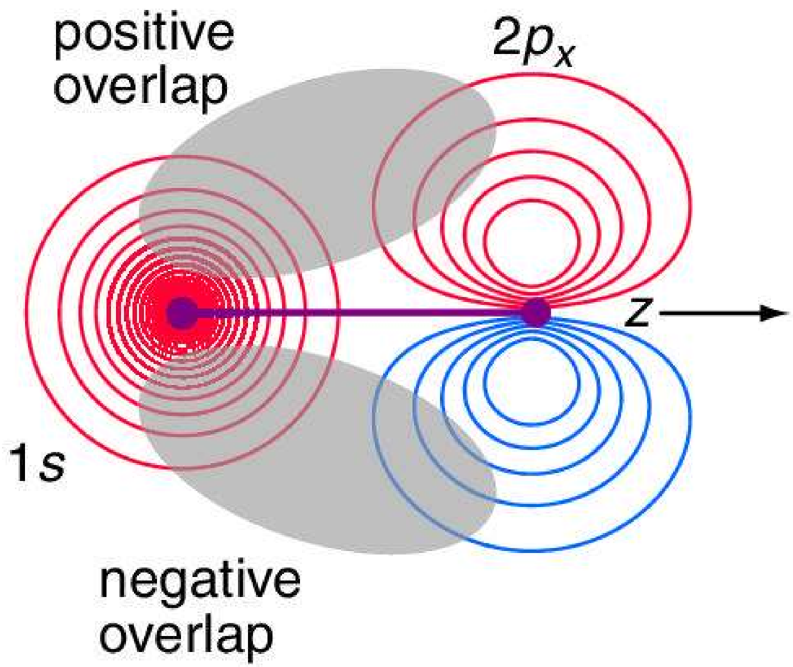
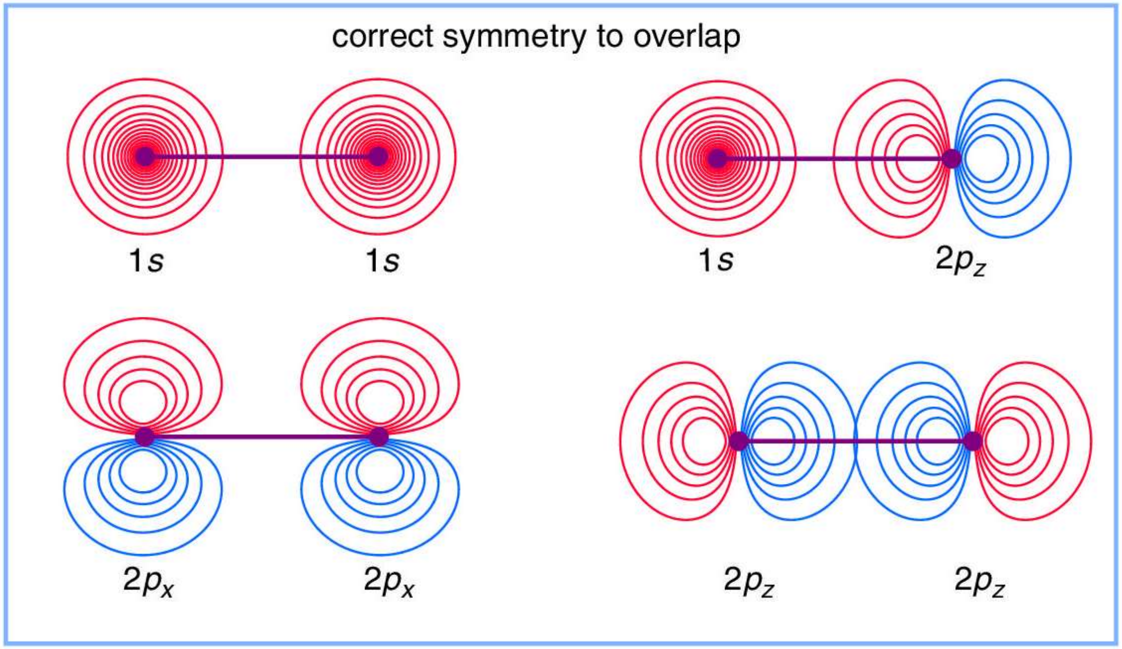
Review: Rules for Forming MOs: 1

