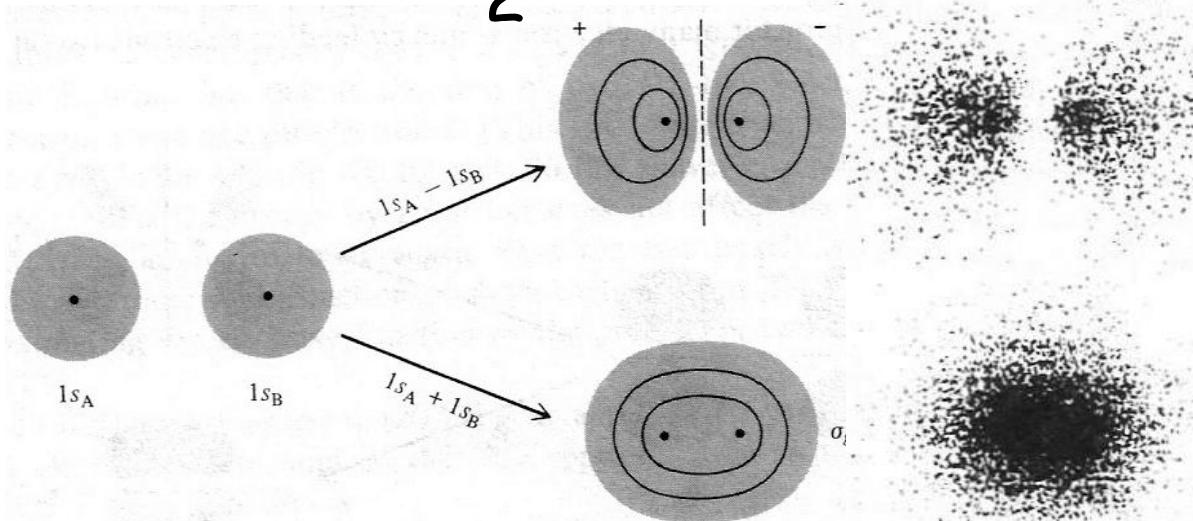


H_2^+ Molecular Orbitals



$$\varphi_- = \frac{1}{\sqrt{2 - 2S(R)}} (\psi_{1s_A} - \psi_{1s_B})$$

$$\varphi_+ = \frac{1}{\sqrt{2 + 2S(R)}} (\psi_{1s_A} + \psi_{1s_B})$$

$$\langle E \rangle_+ = \langle \varphi_+ | \hat{H} | \varphi_+ \rangle = \left\langle \frac{1}{\sqrt{2 + 2S}} (\psi_{1s_A} + \psi_{1s_B}) \middle| \hat{H}_{H_2^+} \middle| \frac{1}{\sqrt{2 + 2S}} (\psi_{1s_A} + \psi_{1s_B}) \right\rangle$$

$$\langle E \rangle_+ = \frac{1}{2(1+S)} \left[\langle \psi_{1s_A} | \hat{H} | \psi_{1s_A} \rangle + \langle \psi_{1s_B} | \hat{H} | \psi_{1s_B} \rangle + \langle \psi_{1s_A} | \hat{H} | \psi_{1s_B} \rangle + \langle \psi_{1s_B} | \hat{H} | \psi_{1s_A} \rangle \right]$$

Let $H_{ii} = \langle \psi_{1s_i} | \hat{H} | \psi_{1s_i} \rangle$ and $H_{ij} = \langle \psi_{1s_i} | \hat{H} | \psi_{1s_j} \rangle$

$$\Rightarrow \langle E \rangle_+ = \frac{H_{ii} + H_{ij}}{1+S_{ij}} \text{ and } \langle E \rangle_- = \frac{H_{ii} - H_{ij}}{1-S_{ij}}$$

Stabilization due to Bond Formation

$$\hat{H} \sim \left(-\nabla^2 - \frac{1}{r_{eA}} \right) + \frac{1}{R_{AB}} - \frac{1}{r_{eB}} = \hat{H}_{H(1e)} + \frac{1}{R_{AB}} - \frac{1}{r_{eB}}$$

$$\langle E \rangle_+ = \frac{\frac{H_{ii} + H_{jj}}{2}}{1+S_{..}}; \langle E \rangle_- = \frac{\frac{H_{ii} - H_{jj}}{2}}{1-S_{..}}$$

$$H_{ii} = \langle \psi_{1S_A} | \hat{H} | \psi_{1S_A} \rangle = \left[\langle \psi_{1S_A} | \hat{H}_{H(1e)} | \psi_{1S_A} \rangle + \frac{1}{R_{AB}(\text{const.})} \langle \psi_{1S_A} | \psi_{1S_A} \rangle - \langle \psi_{1S_A} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle \right]$$

$$H_{ii} (\text{or } H_{AA} = H_{BB}) = E_{1S(1e)} + \frac{1}{R_{AB}} - J \quad \text{where } J = \langle \psi_{1S_A} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle \Rightarrow \text{Coulomb Integral}$$

Interaction energy viewed as a -ve charge cloud with a +ve charged nucleus

$$H_{ij} = \langle \psi_{1S_B} | \hat{H} | \psi_{1S_A} \rangle = \left[\langle \psi_{1S_B} | \hat{H}_{H(1e)} | \psi_{1S_A} \rangle + \frac{1}{R_{AB}(\text{const.})} \langle \psi_{1S_B} | \psi_{1S_A} \rangle - \langle \psi_{1S_B} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle \right]$$

$$H_{ij} (\text{or } H_{BA}) = \langle \psi_{1S_B} | E_{1S(1e)} | \psi_{1S_A} \rangle + \frac{1}{R_{AB}} \langle \psi_{1S_B} | \psi_{1S_A} \rangle - \langle \psi_{1S_B} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle$$

$$H_{ij} = E_{1S(1e)} S + \frac{S}{R_{AB}} - K, \quad \text{where } K = \langle \psi_{1S_B} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle$$

$K \Rightarrow$ Exchange Integral or Resonance Integral:
Lowering of energy leads to bond formation.

**K is purely quantum-mechanical concept:
No Classical analogue**

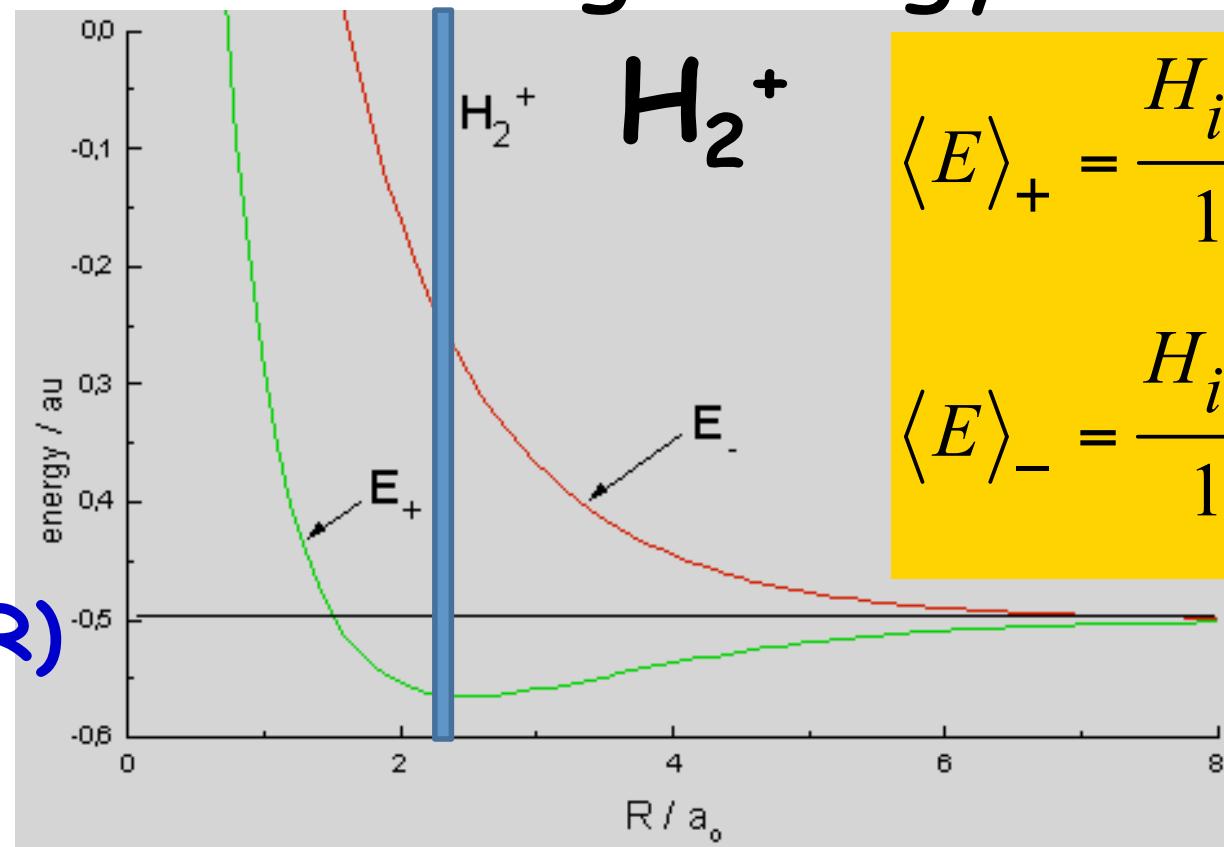
Bonding/Anti-bonding energy is $f(R_{AB})$

$$S = f(R)$$

$$H_{ii} = H_{ii}(R)$$

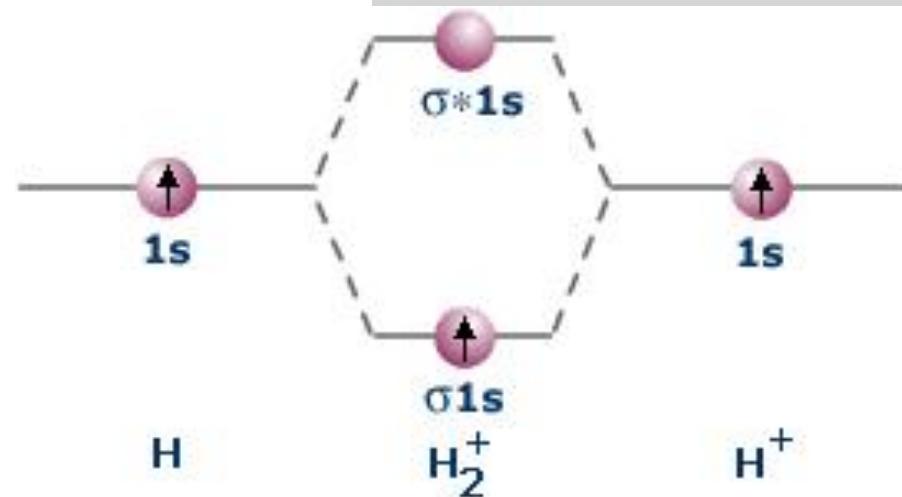
$$H_{ij} = H_{ij}(R)$$

$$\text{Energy} = E(R)$$



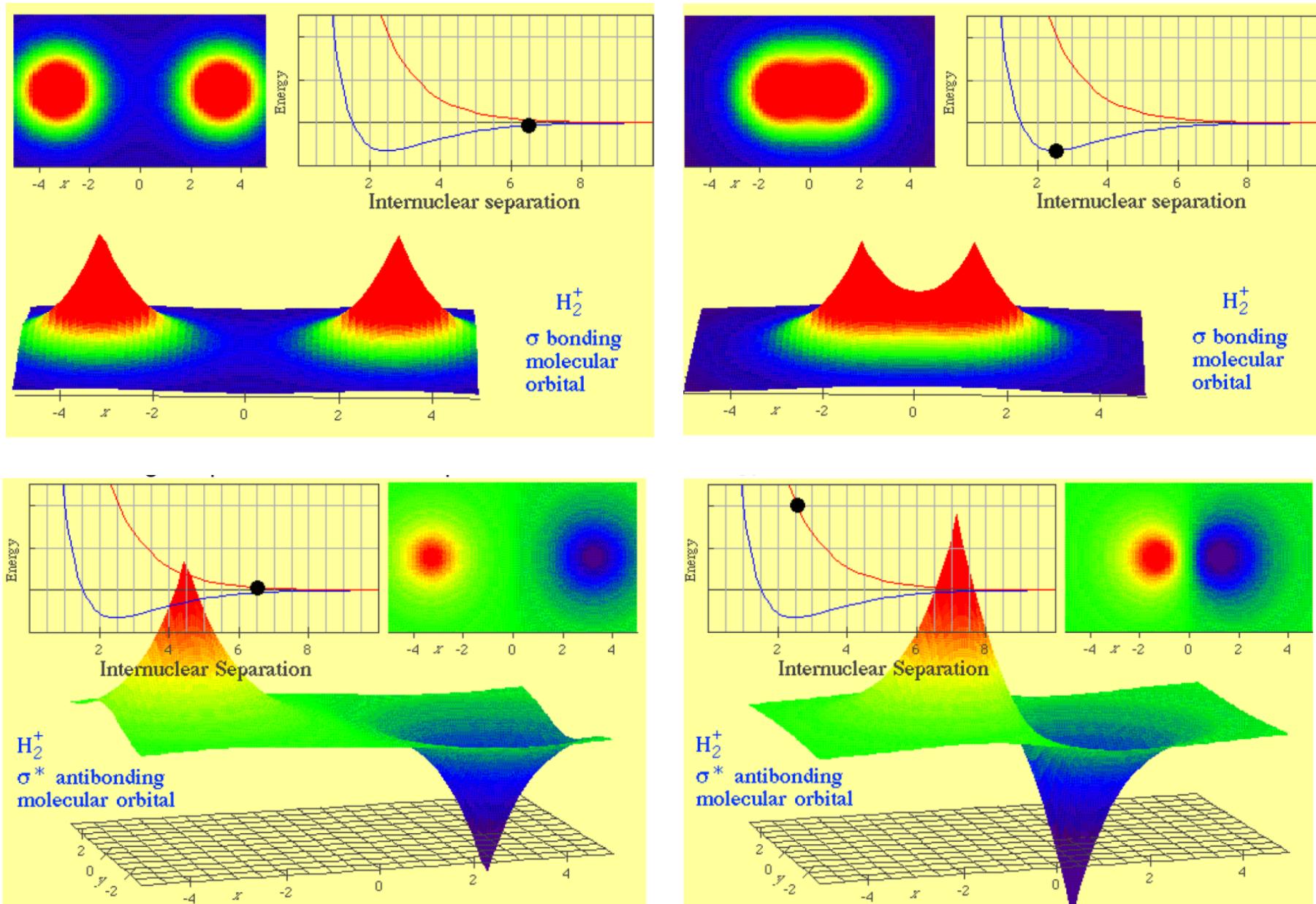
$$\langle E \rangle_+ = \frac{H_{ii} + H_{ij}}{1 + S_{ij}}$$

