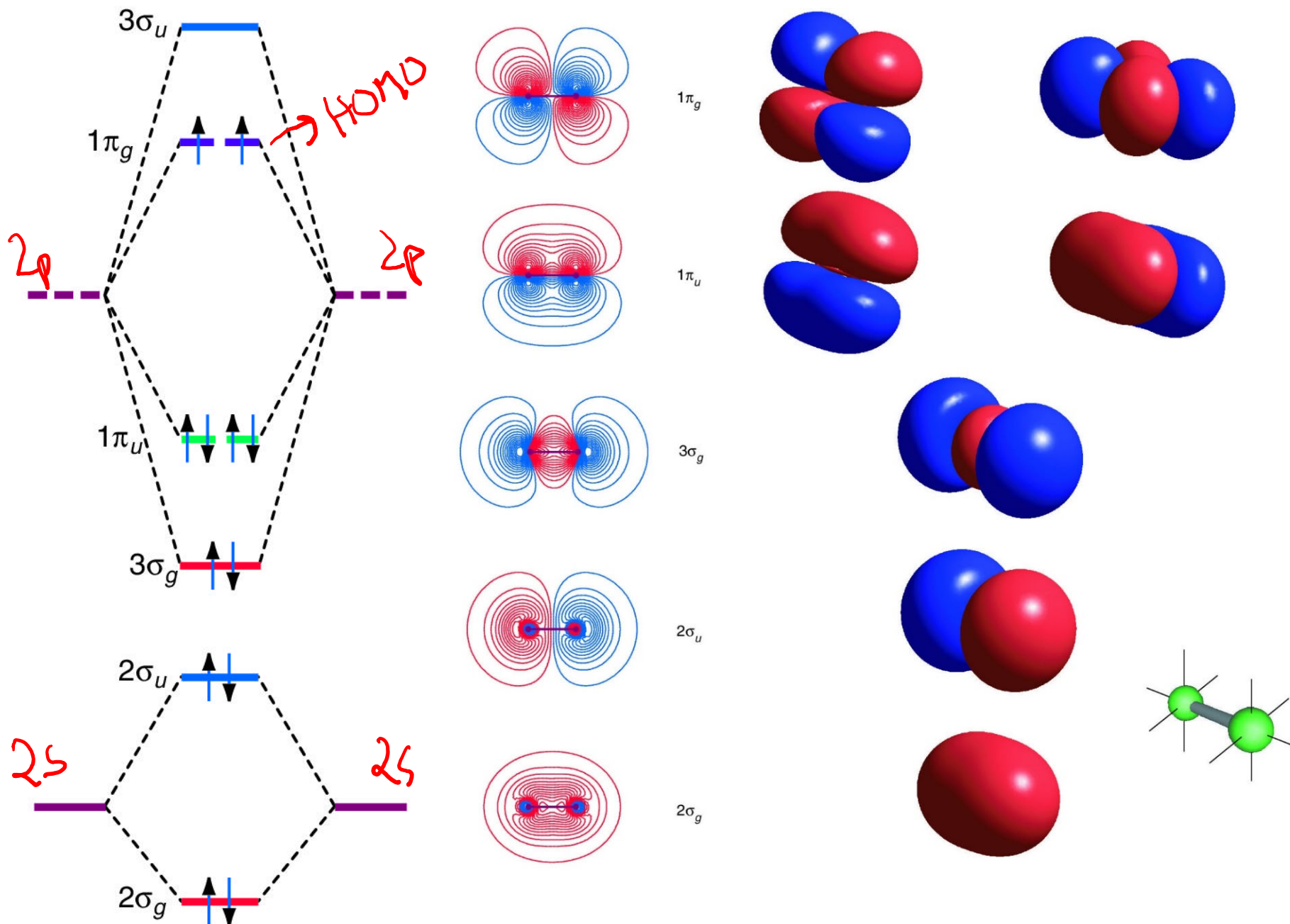


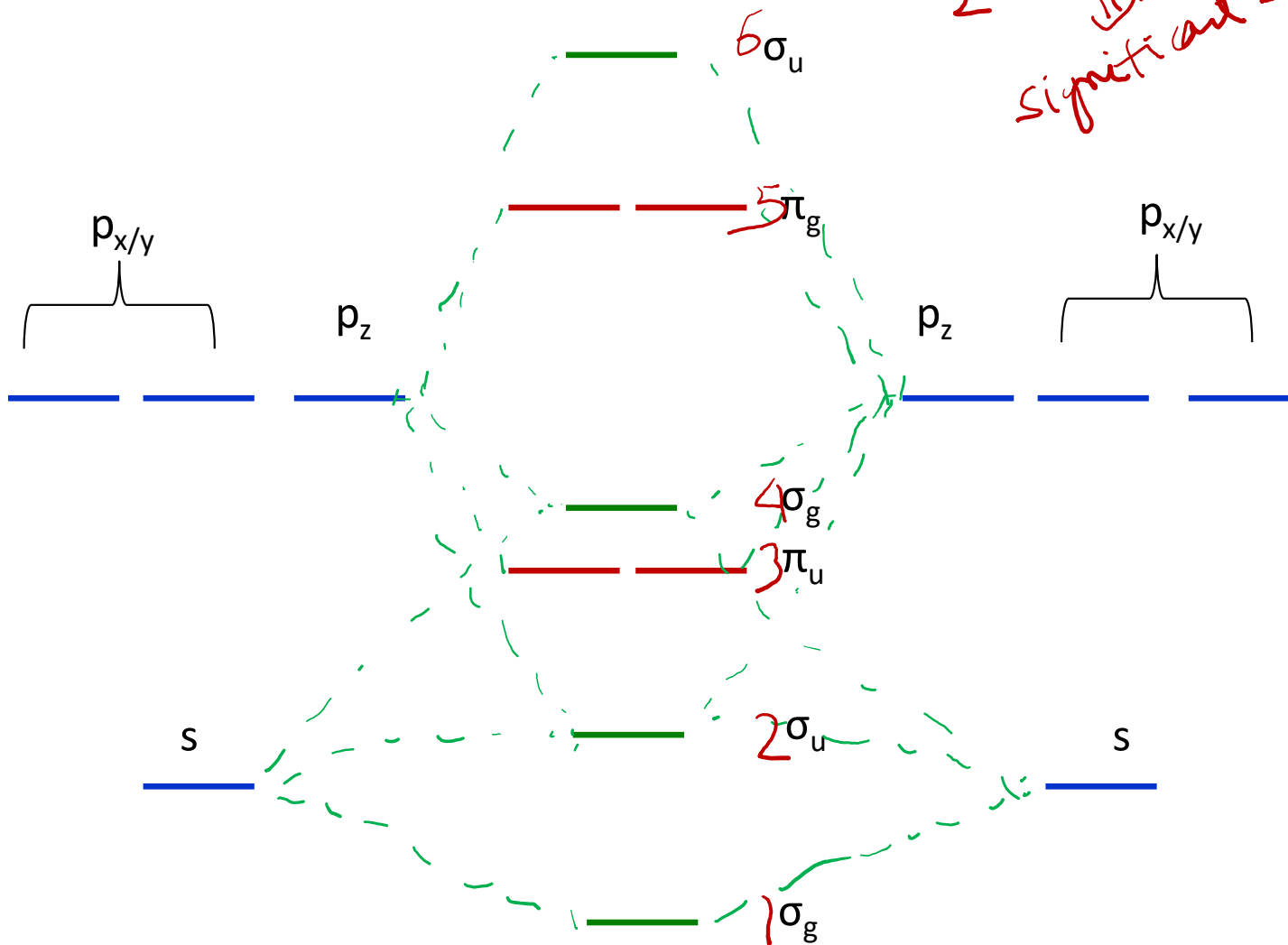
Review : Idealized MO Diagrams: O_2



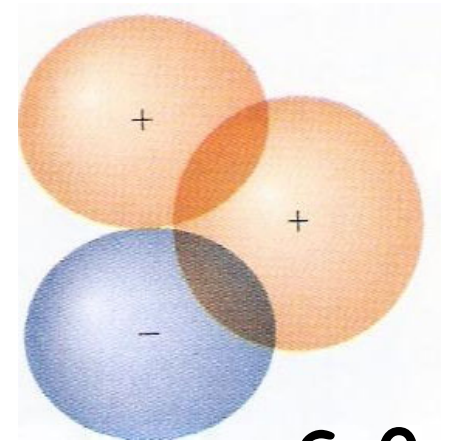
For 3D view: <https://www.chemtube3d.com/orbitalsfluorine/>

MO of N₂

*2σ_u & 3σ_g
significant s-p mixing*

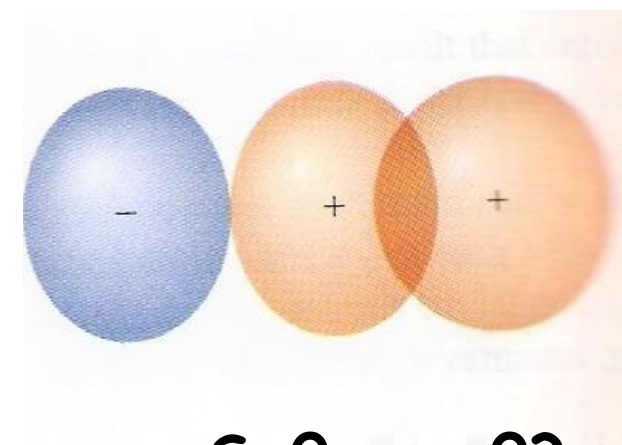


$p_{x/y} + s$



