Review : Idealized MO Diagrams: O₂

For 3D view: https://www.chemtube3d.com/orbitalsfluorine/
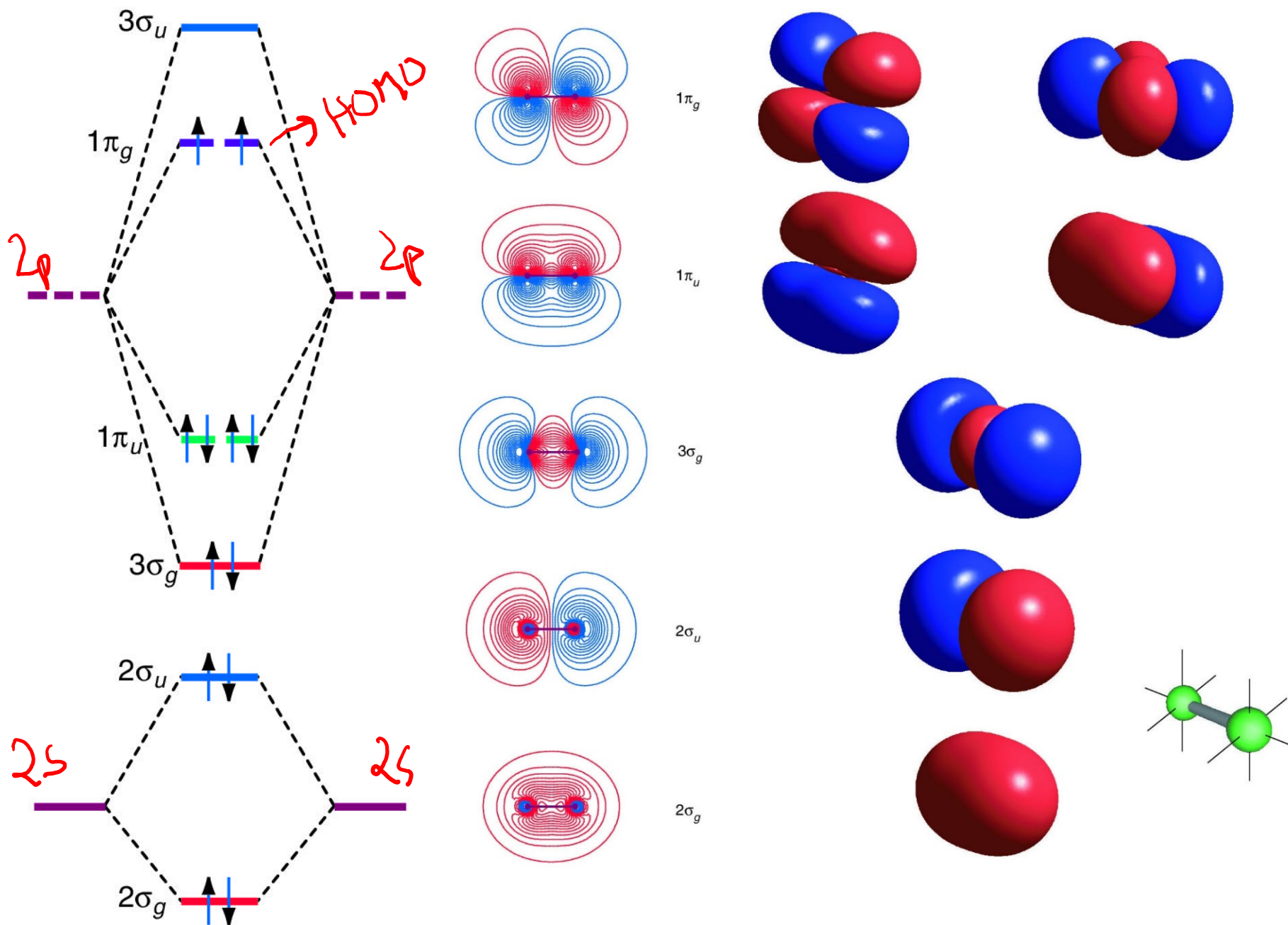
Expected MO and Energies for N_2

$\epsilon_{3\sigma_u} = 1.2262\ E_h$

$\epsilon_{1\pi_g} = 0.3002\ E_h$

$\epsilon_{1\pi_u} = -0.5454\ E_h$

$\epsilon_{3\sigma_g} = -0.5555\ E_h$

$\epsilon_{2\sigma_u} = -0.7137\ E_h$

$\epsilon_{2\sigma_g} = $ ...

N_2

N_A N_B

$\sigma_u^*(2p)$

$\pi_g^*(2p)$

$2p$

$\pi_u(2p)$

$\sigma_g(2p)$

$\sigma_u^*(2s)$

$2s$

$\sigma_g(2s)$
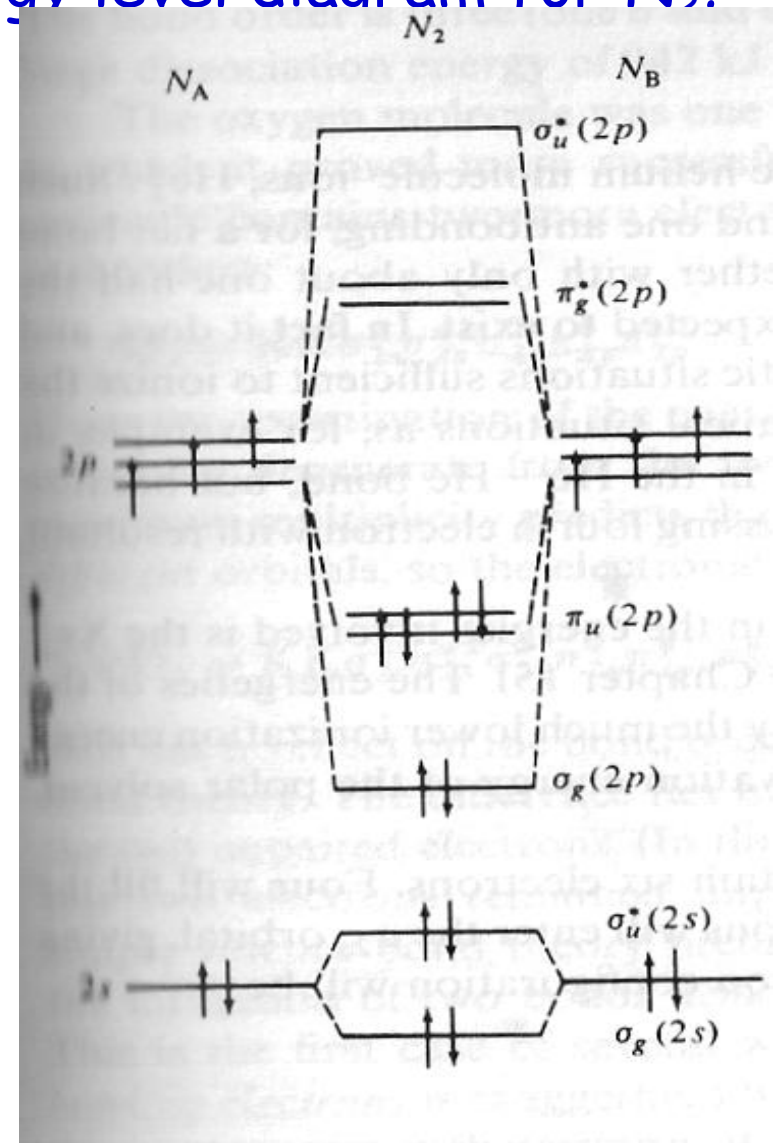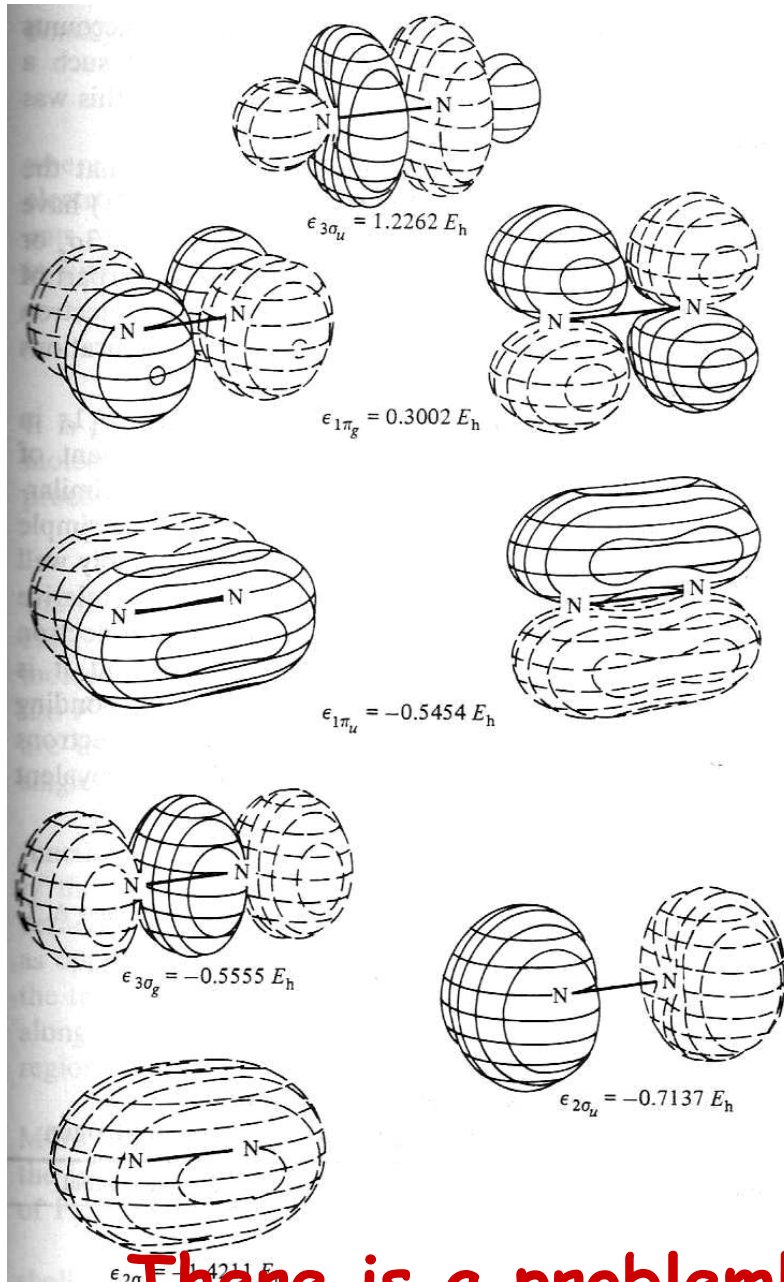
There is a problem! Spectroscopy says NO!