$$\langle E \rangle_- = \frac{H_{ii} - H_{ij}}{1 - S_{ij}}$$

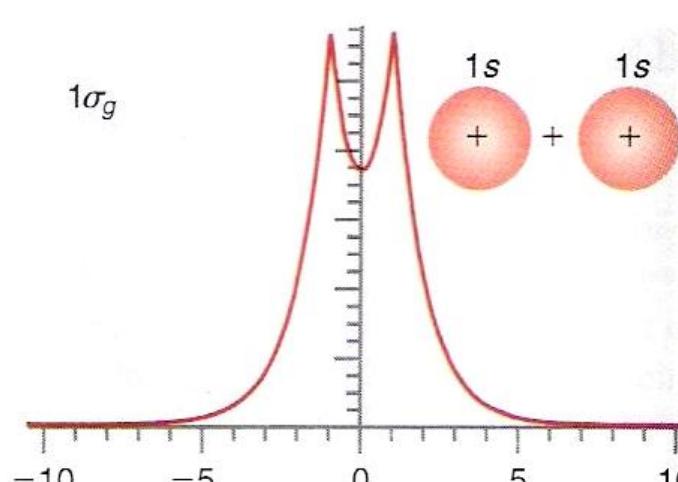
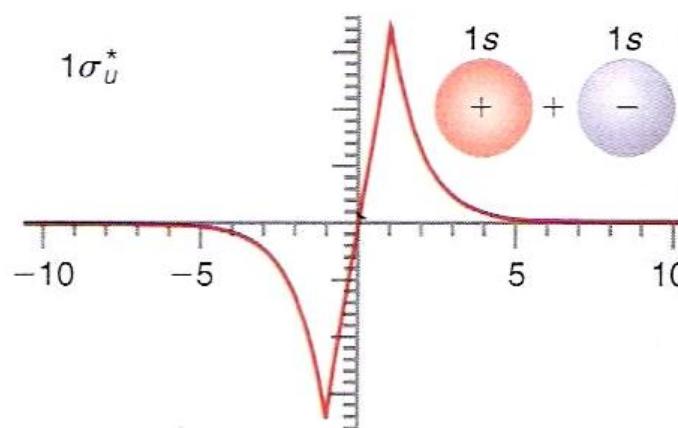
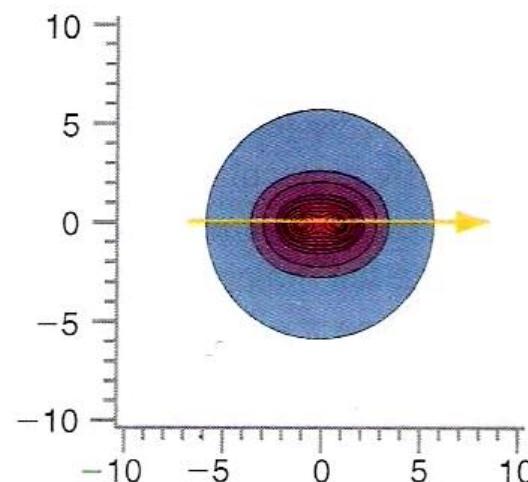
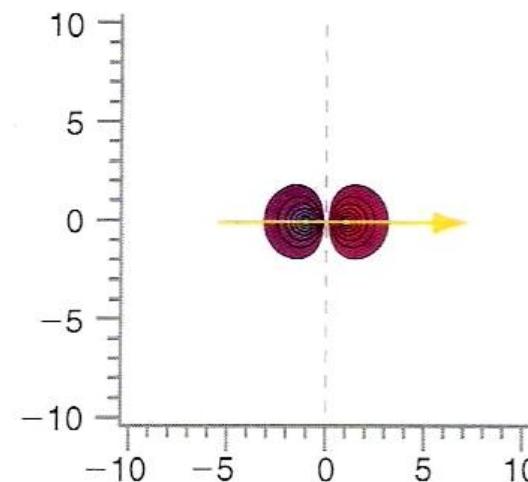


Represents the energies of bonding and anti-bonding levels at equilibrium R_{AB}

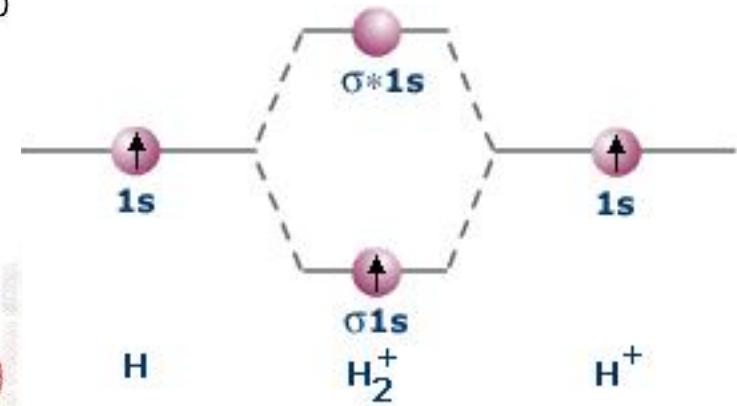
Electron Density and Energy: $f(R_{AB})$



H_2^+ σ -bonds: Electron Density/Energy at Equilibrium Bond distance (R_{Eq})



At R_{Eq} Anti-Bonding:
Electron density = 0
At midpoint between
nuclei, i.e., Nodal
plane present

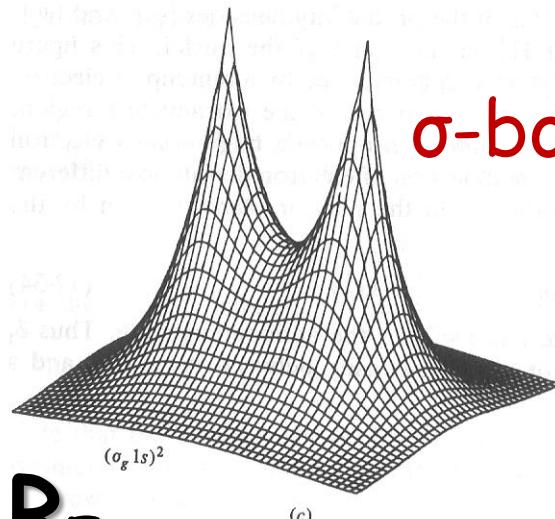


At R_{Eq} Bonding state:
Electron density non-
Zero at midpoint
between nuclei \rightarrow No
nodal plane!

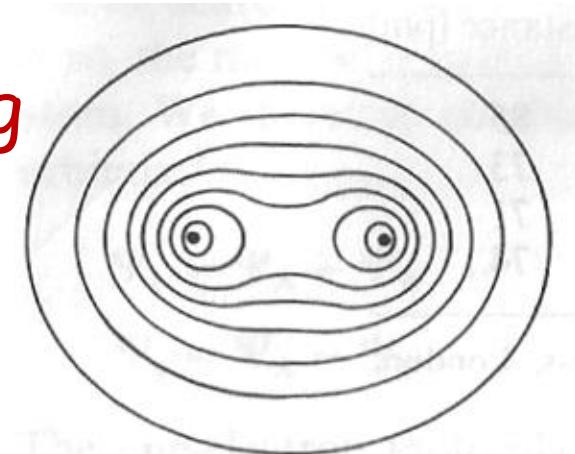
Surface/Contours of electron density

$\varphi_{Bonding}$

$$= \psi_{1S_A} + \psi_{1S_B}$$



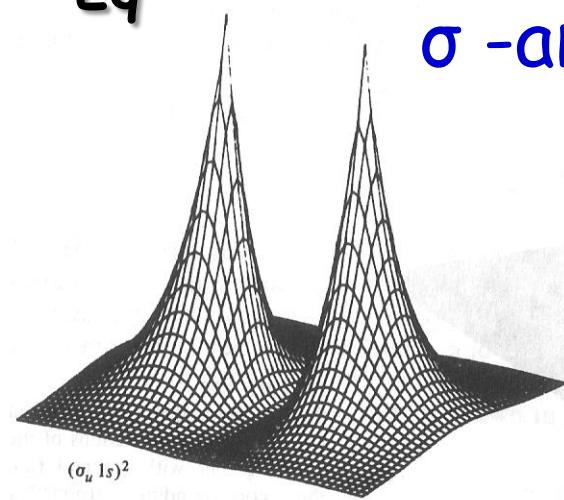
σ -bonding



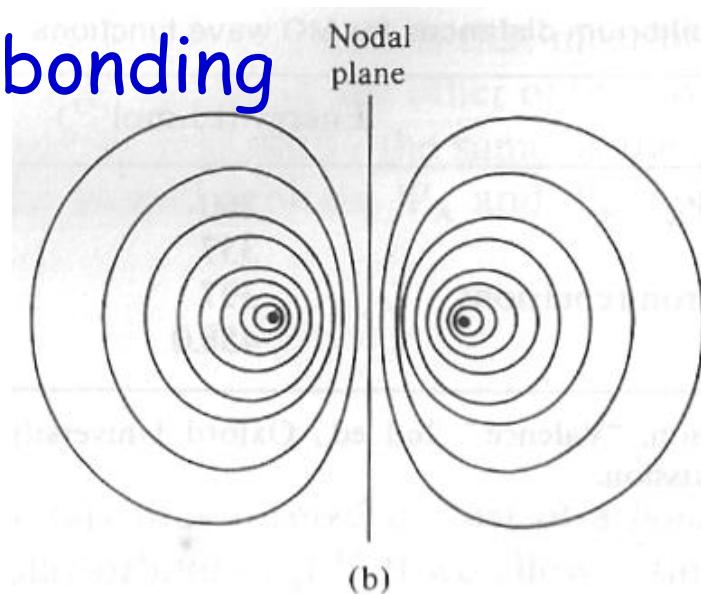
At R_{Eq}

$\varphi_{Anti-bonding}$

$$= \psi_{1S_A} - \psi_{1S_B}$$

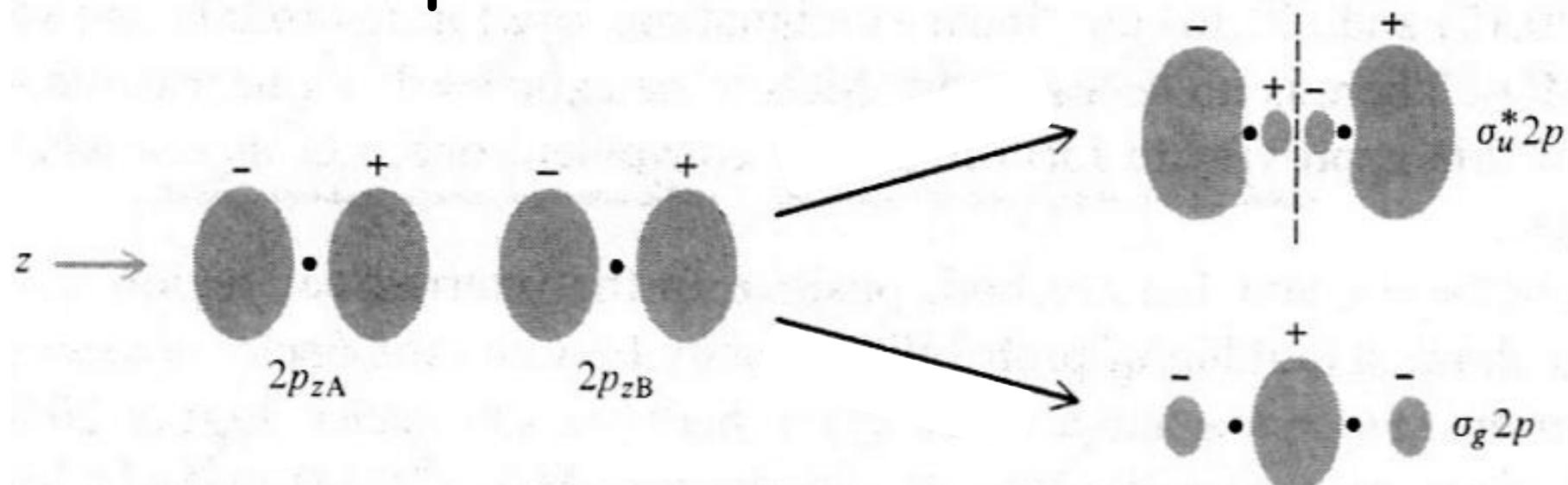


σ -antibonding

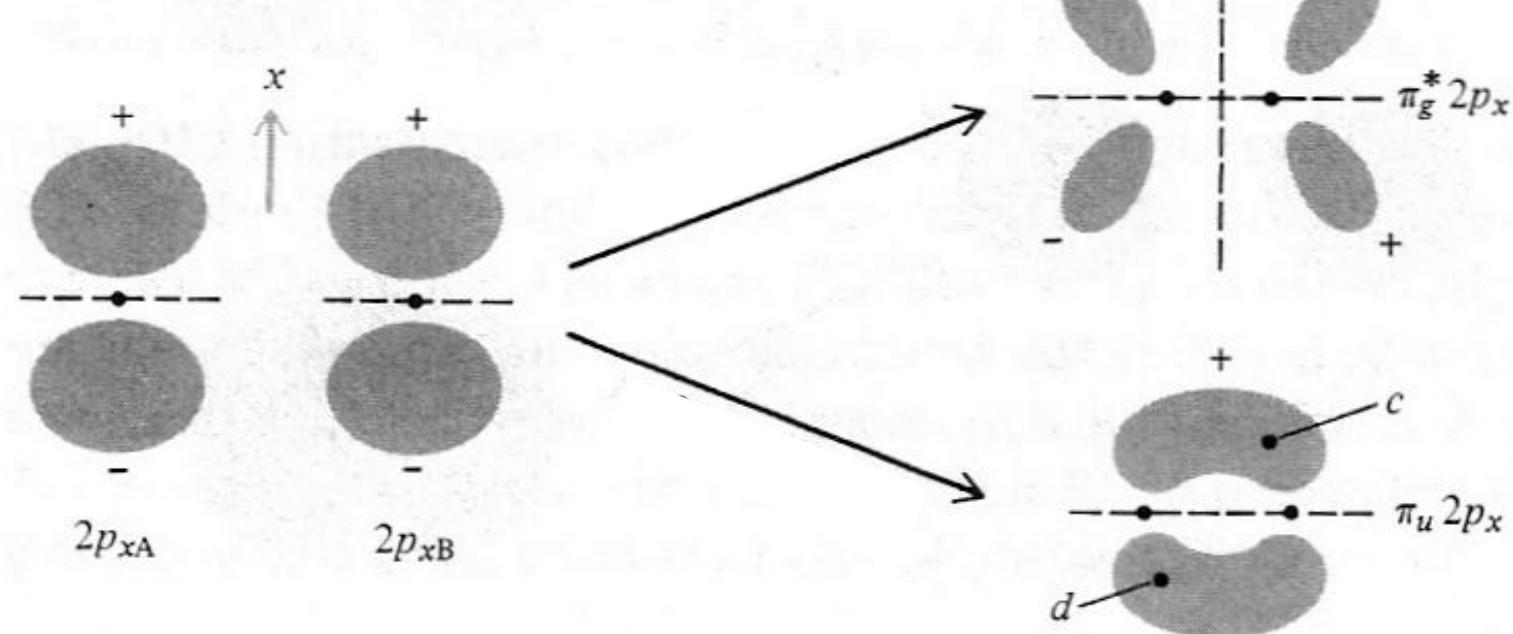


Electron density delocalized over entire molecule
Localized in different manner for bonding and antibonding

LCAO of p-orbitals: σ - and π - bonds



Note the signs, symmetries and nodes



Symmetry and Nomenclature of MOs

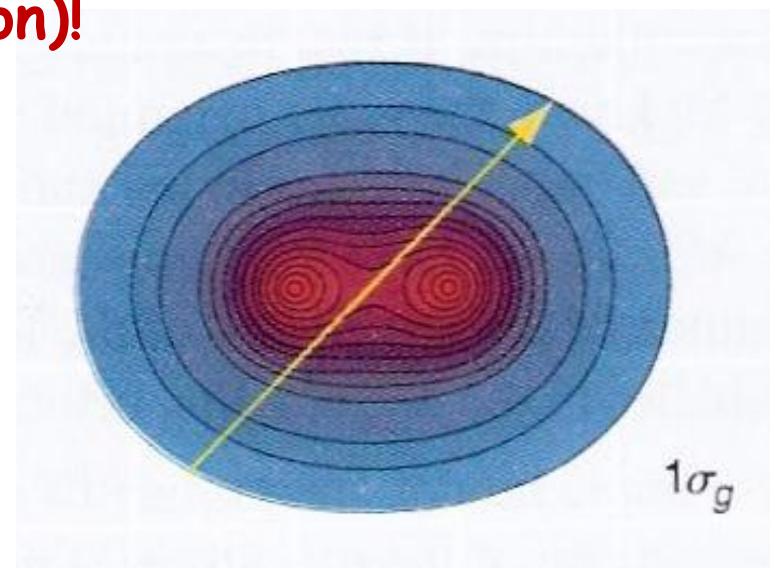
Gerade (g) (symmetric) and Ungerade (u) (antisymmetric)
wrt inversion of coordinates (operation)!