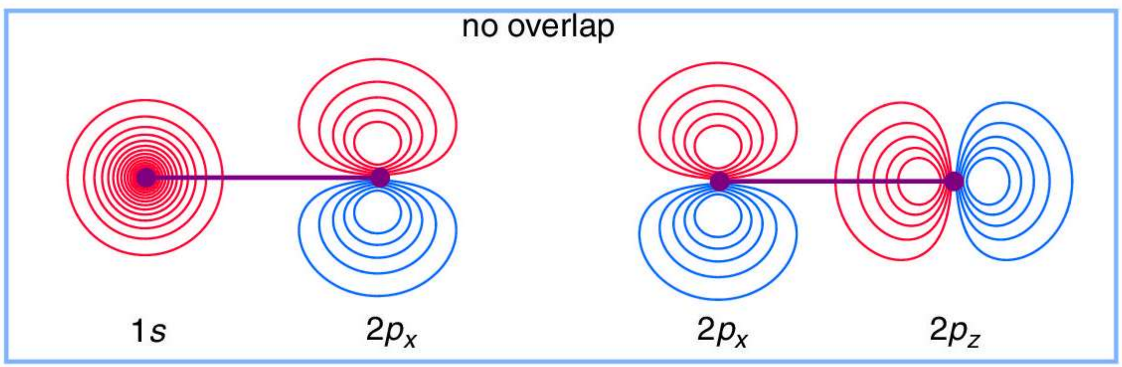
Combining certain number of AO’s produces the same number of MO’s e.g. combining 4 AOs give 4 MOs

Rules for Forming MOs: 2

Recall: Only AO's of the correct symmetry will give MOs



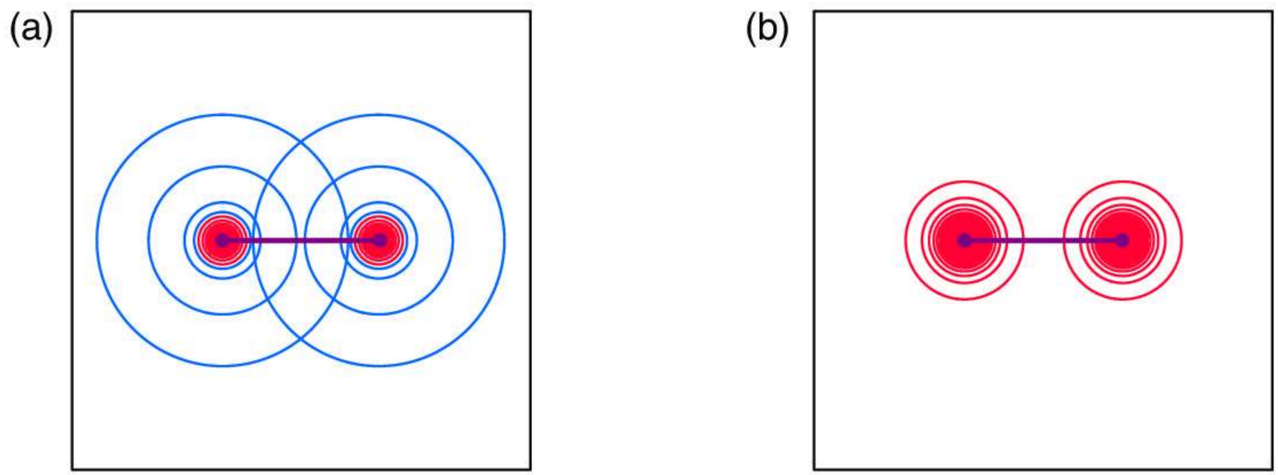




Rules for Forming MOs: 3

Size: In order to interact for form MOs, the AOs must overlap significantly- high S