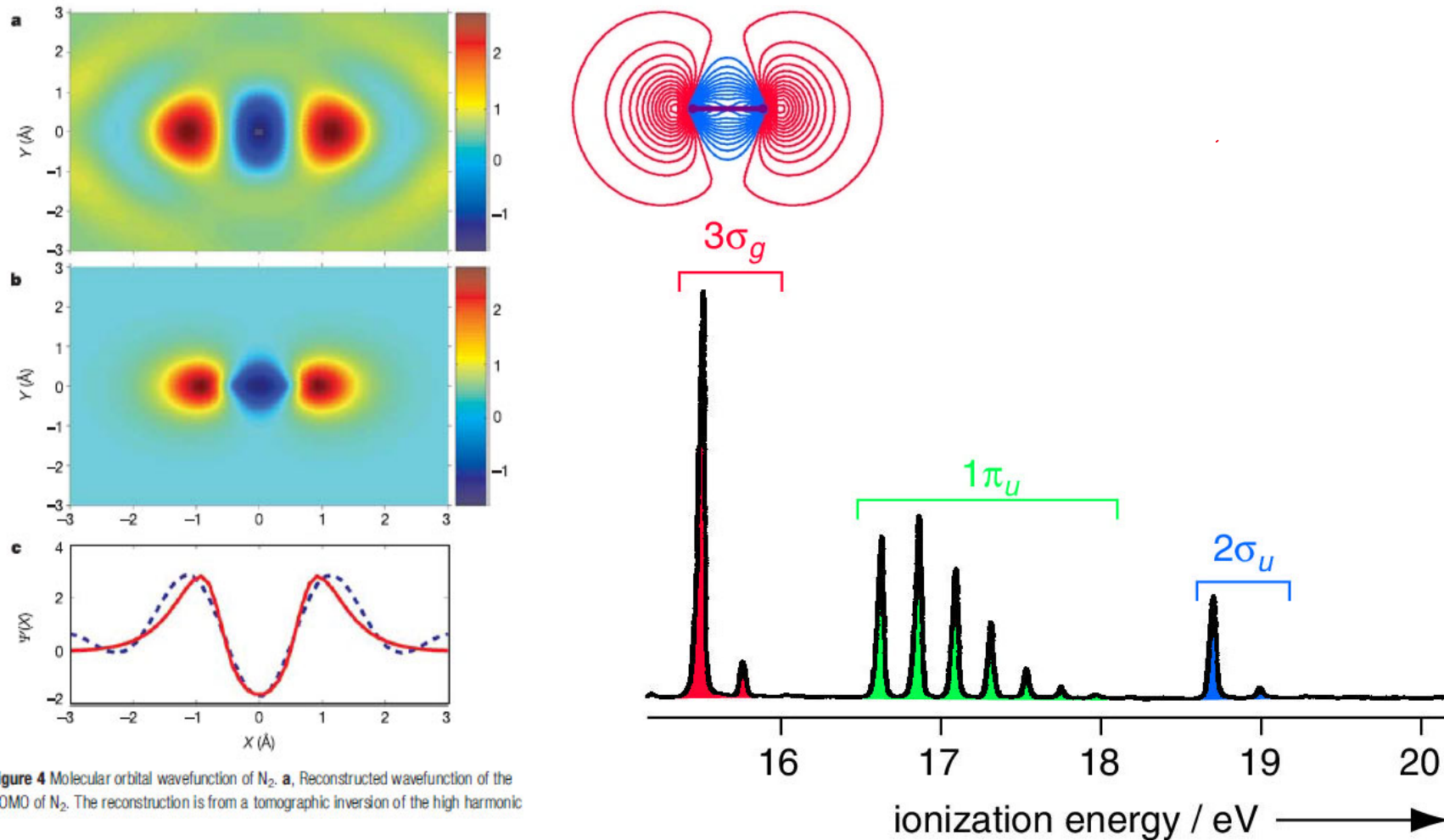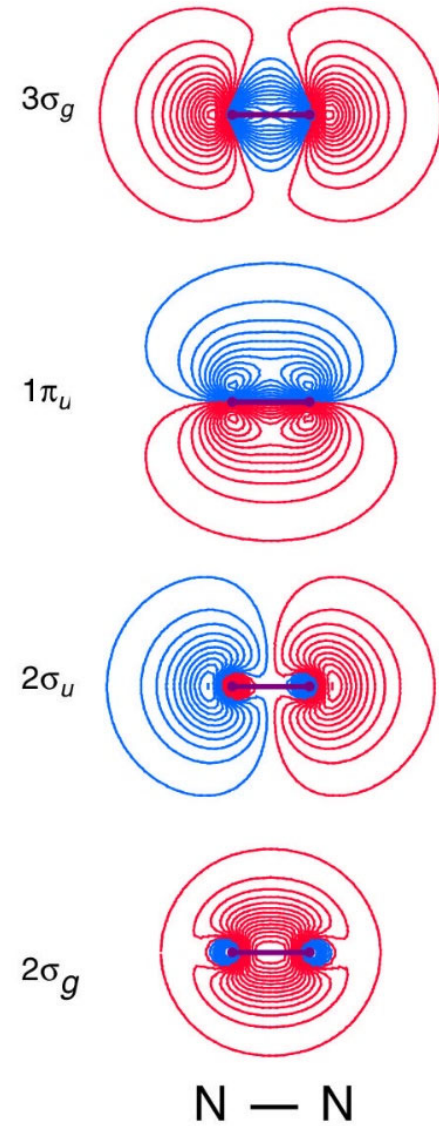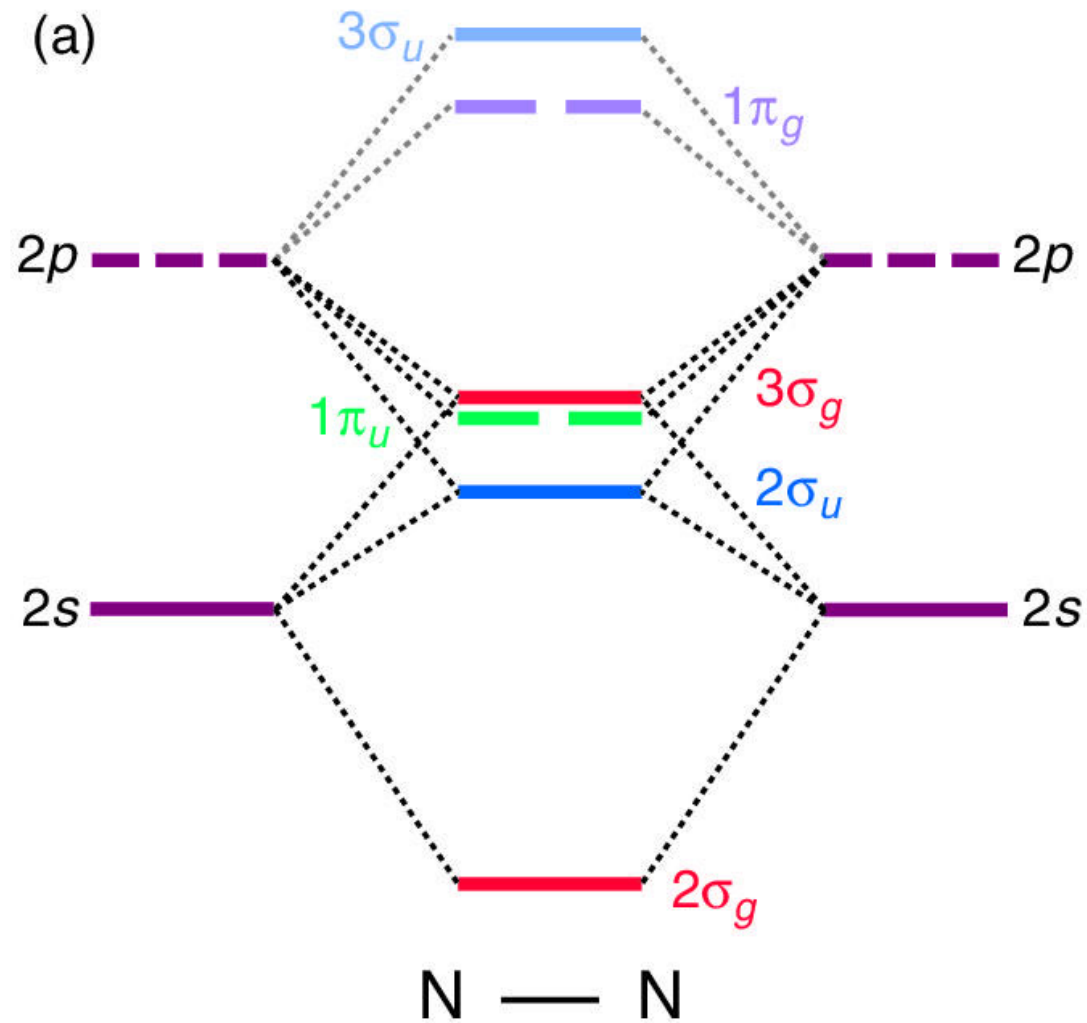# Actual MO and Energy Diagram for N_2