Inversion Operation : \hat{I}

$$\hat{I} \Rightarrow (+x, +y, +z) \rightarrow (-x, -y, -z)$$

$$\hat{I}\Psi(\vec{r}) = \Psi(-\vec{r}) = +\Psi(\vec{r}): \text{Symmetric}$$

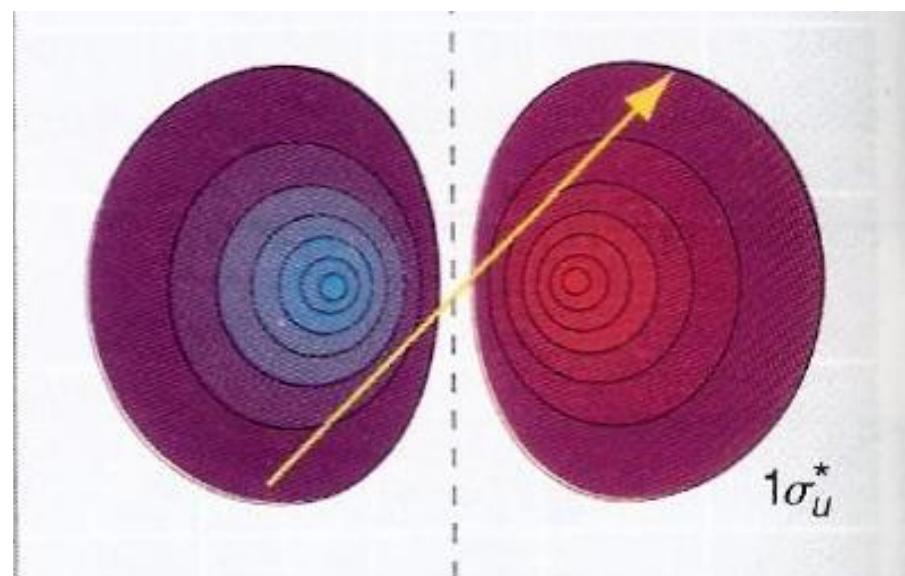
$$\hat{I}\Psi(\vec{r}) = \Psi(-\vec{r}) = -\Psi(\vec{r}): \text{Anti-sym}$$



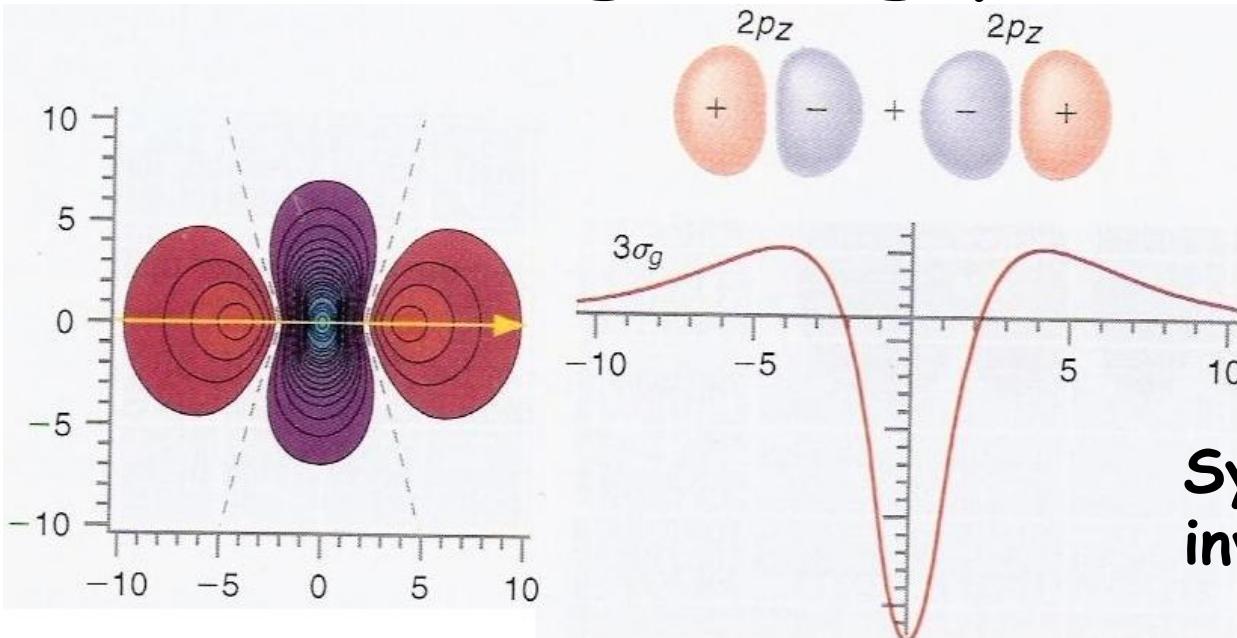
Hydrogen molecule ion:

"b" → Bonding using s:
symmetric → σ_g

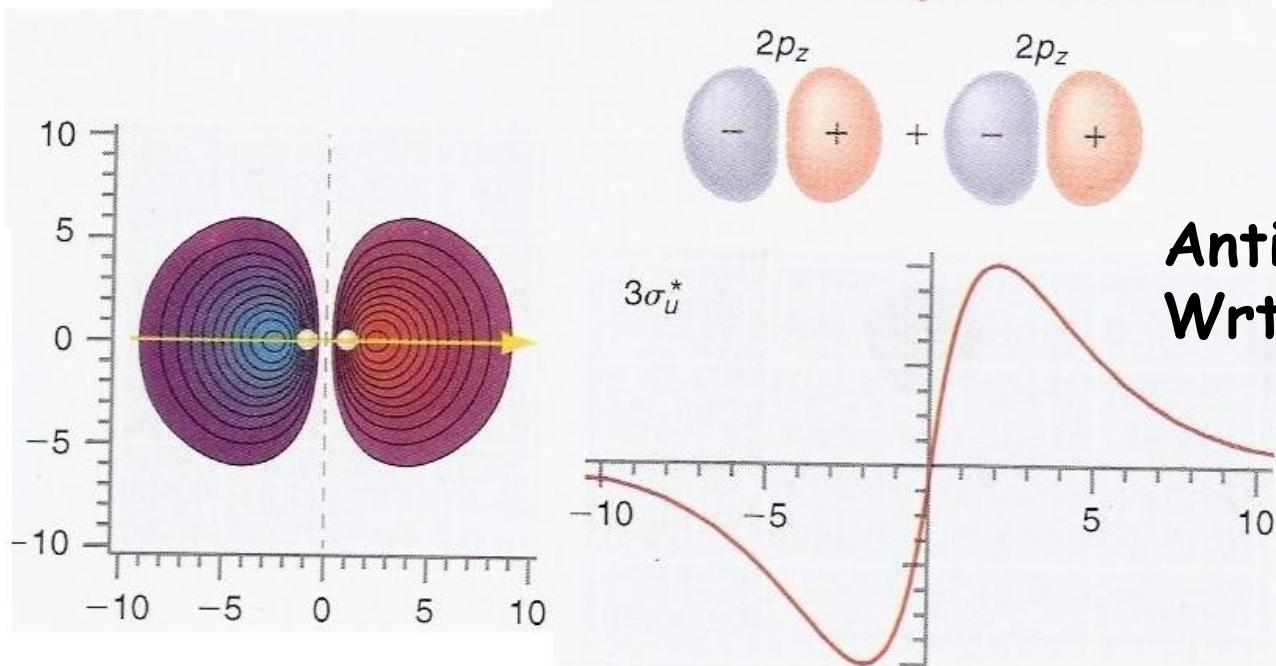
"a" → antibonding using s:
antisymmetric → σ_u^*



σ -bonding using p-orbitals

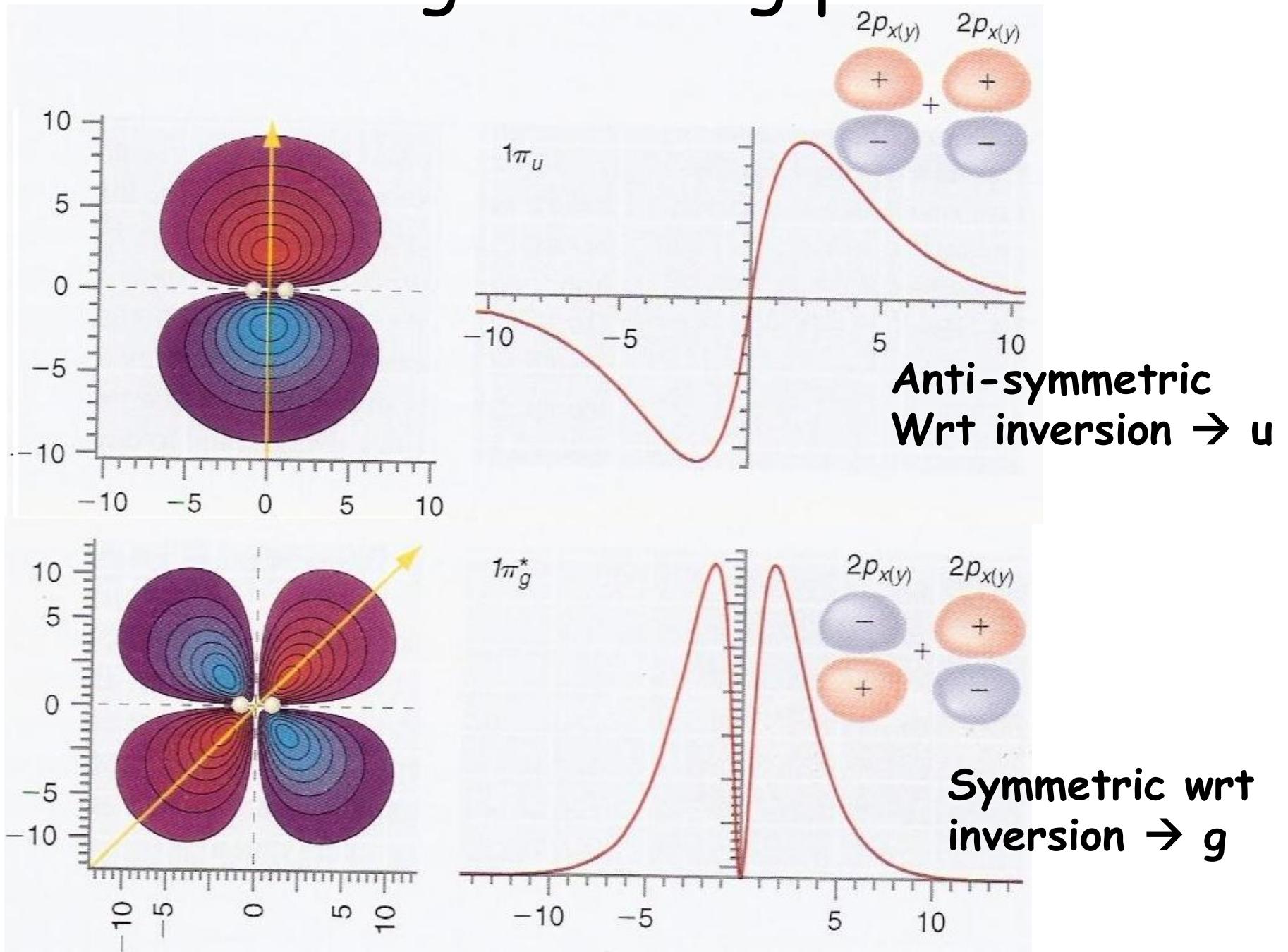


Symmetric wrt
inversion $\rightarrow g$

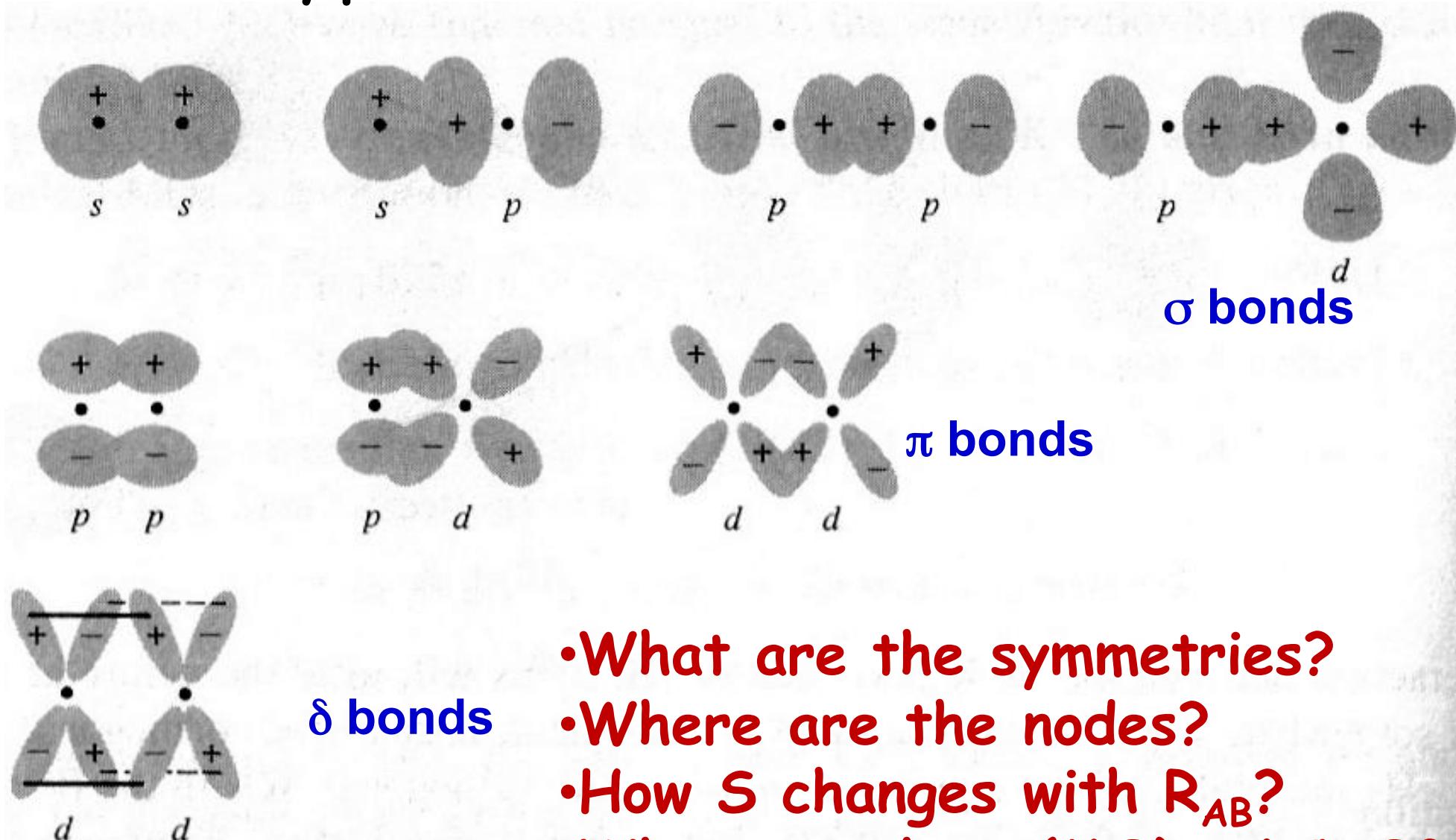


Anti-symmetric
Wrt inversion $\rightarrow u$

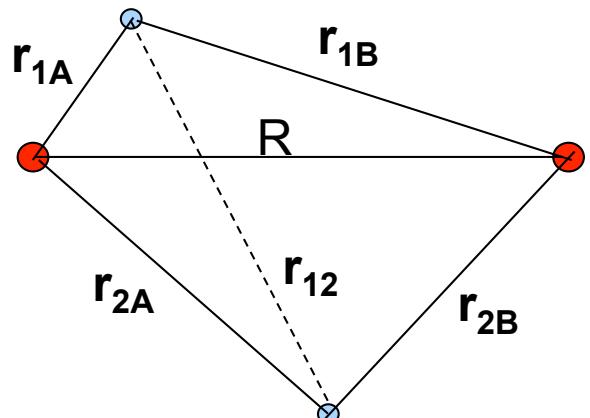
π -bonding involving p-orbitals



Types of Covalent Bonds



Dihydrogen Molecule (H_2)



$$\hat{H}_{H_2} \sim \left(-\nabla_1^2 - \frac{1}{r_{1A}} \right) + \left(-\nabla_2^2 - \frac{1}{r_{2B}} \right) - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{R_{AB}} + \frac{1}{r_{12}}$$

$$\hat{H}_{H_2} = \hat{H}_{H(1e)} + \hat{H}_{H(1e)} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} + \frac{1}{R_{AB}} + \frac{1}{r_{12}}$$