$S=0$

$p_z + s$

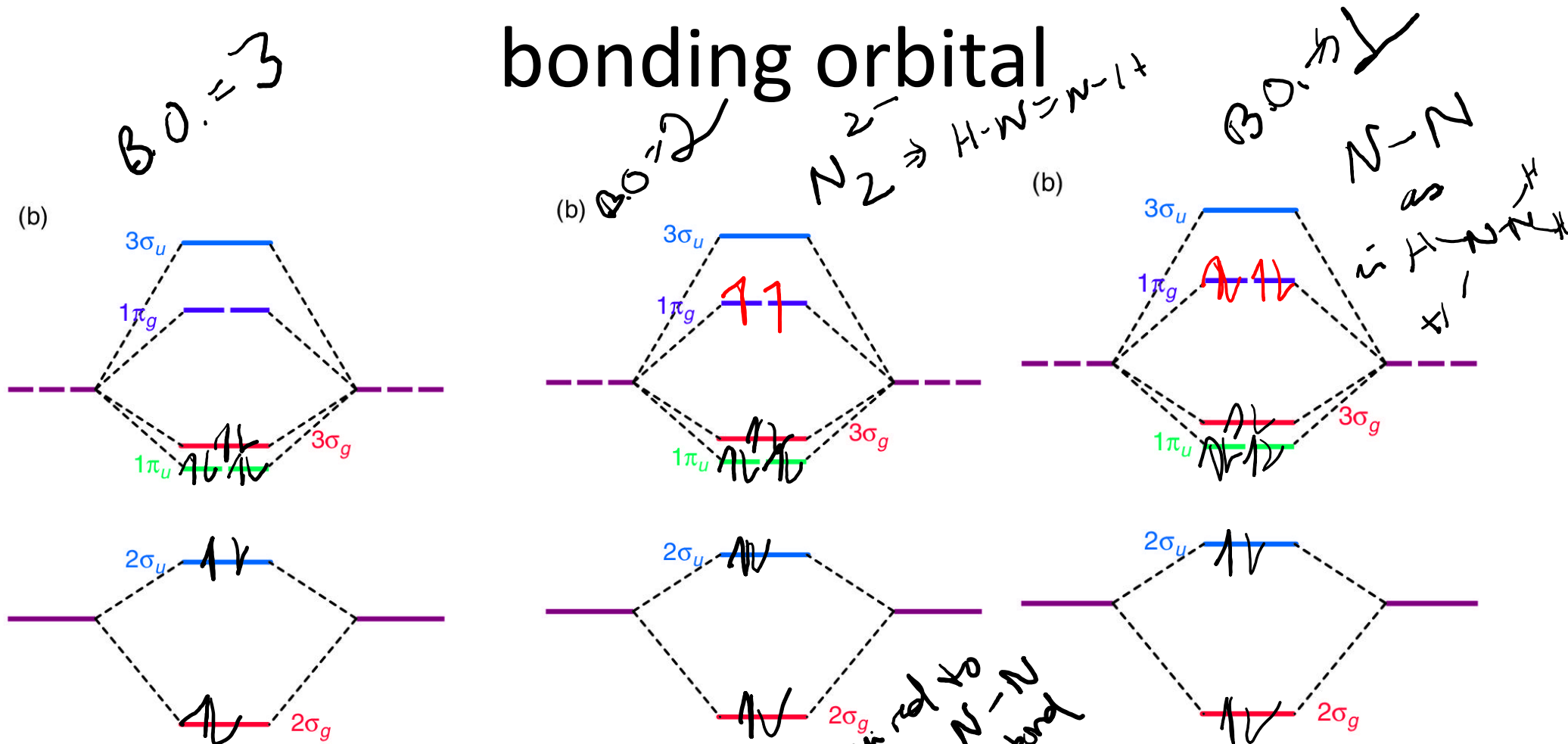


$S > 0$ or < 0 ?

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

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

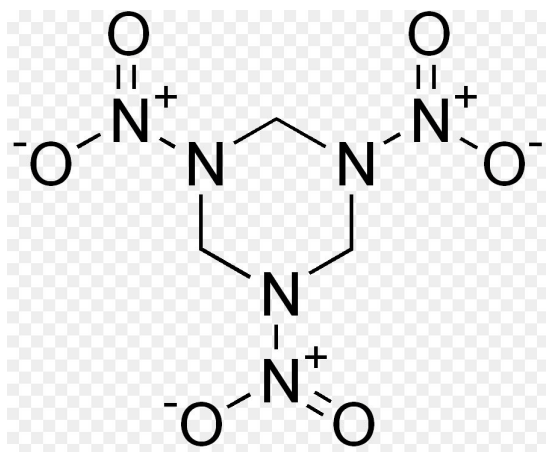
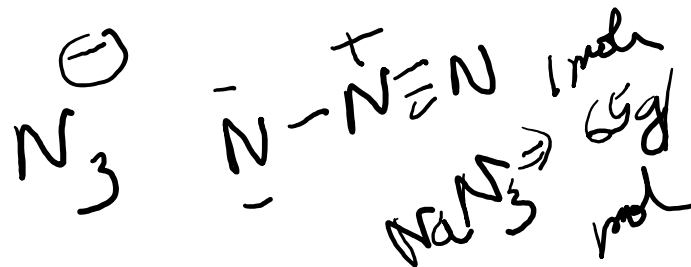
Consequences of Occupying Anti-bonding orbital