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Figure 4 Molecular orbital wavefunction of N_2. a, Reconstructed wavefunction of the HOMO of N_2. The reconstruction is from a tomographic inversion of the high harmonic
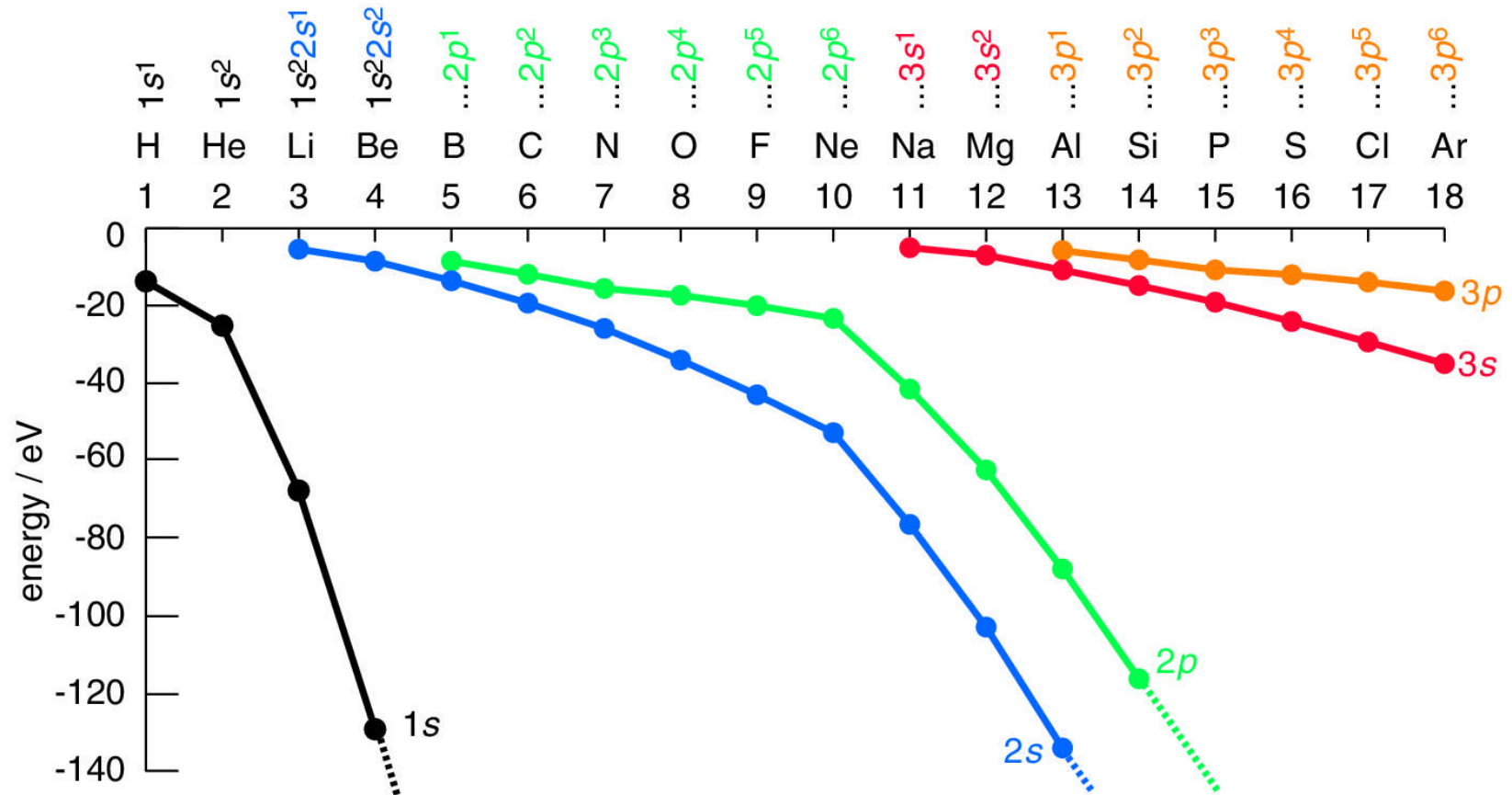
- Mixing of 2S and $2P_z$ orbital → due to small energy gap
  - 2s and $2p_z$ electrons feels not so different Z_{eff}
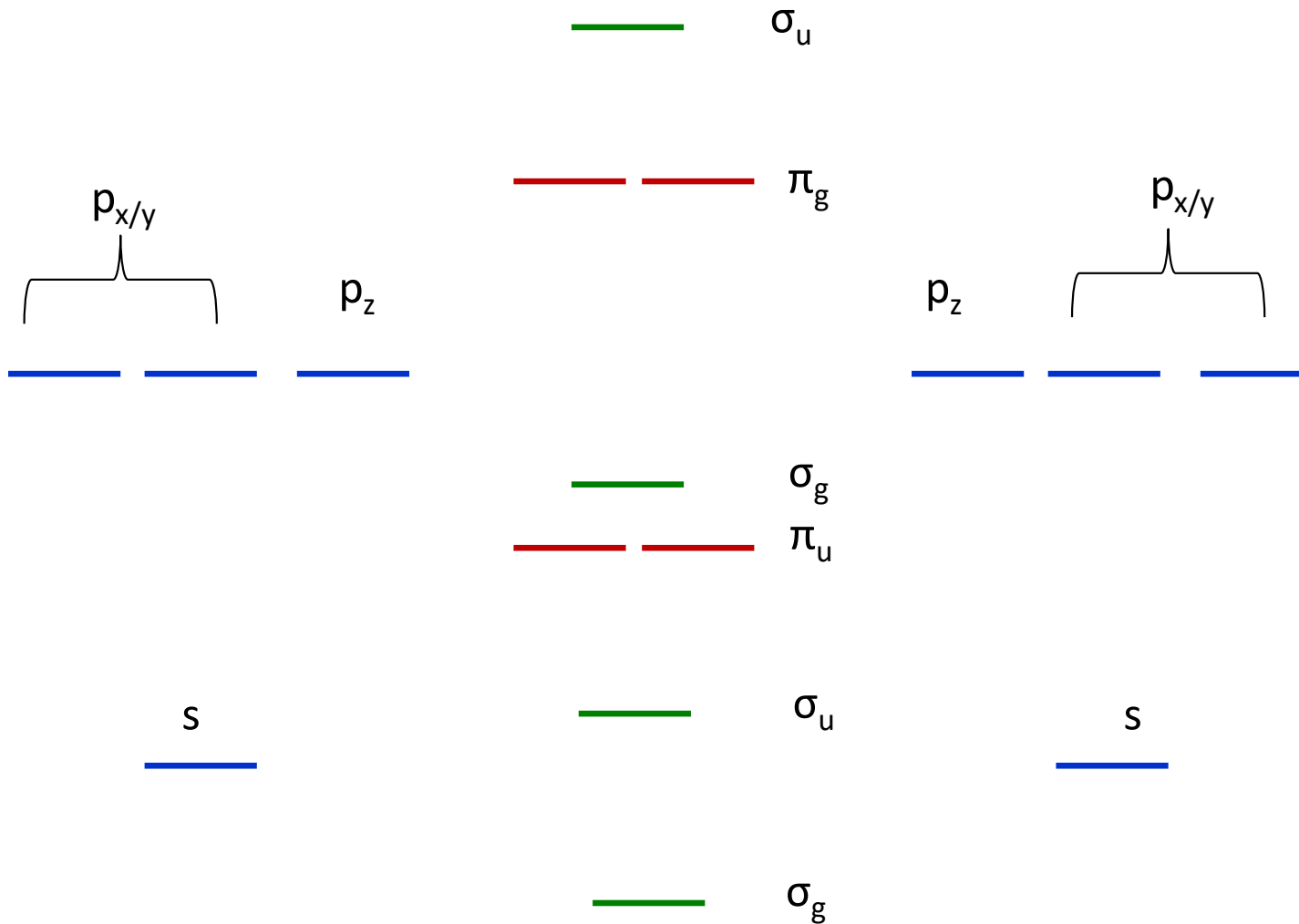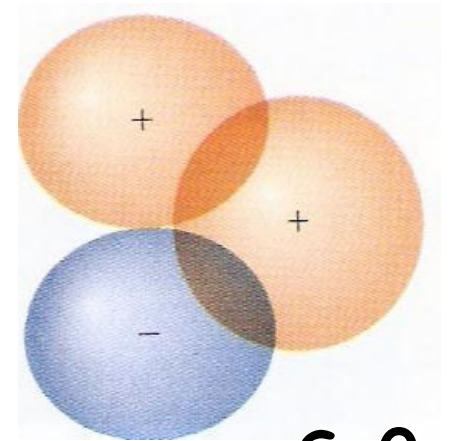
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Actual MO and Energy Diagram for N$_2$