Can not be solved exactly → Approximate

Place 2e with opp. spin in bonding orbital of H_2^+

$$\varphi_b^{1e} = \frac{1}{\sqrt{2(1+S)}} [1s_A + 1s_B]$$

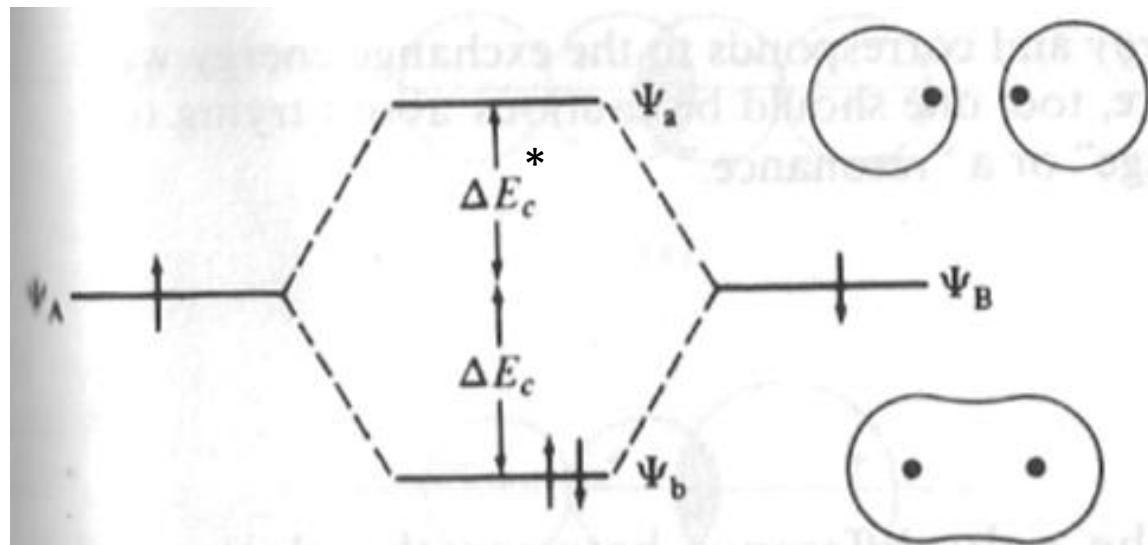
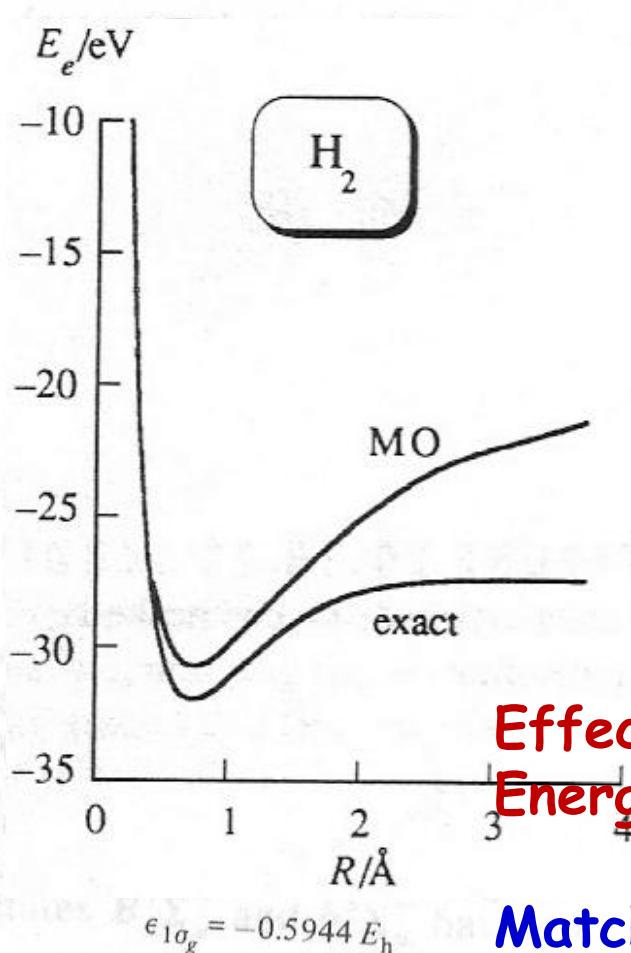
Space+Spin $\varphi_{bonding} = [\psi_b(1)\psi_b(2)] \bullet \left[\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \right]$

Spatial part! $\varphi_{H_2}^{MO} = \frac{1}{2(1+S)} [1s_A(1) + 1s_B(1)][1s_A(2) + 1s_B(2)]$

$$\varphi_{H_2}^{MO} = \frac{1}{2(1+S)} [1s_A(1)1s_A(2) + 1s_B(1)1s_B(2) + 1s_A(1)1s_B(2) + 1s_B(1)1s_A(2)]$$

MOT overemphasizes ionic terms in a covalent bond! VBT better?

Dihydrogen Molecule: One more electron goes to bonding orbital

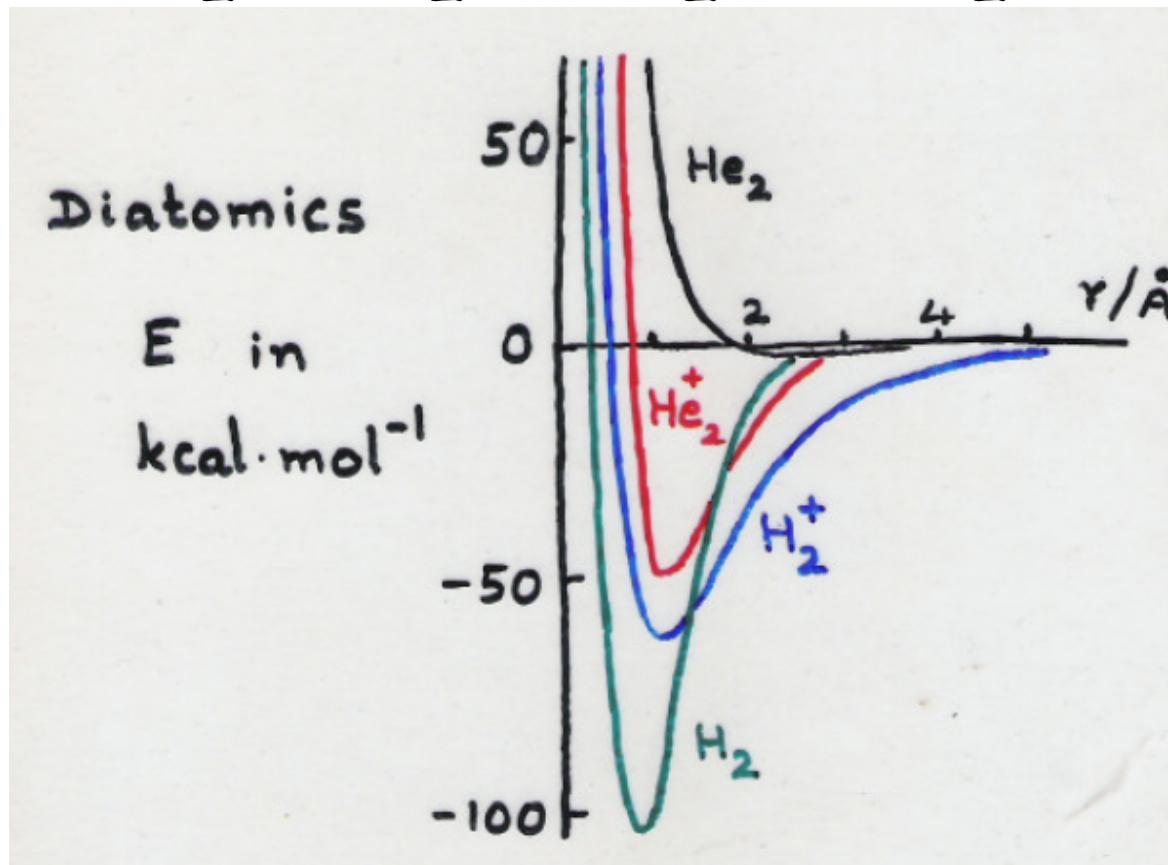
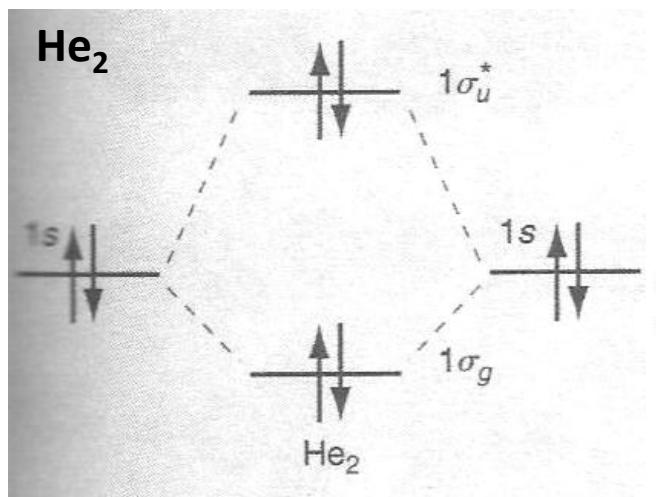
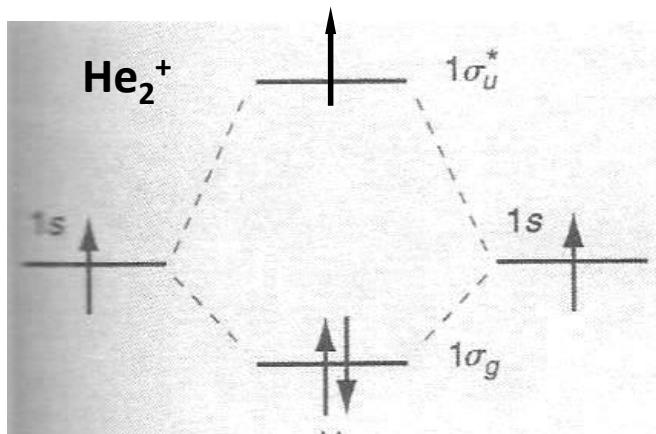


Bond strength increases: Bond order=1

Effective nuclear charge changes the absolute Energy levels and the orbitals!

Matching of energies of AO important for LCAO-MO
If energies are not close to each other, they would Not interact to form MOs.

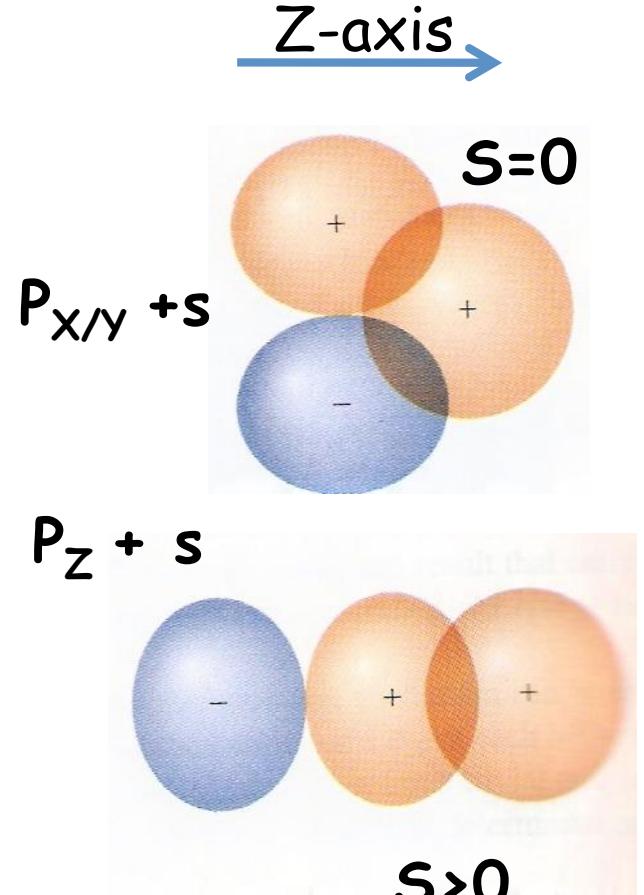
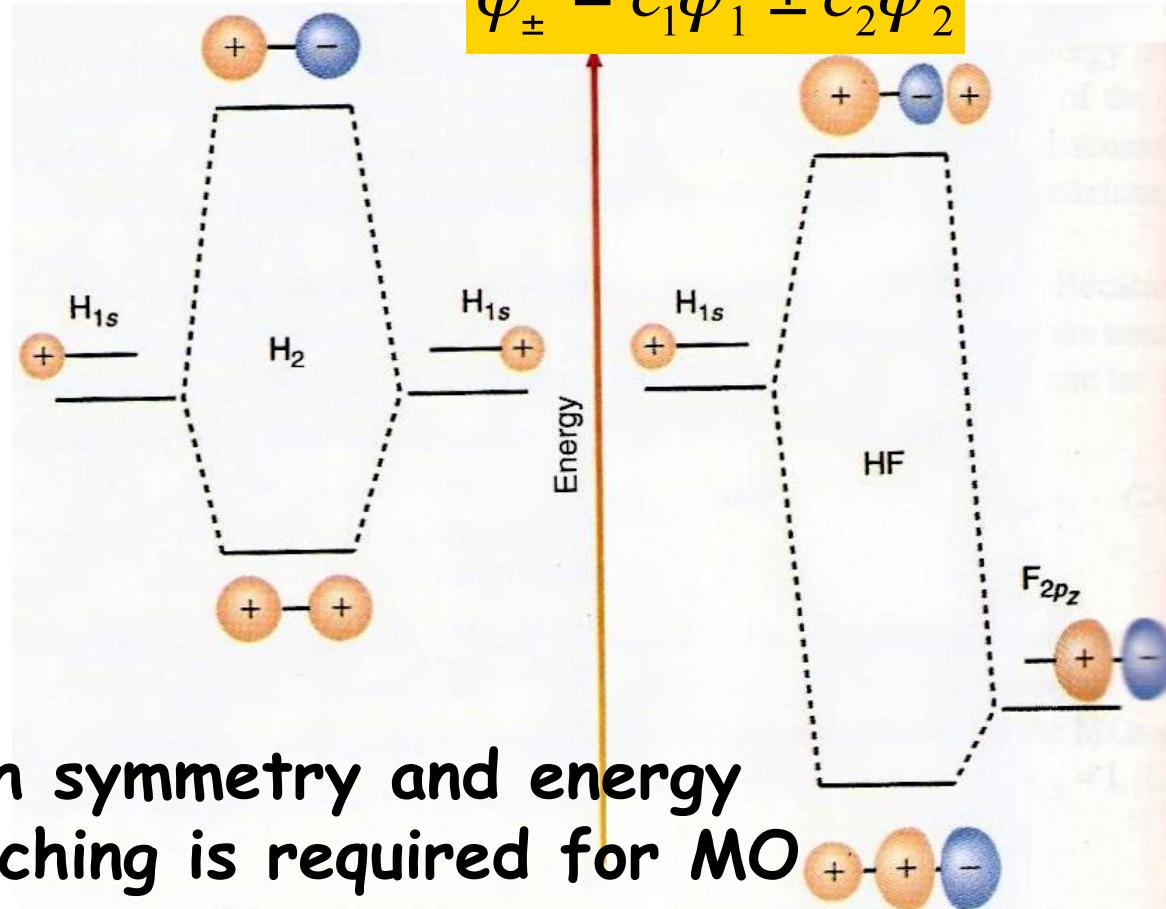
Energies of H_2^+ , H_2 , He_2^+ , He_2



Molecular properties of H_2^+ , H_2 , He_2^+ , and He_2 .

| Species | Number of electrons | Ground-state electron configuration | Bond order | Bond length/pm | Binding energy/kJ·mol ⁻¹ |
|-----------------|---------------------|-------------------------------------|------------|----------------|-------------------------------------|
| H_2^+ | 1 | $(\sigma_g 1s)^1$ | 1/2 | 106 | 268 |
| H_2 | 2 | $(\sigma_g 1s)^2$ | 1 | 74 | 457 |
| He_2^+ | 3 | $(\sigma_g 1s)^2 (\sigma_u 1s)^1$ | 1/2 | 108 | 241 |
| He_2 | 4 | $(\sigma_g 1s)^2 (\sigma_u 1s)^2$ | 0 | ~6000 | $\ll 1$ |