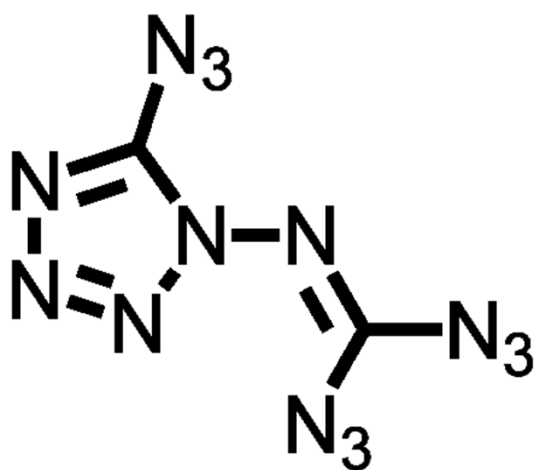
Example: Bond Dissociation energy of N_2 is 945 kJ/mol; $N=N$ is 418 kJ/mol and $N-N$ is 167 kJ/mol

\rightarrow energy required to break $N-N$ bond
 \rightarrow writing reports of very reducing

Sodium Azide: Airbags in vehicles



RDX

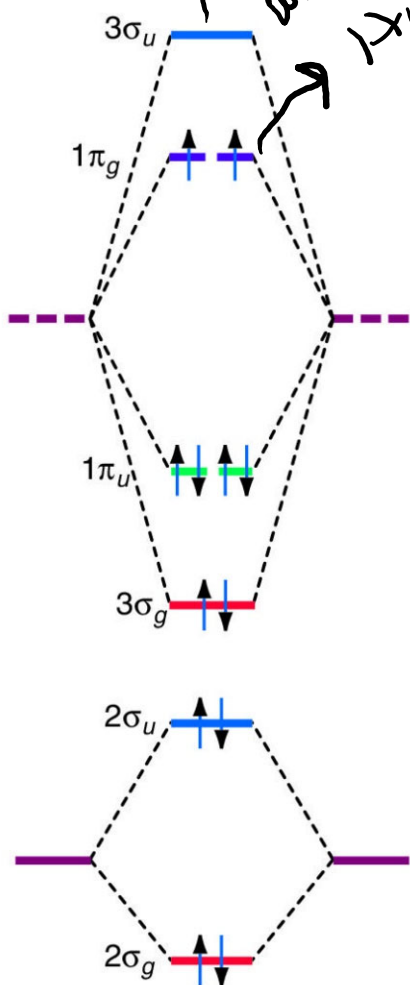


Azidoazide azide

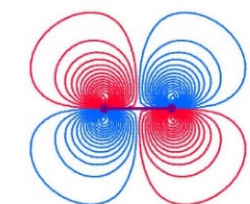
You would never see these kinds of molecules in nature due to their incredible instability, but they were made in a German research lab by Thomas Klapötke's group as recently as 2011. Attempts to touch or handle this chemical (and some may say so much as even look at) can cause it to detonate, breaking those bonds and turning them into multiple molecules of rapidly expanding nitrogen gas.

Lessons from the MO

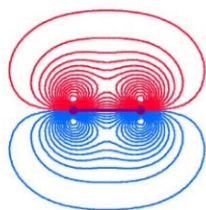
LUMO
 ↑ Lowest unoccupied MO
 HOMO → Highest Occupied MO



