

# Bonds to Bands

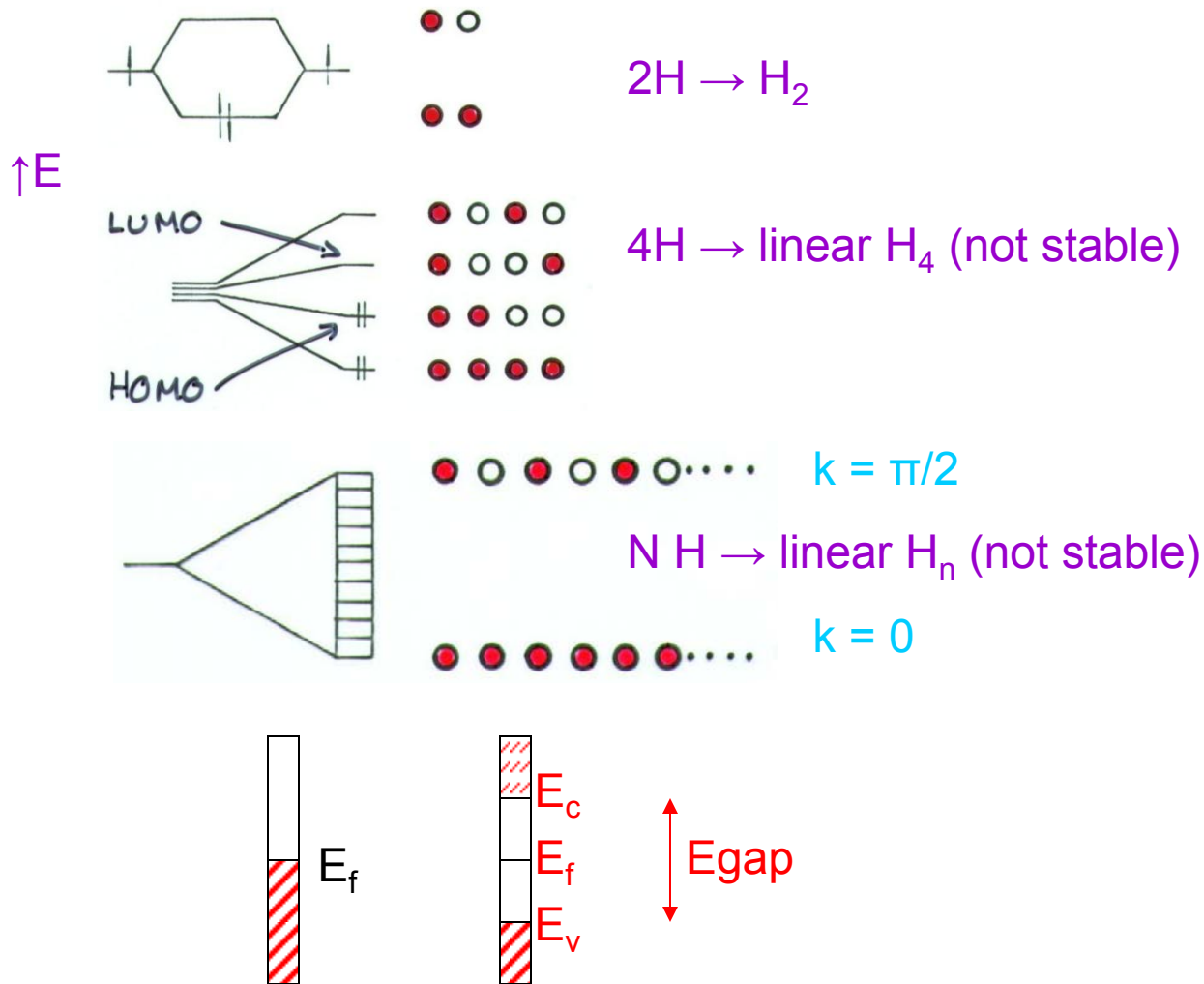
An introduction to basic concepts in solid state and surface bonding and electronic structure.

- Basic classes of bonding
- Basic concepts in quantum chemistry – LCAO and molecular orbital theory (Huckel)
- The tight binding model of solids – bands in 1, 2, and 3 dimensions
- Surfaces – molecular adsorption

## Suggested Readings:

- R. Hoffmann, “Solids and Surfaces: A chemists view of bonding in extended structures” VCH, 1988, pp 1-55, 65-78.
- P.A. Cox, “The Electronic Structure and Chemistry of Solids”, Oxford, 1987, Chpts. 1, 2(skim), 3 (esp. 45-62), and 4 (esp. 79-88).
- Kittel, “Introduction to Solid State Physics” (or Ashcroft and Merman), useful background reading.

# Bonds to Bands - big picture



# Bonds to Bands

- Forces between atoms (chemistry)
  - Covalent
  - Polar covalent
  - Ionic
  - Weak (London/dispersion, dipole...)
- Forces in solids
  - Covalent – Si, C ...
  - Ionic – NaCl, MgO ...
  - Metallic – Cu, Na, Al ...
  - Molecular (weak) – N<sub>2</sub>, benzene

- $E_{\text{disp}} \sim -3/16 \pi E_0 (h\nu_0) \alpha^2 / R^6$

avg. excitation term

polarization term

# Bonds to Bands

- Two main approaches to surface problems in electronic structure calculations:
  - Build up from atom – atomic orbitals + ...
  - Infinite solid down – plane waves + ...
- Interested in energies + positions of electrons

- $E_{\text{class}} = H(r, p) = T + V$  (KE + PE)

- Q.M. teaches us:  $E \Rightarrow i\hbar \frac{\partial}{\partial t}$   
 $t \rightarrow t$

$$x \rightarrow \hat{x}$$

$$P_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x}$$

$$H_{\text{class}} \Rightarrow \hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \text{ or } -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(r)$$

# Bonds to Bands

- 3 postulates in Q. M. (of many)

$$H\psi(r,t) = i\hbar \frac{\partial \psi(r,t)}{\partial t} \quad \text{many Q. Chem. problems use t-independent Schrod. eqn.)}$$

$\psi^2 =$  prob. density of system

- $\alpha\psi_i = a_i\psi_i$  only observable values of system are eigenvalues ( $a_i$ ) of corresponding operator ( $\alpha$ )

$$\begin{aligned} \langle A \rangle &= \int \psi^* \alpha \psi dV \quad (\text{and, if } \psi \text{ is eigenfnc. of } \alpha \text{ operator}) \\ &= \int \psi^* a_i \psi dV = a_i \quad (\text{average, exp. value}) \end{aligned}$$

# Bonds to Bands

- Skip over: particle in a box, harmonic oscillator, rigid rotor, Heisenberg, angular momentum...
- H atom – can do exactly!

$$E = \frac{-\mu Z^2 e^4}{2\hbar^2 n^2} \quad (n = 1, 2, 3, \dots) = \frac{-z^2 e^2}{2n^2 a_0}$$

- Also get  $\psi$ 's e.g.  $\psi(1S) = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$   
 $\psi(2S) = \dots$

# Bonds to Bands

- But for most problems we use some approximate methods:
  - Two common methods used in Quant. Chem. are **variational** and **perturbation** theory methods.
  - Pert. Theory:  $H = H^0 + \lambda H^1 + \lambda^2 H^2 + \dots$

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \text{ (often known)}$$

# Bonds to Bands

- Variational method

- Use matrix notation  $\psi = |\psi\rangle$

$$H|\psi\rangle = E|\psi\rangle \quad (\text{time indep. Sch. Eqn.})$$

- For stationary states, if  $\psi$  is normalized, well-behaved function, it can be shown that

$$\langle \psi^* | H | \psi \rangle = \langle \psi^* | E | \psi \rangle = E \langle \psi^* | \psi \rangle$$

$$\Rightarrow E = \frac{\langle \psi^* | H | \psi \rangle}{\langle \psi^* | \psi \rangle} \quad \begin{array}{l} \leftarrow \text{variational integral} \\ \leftarrow \text{overlap integral} \end{array}$$

- Minimize variational integral to get ground st  $\psi$ 's.



# Bonds to Bands

- Best to start to solve Sch. Eqn. by choosing good  $\psi$ 's!

$$\psi = \sum_n c_n \phi_n \quad (\text{also basic QM postulate})$$

- Any  $\psi$  can be expanded from set of orthonormal functions  $\phi_n$  (satisfying appropriate boundary conditions)

# Bonds to Bands

- In Quantum Chemistry, often use hydrogen-like “atomic orbitals”  $\phi_n$  (s, p, d...) to study molecules (molec.  $\psi$ 's).
- This approach is called LCAO – linear combination of atomic orbitals
- General problem is to minimize variational integral by finding coefficients  $c_n$  that make variational integral stationary:

$$\frac{\partial c_n}{\partial E} = 0!$$

# Bonds to Bands

$$H\psi = E\psi \Rightarrow$$

$$H \sum_n c_n \phi_n = E \sum_n c_n \phi_n$$

$$(H - E) \sum_n c_n \phi_n = 0$$

$$\sum_n c_n (H\phi_n - E\phi_n) = 0$$

$$\sum_n c_n \left( \int \phi_m^* H \phi_n^* d\nu - \int \phi_m^* E \phi_n^* d\nu \right) = 0$$

$$\sum_n c_n (H_{mn} - E\delta_{mn}) = 0 \quad \text{if } \phi_{nm} \text{ orthonormal, if not:}$$

$$\sum_n c_n (H_{mn} - ES_{mn}) = 0$$

(Consult QM book for derivations!)

# Var. Method

- The nontrivial solution for complex systems is  $|H_{mn} - ES_{nm}| = 0$  can be a big determinant
- Solutions yield  $E_i$ 's, which then yield  $c_i$ 's (normalize with  $\sum c_i^2 = 1$ )
- Computationally hard part is determination of  $H_{mn}$  and diagonalization of matrix.

# Bonds to Bands

- Most simple molecular system  $\text{H}_2^+$   
(molecule ion with one electron)

$$\hat{H}_{elec} = \underbrace{-\frac{\hbar^2}{2m}\nabla^2}_{\text{Kin. En.}} - \underbrace{\frac{e^2}{r_{IA}} - \frac{e^2}{r_{IB}}}_{\text{Elect.-nuc. attract.}} + \underbrace{\frac{e^2}{r_{AB}}}_{\text{nucl. rep.}} \left( + \frac{2e^2}{r_{12}} + \dots \right)$$

repulsion for  $\text{H}_2$  electronic or larger systems

- For trial functions choose 2 simple 1s atomic orbitals.

$$\psi_i = c_{Ai}\phi_{ISA} + c_{Bi}\phi_{ISB}$$

let

$$H_{AA} = \langle \phi_{ISA}^* | H | \phi_{ISA} \rangle = H_{BB}$$

$$H_{AB} = \langle \phi_{ISB}^* | H | \phi_{ISA} \rangle = H_{BA}$$

$$S_{AB} = \langle \phi_{ISB}^* | \phi_{ISA} \rangle = S_{BA}$$

$$S_{AA} = 1$$

# Bonds to Bands

- For a simple diatomic, the determinant becomes:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0$$

$$(H_{AA} - E)(H_{BB} - E) - (H_{AB} - ES_{AB})^2 = 0$$

$$(1 - S_{AB}^2)E^2 + (2H_{AB} - 2H_{AA})E + (H_{AA}^2 - H_{AB}^2) = 0$$

solve quadratic and get 2 solutions:

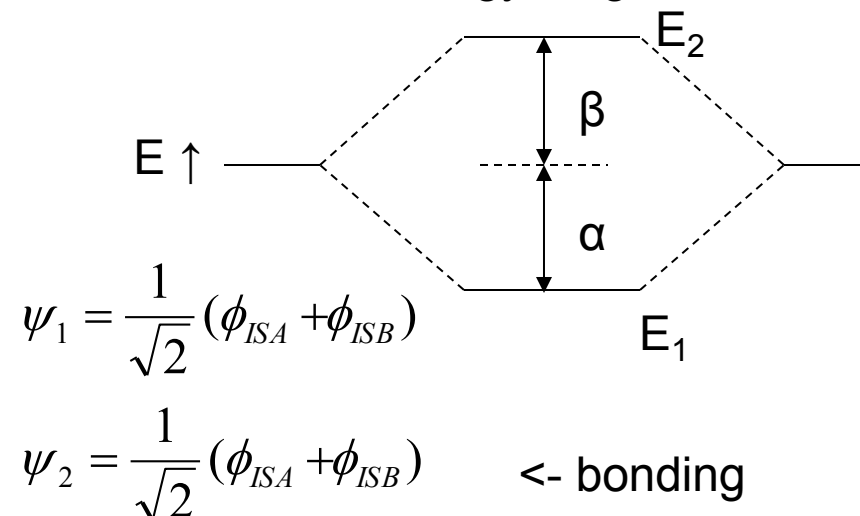
$$E = \frac{H_{AA} - H_{AB}S_{AB} + H_{AB} - H_{AA}S_{AB}}{(1 - S_{AB})(1 + S_{AB})} \quad + \text{ sol'n}$$

$$E = \frac{H_{AA} - H_{AB}S_{AB} - H_{AB} + H_{AA}S_{AB}}{(1 - S_{AB})(1 + S_{AB})} \quad - \text{ sol'n}$$

$$\Rightarrow E_1 = \frac{H_{AA} + H_{AB}}{(1 + S_{AB})} \quad (+)$$

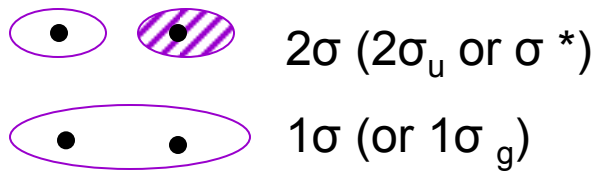
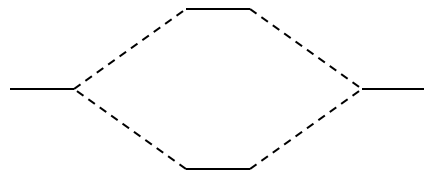
$$\Rightarrow E_2 = \frac{H_{AA} - H_{AB}}{(1 - S_{AB})} \quad (-)$$

Can draw correlation energy diagram:



# Bonds to Bands

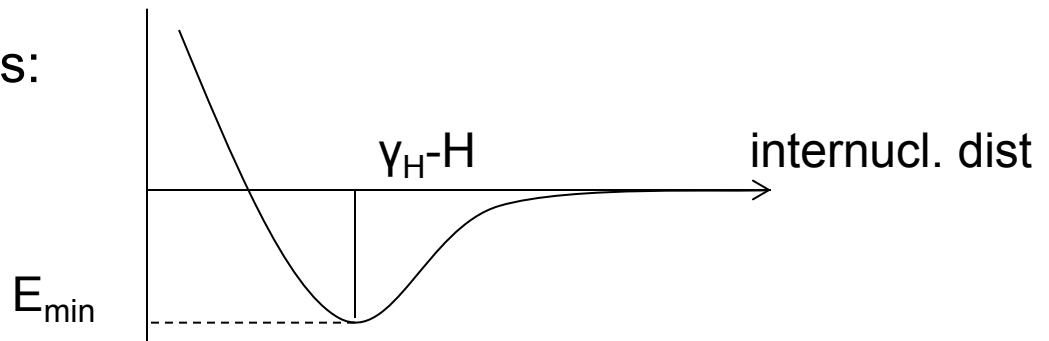
- $\Psi_1$  is called bonding orbital
- $\Psi_2$  is called anti-bonding orbital



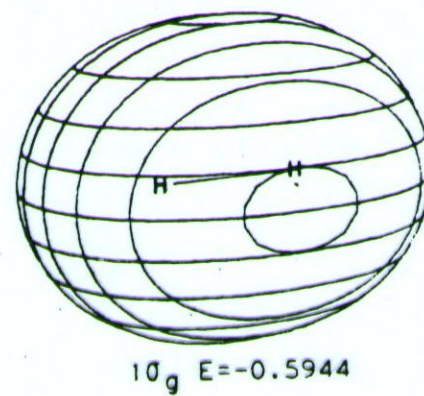
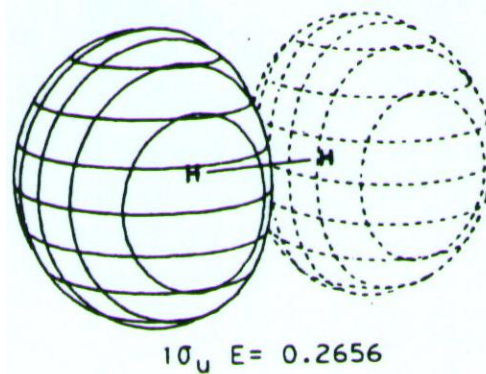
(phase  $\neq$  spin)

- Remember: each orbital can have 2 electrons. (Pauli)
- For ( $2^+$ ) electron systems must add elec: - elec. repulsion + screening of core  $Z_{\text{eff}}$  concepts (and more)

- Potential energy diagrams:

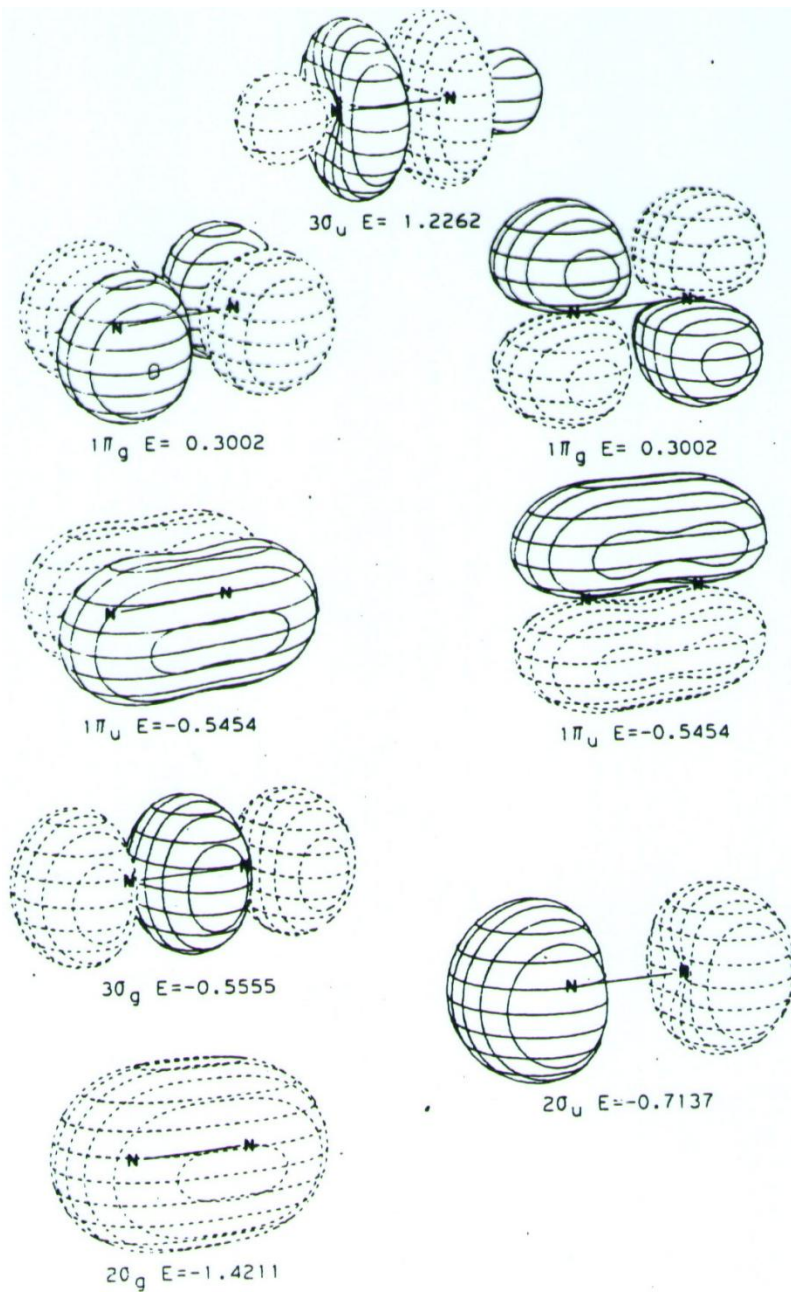


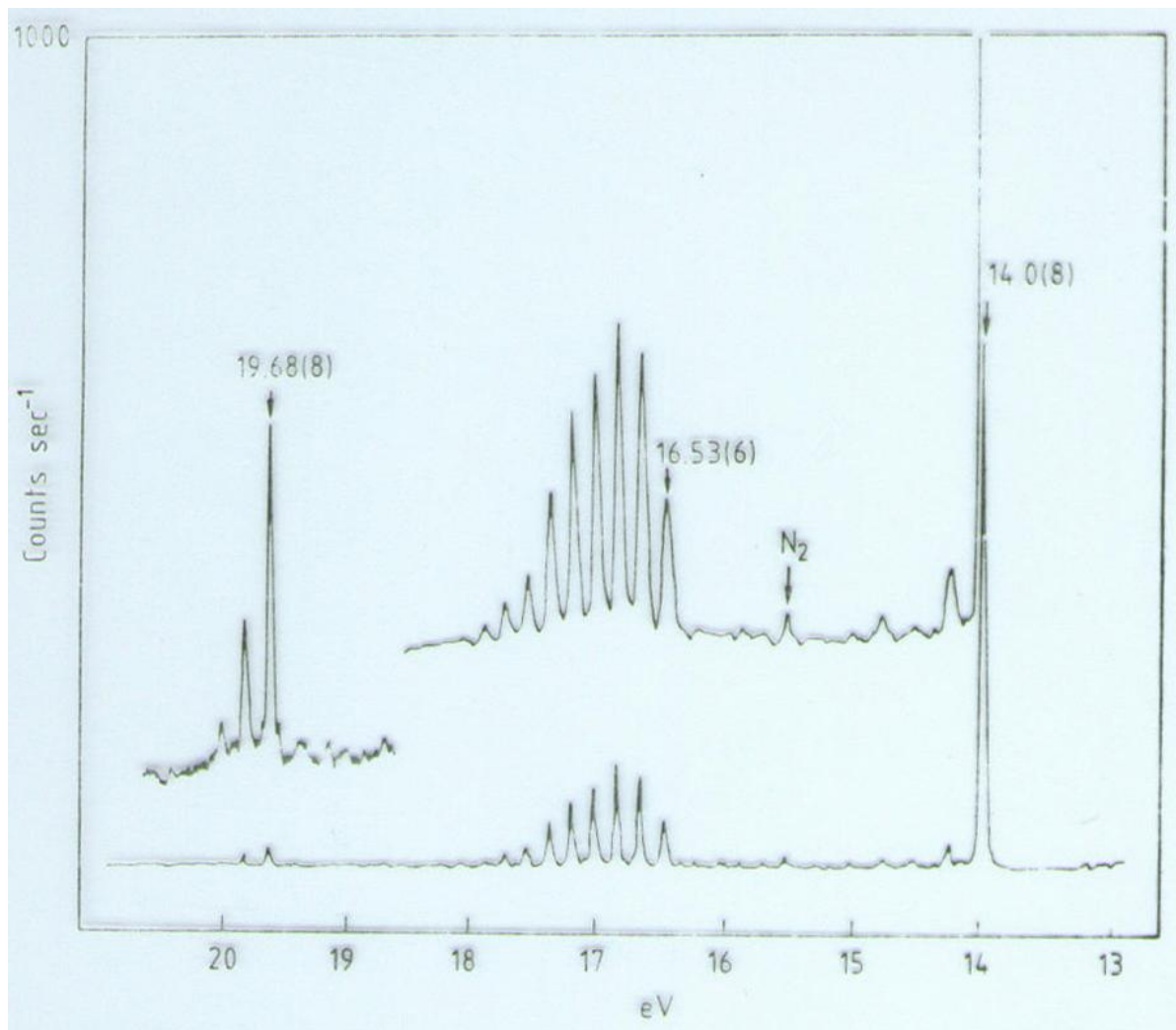
# Hydrogen



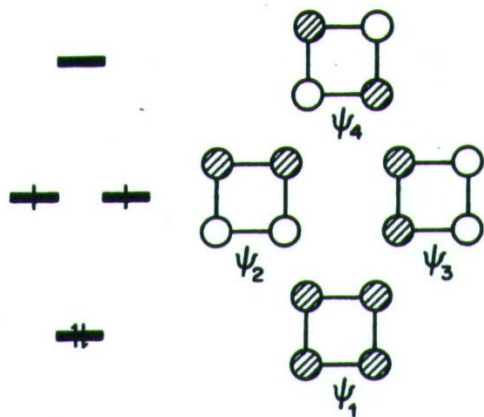


# Nitrogen

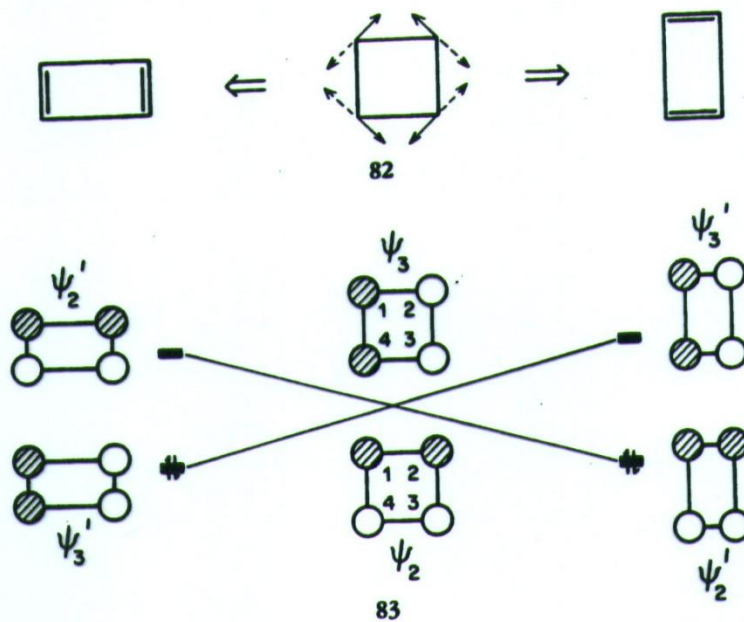


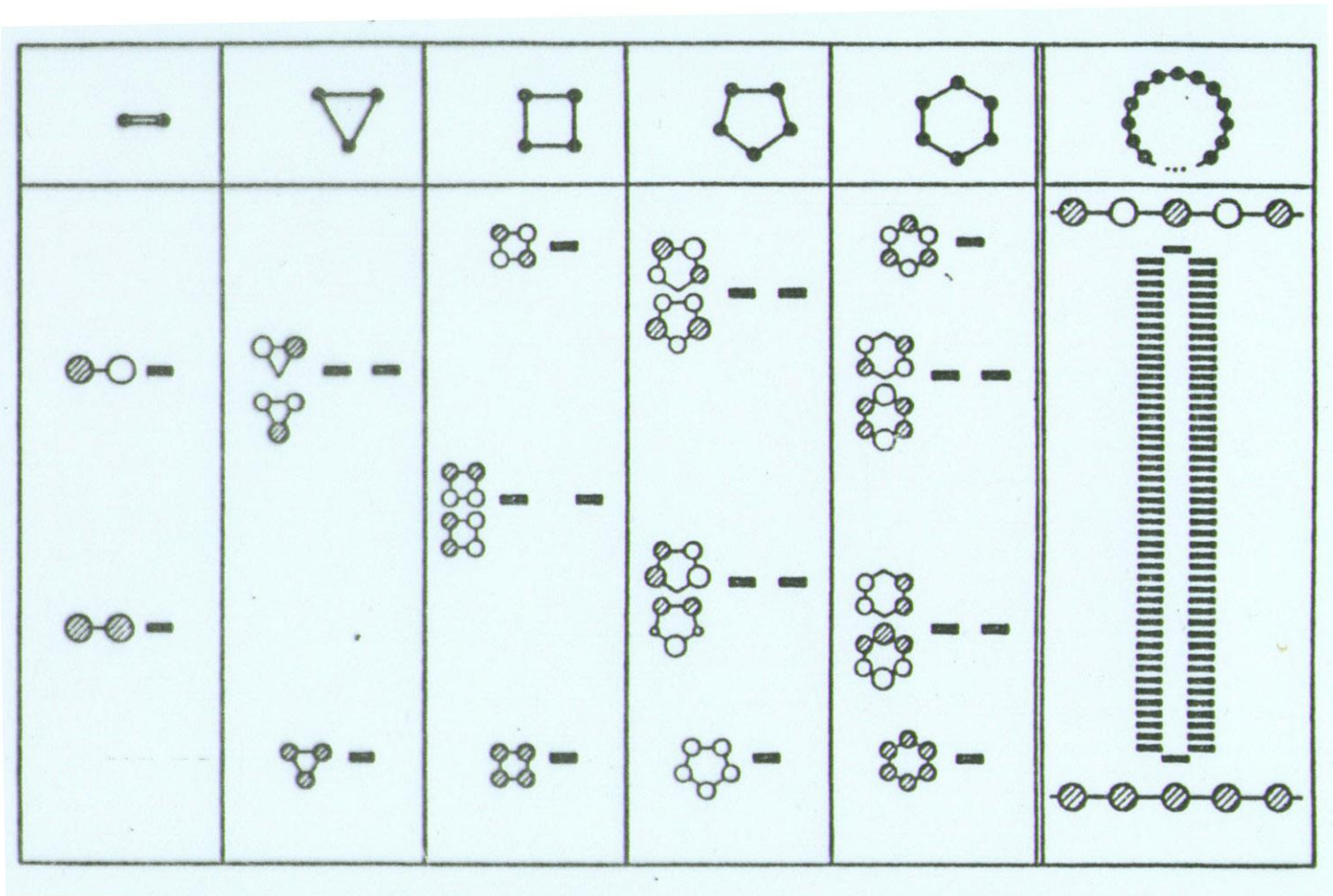


Can use photoemission to determine energy levels. Above is the He 1 ultraviolet photoelectron spectrum of CO. Note the vibrational fine structure of the ionic states. From Turner et. al.