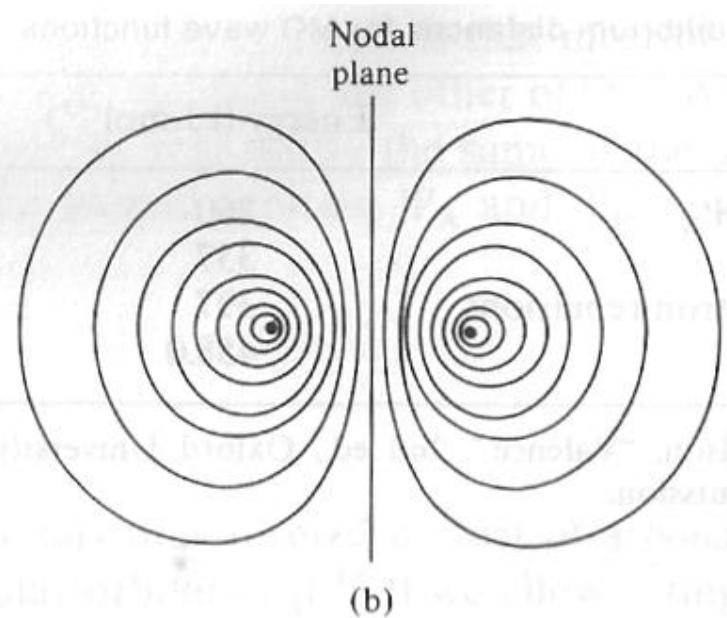
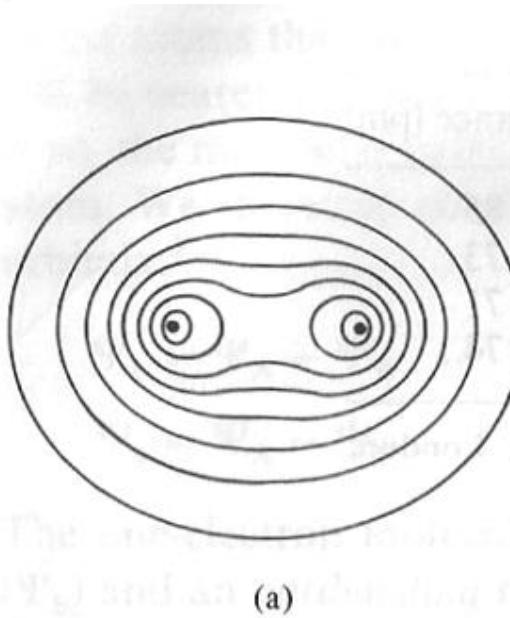
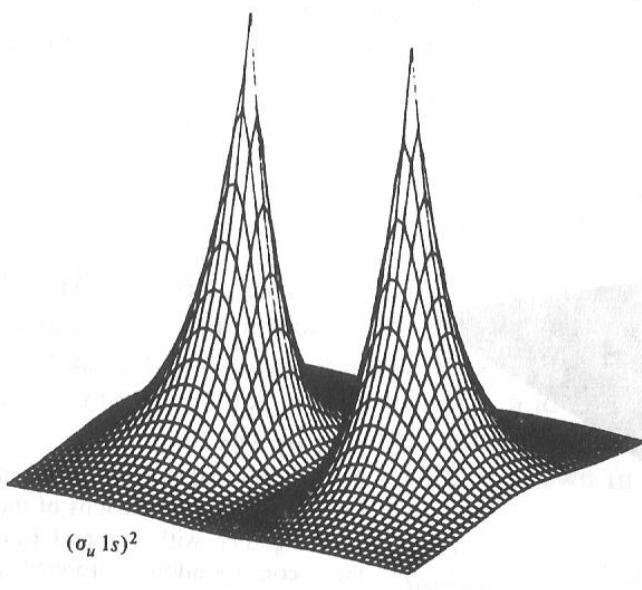
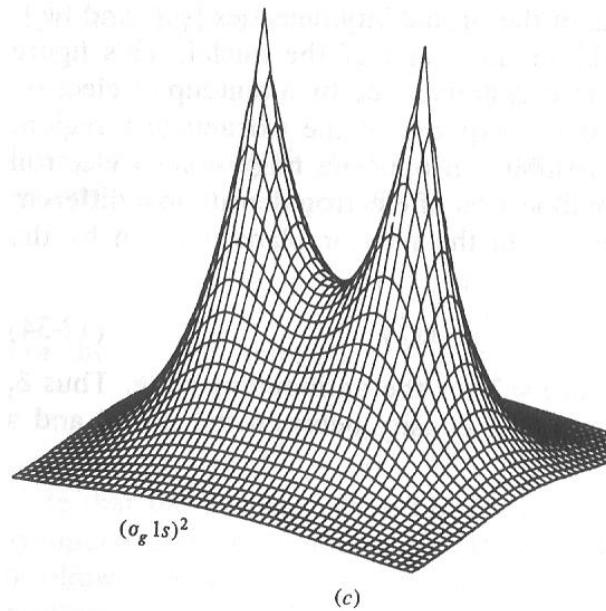
Matching of AO energies for MO



Valence electrons are most important for bonding

- Due to large difference in energy of 1s(H) and 1s(F), LCAO-MO for both 1S is not feasible in HF.
- Rather only 2P_z(F) [NOT 2P_{x/y}(F)] and 1S(H) form a σ -bond.

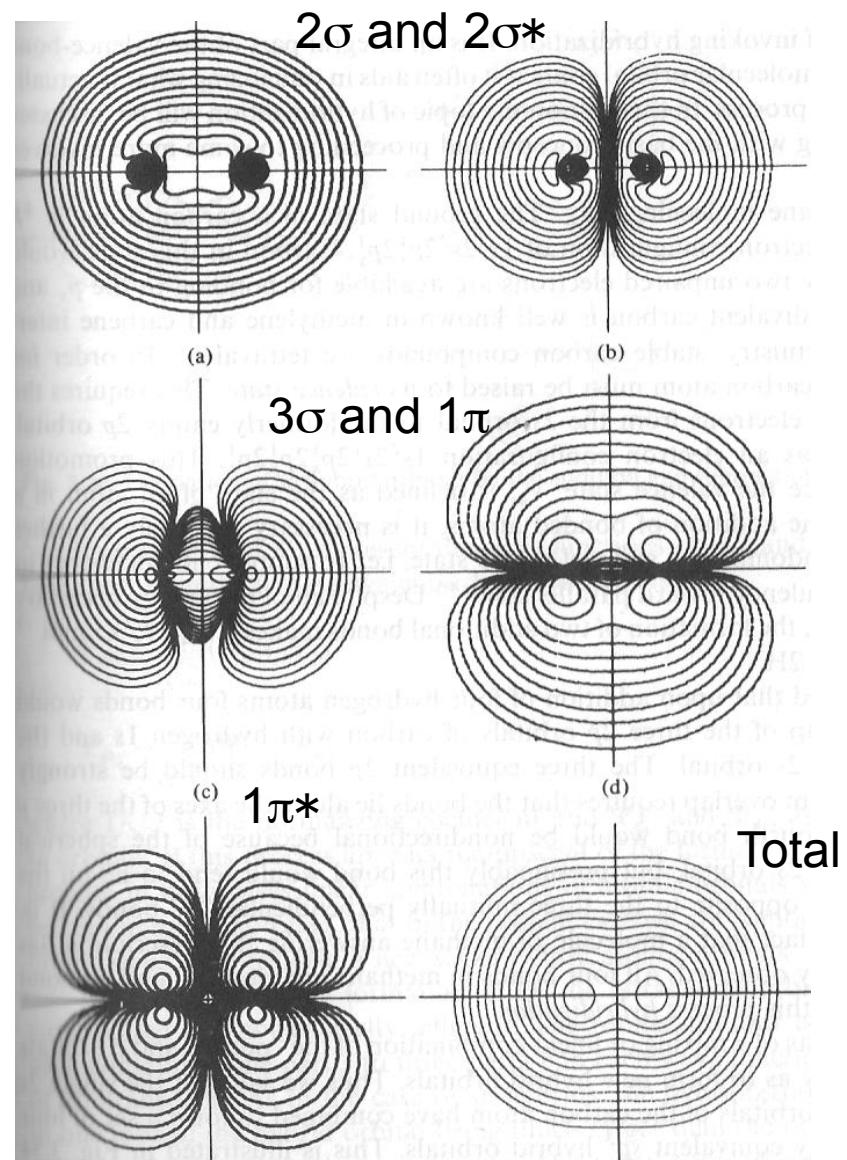
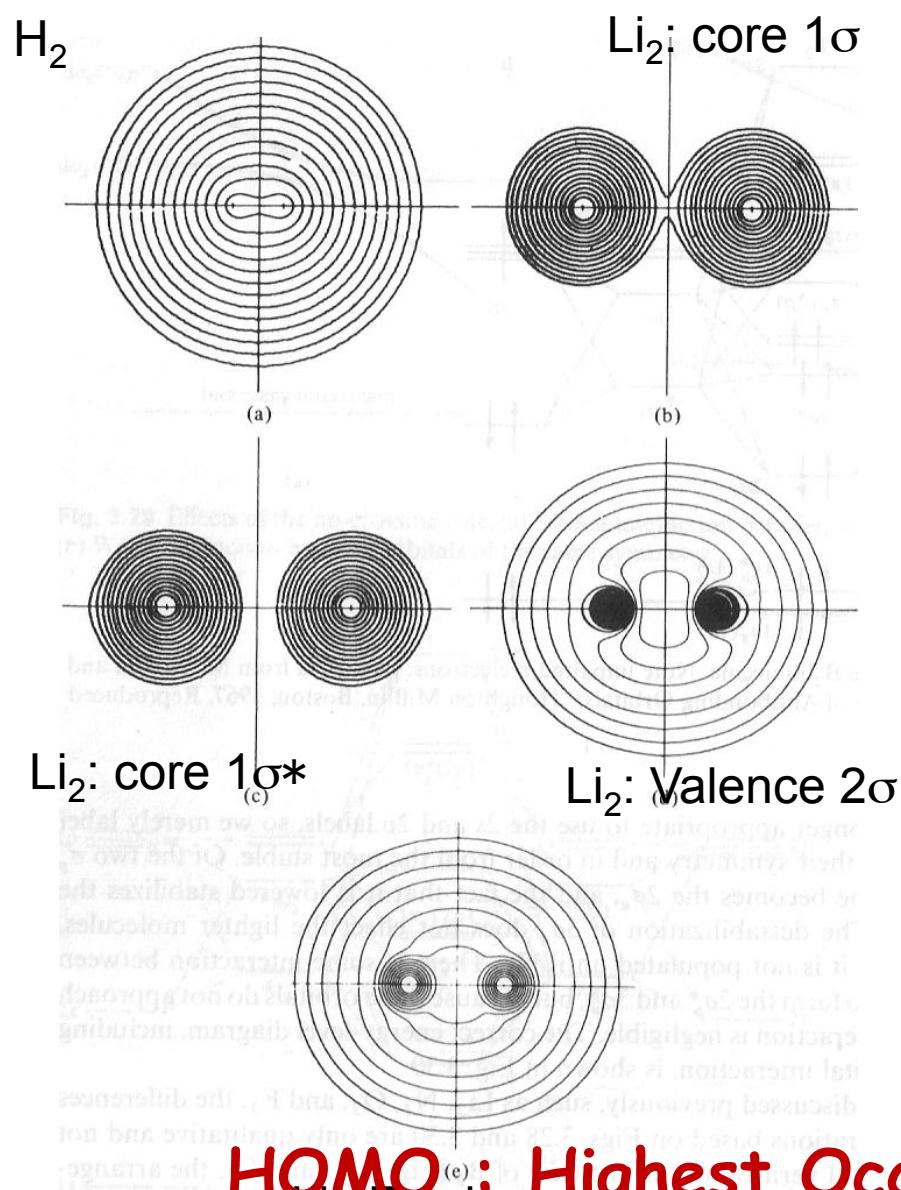
Electron Density Maps/Contours



Probability of finding an electron is equal
For each line drawn in the contour plot.

Value of probability higher close to the
Nucleus and decreased radially (outward)

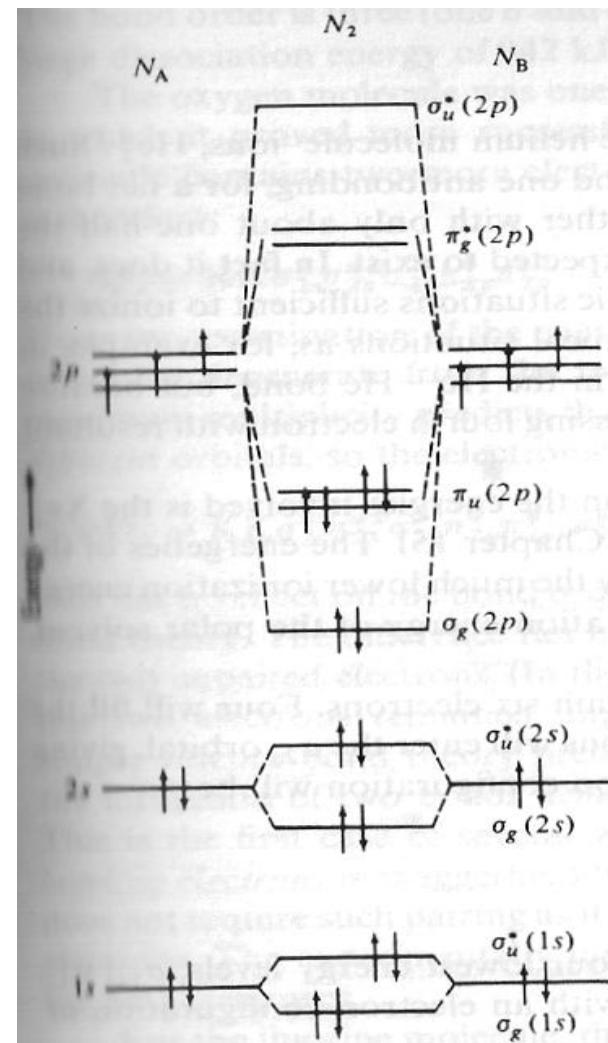
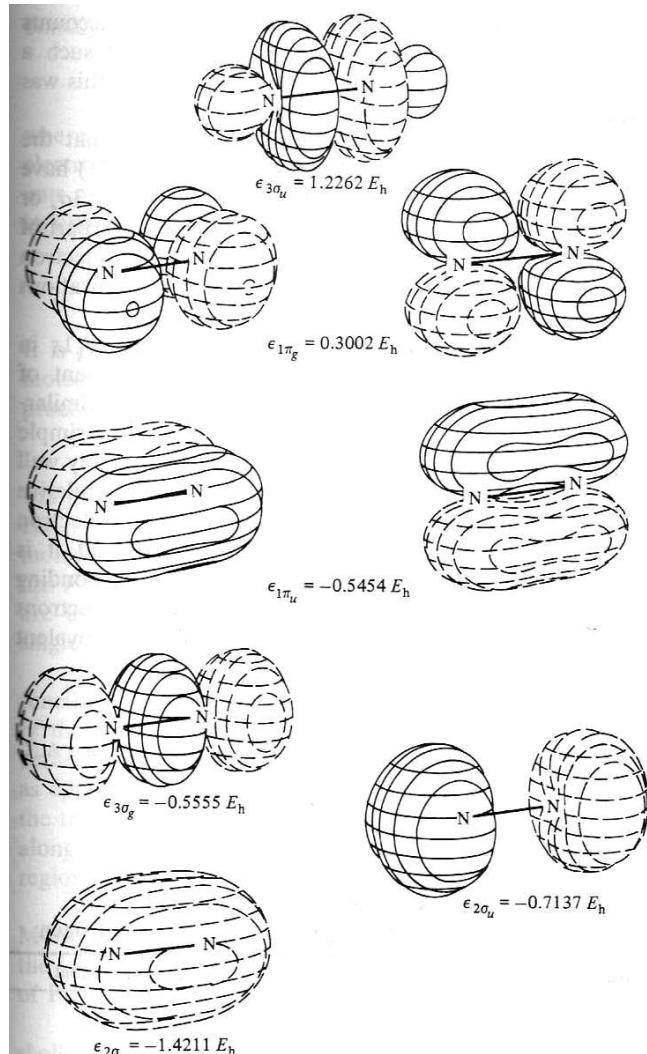
MO Contours show electron density maps



HOMO: Highest Occupied Molecular Orbital
LUMO : Lowest Unoccupied Molecular Orbital