(a)

$3\sigma_u$

$1\pi_g$

$2p$ $2p$

$1\pi_u$ $3\sigma_g$

$2\sigma_u$

$2s$ $2s$

$2\sigma_g$

N — N

$3\sigma_g$

$1\pi_u$

$2\sigma_u$

$2\sigma_g$

N — N

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S-P Mixing in Atomic Orbitals

Recall:

MO of N$_2$

$P_{X/Y}$ +s

σ_u

π_g

$p_{x/y}$

p_z

p_z

$p_{x/y}$

S=0

P_Z + s

σ_g

π_u

s

σ_u

s

S>0 or <0?

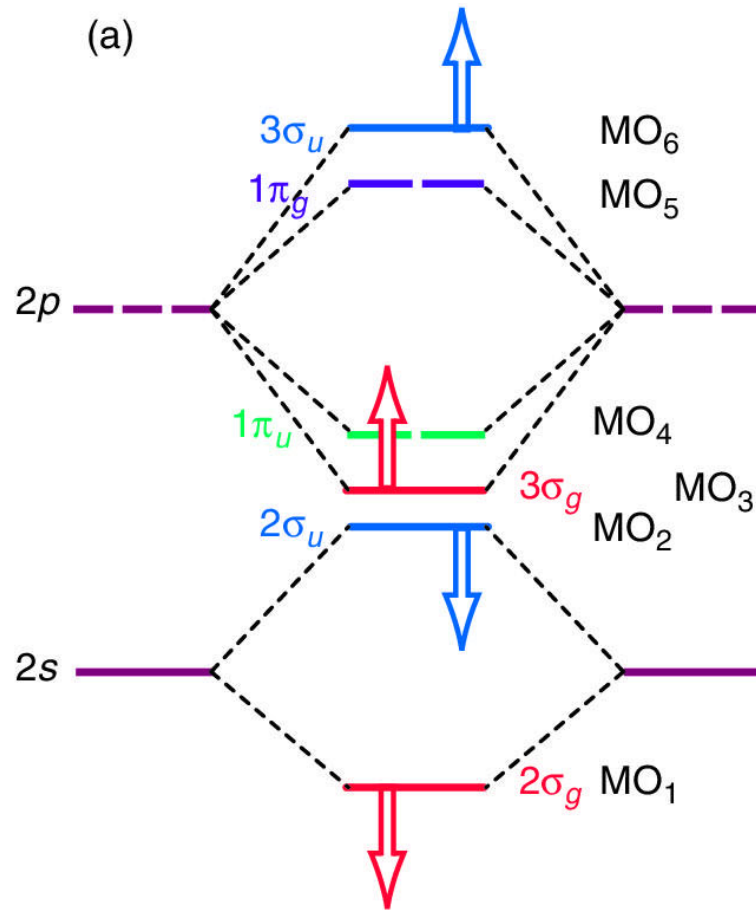σ_g
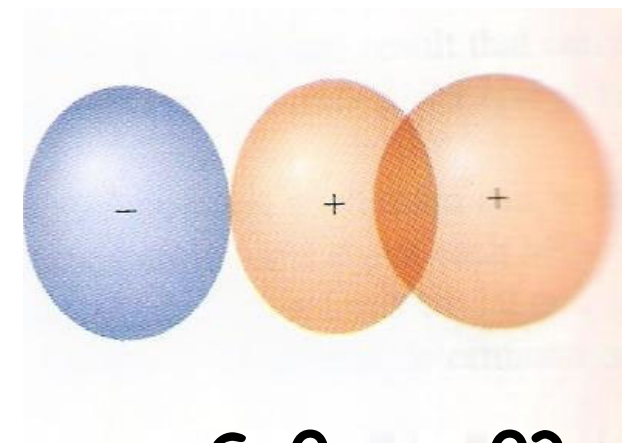
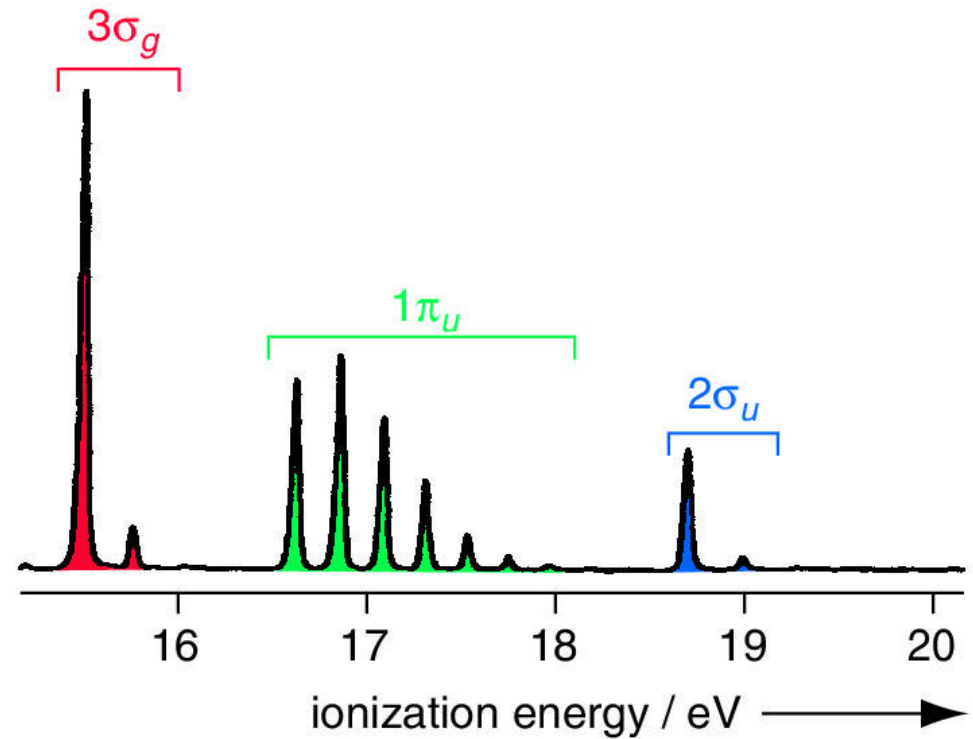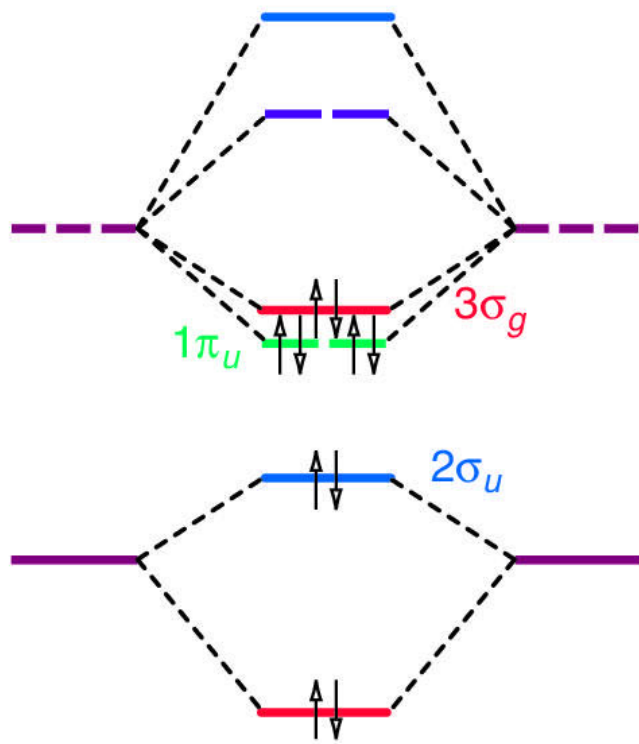4 MO's can be constructed from 2s (two) and $2p_z$ (two)