Qualitative electronic structure and energy minimization of cyclobutadiene; symmetry breaking

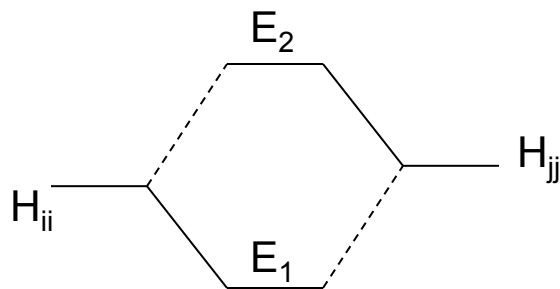




Energy levels and symmetry of multi-atom ring systems

# Extended Hückel Theory - EHT

- Quantum chemical approximation technique.
- Semi-empirical.
- Study only valence (i.e. bonding) orbitals.
- Solve the problem  $H_4=E_4$  with LCAO variational method, but using ideas from perturbation theory.



- The initial state orbitals are atomic slater type orbitals – STOs
$$X_i = A r^{n-1} e^{-5r/n_0} Y_{lm}(\theta, \varphi)$$
- The initial state energies,  $H_{ii}$  are taken as  $-I.P.$  from experiment or some other calculation.

# Extended Hückel Theory - EHT


- Intuitive idea is that the strength of a bond, as represented by the off-diagonal matrix elements  $H_{ij}$ , should be proportional to the extent of overlap ( $S_{ij}$ ) and the mean energy of the interacting orbitals  $(H_{ii}+H_{jj})/2$ .

$$H_{ij} = K \frac{(H_{ii} + H_{jj})}{2} S_{ij}$$

- K is an empirical parameter between 1 and 2.
- Problems:
  - $H_{ij}$  is not exact
  - No charge self consistency
  - $H_{ij}$  increases with overlap causing system to show minimum energy when atoms collapse.
  - No core-core repulsion
  - Etc.
- But... EHT does usually show qualitatively correct trends in an easily interpretable manner.

phase factor


$$k=0 \quad \psi_0 = \sum_n \underbrace{e^{i0n}} \chi_n = \sum_n \chi_n$$

$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$


“bonding”

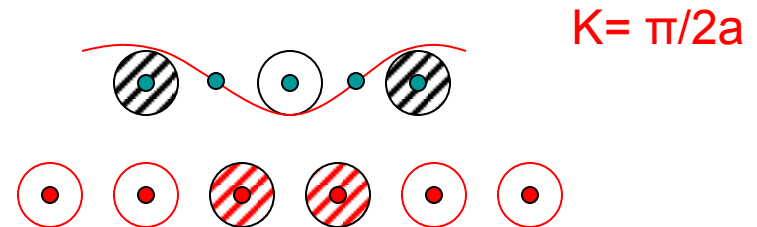
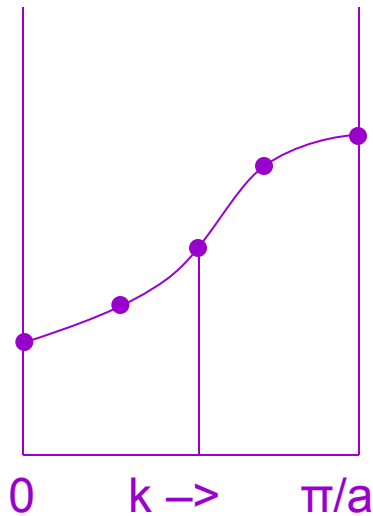
neighboring orbitals in lattice  
“in-phase”

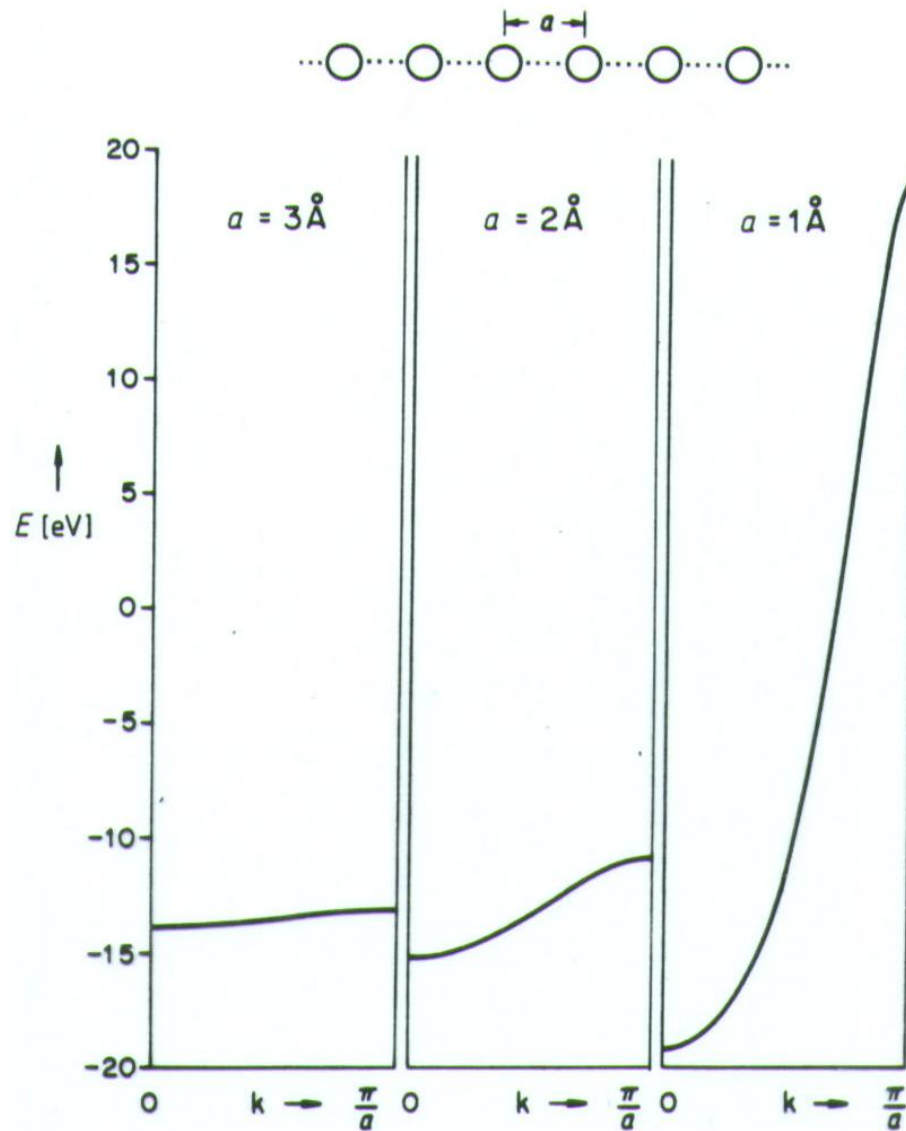
$$k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n \underbrace{e^{i\pi n}} \chi_n = \sum_n (-1)^n \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$


“anti-bonding”

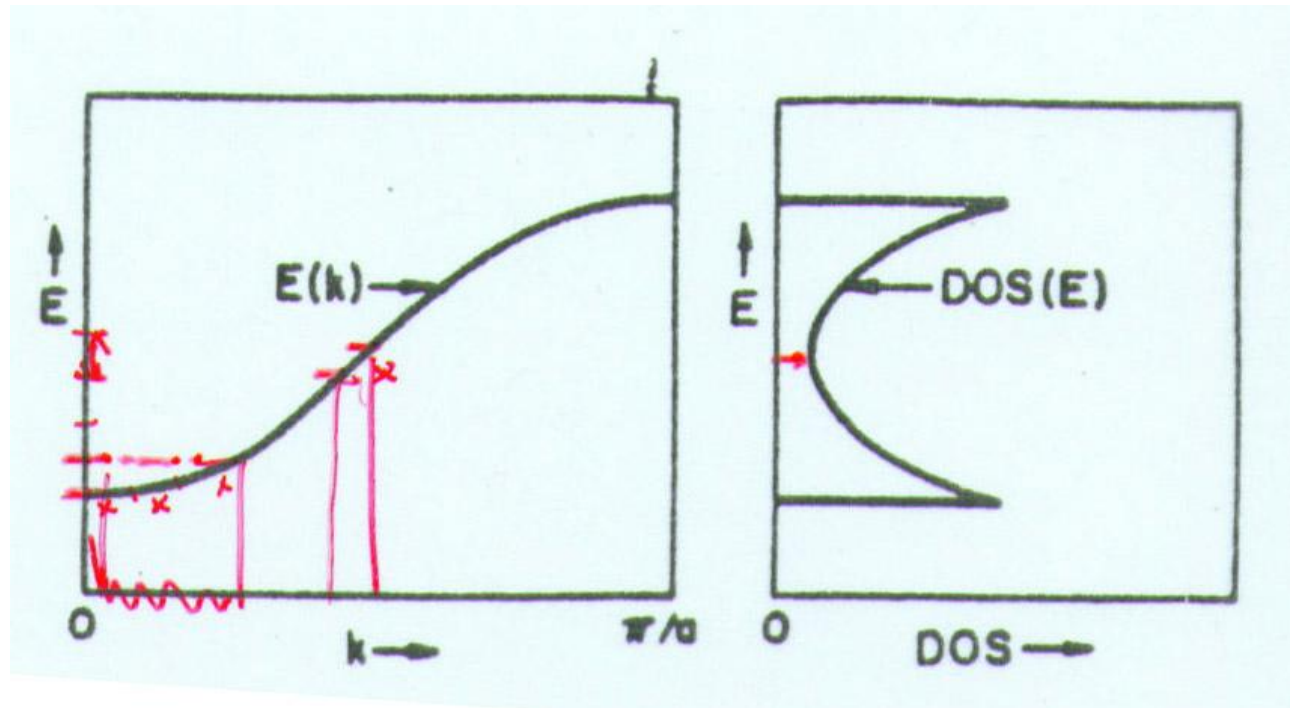
neighboring orbitals in lattice  
“out-of-phase”



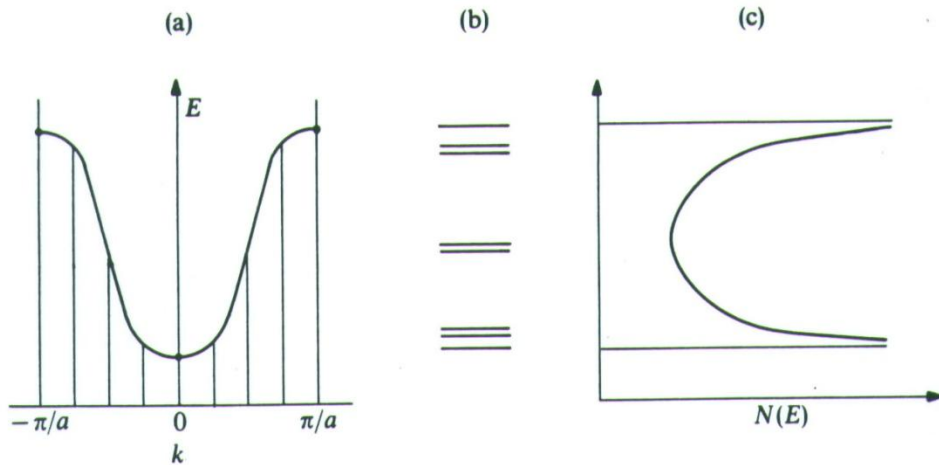


The band structure of a chain of hydrogen atoms spaced 3, 2, and 1 Å apart. The energy of an isolated H atom is -13.6 eV.

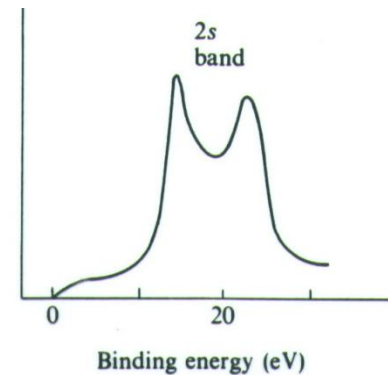




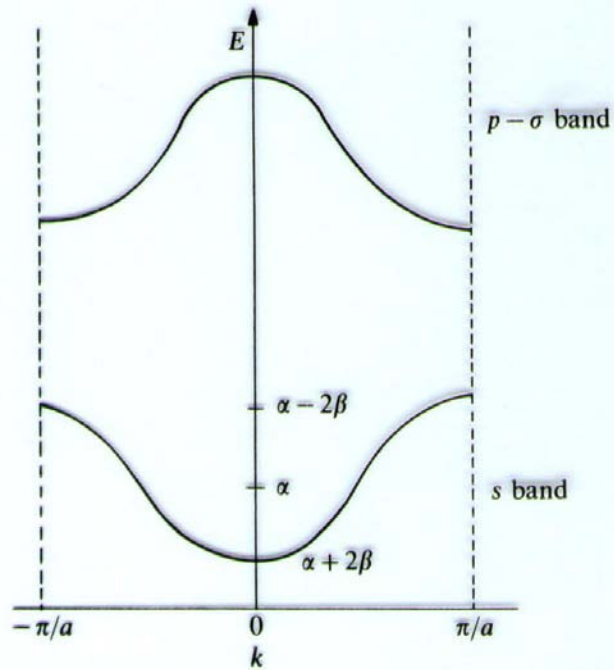
Density of States (DOS) Concept



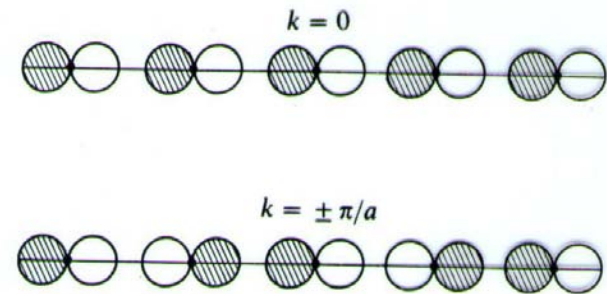
(a)  $E(k)$  curve showing the allowed  $k$  values for a chain with  $N=8$  atoms. (b) Orbital energies for eight-atom chain, showing clustering at the top and bottom of the band. (c) Density of states for a chain with very large  $N$ .