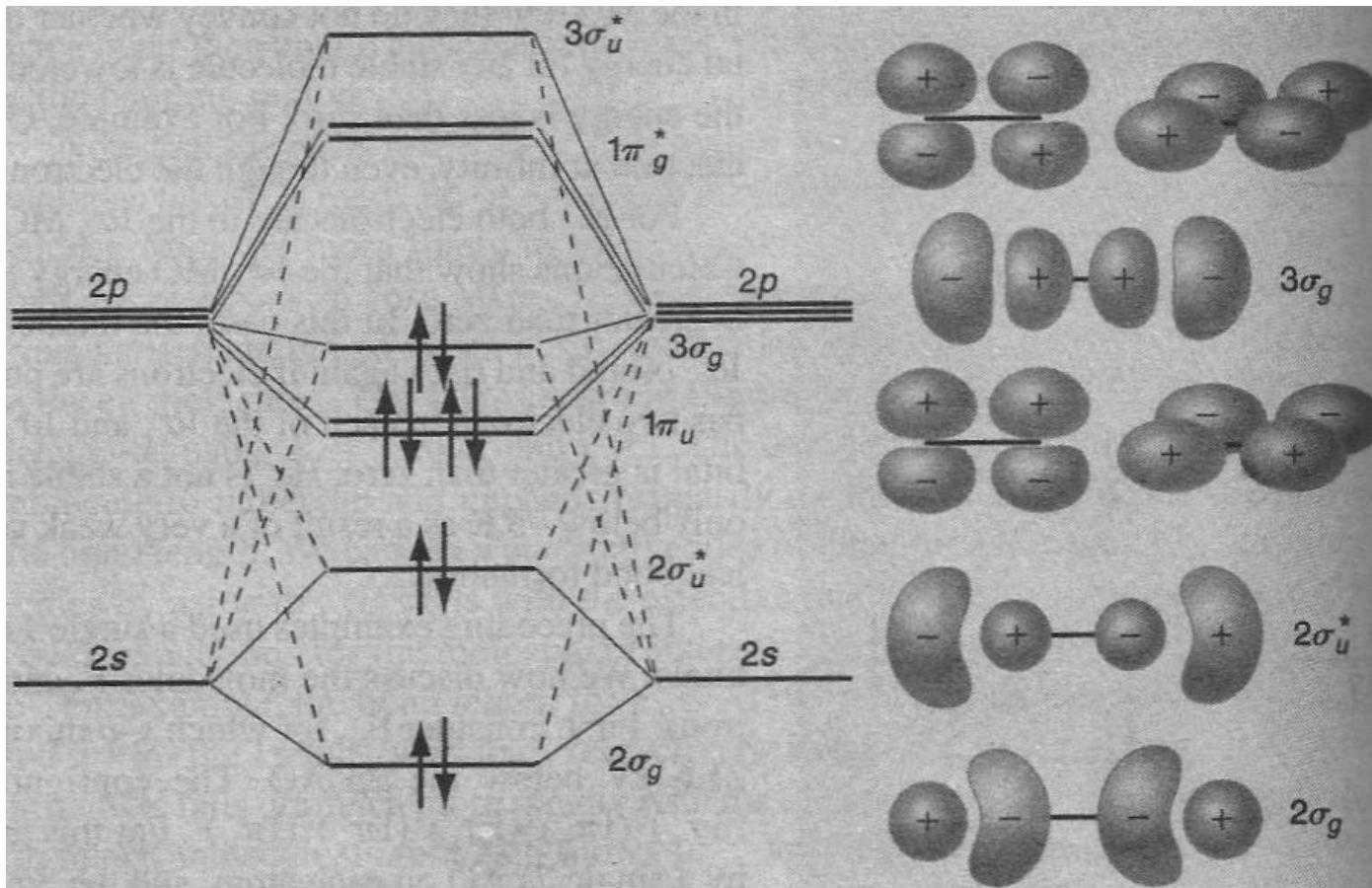
Expected MO and Energies for Dinitrogen

Is this a correct energy level diagram for N_2 ?



There is a problem! Spectroscopy says NO!

Actual MO and Energy Diagram for N₂



Nature 2004 vol 432 867

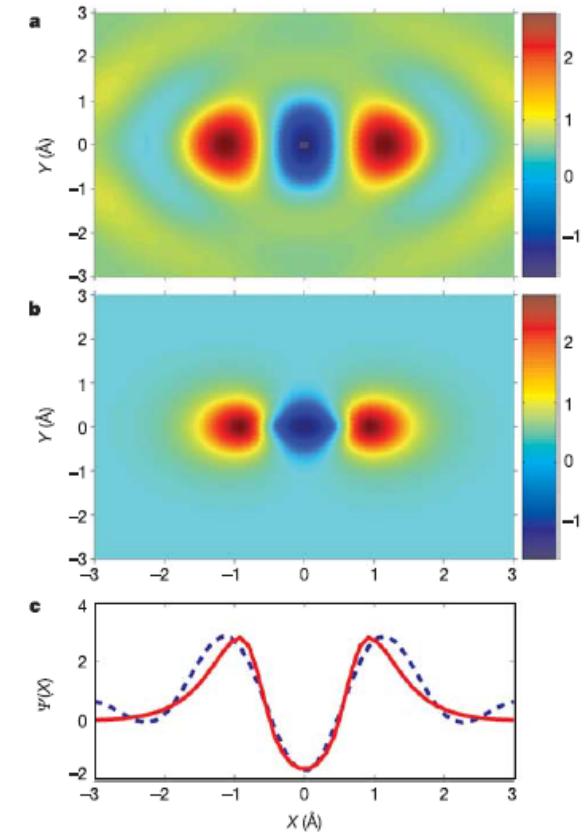


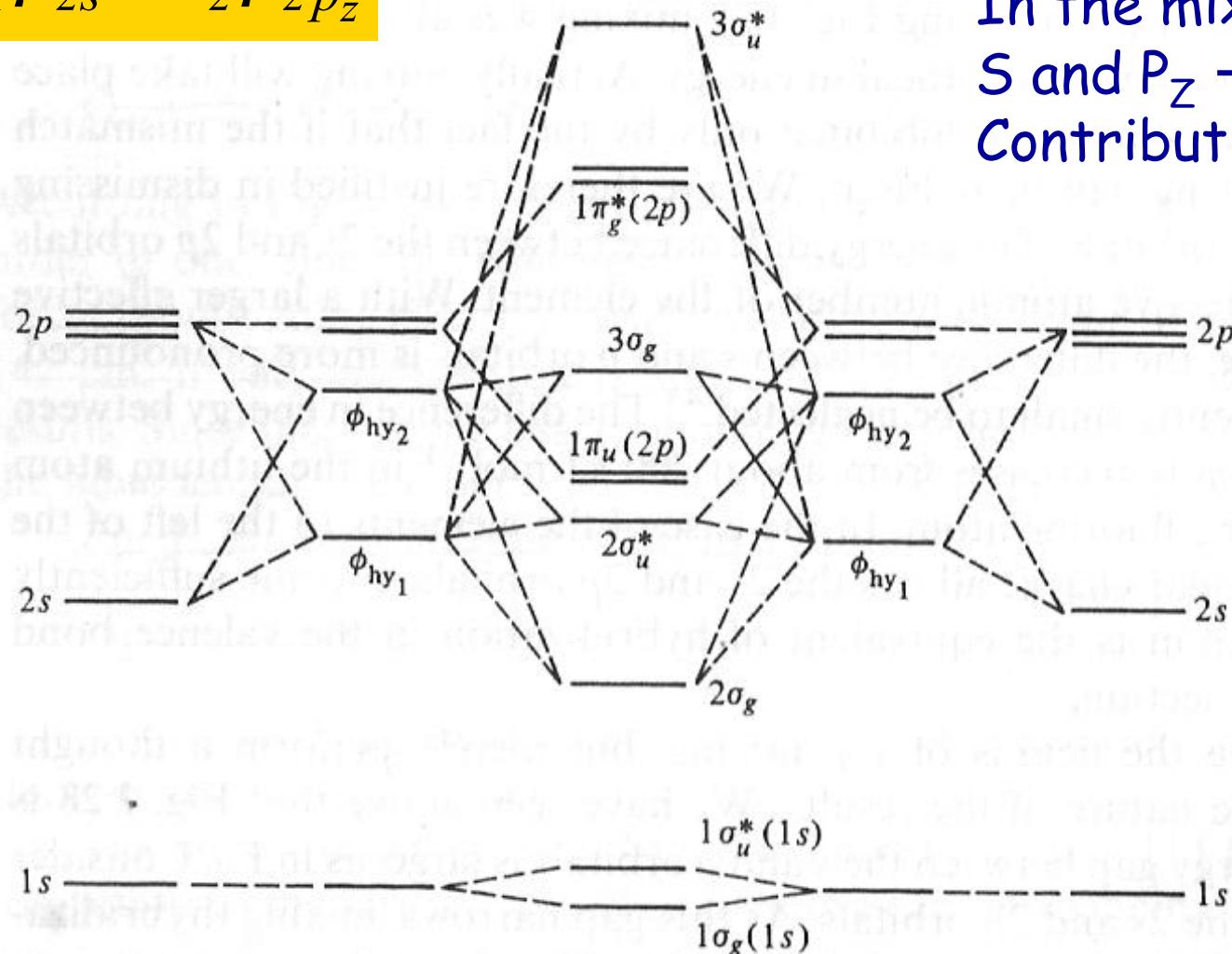
Figure 4 Molecular orbital wavefunction of N₂. a, Reconstructed wavefunction of the HOMO of N₂. The reconstruction is from a tomographic inversion of the high harmoni

Mixing of 2S and 2P orbital occur because of small energy gap between them. 2s and 2p electrons feels not so different effective nuclear charge.

S-P Mixing in Atomic Orbitals

$$\psi_{\pm}^{SP_z} = c_1 \psi_{2s} \pm c_2 \psi_{2p_z}$$

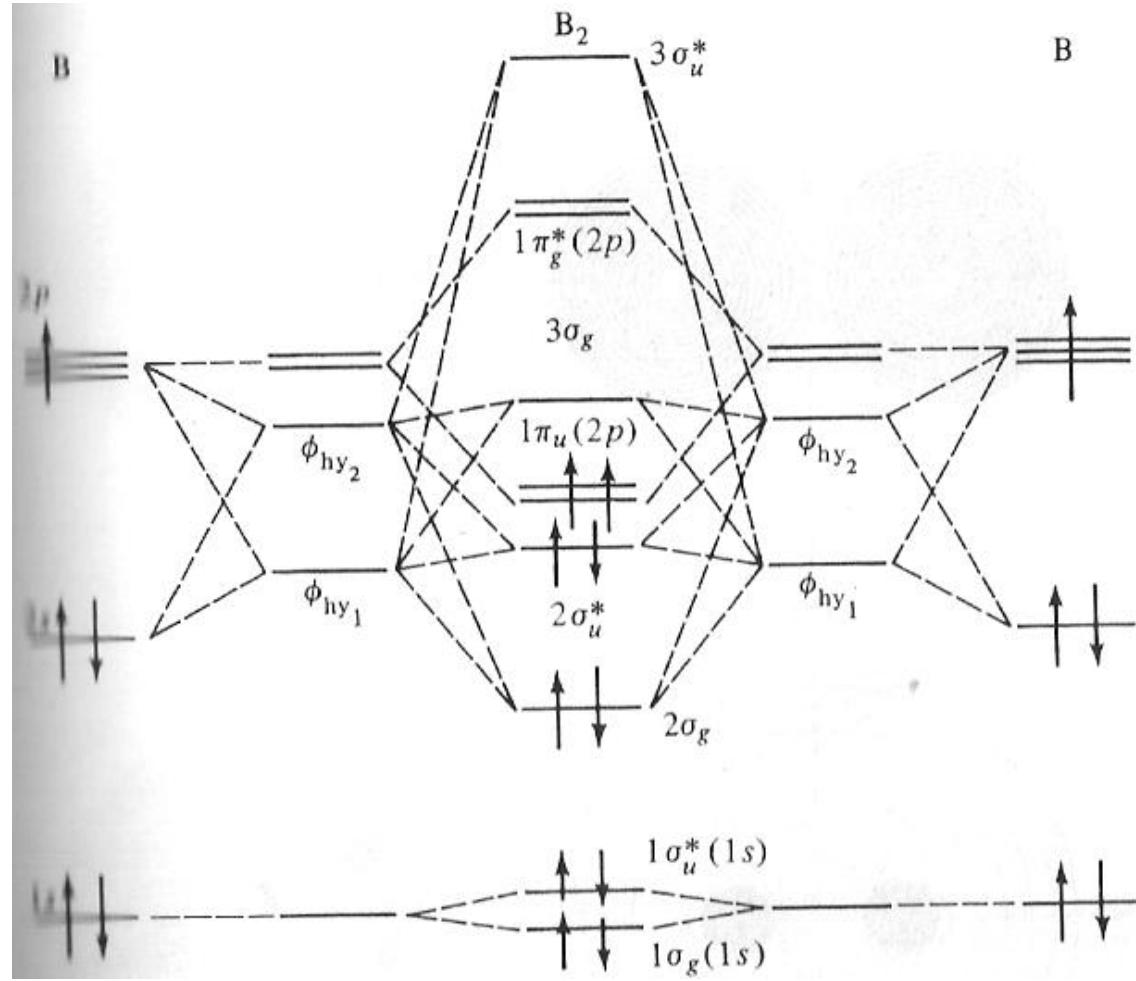
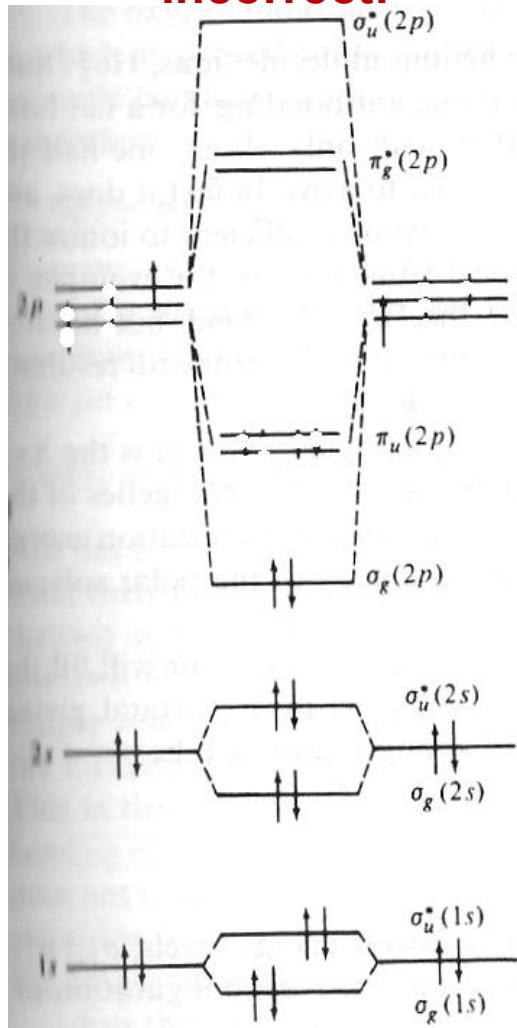
C_1 and C_2 not equal -
In the mix orbital:
 S and $P_z \rightarrow$ different
Contributions in mix



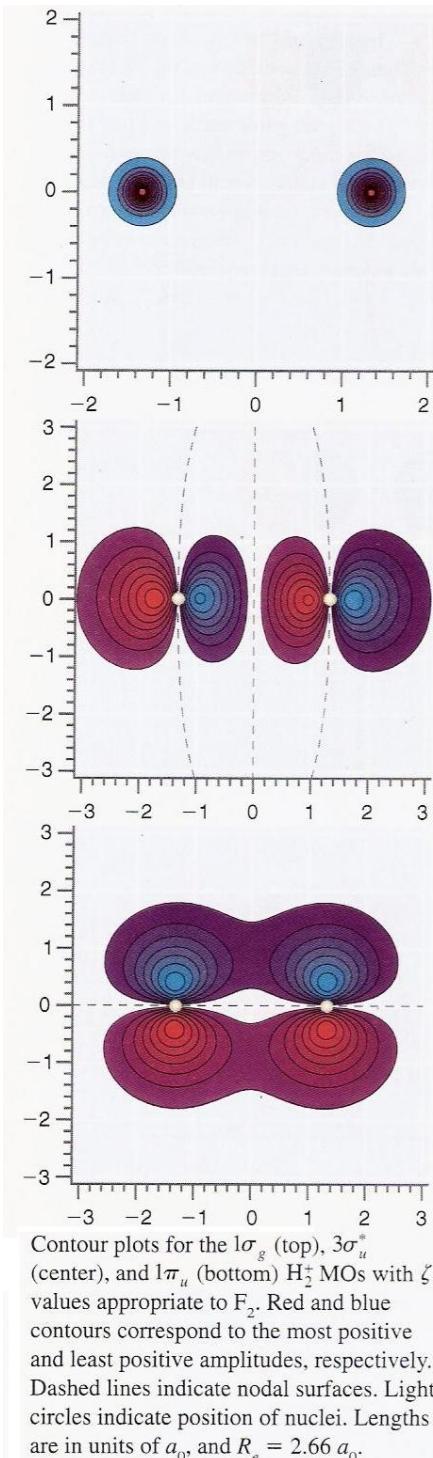
2S and 2P AOs MIX due to less energy gap \rightarrow 2s and 2p e feels not so different Z_{eff} . \rightarrow Mixed states can form MOs

s-p Mixing: B_2 magnetism confirms it!