Example one MO can be $c_1*(2s) + c_2*(2s) + c_3*(2p_z) + c_4*(2p_z)$

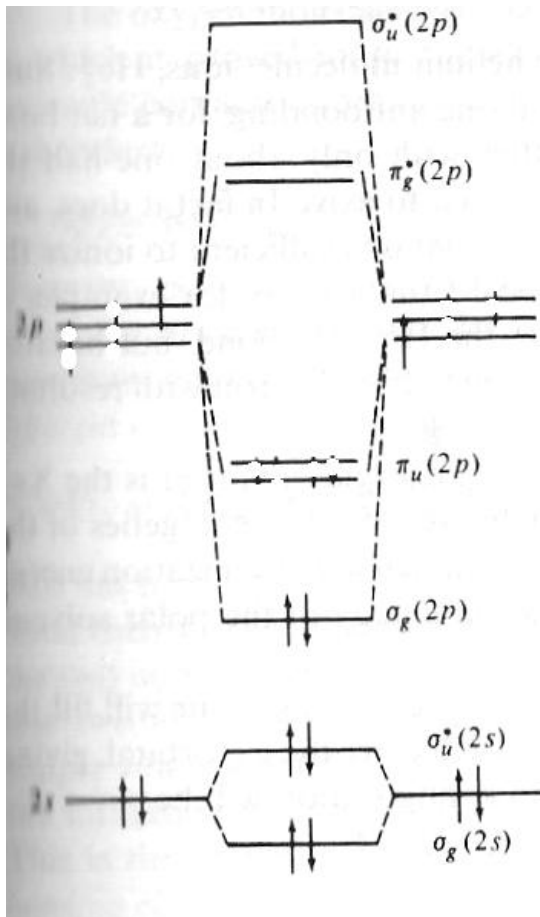# S-P Mixing in Atomic Orbitals
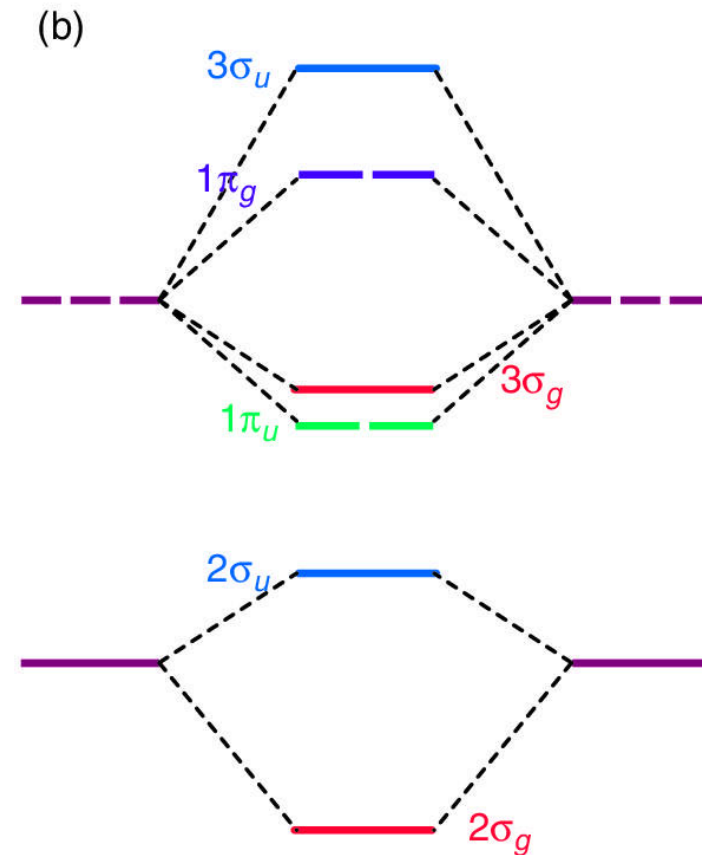
Mixing of 2s and 2p

Actual MO and Energy Diagram for N$_2$
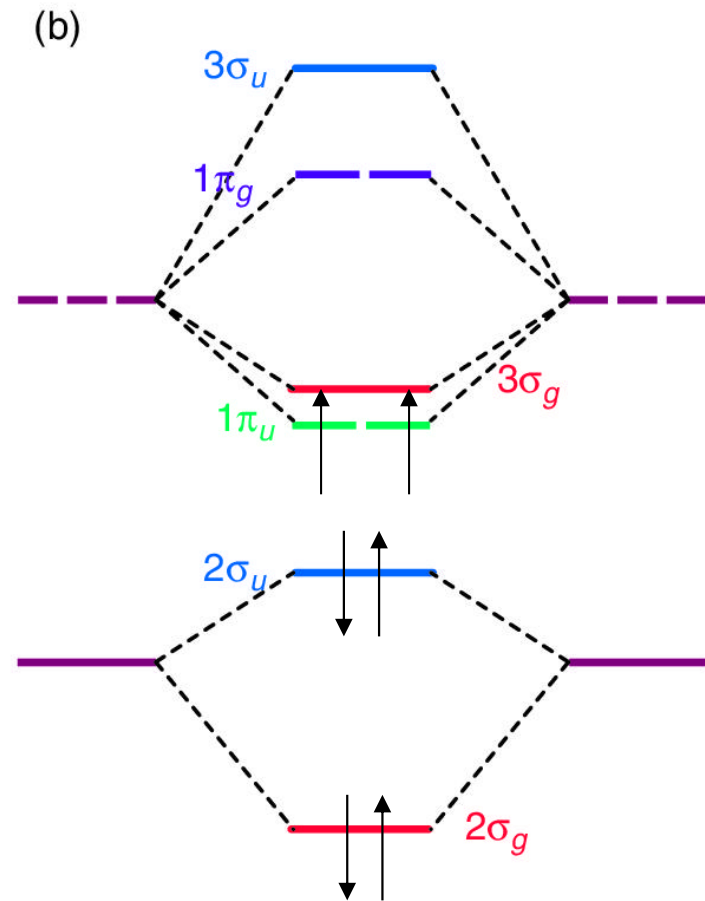
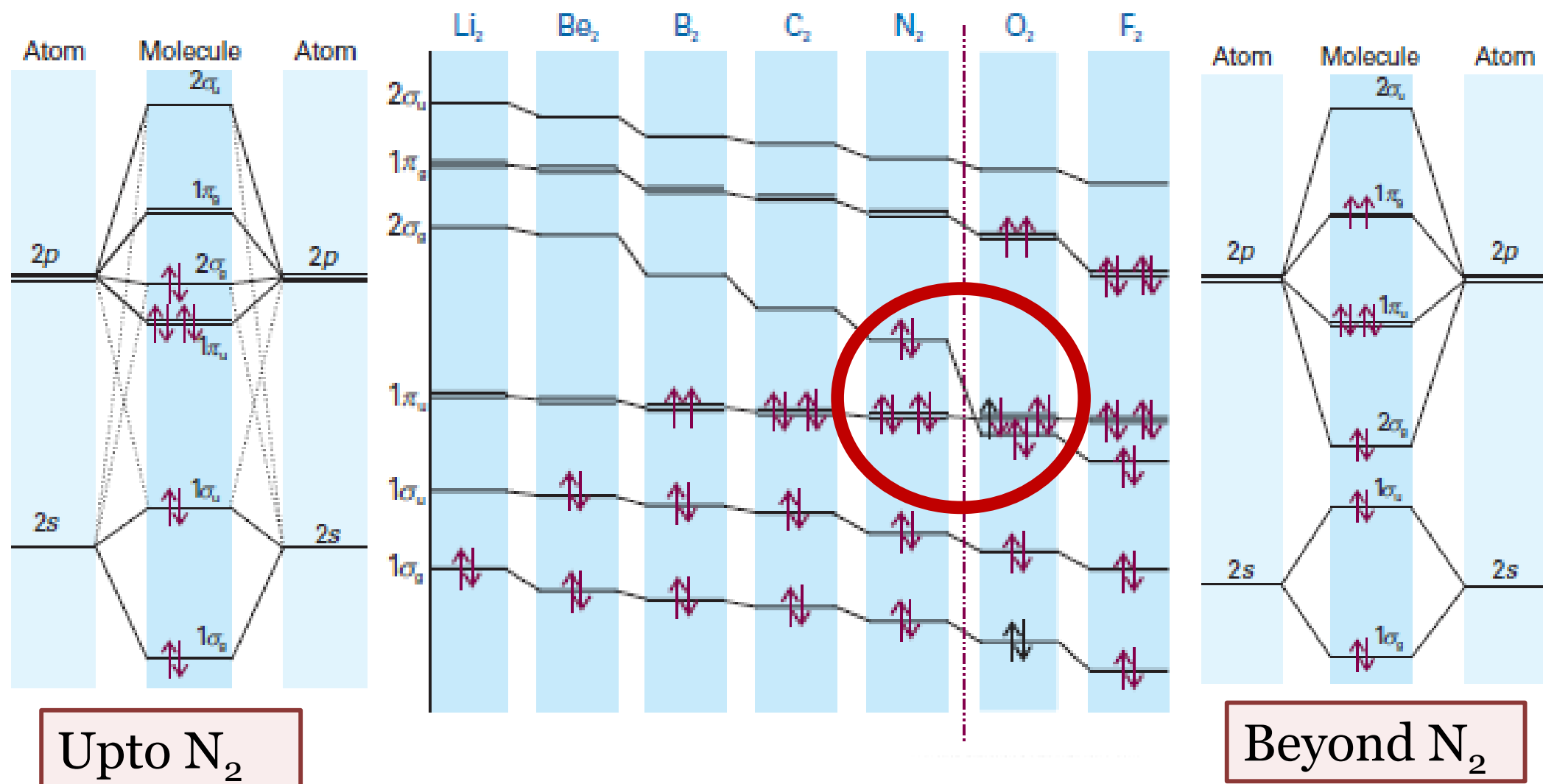# s-p Mixing: B$_2$ magnetism confirms it!