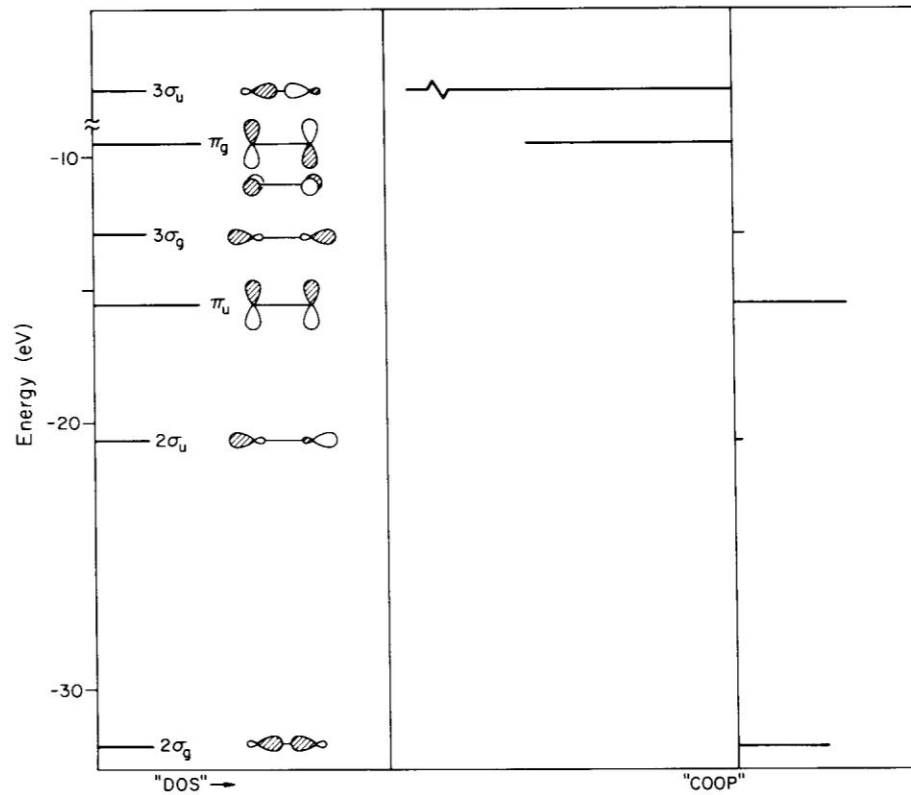
X-ray photoelectron spectrum of the long-chain alkane  $C_{36}H_{74}$ , showing the density of states in the 2s band. (From J.J. Pireau *et. Al.*, *Phys. Rev. A*, 14 (1976), 2133.)



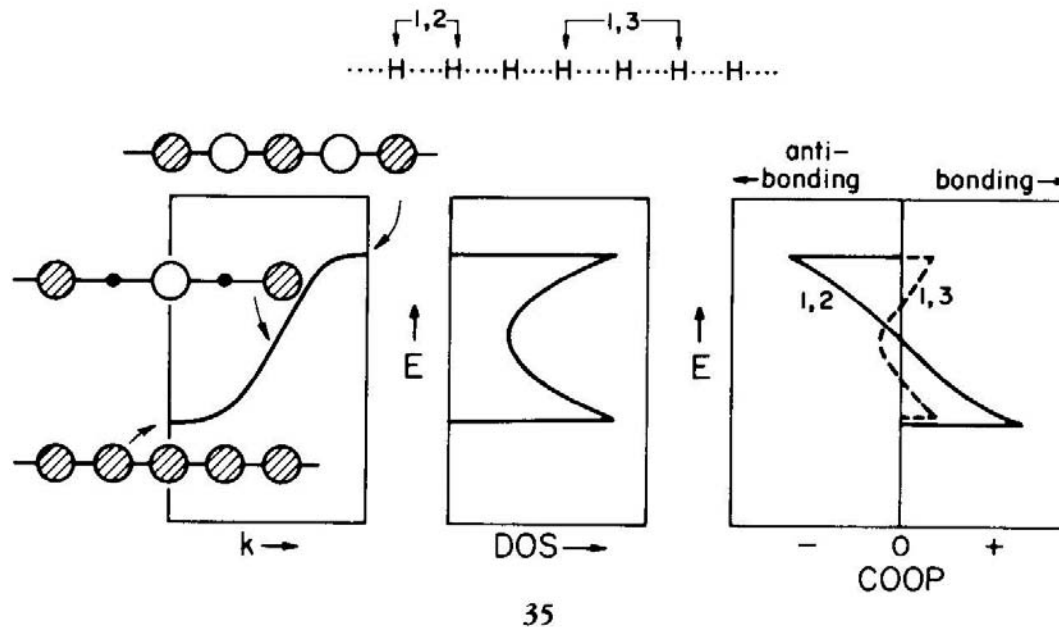
Energy as a function of  $k$  for bands of  $s$  and  $p\sigma$  orbitals in a linear chain.



Overlap of  $p\sigma$  orbitals for  $k = 0$  and  $k = \pm\pi/a$ .



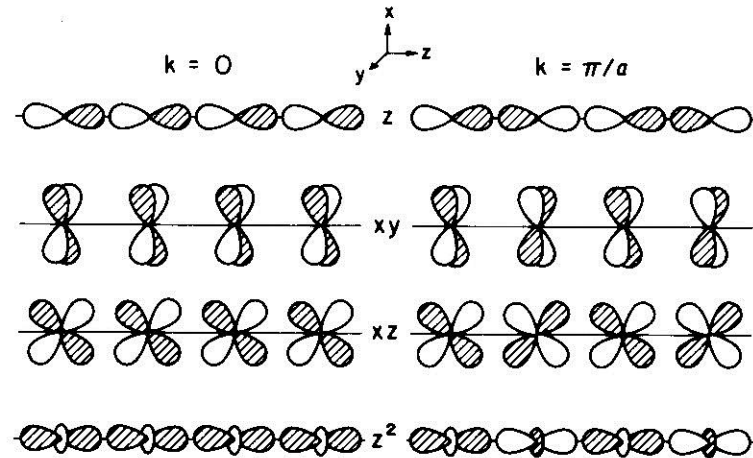
The orbitals of  $N_2$  (left) and a “solid state way” to plot the DOS and COOP curves for this molecule. The  $1\sigma_g$  and  $1\sigma_u$  orbitals are out of the range of this figure.



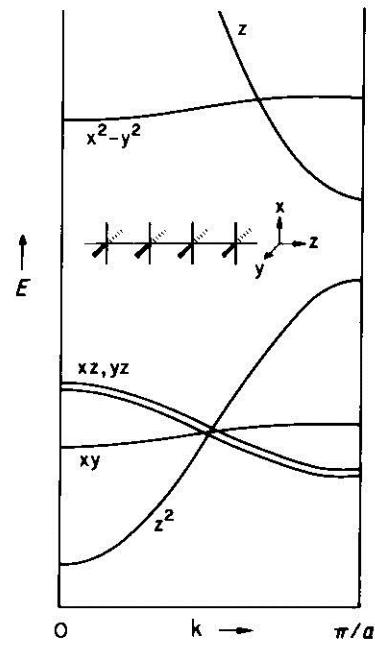
## Crystal Orbital Overlap Population – COOP

Better than DOS for determining extent of bonding and antibonding interactions

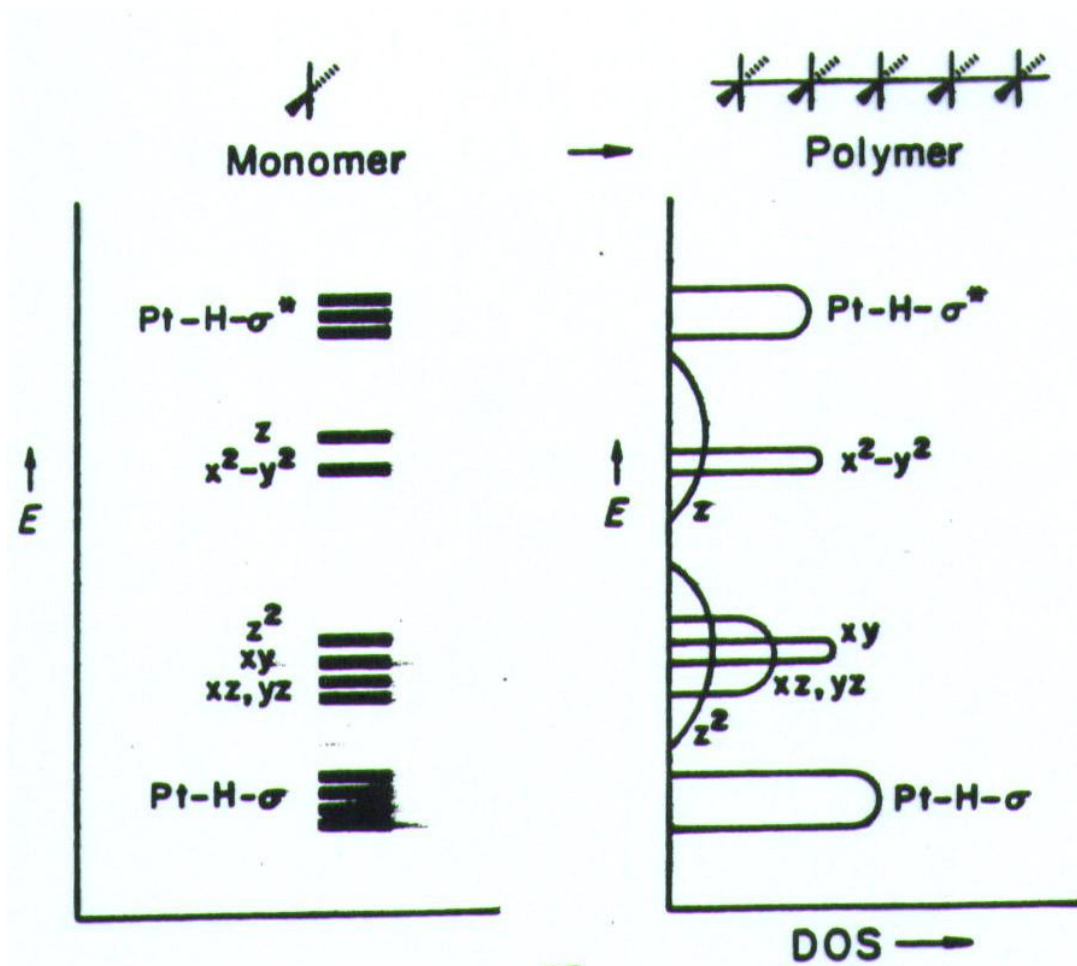
# p and d orbitals (in addition to s) – for the linear chain

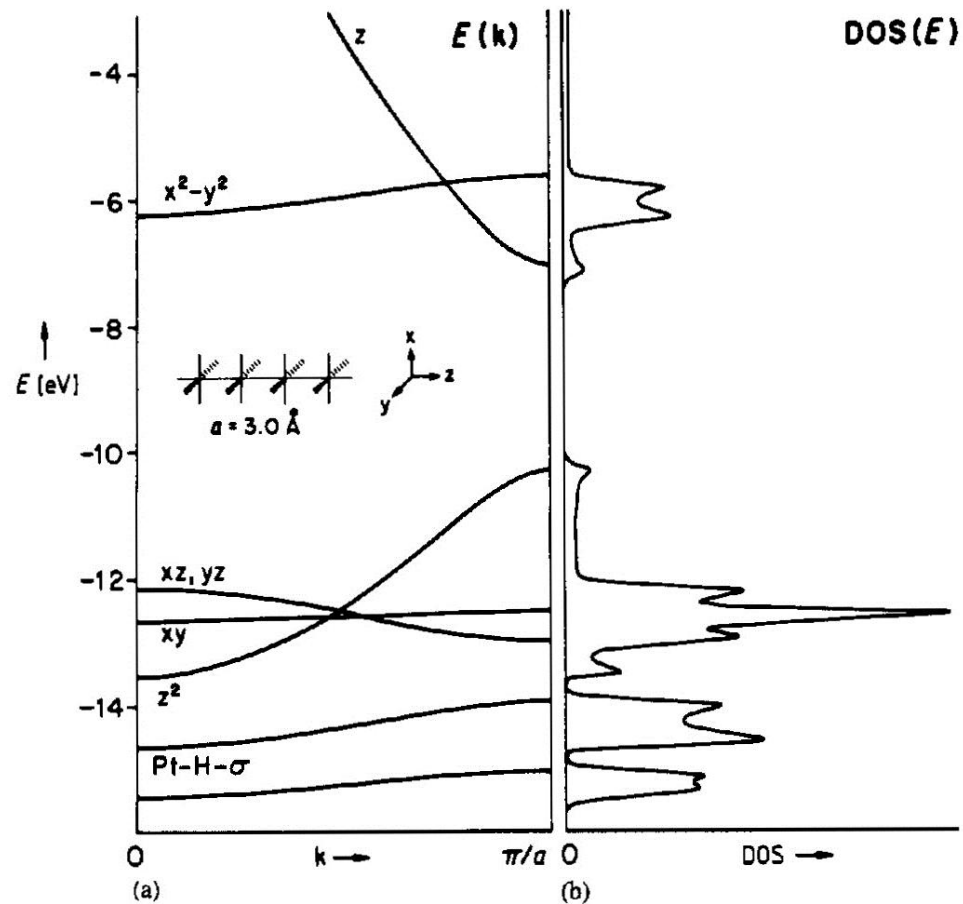


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A polymer - linear array of PtH<sub>4</sub> molecules