Example: Look at the MO formed from 2s AO's and 1s AO's of Li

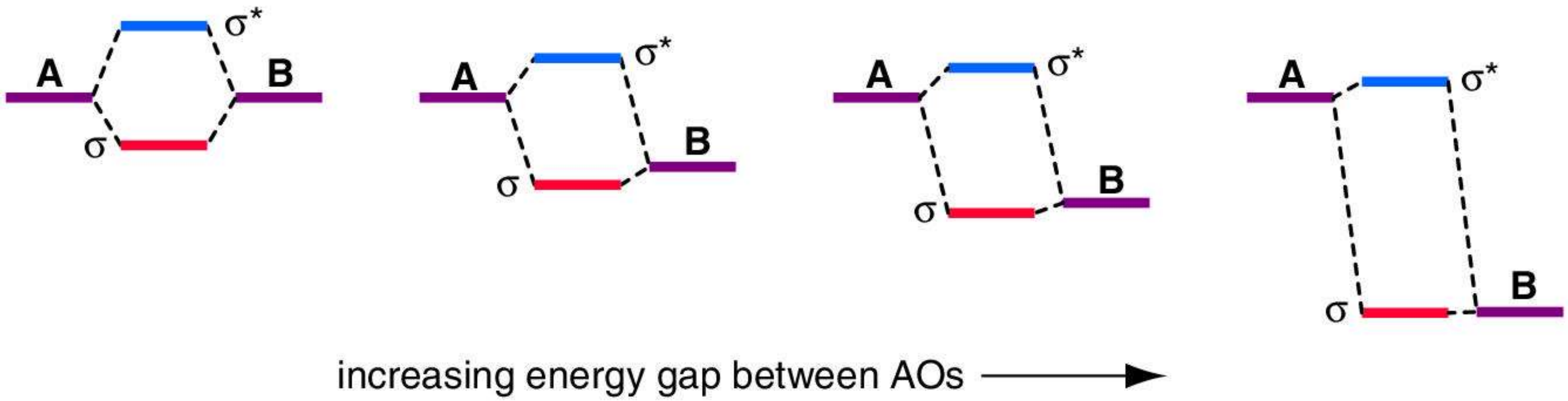


2s 1s

- The 2s AO's overlap significantly- the resulting bonding and anti-bonding MO will be significantly shifted from the energy of AO's
- For the 1s's, even though symmetry is correct to overlap, S will be zero

Rules for Forming MOs: 4

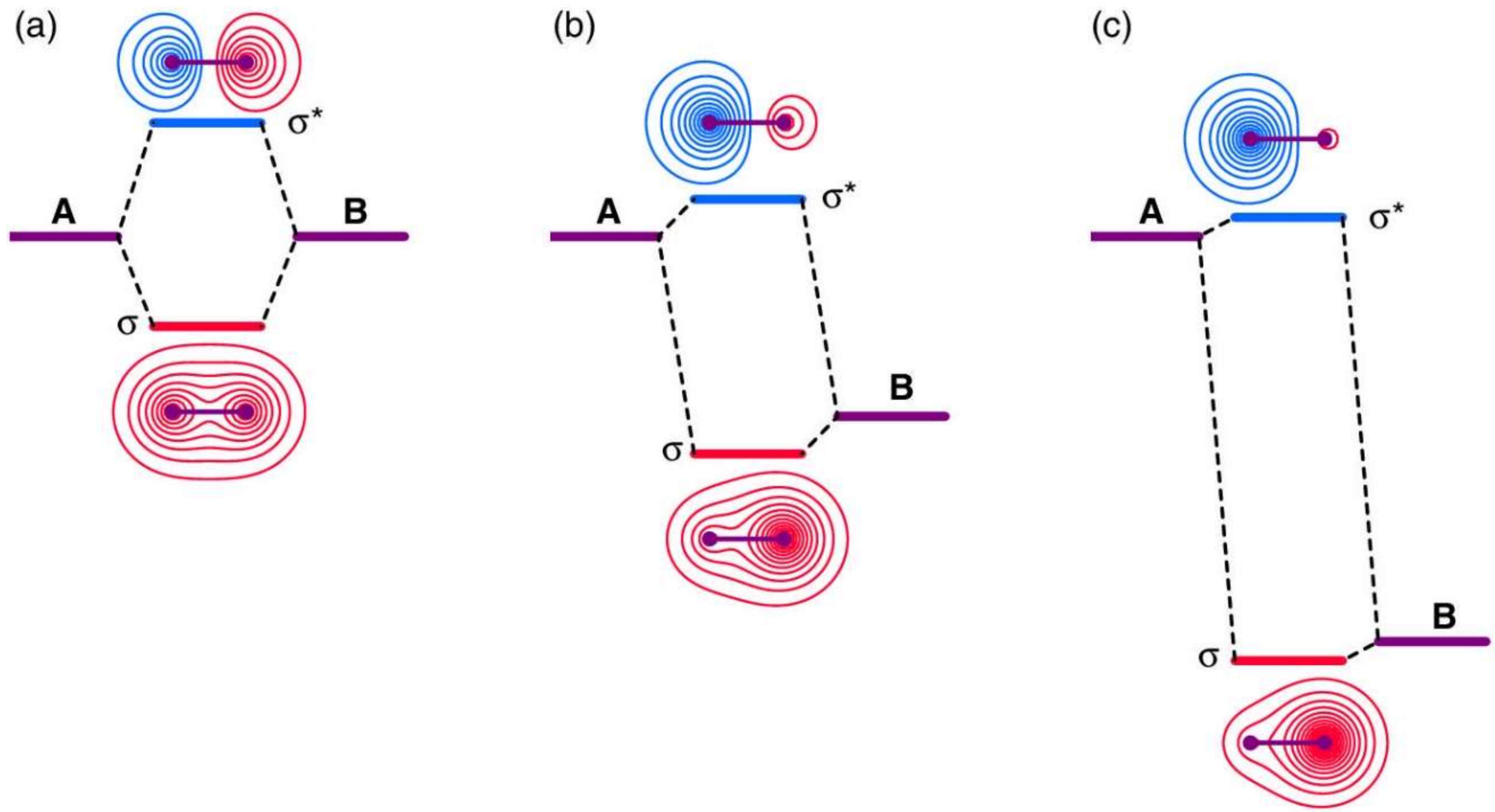
Energy match and contribution from different AOs