Incorrect!

Correct!

Boron is paramagnetic. This can only happen if the two electrons with parallel spin are in the π-orbitals → π-bonding energies lower than σ*?
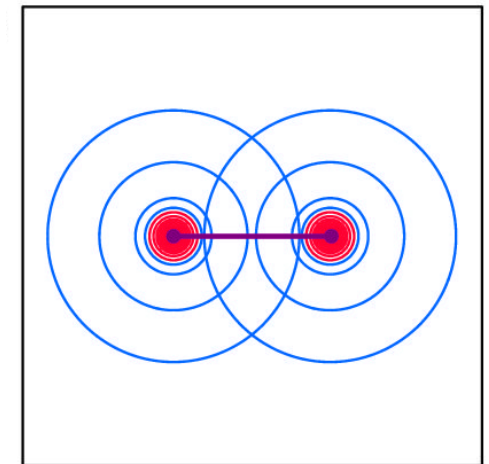
MO Energy Diagram (Homo-Diatomics)

Upto N$_2$
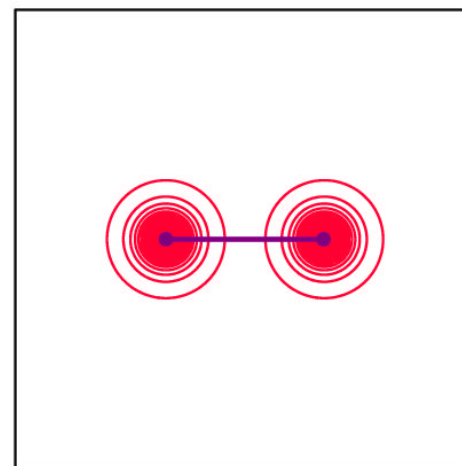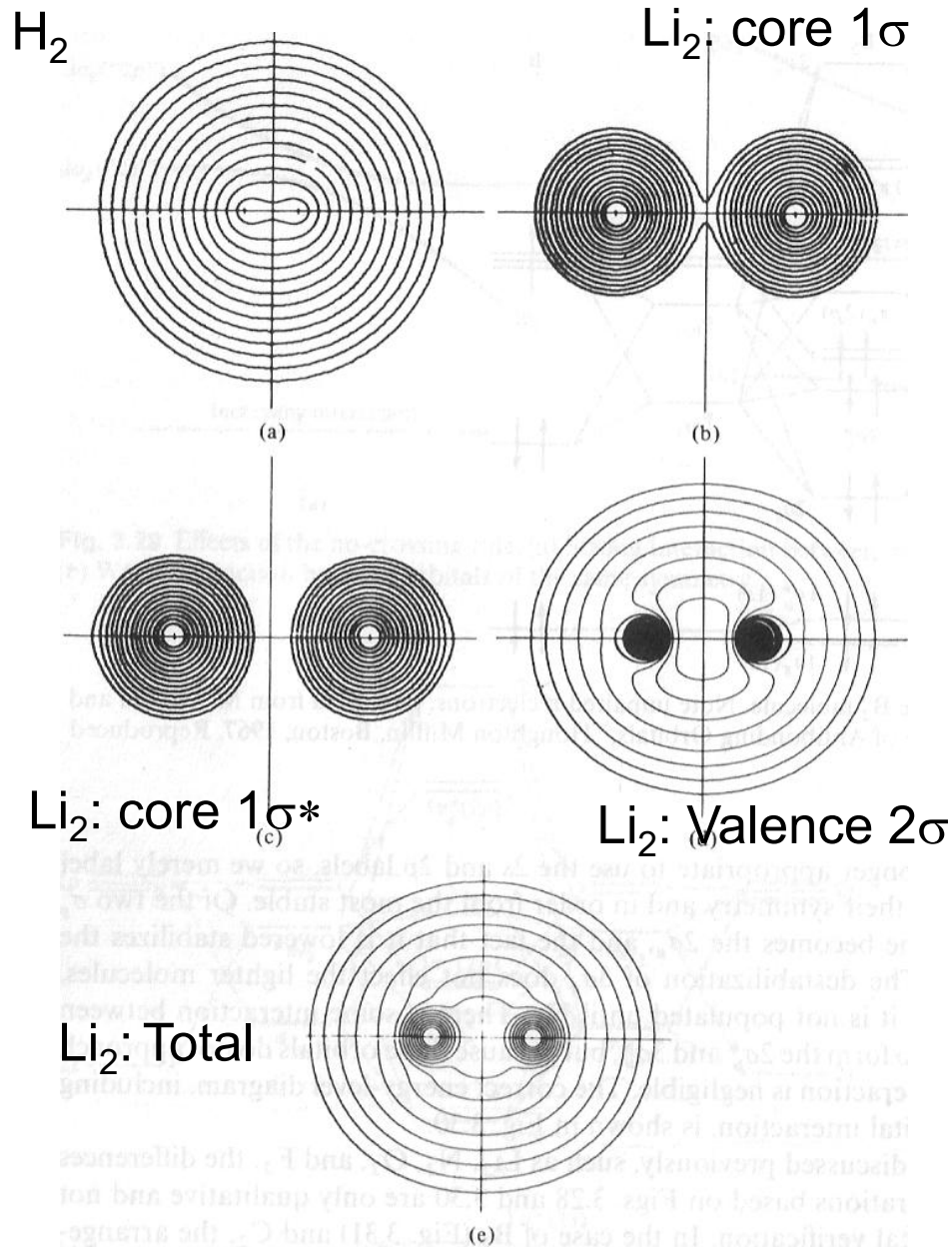
Beyond N$_2$