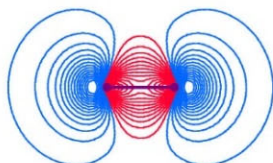
O₂



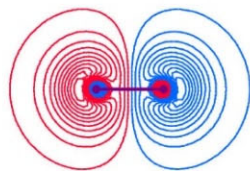
HOMO of O₂



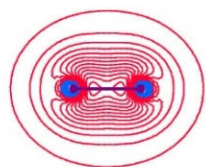
1π_u



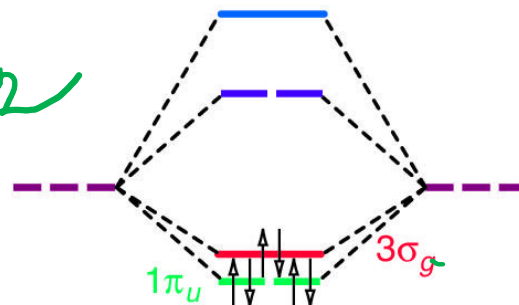
3σ_g



2σ_u



2σ_g



N₂

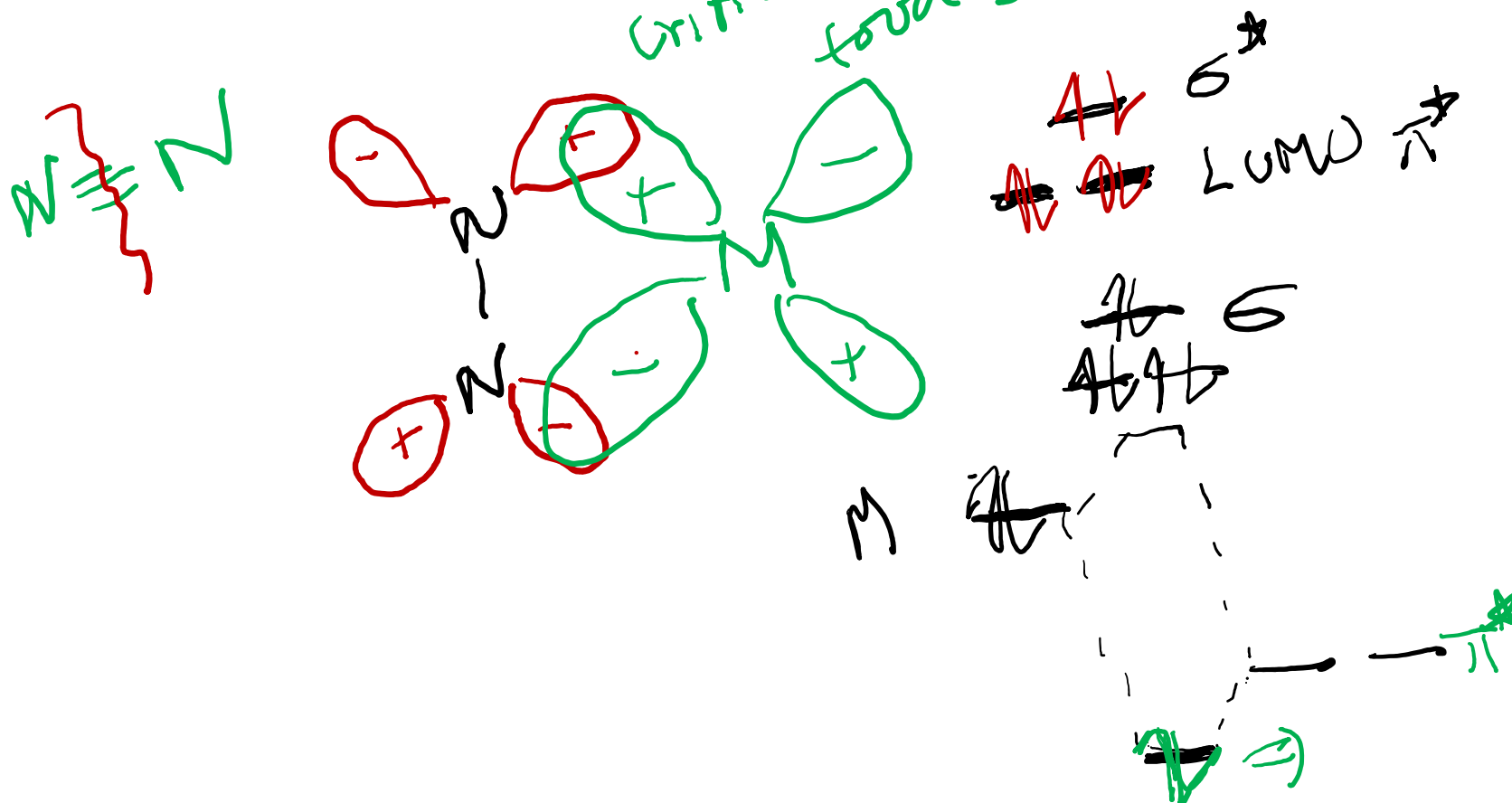
HOMO of N₂

O₂ is a good Lewis base
 but
 N₂ is NOT

Thoughts about N₂ Reduction

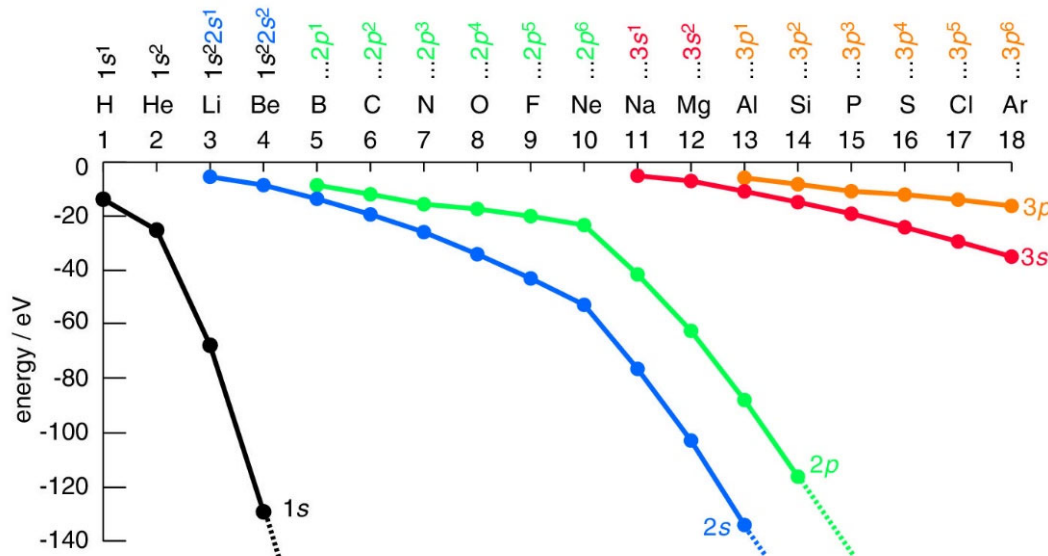
Reduction of N₂ to NH₃

↓
Critical to our food security.



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

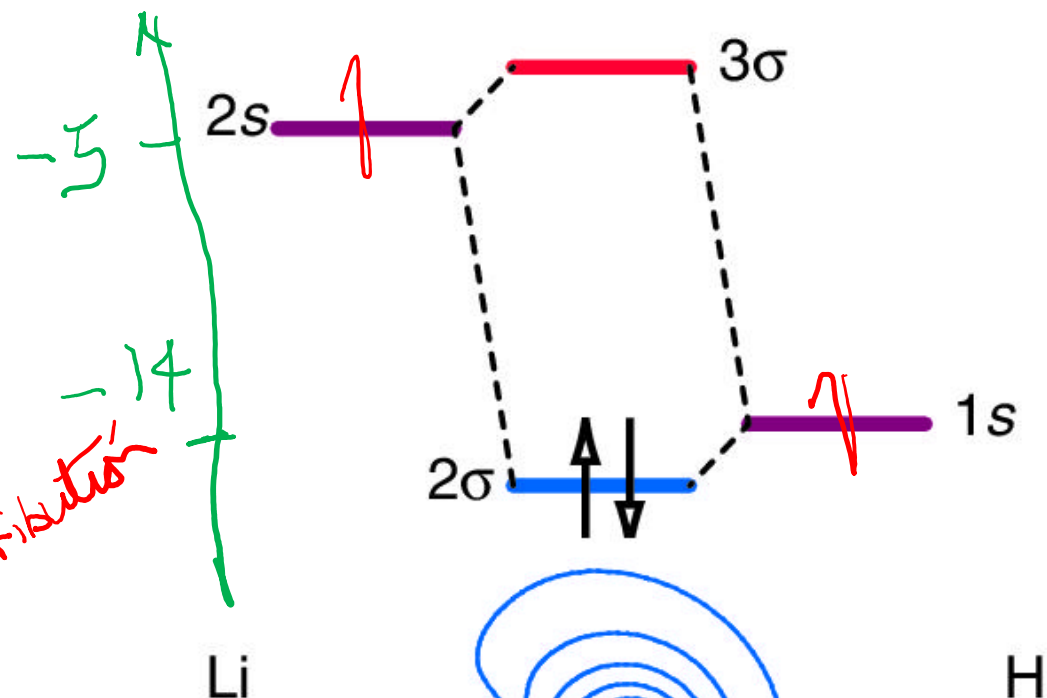
Li (1s) > -60 eV

Hydrides: Li-H and H-F

$$\text{Li (2s)} = -5 \text{ eV}$$

$$\text{H (1s)} = -14 \text{ eV}$$

$$\text{Li (1s)} > -60 \text{ eV}$$

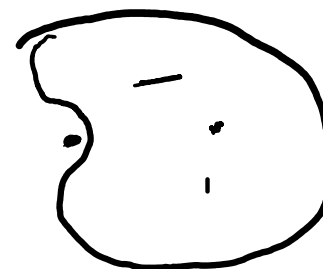
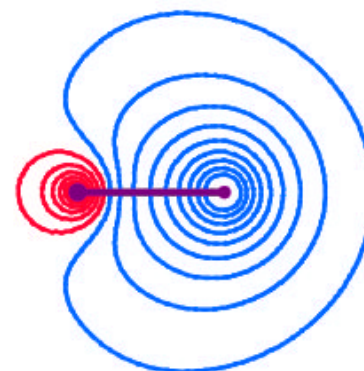
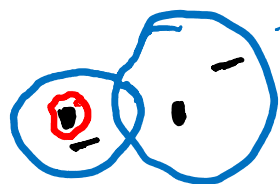