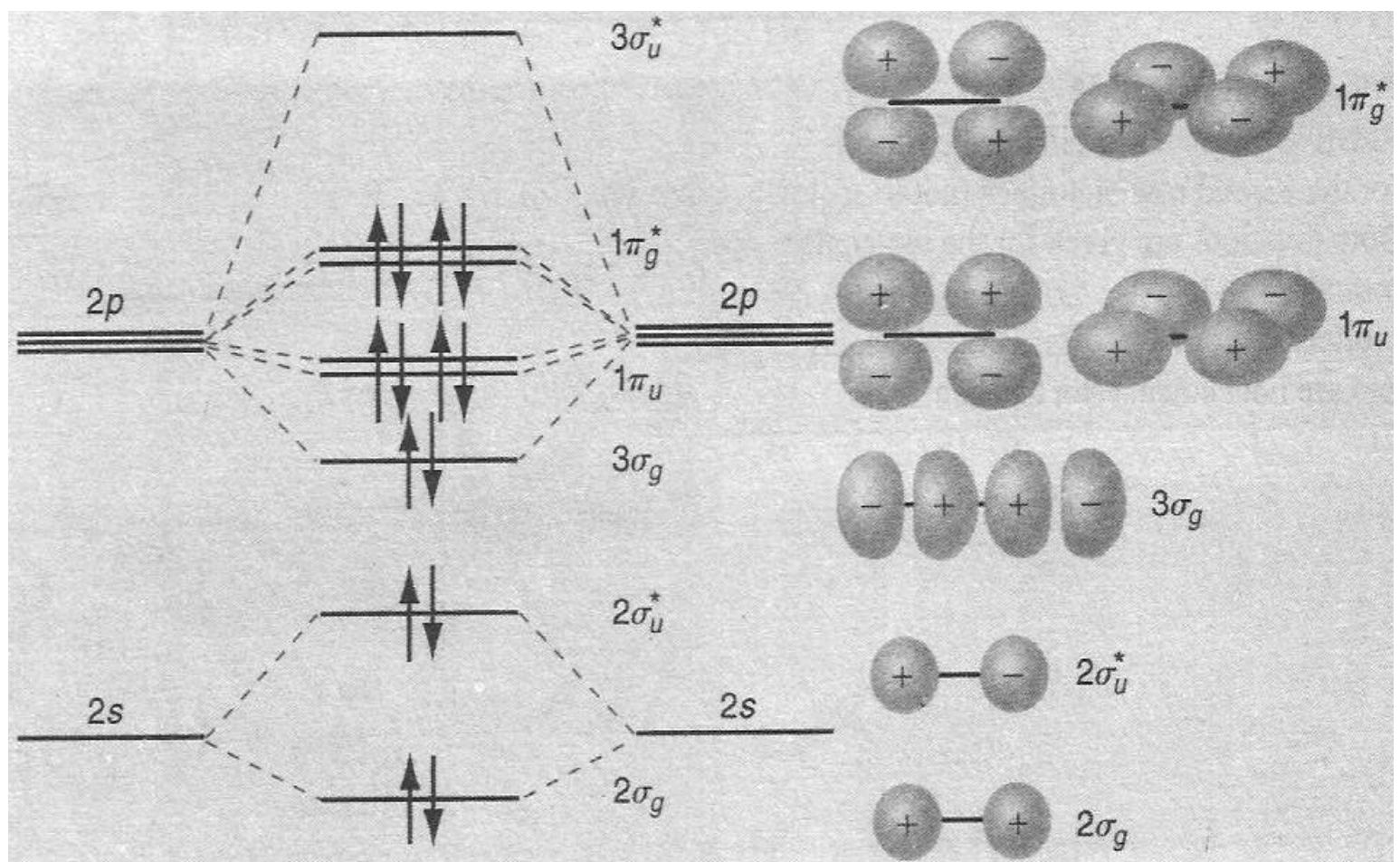
Incorrect!



Boron is paramagnetic. This can only happen if the two electrons with parallel spin are in the π -orbitals $\rightarrow \pi$ -bonding energies lower than σ^* ?

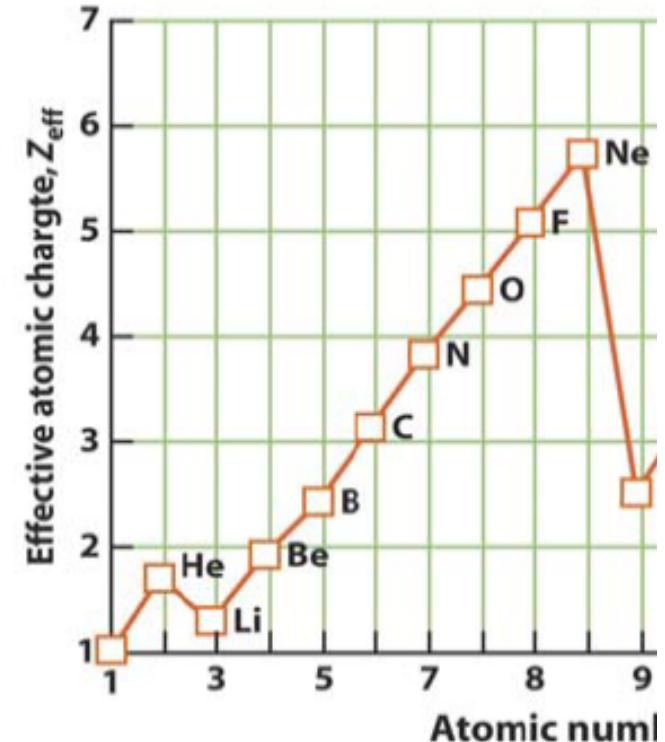
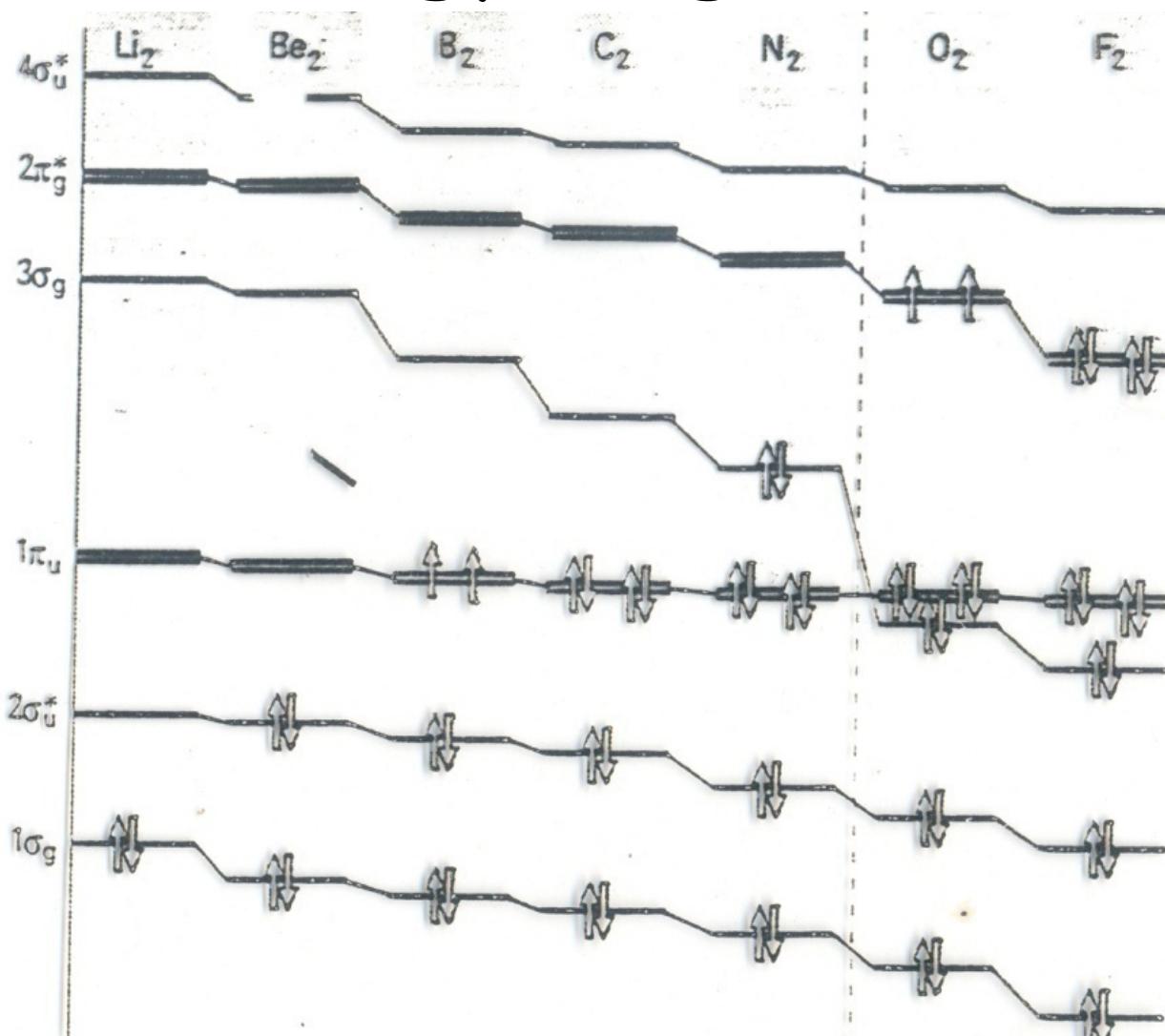


MO Energy Diagram for F_2



Less mixing of S and P orbital because of higher energy Gap between 2S and 2P levels in Oxygen and Fluorine!
2s and 2p electrons feels very different nuclear charge

MO Energy Diagram (Homo-Diatomics)

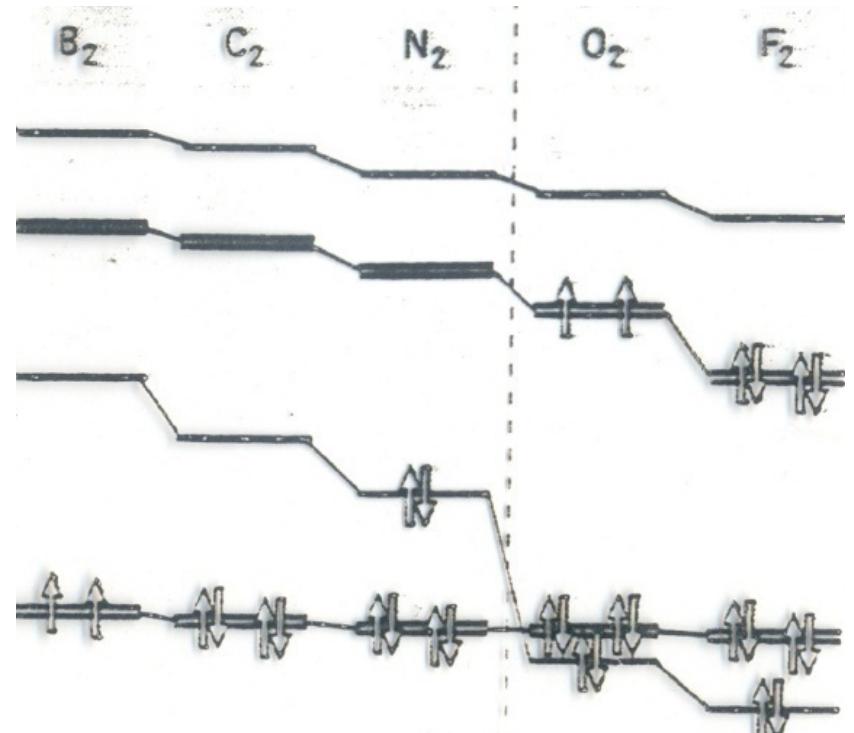
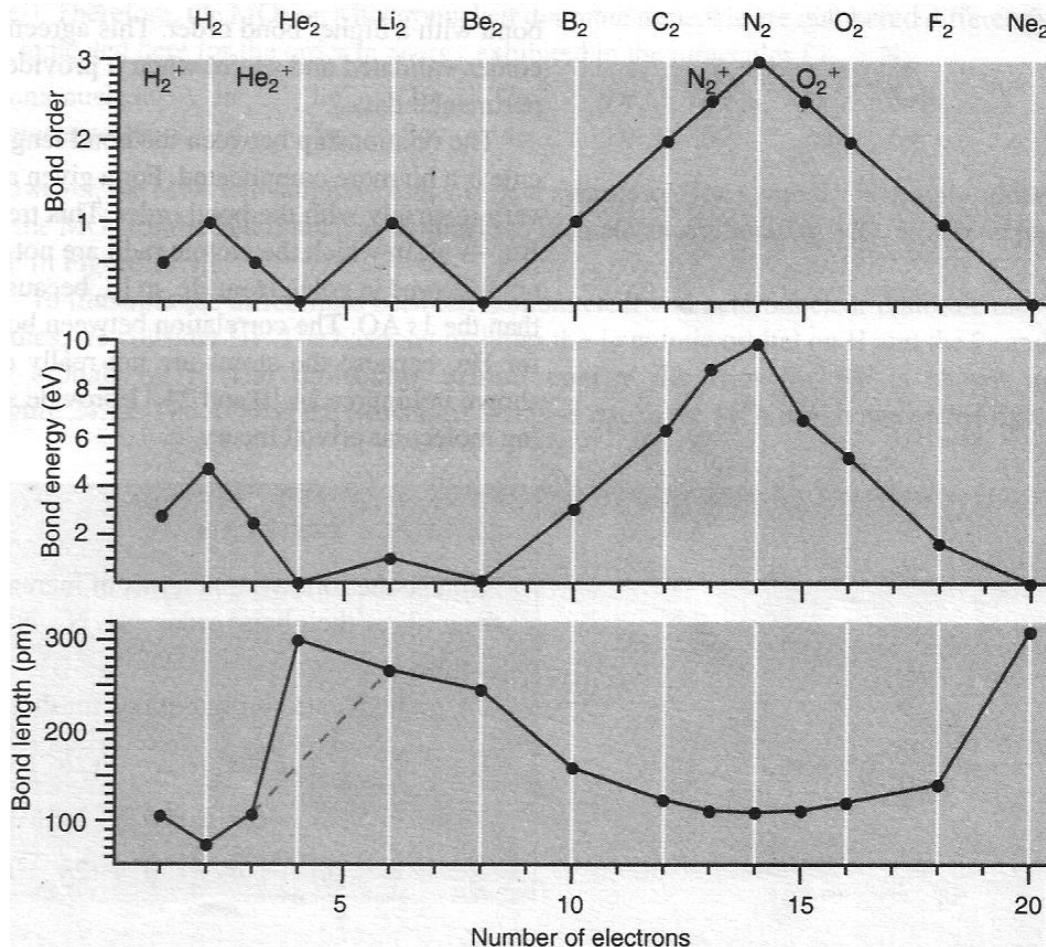


Bond Order = $\frac{1}{2}$ (# of bonding electrons - # of antibonding electrons)