- When AOs are closely matched in energy, the bonding and anti-bonding MOs lie significantly above and below the AOs
- The bonding MO lies closer in energy to that of the lower energy AO
- The anti-bonding MO lies closer in energy to that of the higher energy AO

Rule 5 for Forming MOs

Energy match and contribution from different AOs

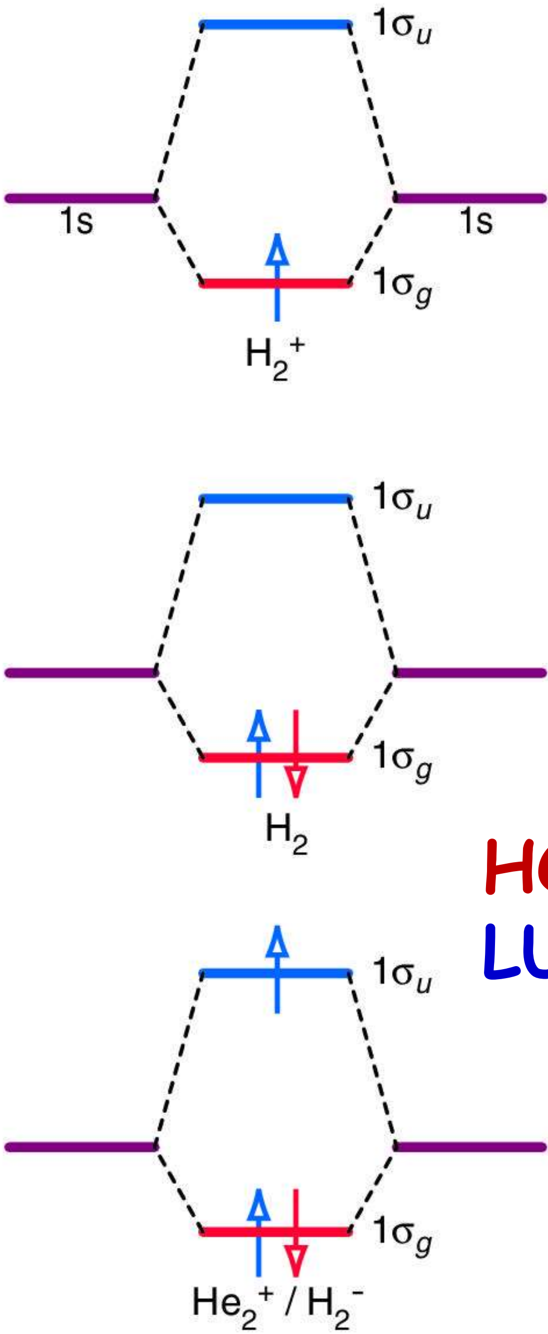


- Contribution to the bonding MO from the lower energy AO increases, while from the higher energy AO decreases
- Contribution to the anti-bonding MO from the higher energy AO increases, while from the lower energy AO decreases

Dihydrogen Molecule: Orbital Interaction Diagram

1. Plot atomic valence orbital energies
2. Determine which orbitals can interact (those with S>0).
3. Plot MO energies and draw orbitals Interaction
4. Use Aufbau principle to fill in electrons

H_2, He and their Ions



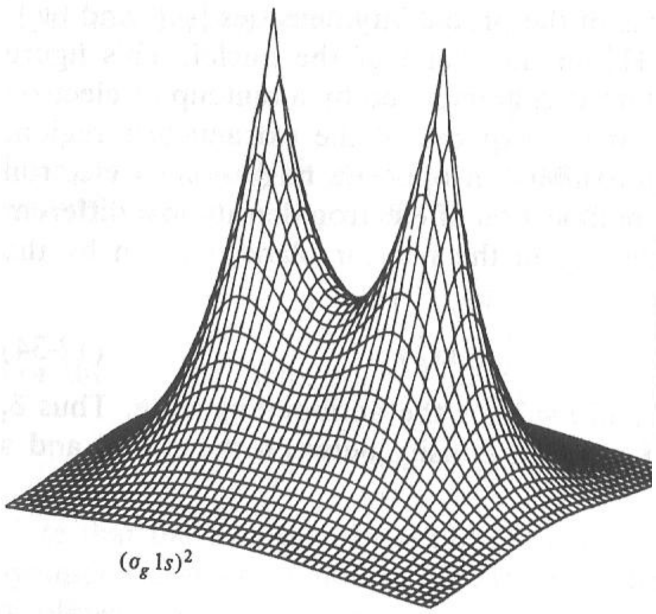
Molecule	BDE (kJ/mol)	Bond length (pm)
H_2^+	256	106
H_2	432	74
He_2^+	241	108
He_2	Not Observed	Not Observed