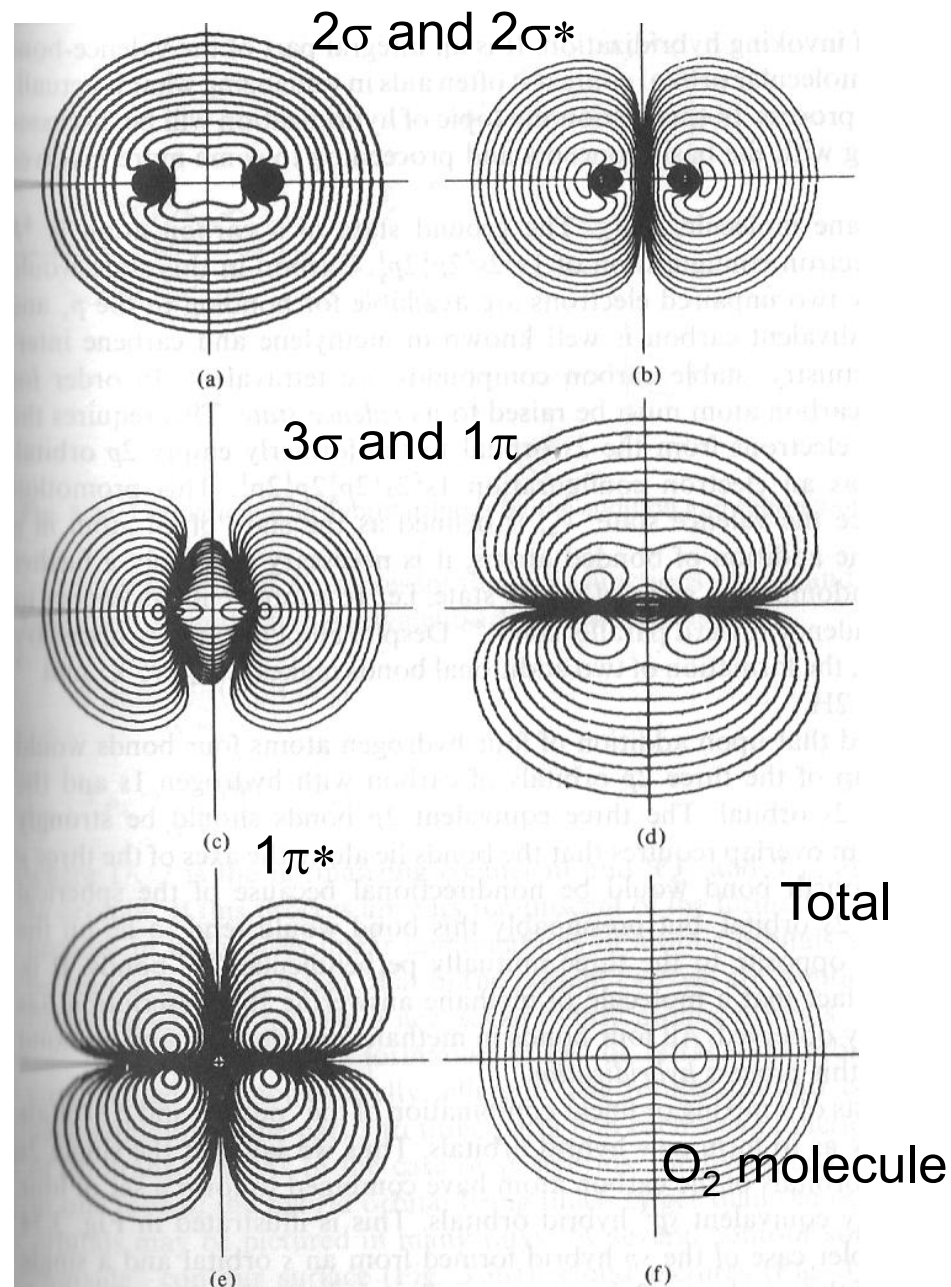Bond Order = 0.5 x (bonding electrons - antibonding electrons)
Bond order = 0 → molecular can not exist – No bond formation
Bond order higher → stronger bond, shorter bond length
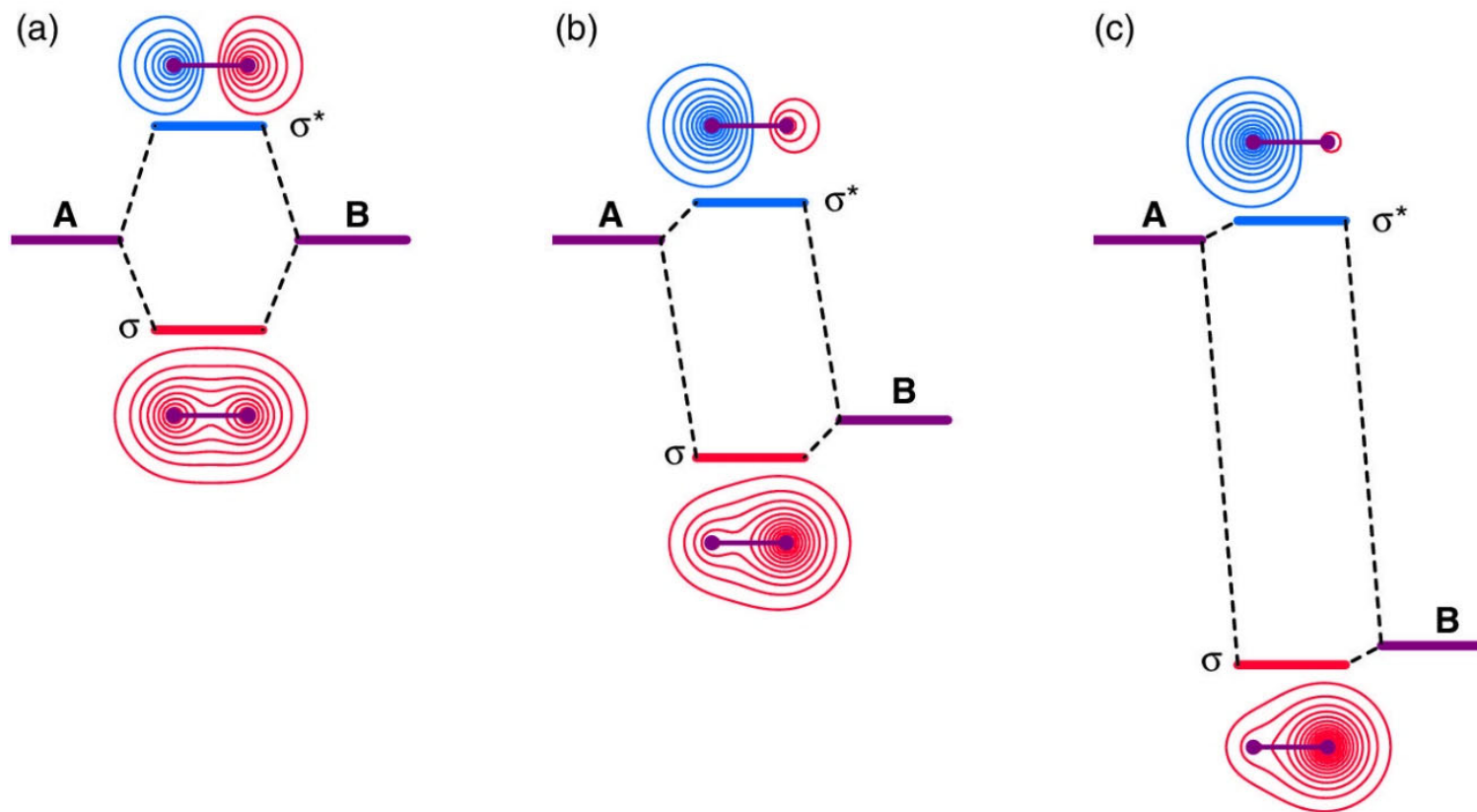
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MO Contours→ electron density maps

H₂

Li₂: core 1σ

Li₂: core 1σ*

Li₂: Valence 2σ

Li₂: Total

MO Contours→ electron density maps

2σ and $2\sigma*$

3σ and 1π

$1\pi*$

Total

O_2 molecule

(a)   (b)   (c)   (d)   (e)   (f)

Recall: Rule 4 for Forming MOs

Energy match and contribution from different AOs

- Contribution to the bonding MO from the lower energy AO increases, while from the higher energy AO decreases
- Contribution to the anti-bonding MO from the higher energy AO increases, while from the lower energy AO decreases

Hydrides: Li-H and H-F

	Bond Length	Dipole Moment	Polarity
Li-H	160 pm	5.9 D	H is δ-
F-H	91.7 pm	1.9 D	H is δ+
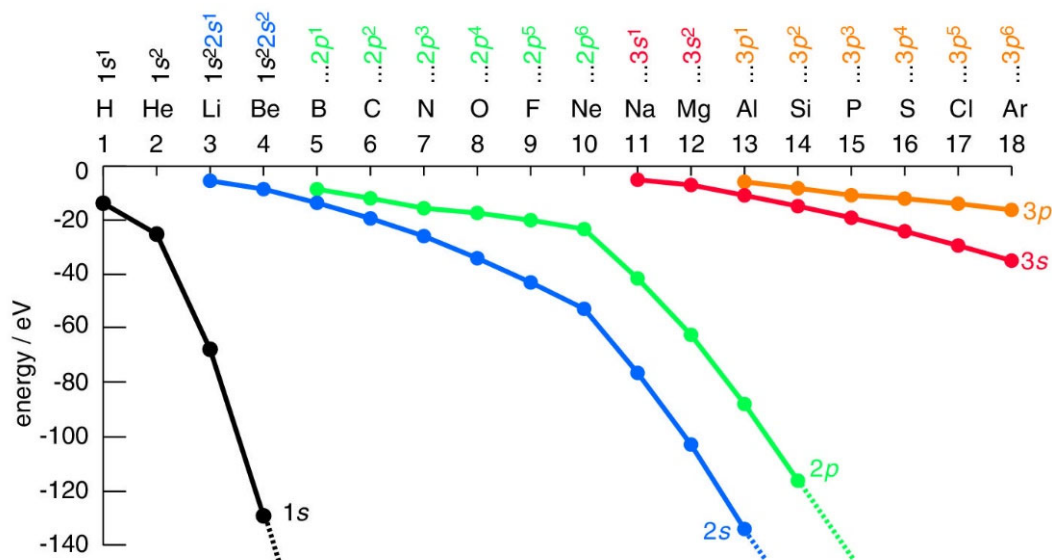
Li (2s) = -5 eV
H (1s) = - 14 eV