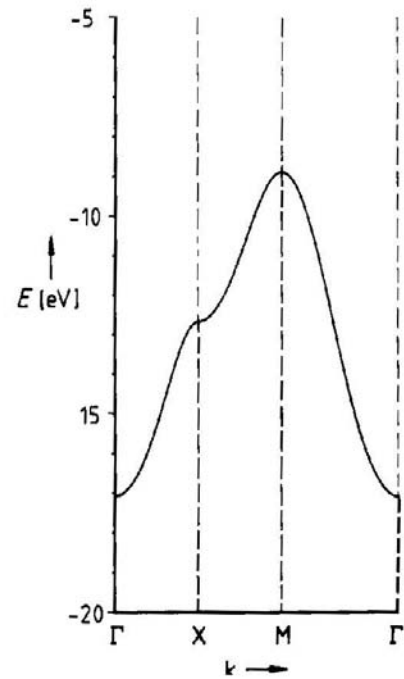
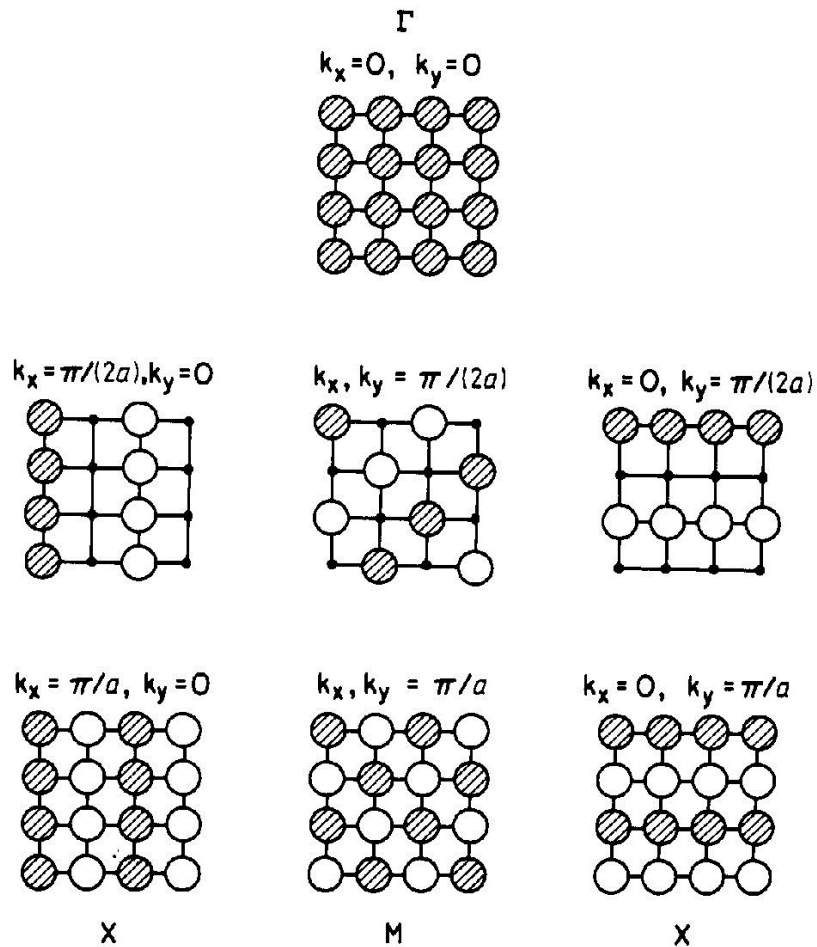




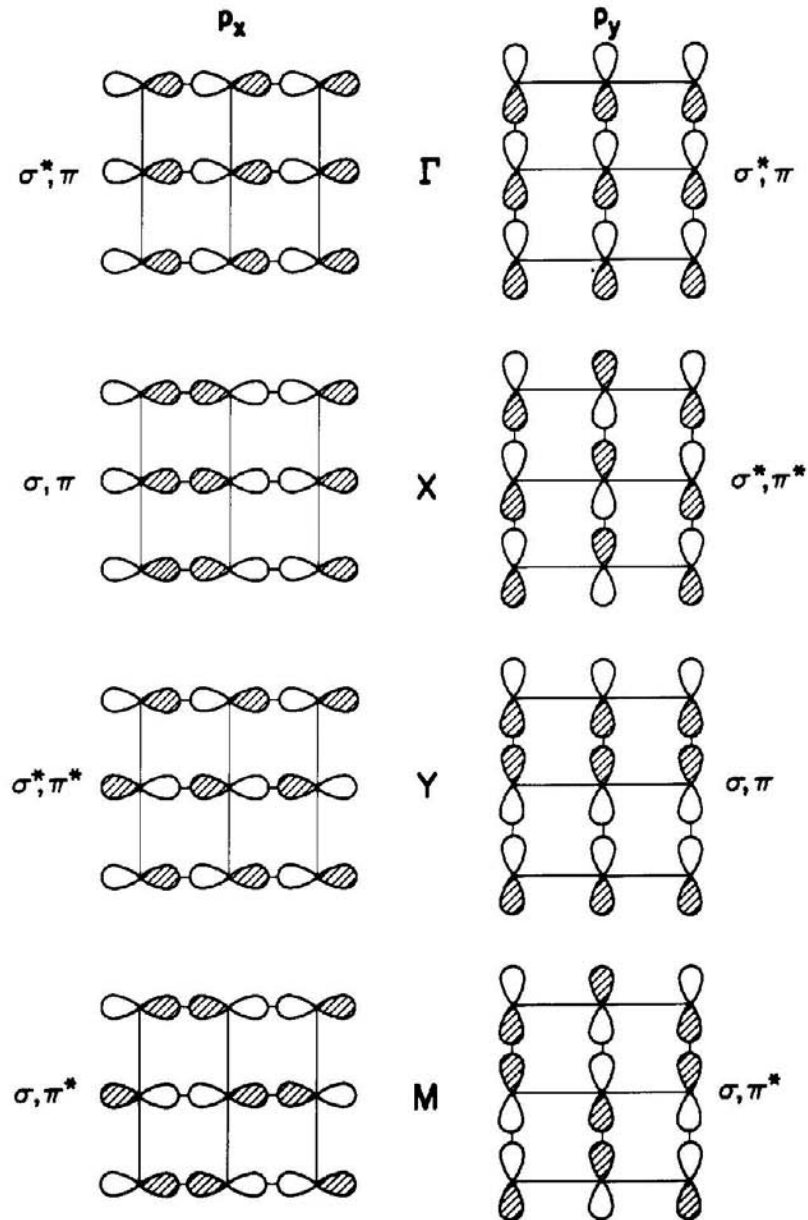
Band structure and density of states for an eclipsed  $\text{PtH}_4^{2-}$  stack. The DOS curves are broadened so that the two-peaked shape of the  $xy$  peak in the DOS is not resolved.

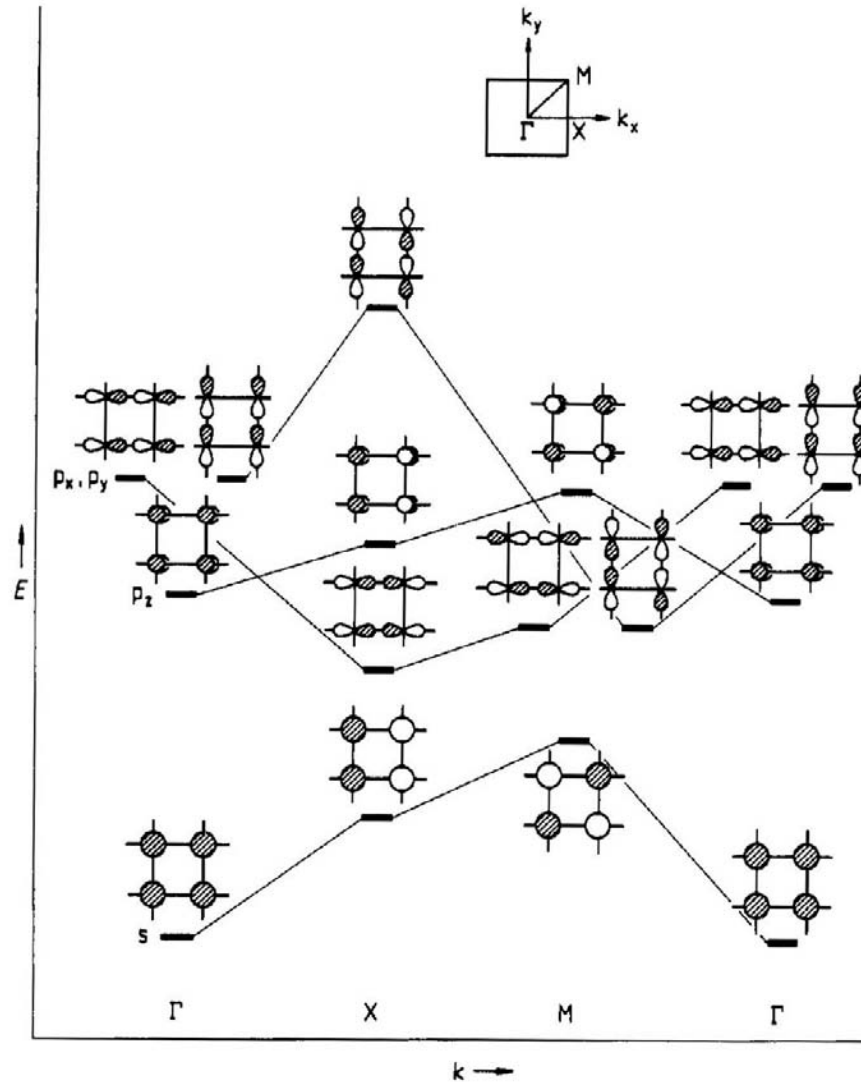


# 2 D array of s orbitals



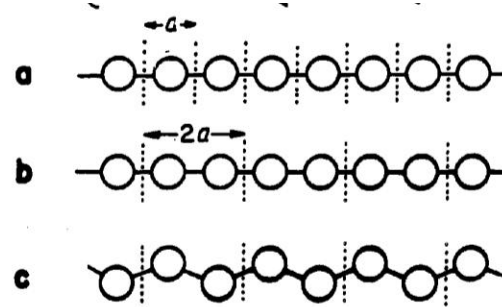
# 2D array of p orbitals ( $p_x$ and $p_y$ )



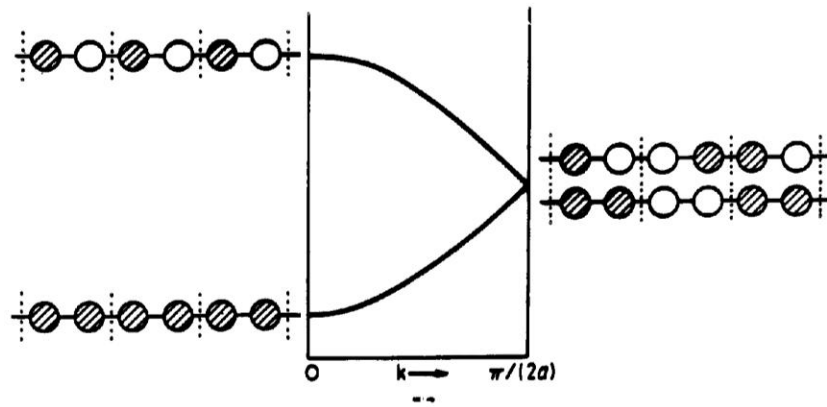


Schematic band structure of a planar square lattice of atoms bearing  $ns$  and  $np$  orbitals. The  $s$  and  $p$  levels have a large enough separation that the  $s$  and  $p$  band do not overlap.

# Buckling of 1D chain to minimize E (periodicity changes – doubles)



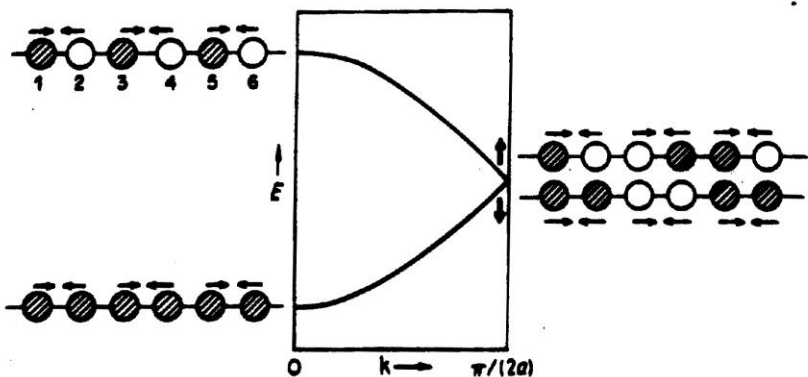
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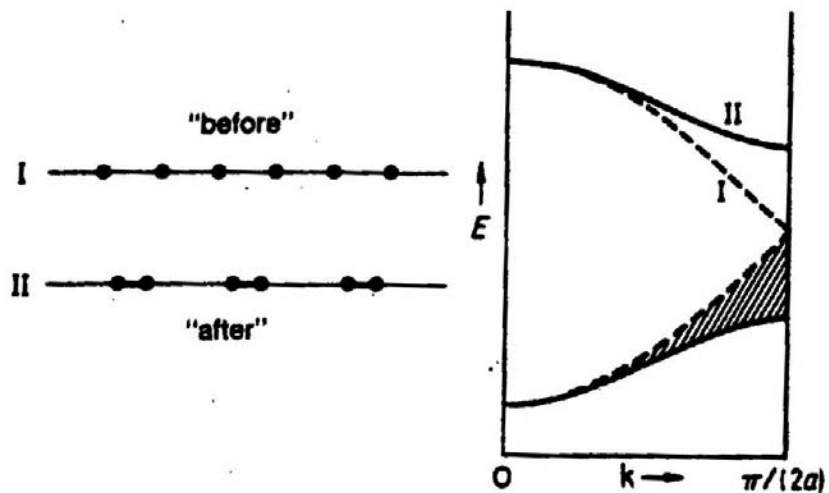
# Energy minimization for I-D chain – Peierls instability