HOMO : Highest Occupied Molecular Orbital

LUMO : Lowest Unoccupied Molecular Orbital

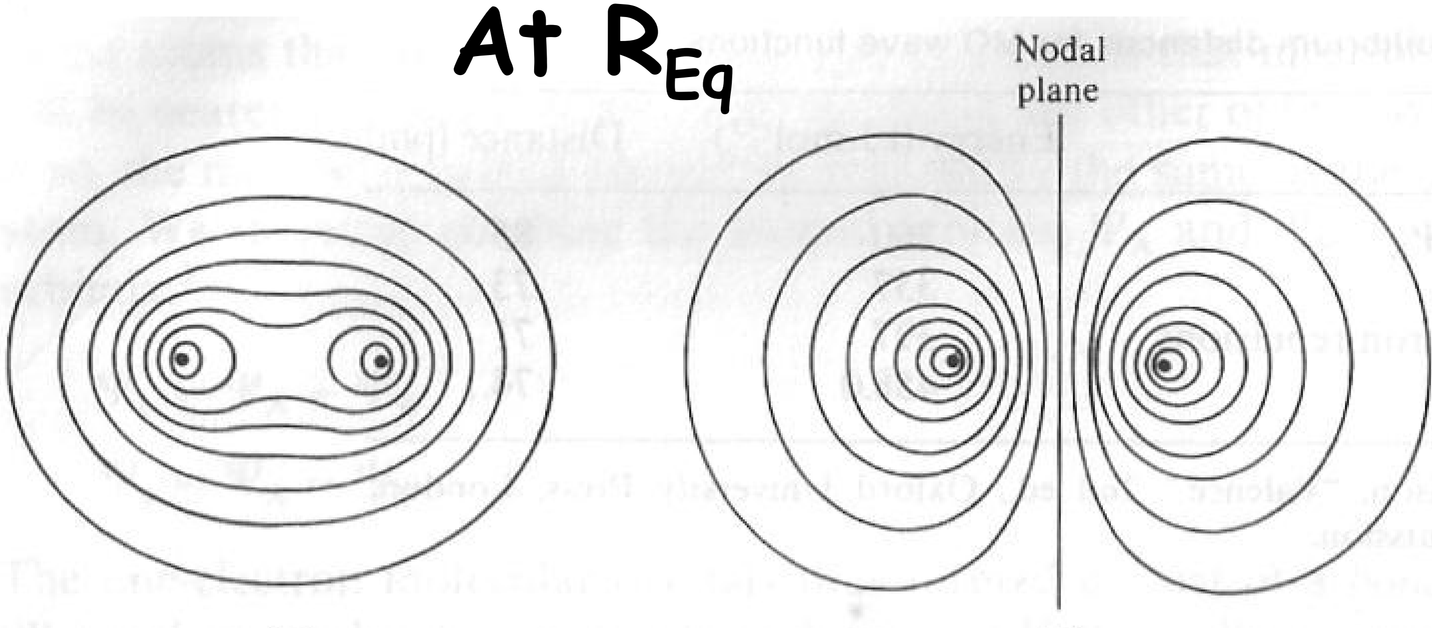
BO = ½(no. of bonding electrons – no. of anti-bonding electrons)

Electron Density Maps/Contours

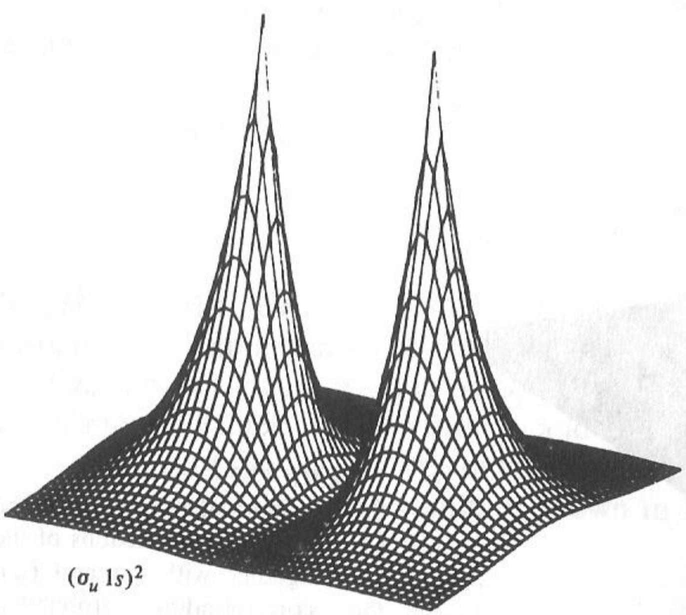


(c)

