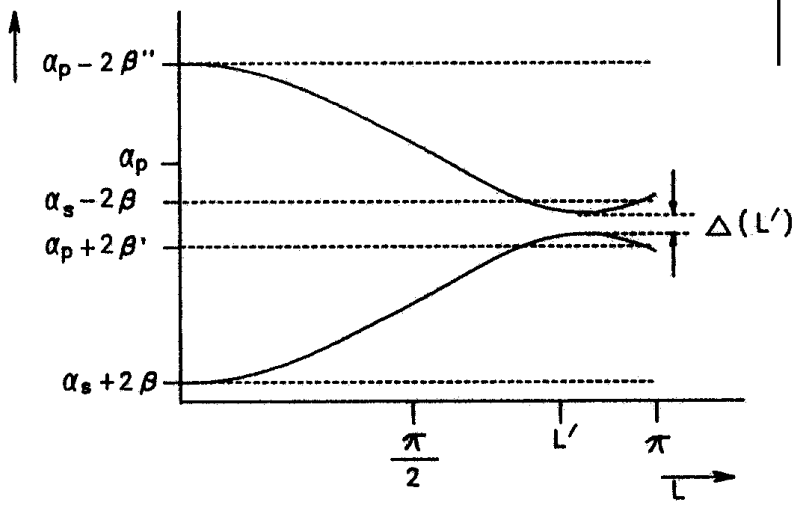
General solution for s-p-interaction

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

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

Ideal hybridisation

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



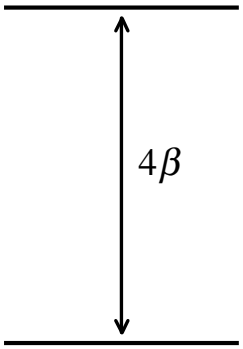
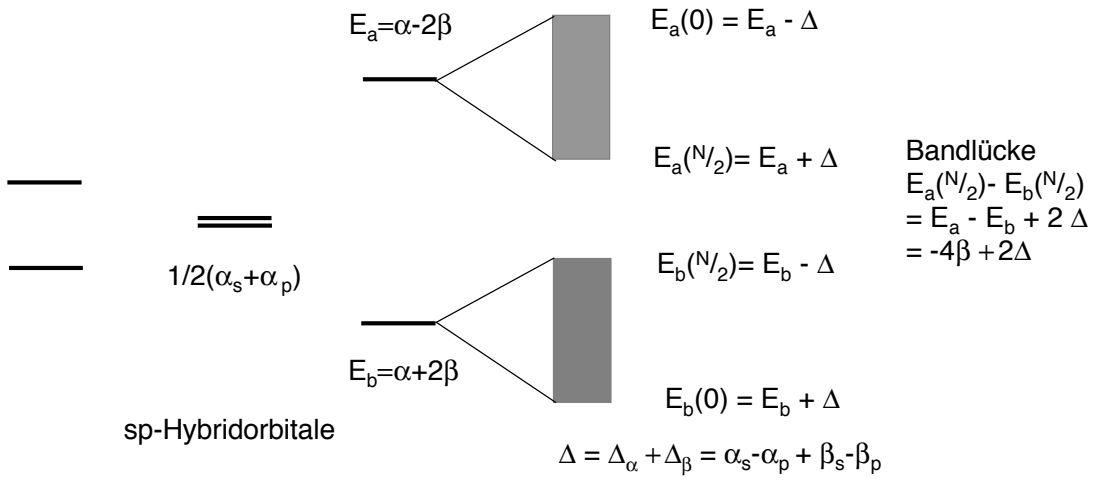


Figure 2.34. Overlapping crossing *s*- and *p*-atomic valence electron bands.

Ketten von sp-Hybridorbitalen - Modelle für Halbleiter (Si) und Isolatoren (C)

Weaire-Thorpe-Modell (3-dim., mit sp^3-Hybriden)



$$\Delta = \Delta_\alpha + \Delta_\beta = \alpha_s - \alpha_p + \beta_s - \beta_p$$

Antibindende u. bindende Linearkomb. von sp-Hybridorbitalen benachbarter Atome

Bänder antibindender und bindender Linear-komb. von sp-Hybrid-orbitalen

Vergleich Si - C (Diamant-Struktur)

Parameter in eV nach Sutton [5]

	Si	C	
-4β	+7,55	+14,5	Überlappung
2Δ	-5,34	-8,9	2s/2p-Aufsplatung
Lücke	2.21	5.6	
Exp.	1.2	5.4	

Shockley-Oberflächenzustand

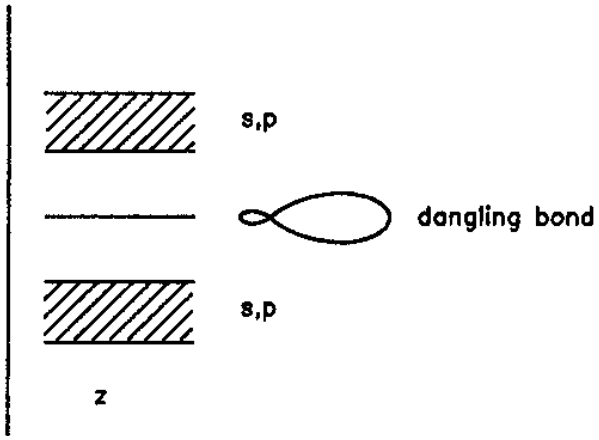


Figure 2.35. Shockley surface state or dangling bond in the almost ideal hybridization limit.

Das Ende einer Kette - Modell für eine Oberfläche
Hybridorbital ohne Bindungspartner besetzt mit einem Elektron
(entspricht einem σ-Radikal)