Bond order = 0 → molecule can not exist - No bond formation

Bond order higher → stronger bond, shorter bond length

Bond order, strength, length... ...magnetism can be explained

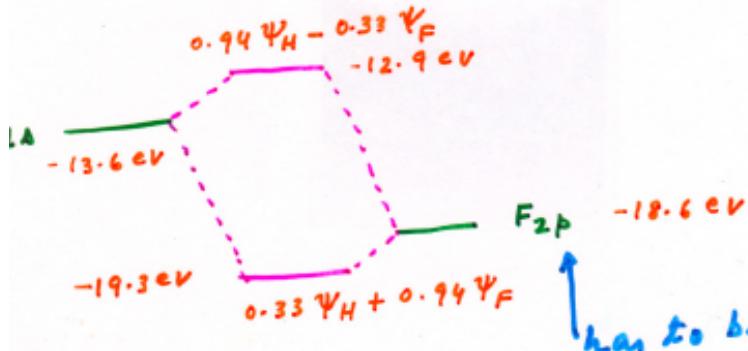


Paired Spins: Diamagnetic
Unpaired spins: Paramagnetic

Hetero-nuclear Diatomics: HF

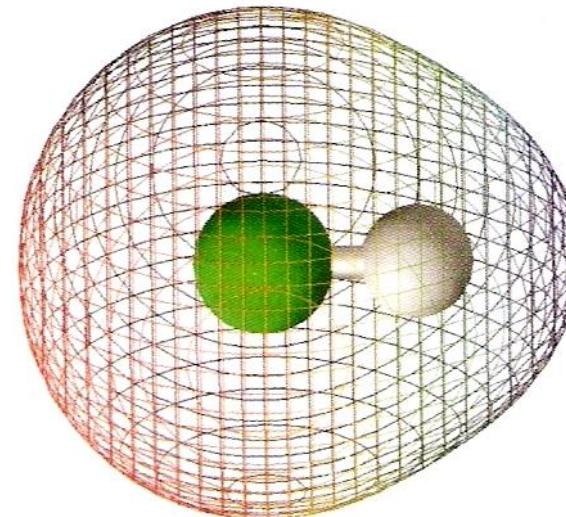
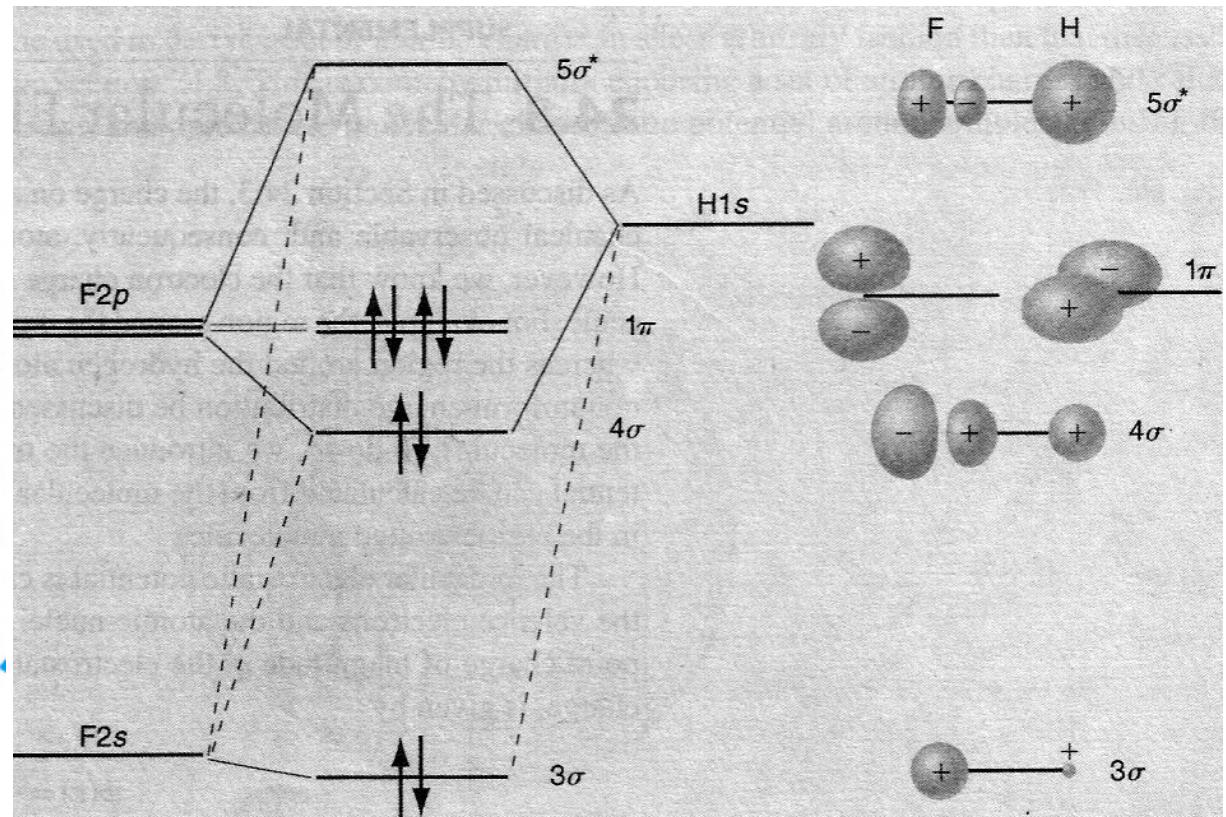
$$\phi_{4\sigma}^b = c_1 \psi_{2s} + c_2 \psi_{2p_z}$$

$$\phi_{5\sigma}^* = c_1 \psi_{2s} - c_2 \psi_{2p_z}$$



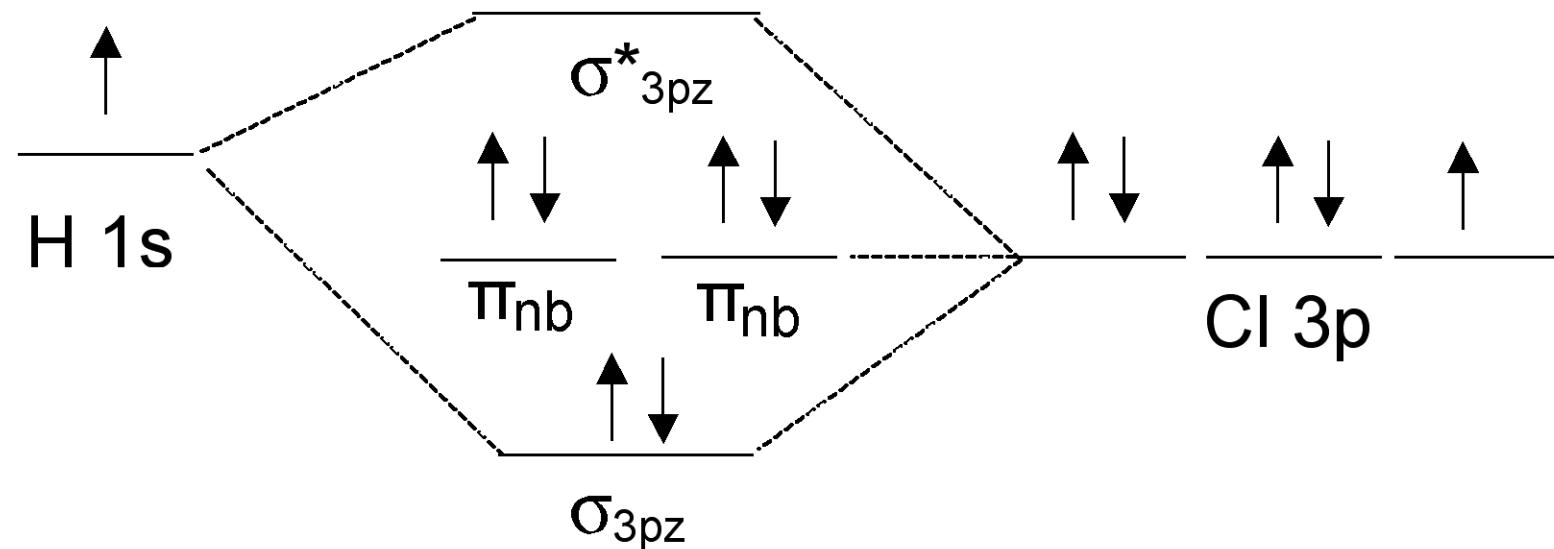
Electronegativity of F
much more than H
(as $Z_{\text{eff}} \gg H$):

Electrostatic potentials
can be computed which
gives a realistic picture
of the electron densities
in HF: "Egg" Shaped



Hetero-nuclear Diatomics: HCl

For Cl \rightarrow 3p states close in energy to the 1s of H



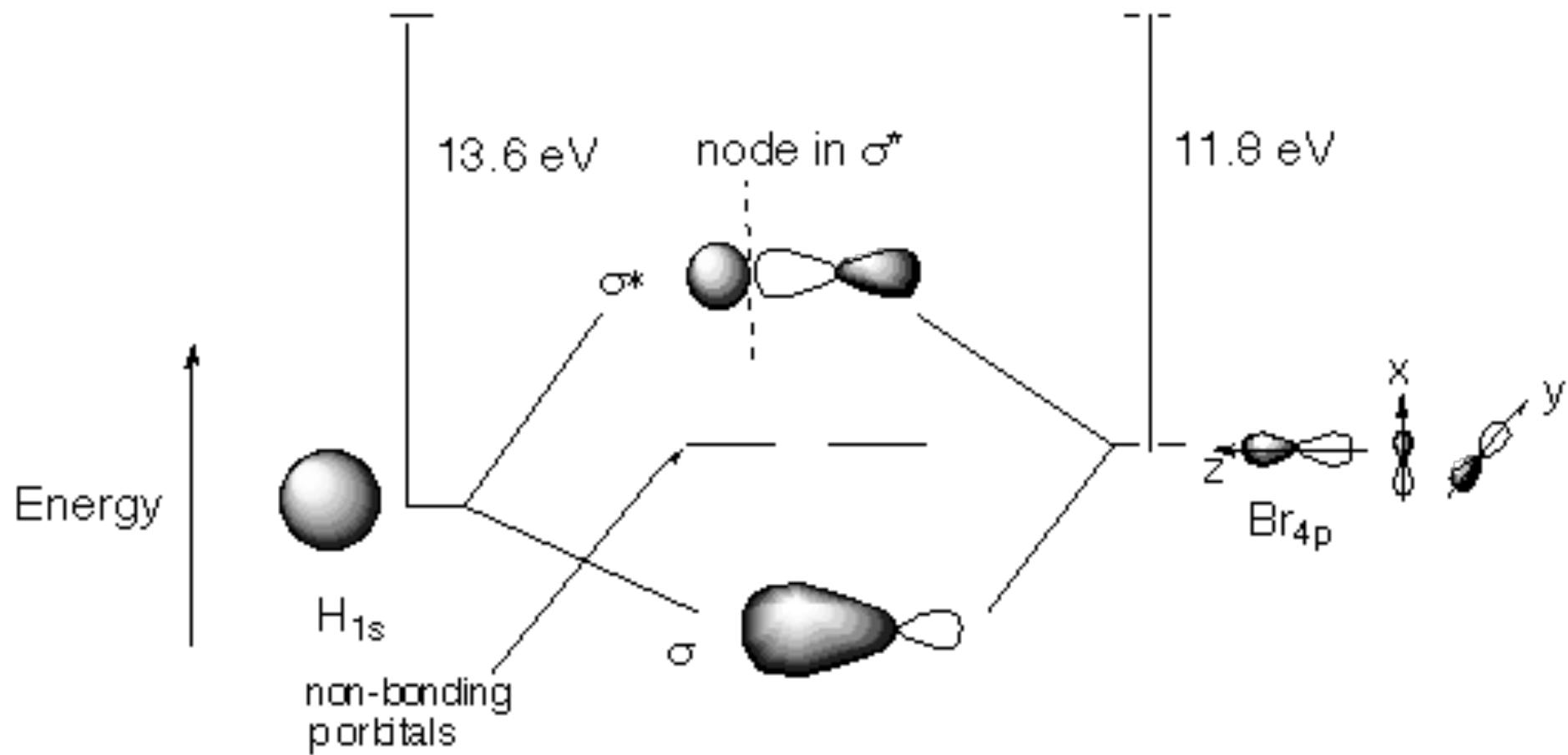
Similar to HF, except for
2p and 3p difference.

Can not tell where absolute
Energy levels will be unless
Spectroscopic evidences
Exists. Or do QM calculations

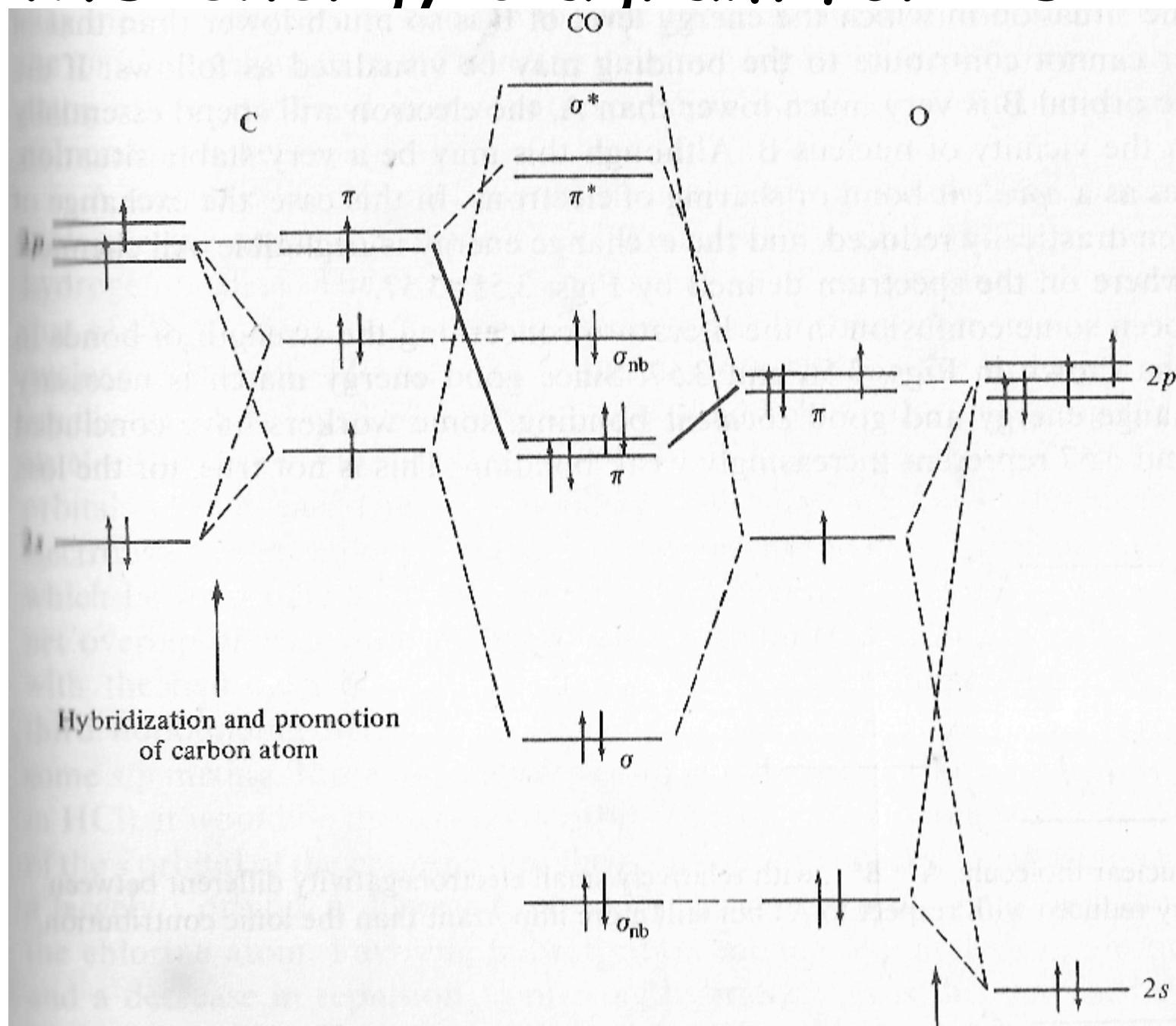


Hetero-nuclear Diatomics: HBr

For Br \rightarrow 4p states close in energy to the 1s of H!
Actually the 4p is higher in energy as opposed to
That of F(2s) and Cl(3s)



MO energy diagram for CO



MO energy diagram for CO