At R_{Eq}



(a) (b)

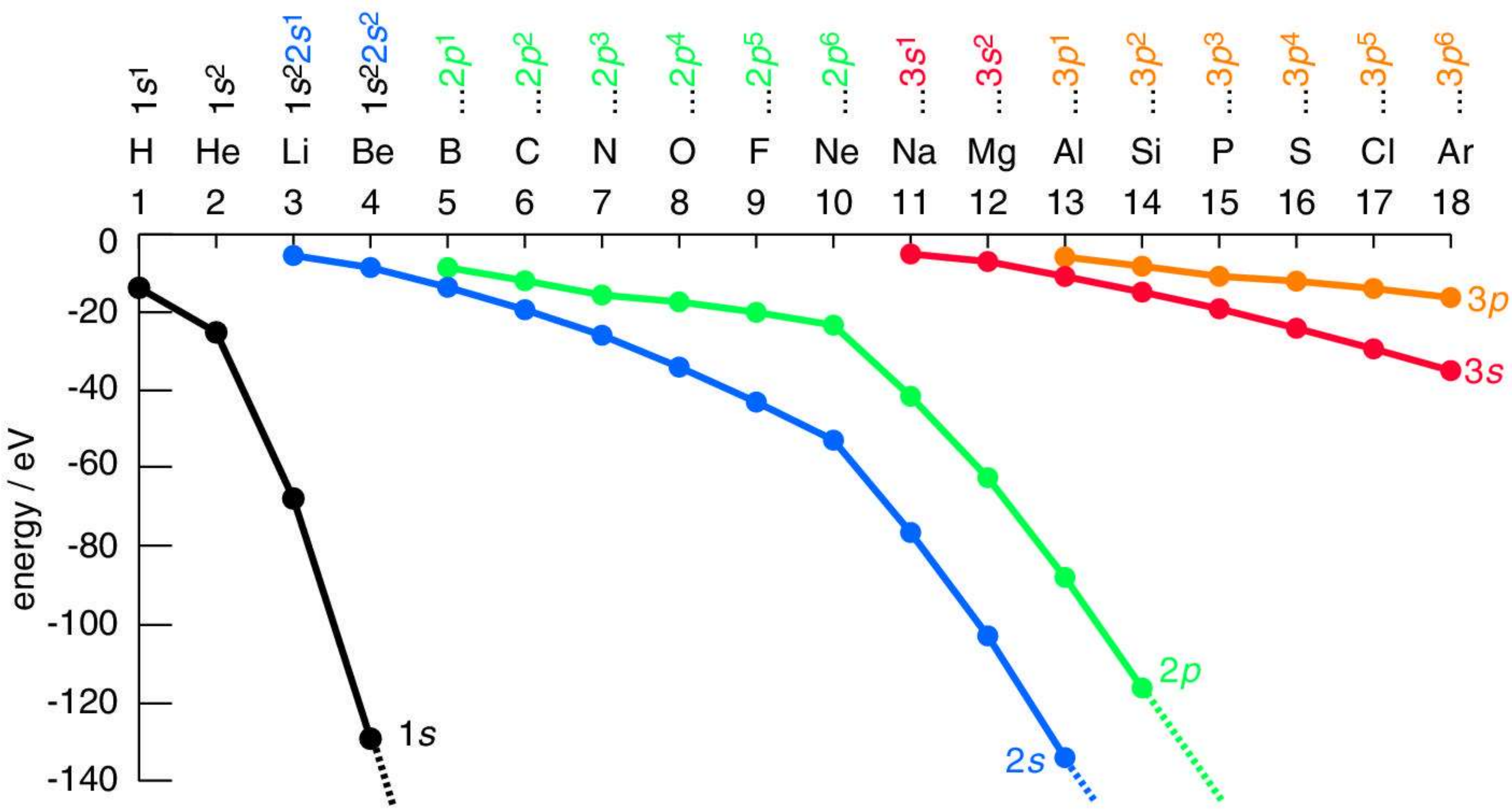


Probability density is equal for each line drawn in the contour plot.