$$\Psi_{2\sigma} = c_1 \Psi_{\text{Li}(2s)} - c_2 \Psi_{\text{H}(1s)}$$

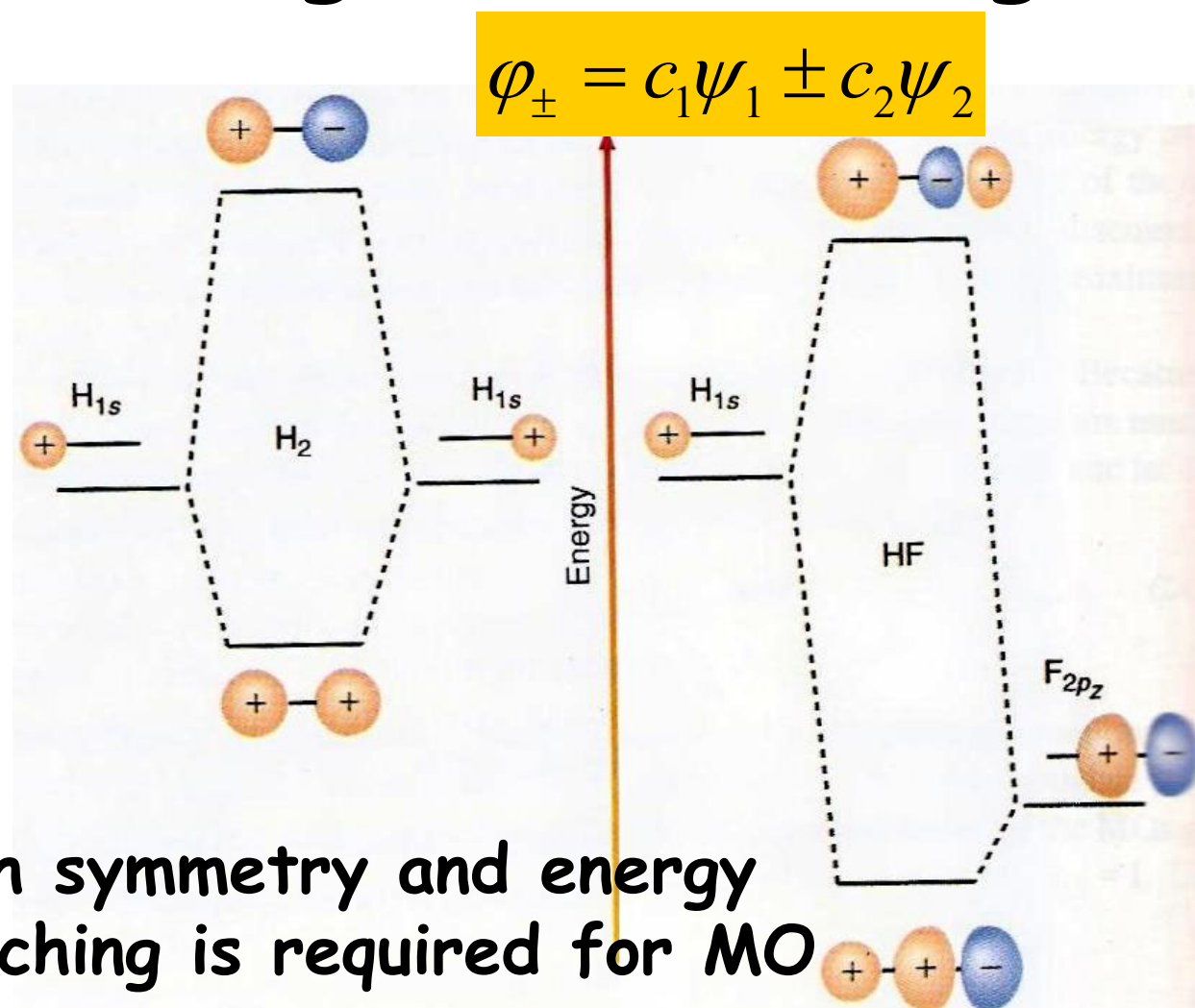
$$\Psi_{3\sigma} = c_3 \Psi_{\text{Li}(2s)} + c_4 \Psi_{\text{H}(1s)}$$