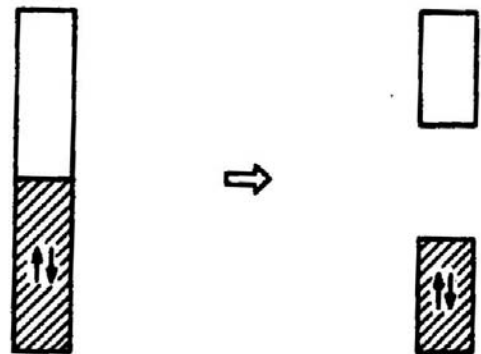
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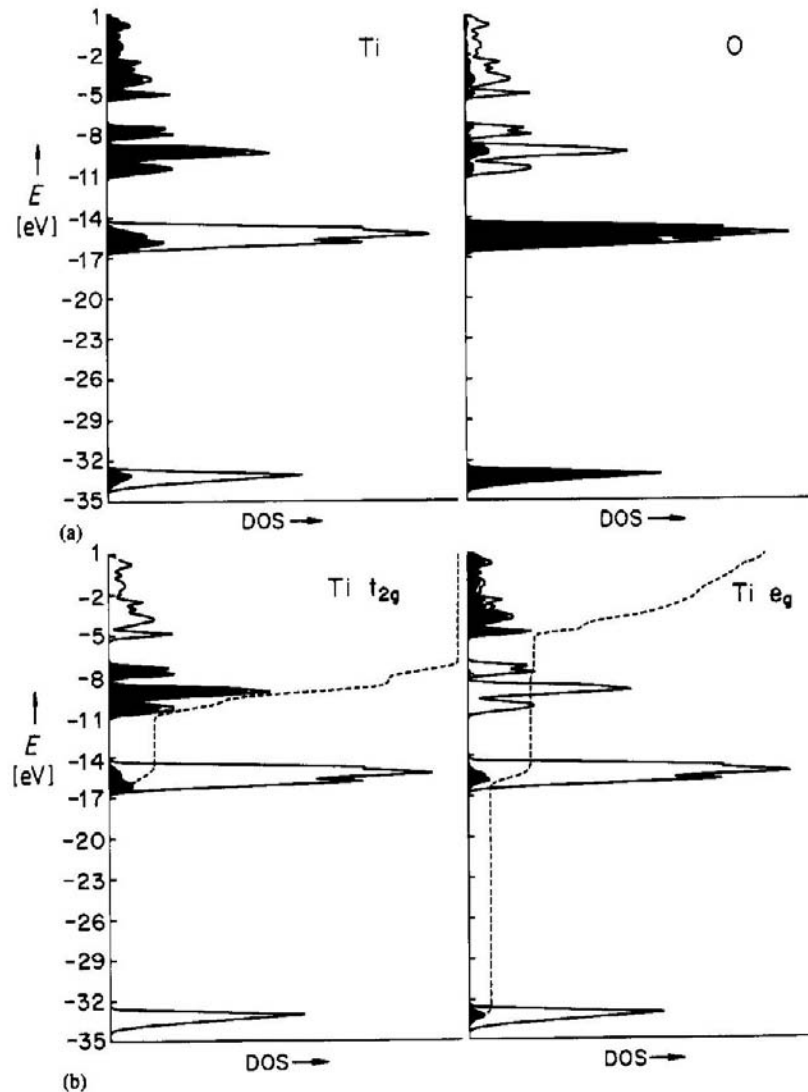


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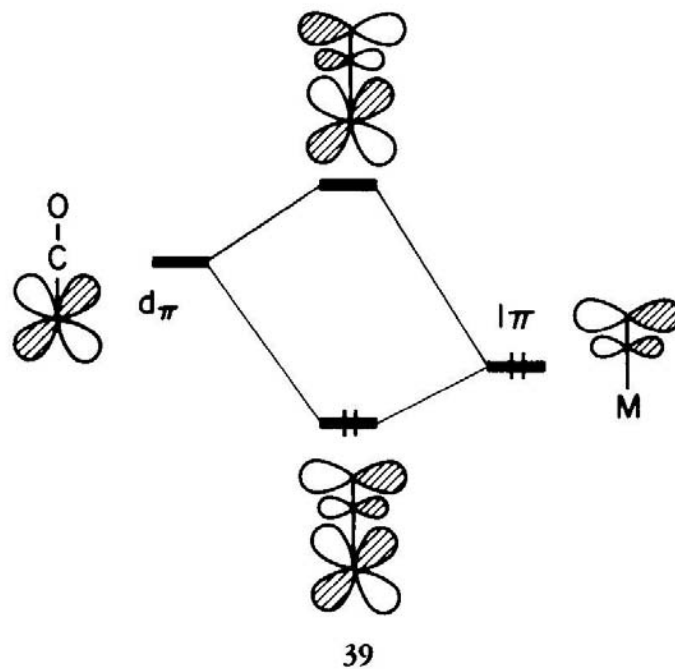
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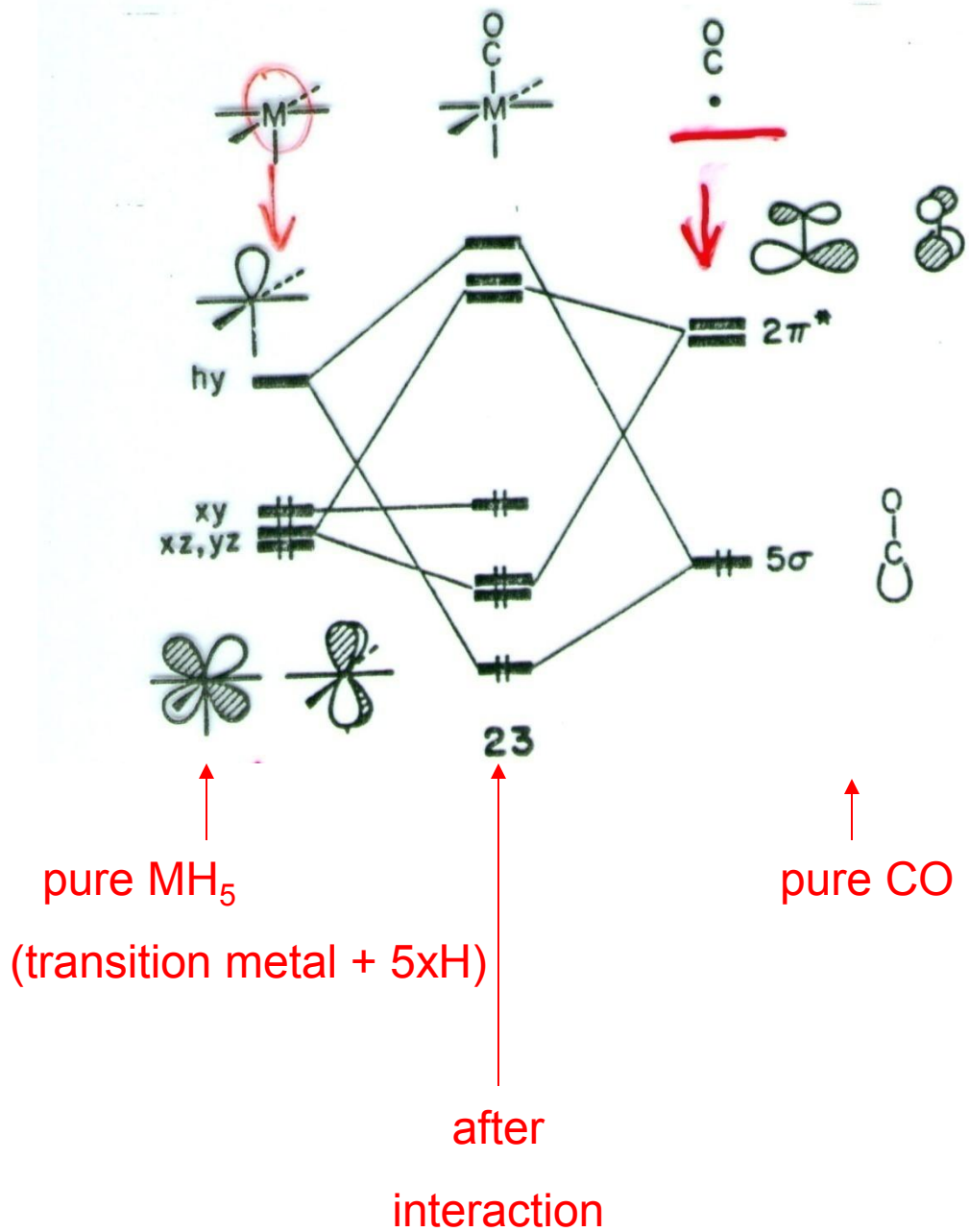




Contributions of Ti and O to the total DOS of rutile,  $\text{TiO}_2$  are shown at top. At bottom, the  $t_{2g}$  and  $e_g$  Ti contributions are shown; their integration (on scale of 0-100%) is given by the dashed line.

# CO bonding to a transition metal





pure MH<sub>5</sub>  
 (transition metal + 5xH)

pure CO

after  
 interaction

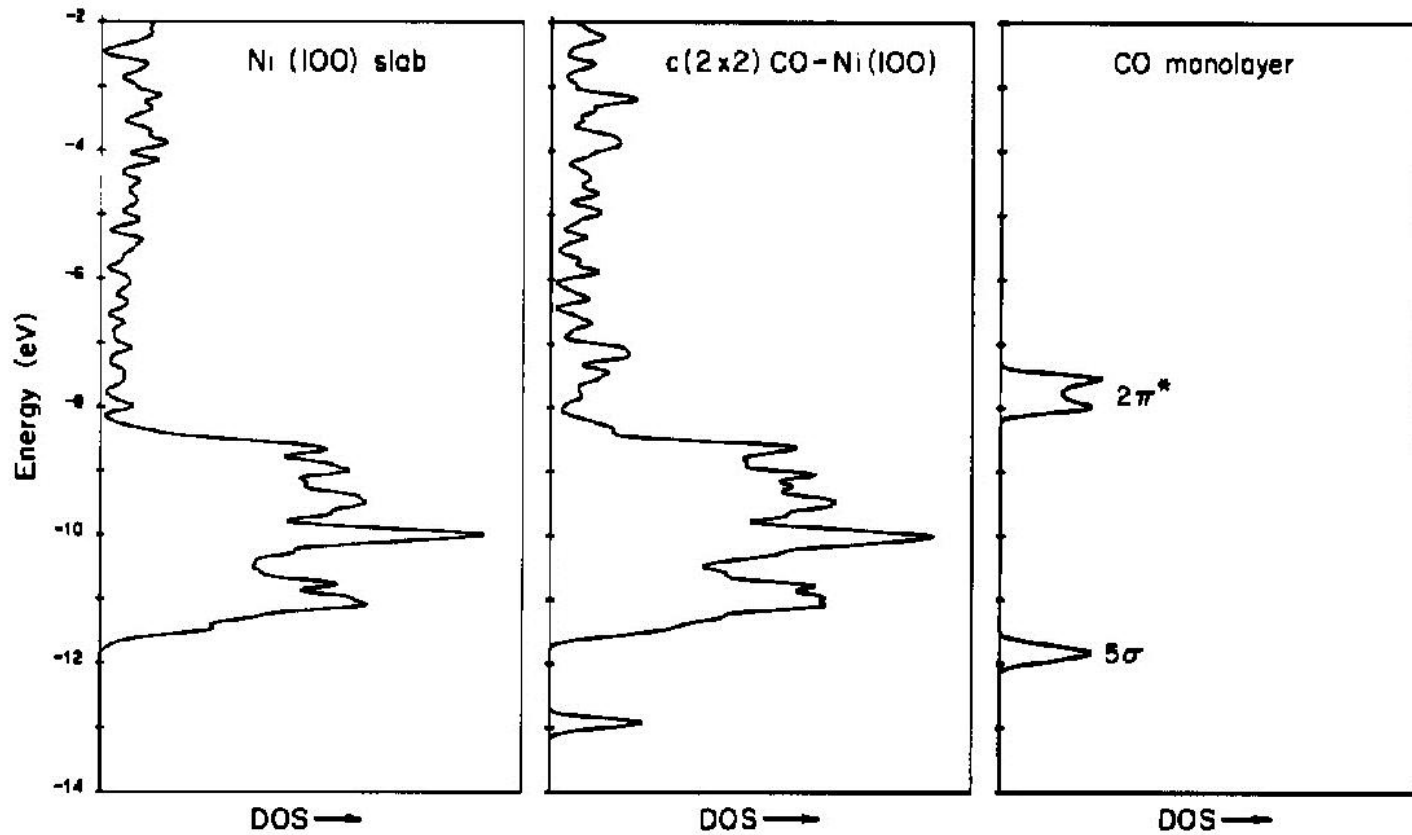


# I. Surface Problems

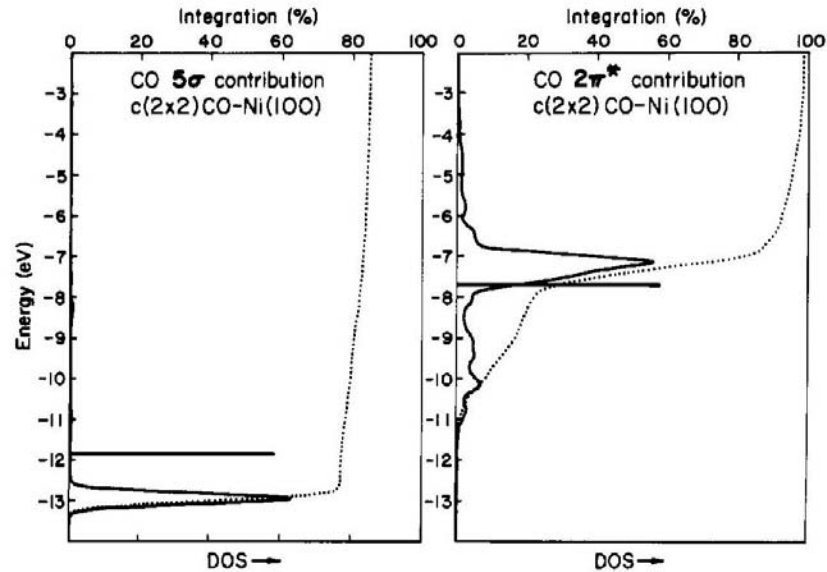
- Slab approach



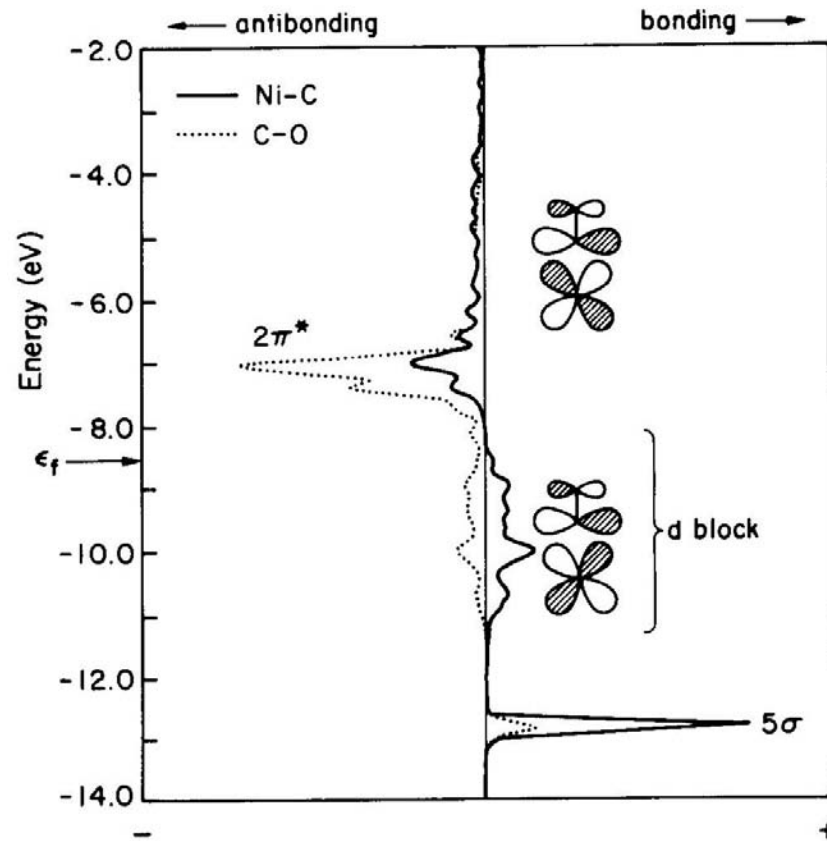
- Take an ordered overlayer, 1-N layers of a metal slab, and construct an infinite 2-D structure by using a lattice basis and Bloch sums. The Fermi level of a slab will differ somewhat from that of a bulk metal, so  $E_f$  should be imposed as the bulk value (calculated in a separate calculation).
- Similar to before, we must sample in k-space, which is now two-dimensional.
- Solution is achieved by solving the matrix and filling the orbitals up to  $E_f$ .