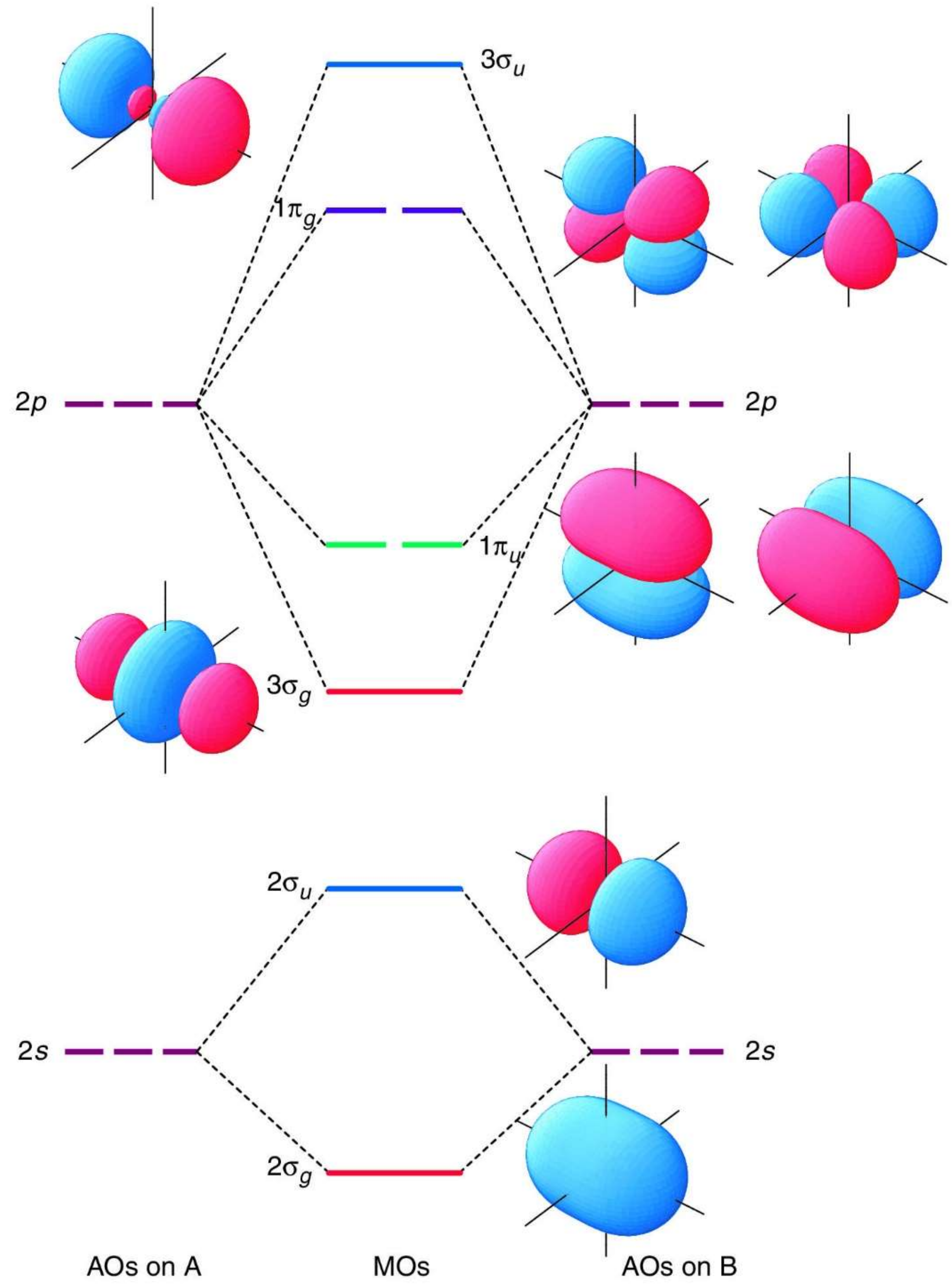
Value of probability density higher close to the Nucleus and decreased radially