Li (1s) >-60 eV

Hydrides: Li-H and H-F
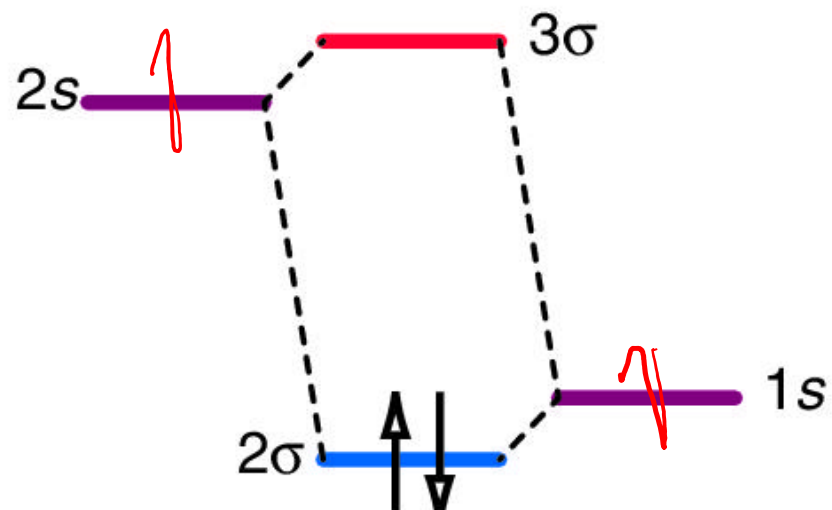
Li (2s) = -5 eV

H (1s) = - 14 eV

Li (1s) >-60 eV

→ higher contribution

$$\Psi_{2\sigma} = c_1 \Psi_{Li(2s)} - c_2 \Psi_{H(1s)}$$

$$\Psi_{3\sigma} = c_3 \Psi_{Li(2s)} + c_4 \Psi_{H(1s)}$$

higher contribution

2s

3σ

1s

2σ

Li

H

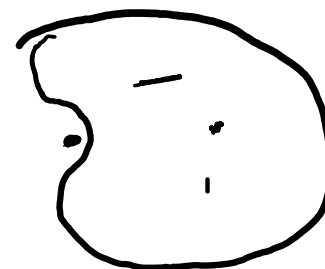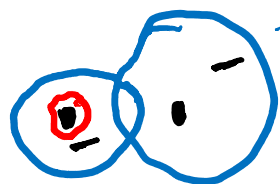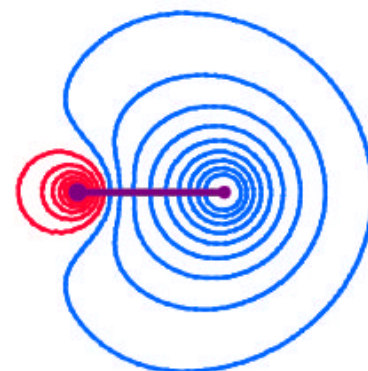Li →

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Matching of AO energies/symmetries

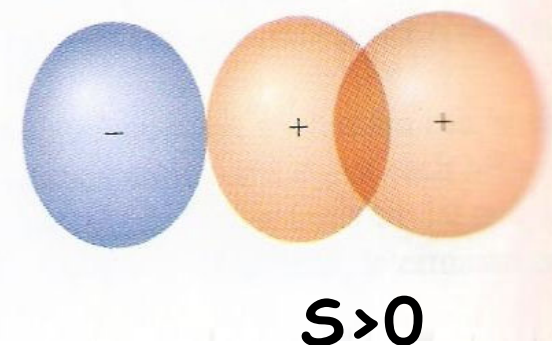$$\varphi_{\pm} = c_1\psi_1 \pm c_2\psi_2$$

Z-axis

$P_{X/Y}$ +s

S=0

P_Z + s

S>0
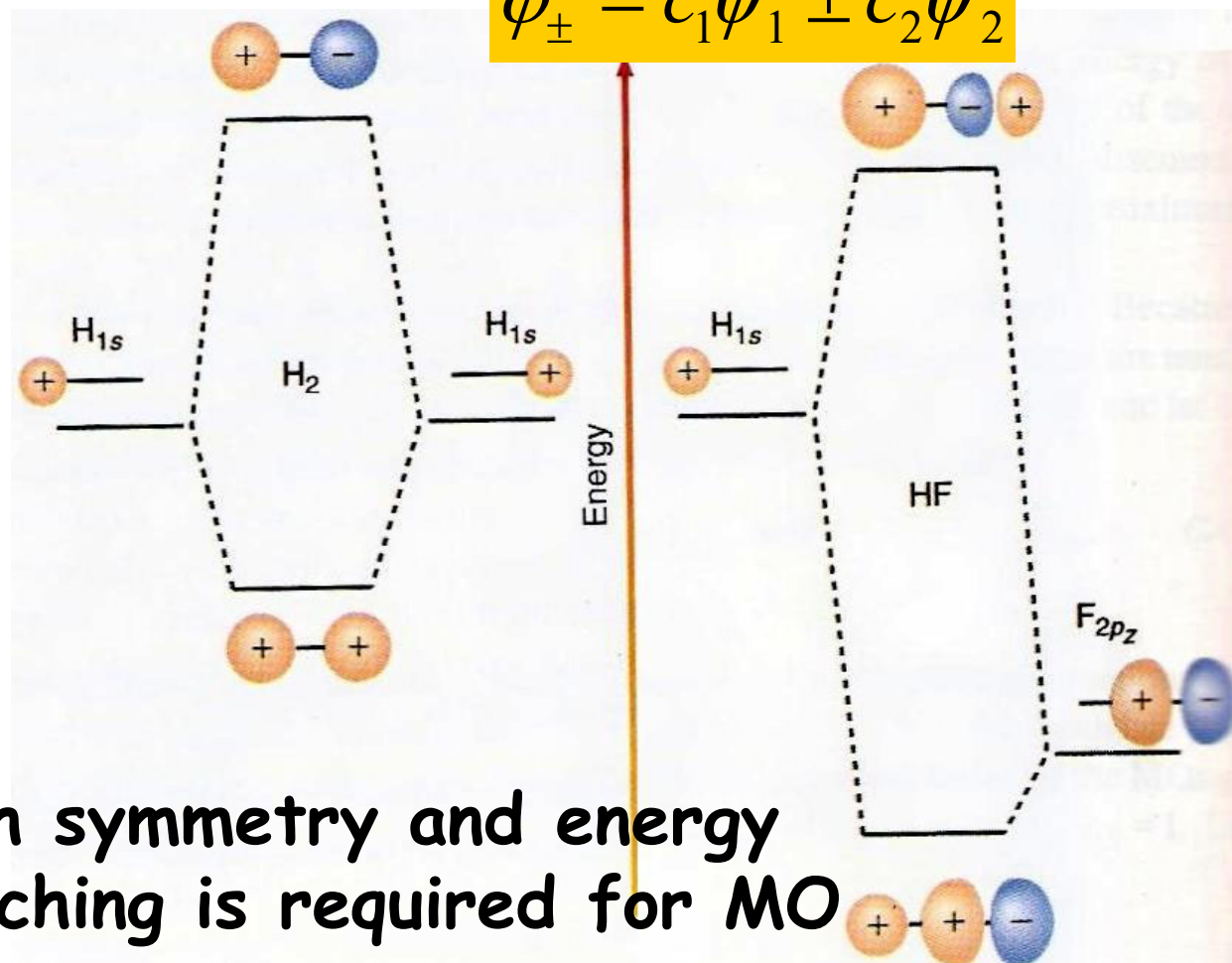
Both symmetry and energy matching is required for MO
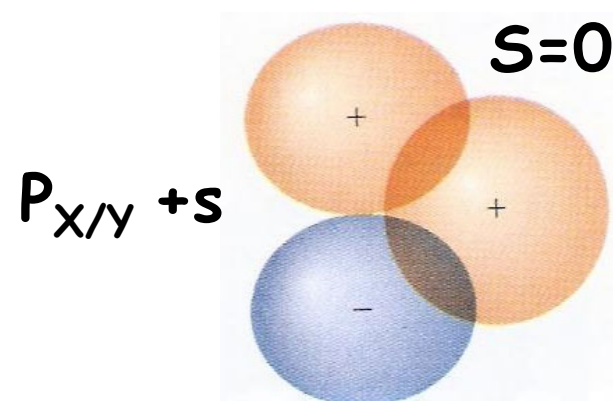
Valence electrons are most important for bonding

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