higher contribution

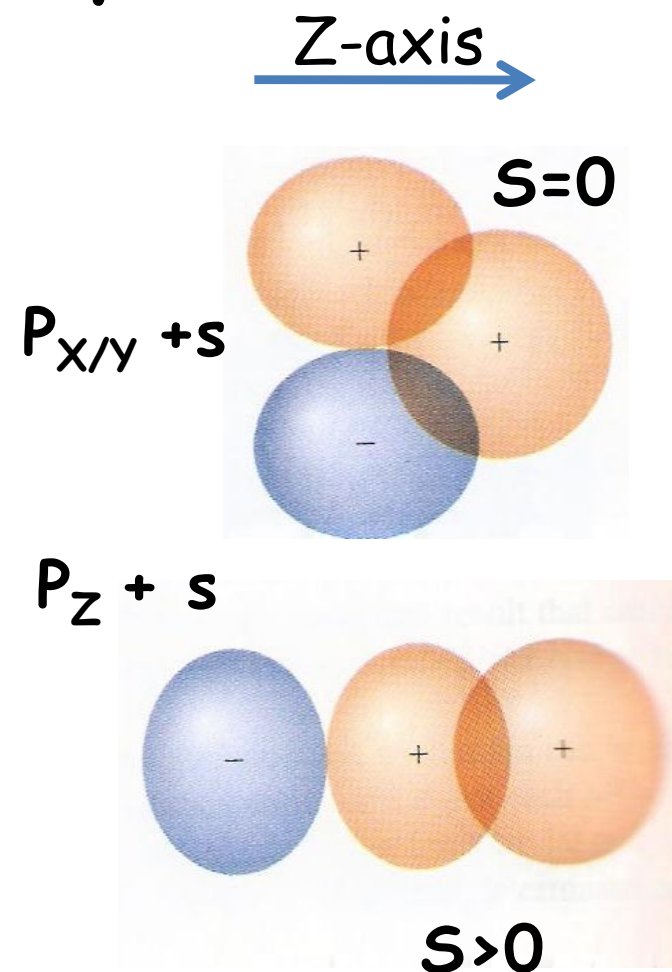
Li



Matching of AO energies/symmetries



Both symmetry and energy matching is required for MO

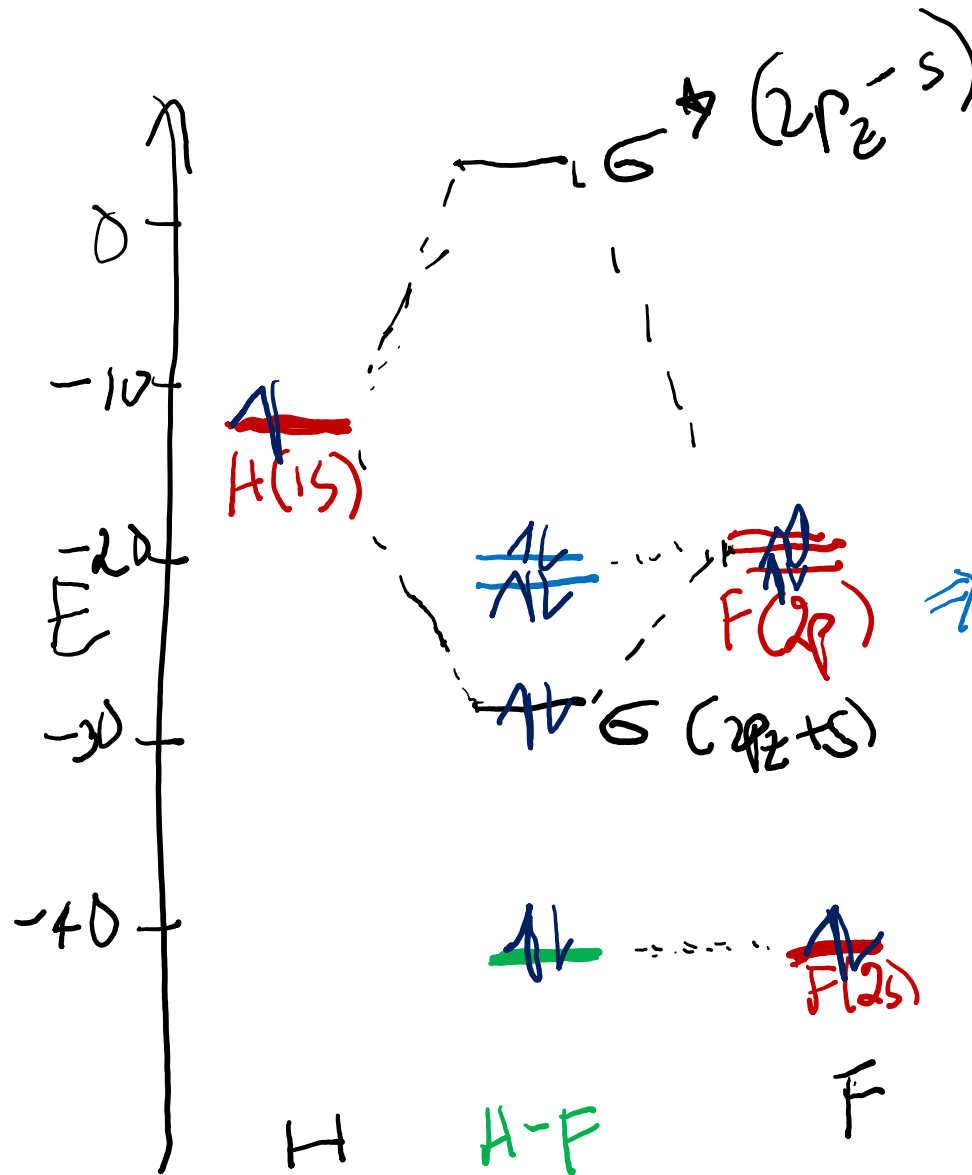


Valence electrons are most important for bonding

- Due to large difference in energy of $1s(H)$ and $1s(F)$, LCAO-MO for both $1s$ is not feasible in HF .
- Rather only $2p_z(F)$ [NOT $2p_{x/y}(F)$] and $1s(H)$ form a σ -bond. 100

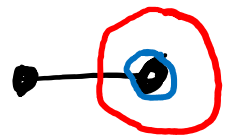
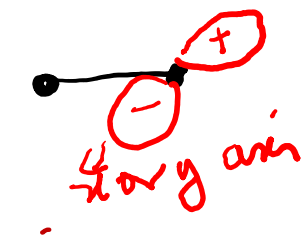
Hetero-nuclear Diatomics: HF

H (1s) -14 eV
F (2s) -43 eV
F (2p) -20 eV



H-F $\rightarrow z$
 $\left. \begin{array}{l} s \text{ and } 2p_z \\ s \text{ and } 2p_z \end{array} \right\}$
 $S=0$