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.

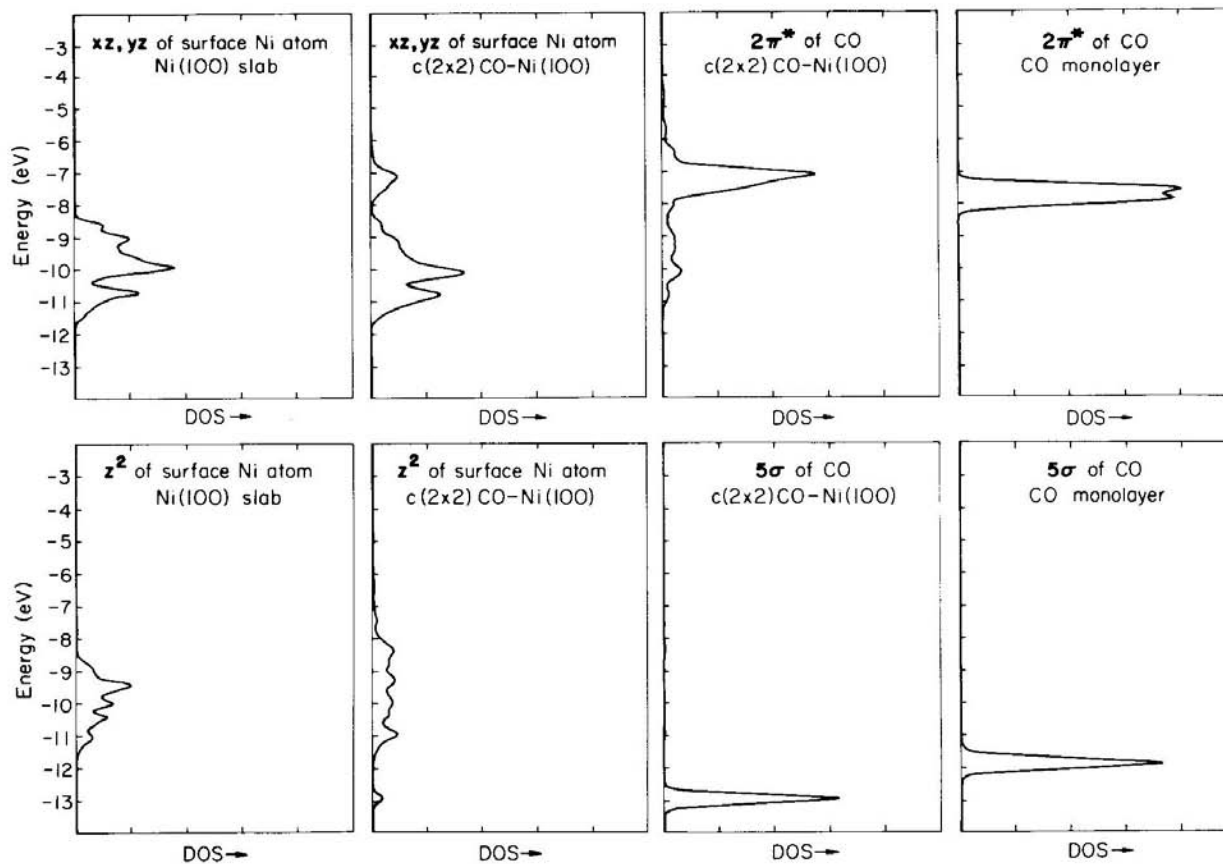


For the  $c(2 \times 2)$ CO-Ni(100) model this shows the  $5\sigma$  and  $2\pi^*$  contributions to the total DOS. Each contribution is magnified. The position of each level in isolated CO is marked by a line. The integration of the DOS contribution is given by the dotted line.

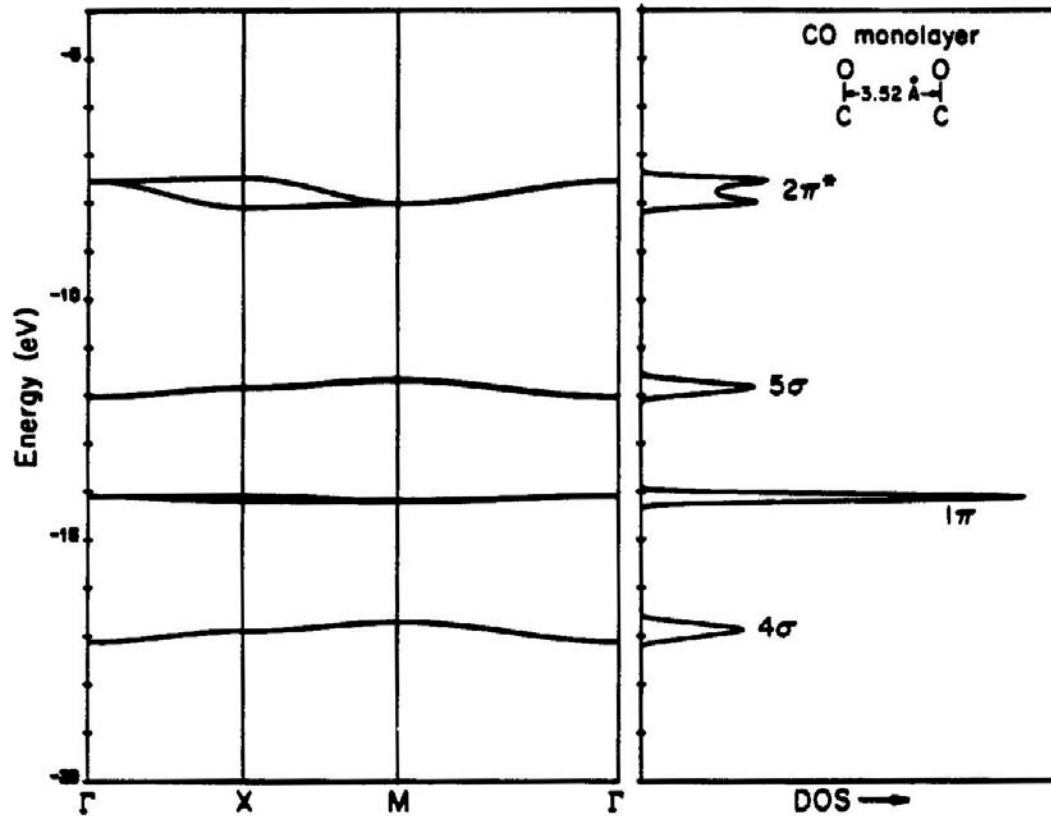


Crystal orbital population of CO, on top, in a  $c(2 \times 2)$ CO-Ni(100) model. Representative orbital combinations are drawn out.

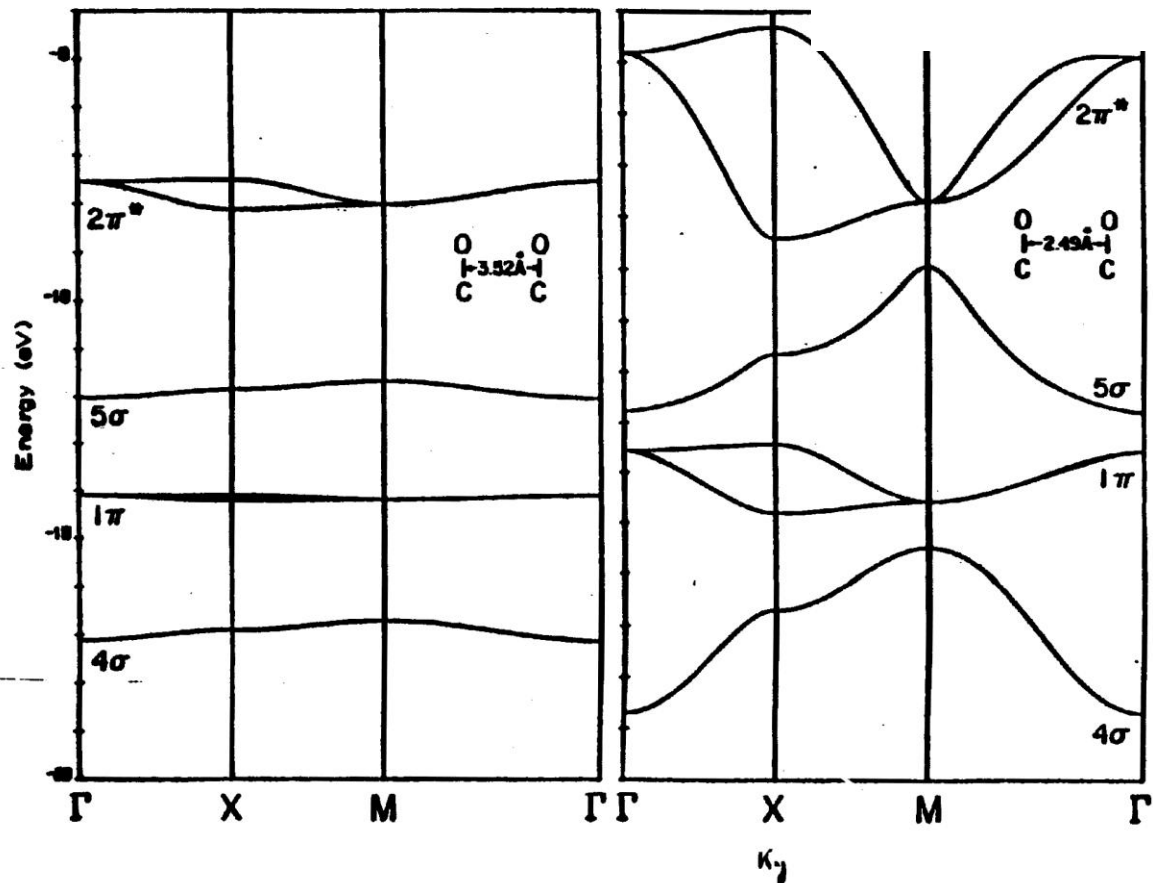
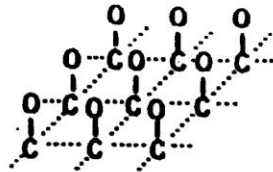
# Molecule-surface orbital interaction diagram



Interaction diagrams for  $5\sigma$  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  $5\sigma$ ,  $xz, yz$  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.

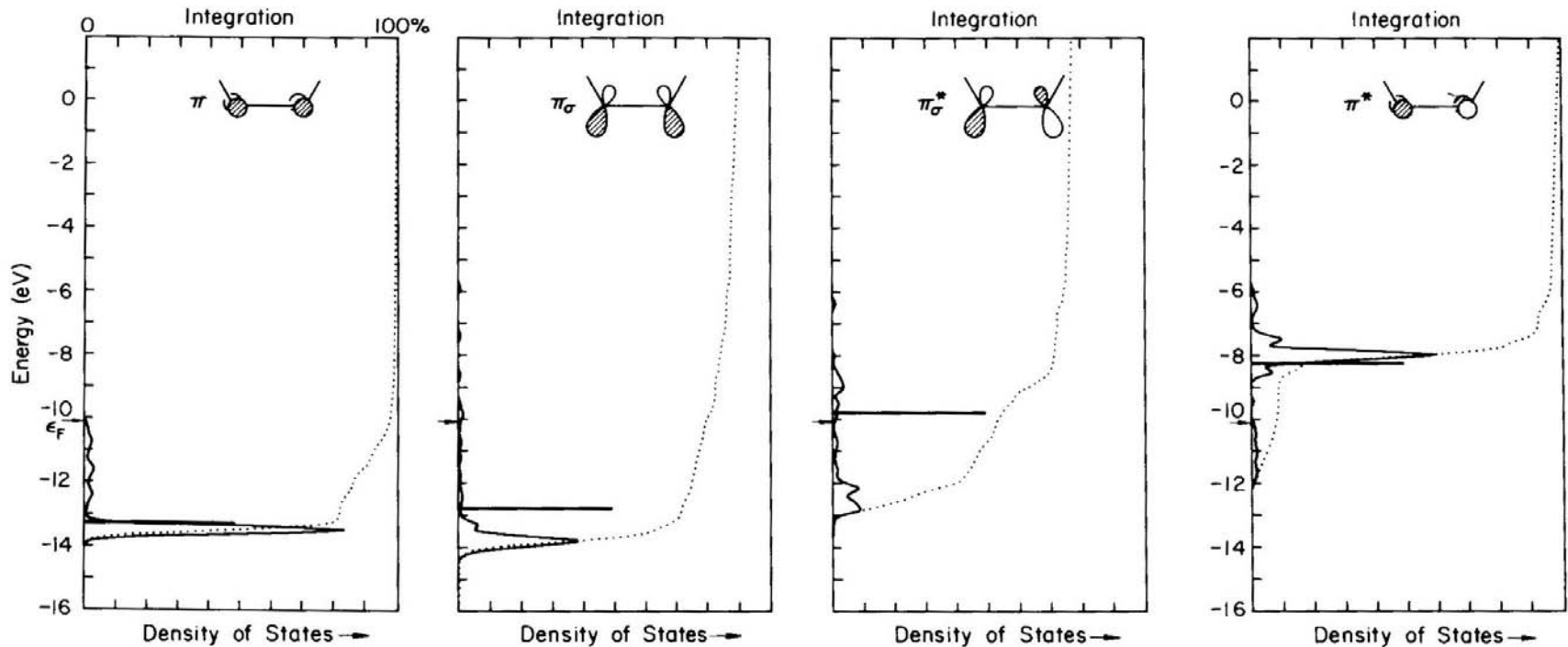


The density of states (right) corresponding to the band structure (left) of a square monolayer of CO's 3.52 Å apart.



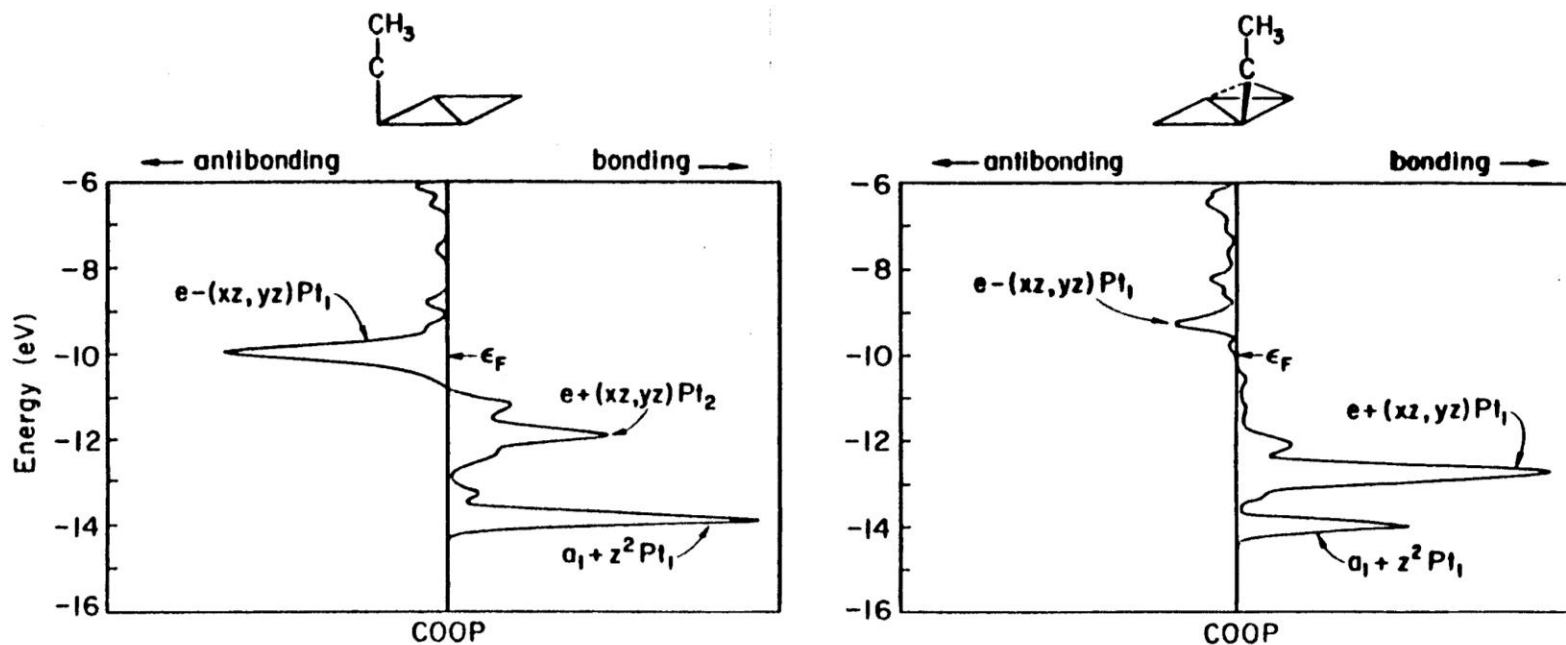
Dispersion of energy bands for square monolayer of CO at two separations: (a) left, 3.52 Å, (b) right, 2.49 Å. These would correspond to  $\frac{1}{2}$  and full coverage of a Ni(100) surface.

# C<sub>2</sub>H<sub>4</sub> bonded to a metal surface



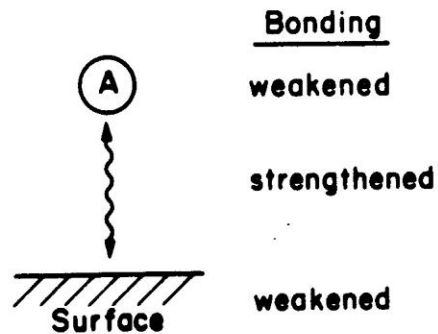
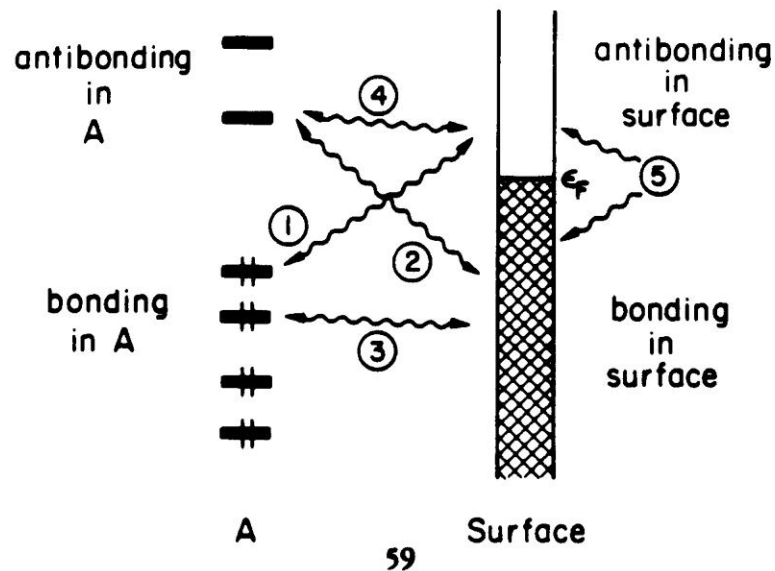
From left to right: contributions of  $\pi$ ,  $\pi_\rho$ ,  $\pi_\rho^*$ , and  $\pi^*$  to the DOS of C<sub>2</sub>H<sub>2</sub> in a two-fold geometry on Pt(111). The lines mark the positions of these levels in a free bent acetylene. The integration of the DOS contributions are indicated by the dotted line.





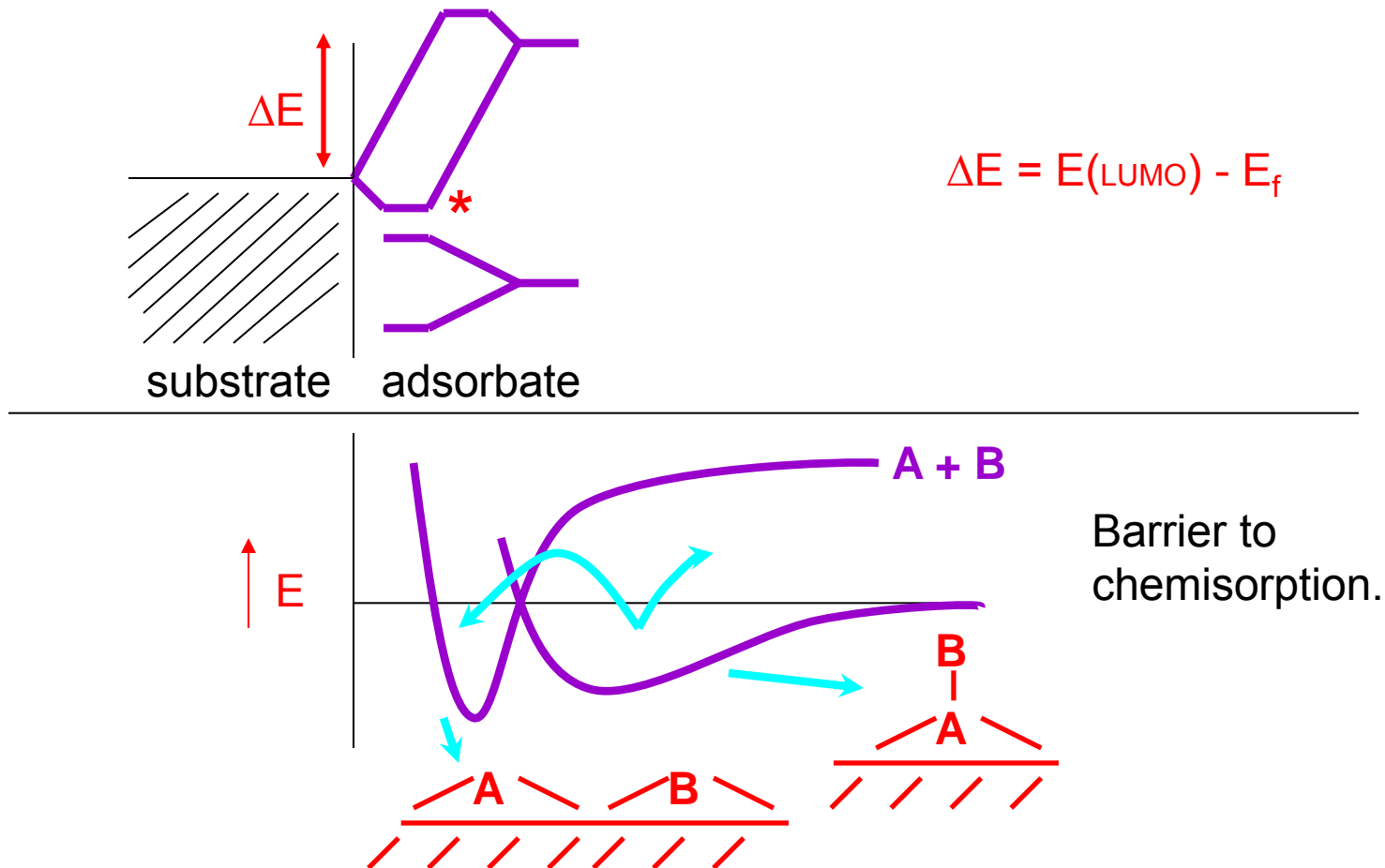
COOP curve for the  $\alpha$ -carbon-Pt<sub>1</sub> bond in the 1-fold (left) and 3-fold (right) geometry of ethylidyne, CCH<sub>3</sub> on Pt(111).

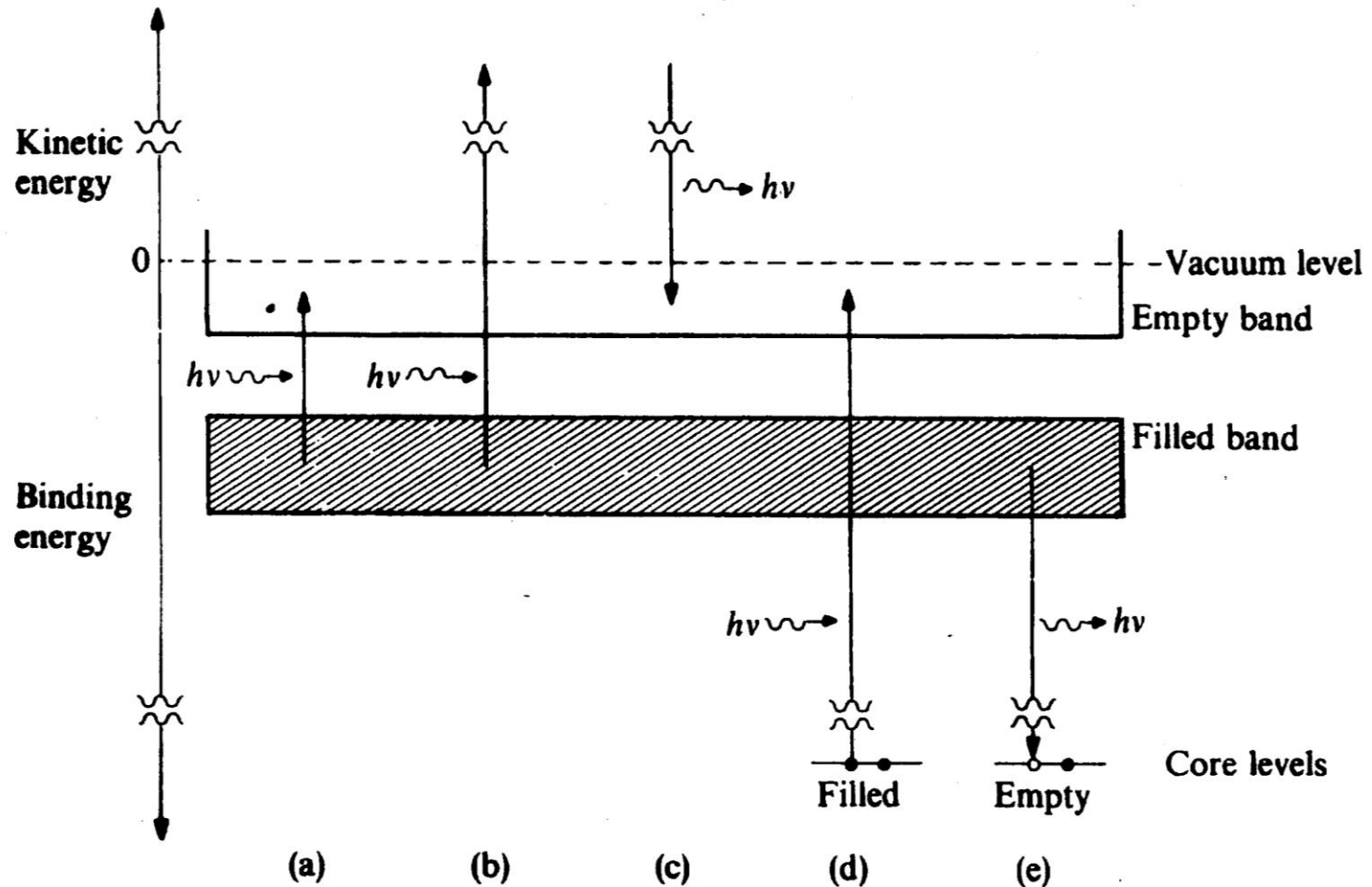
# Different orbital interactions between surface and adsorbate atom or molecule



Unoccupied orbitals often antibonding within a molecule A-B.

Control dissociation of A-B by controlling surface's ability to populate antibonding levels.





Spectroscopic techniques, some of which can be used to determine energy levels. (a) optical absorption in the visible/UV range; (b) photoelectron spectroscopy; (c) inverse photoelectron spectroscopy; (d) X-ray absorption; (e) X-ray emission. Electrons with energies above the vacuum level can enter or leave the solid; in techniques (b) and (c) the scale shows the kinetic energy measured in a vacuum outside the solid.