$2p_x, 2p_y, 2p_z$

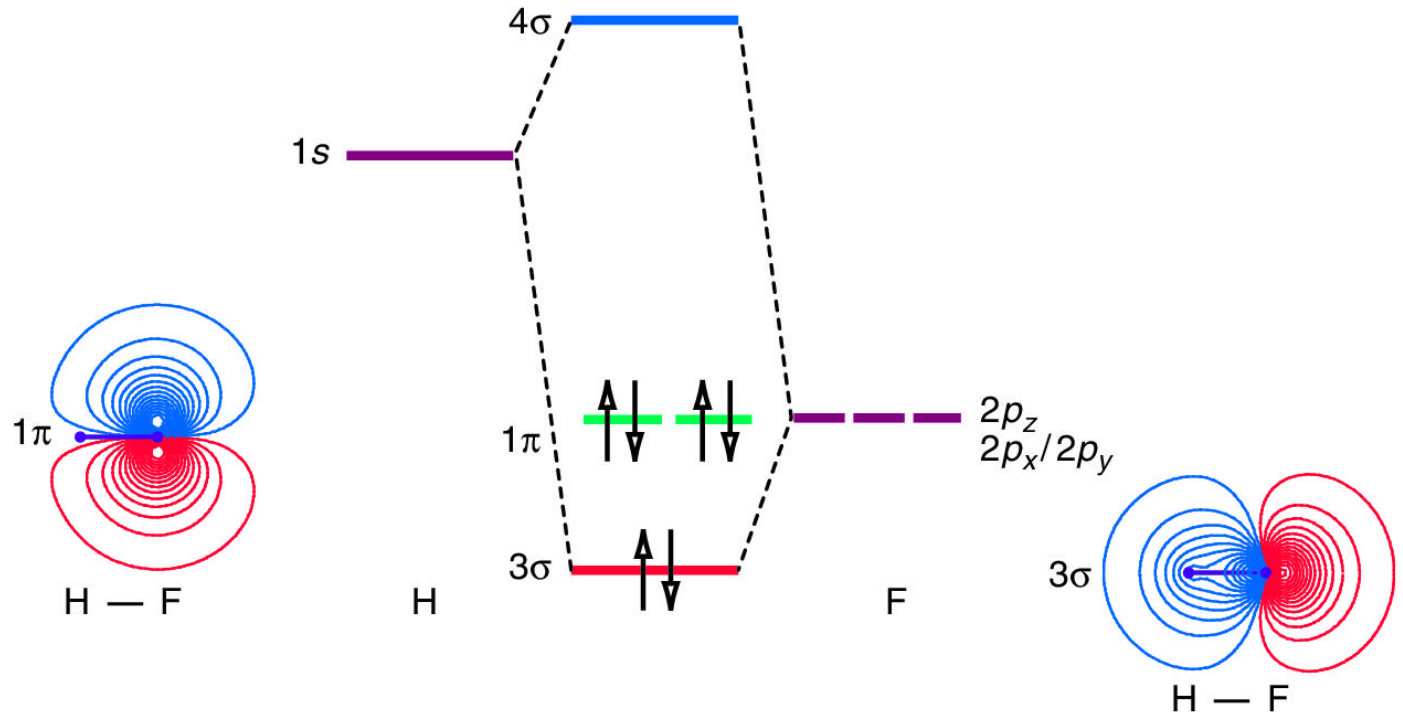


Hetero-nuclear Diatomics: HF

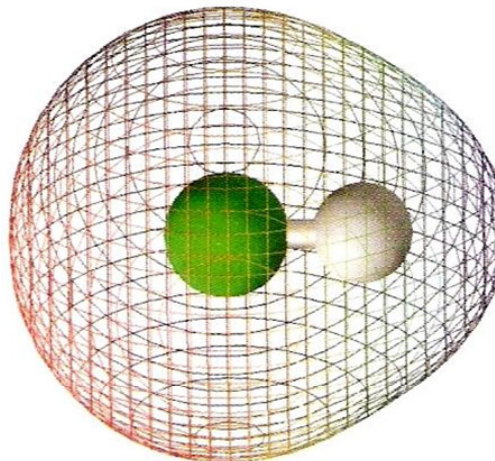
H (1s) -14 eV

F (2s) -43 eV

F (2p) -20 eV

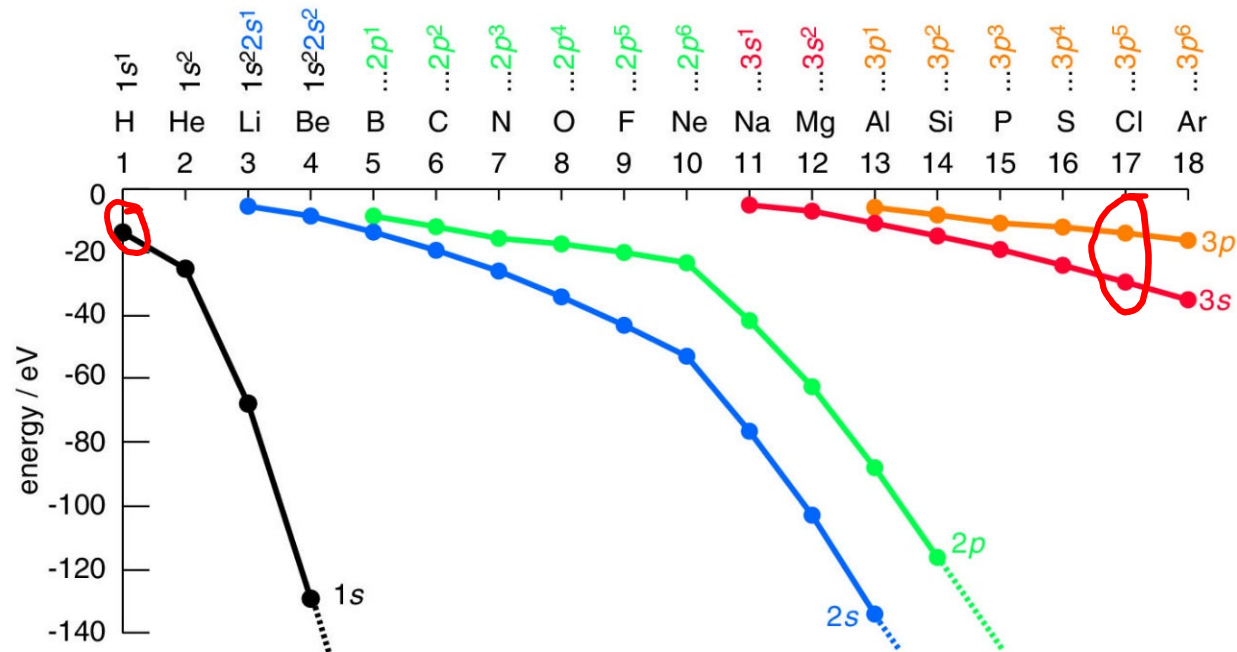


Electrostatic potentials
can be computed which
gives a realistic picture
of the electron densities
in HF: "Egg" Shaped



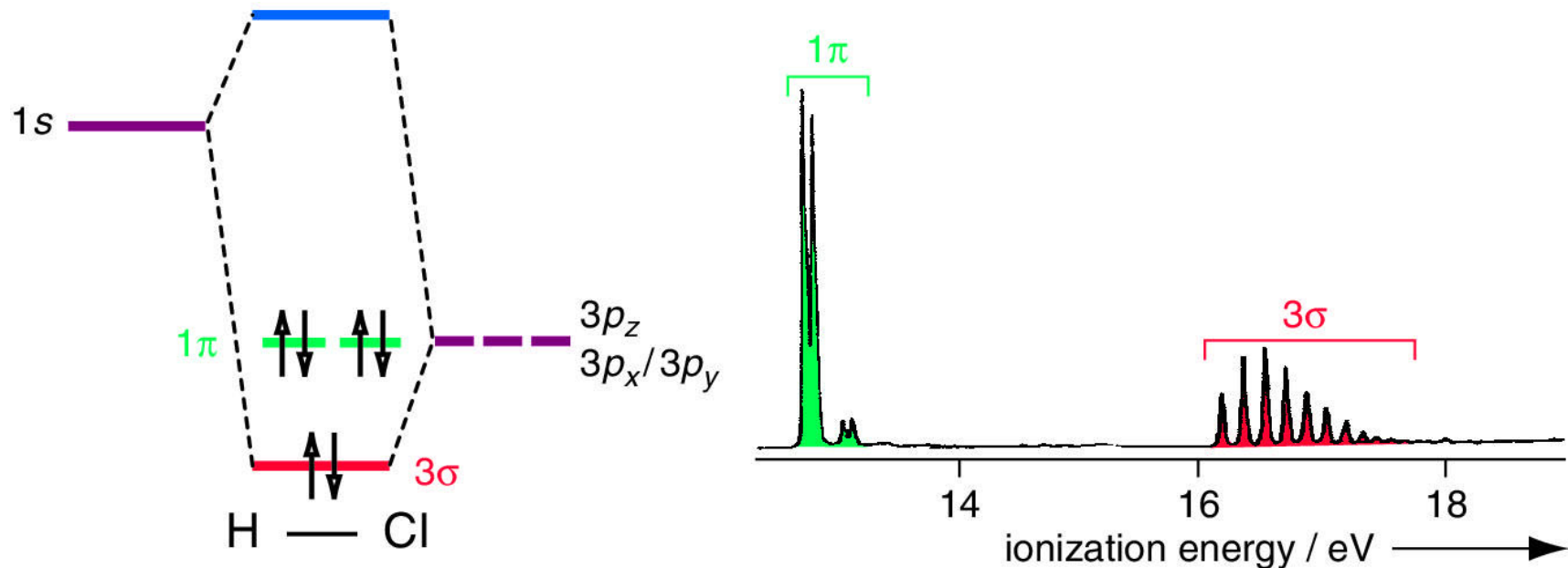
Hetero-nuclear Diatomics: HCl

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



Hetero-nuclear Diatomics: HCl

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

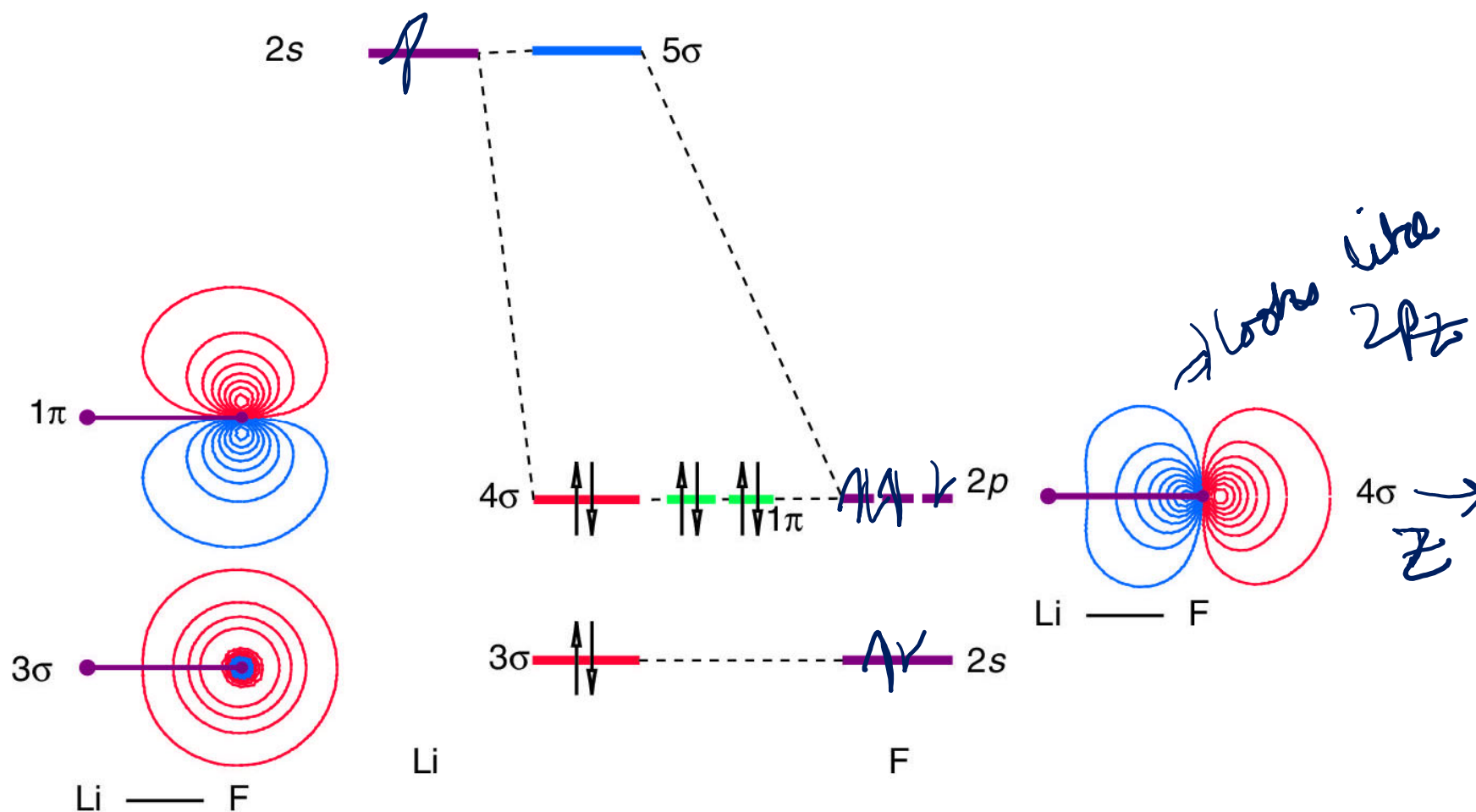


Similar to HF, expect for 2p and 3p difference.

Can not tell where absolute Energy levels will be unless Spectroscopic evidences exist, or perform QM calculations

Li-F

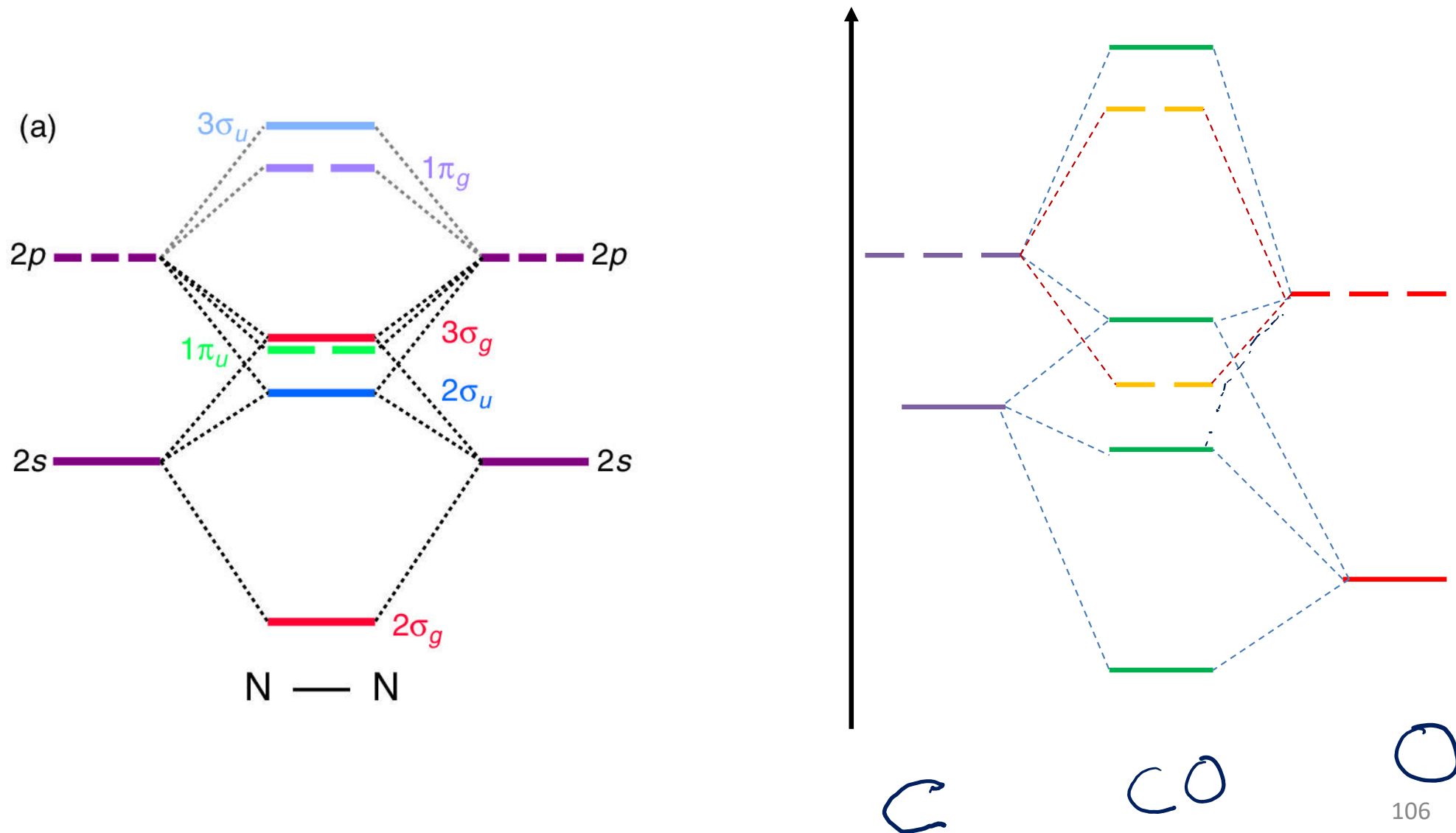
Li 2s (-5 eV), F (2s) -43 eV, F (2p) -20 eV



MO energy diagram for CO

C 2s (-19 eV), 2p (-12 eV)

O 2s (-34 eV), 2p (-17 eV)



MO energy diagram for CO

C 2s (-19 eV), 2p (-12 eV)

O 2s (-34 eV), 2p (-17 eV)