Idealized MO Diagrams: 2^{nd} Row

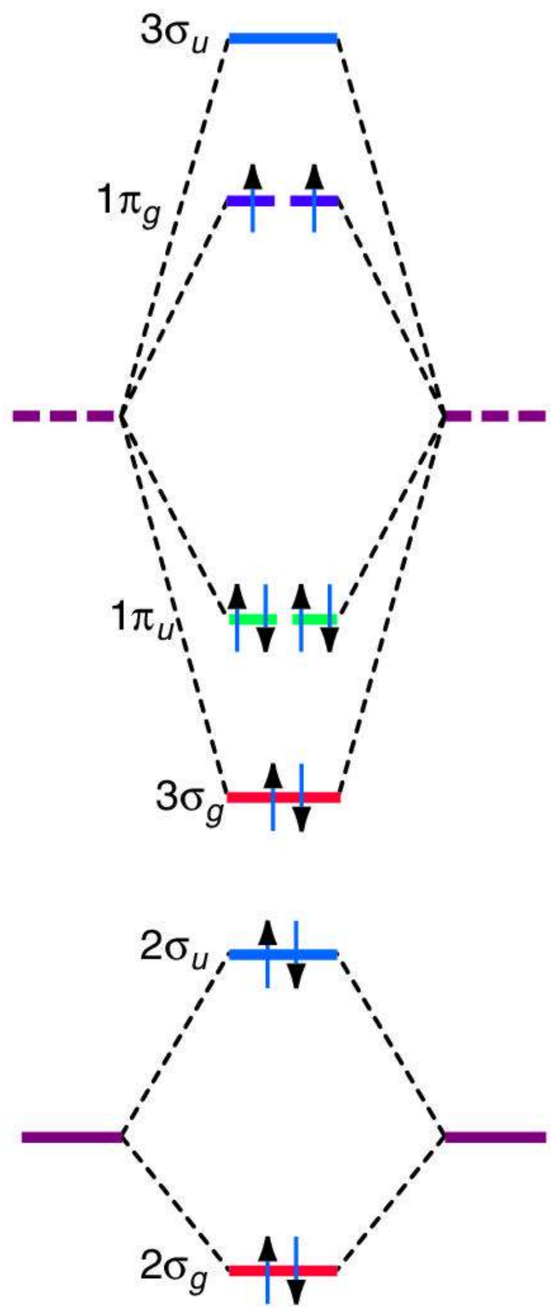
Recall:



Idealized MO Diagrams: 2nd Row



Idealized MO Diagrams: O_2, F_2, Ne_2



Oxygen as a Fuel

Fossil Fuels

Carbohydrates

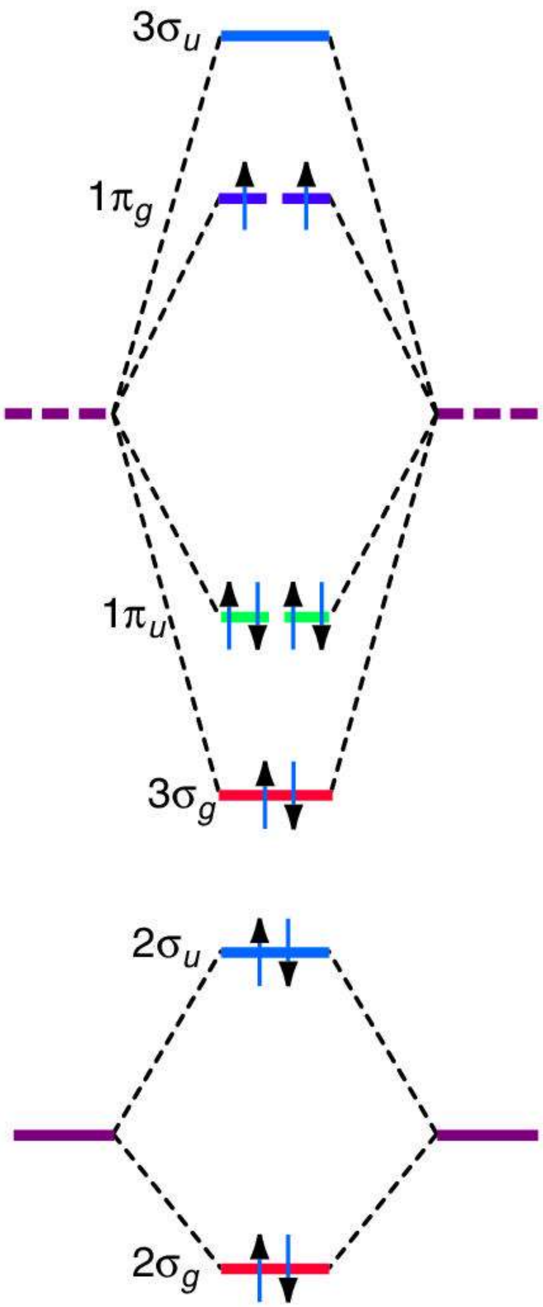
$CH_4 + 2\ O_2 \longrightarrow CO_2 + H_2O$

$\text{Sucrose} + 12\ O_2 \longrightarrow CO_2 + H_2O$

$C_2H_5OH + 3\ O_2 \longrightarrow CO_2 + H_2O$

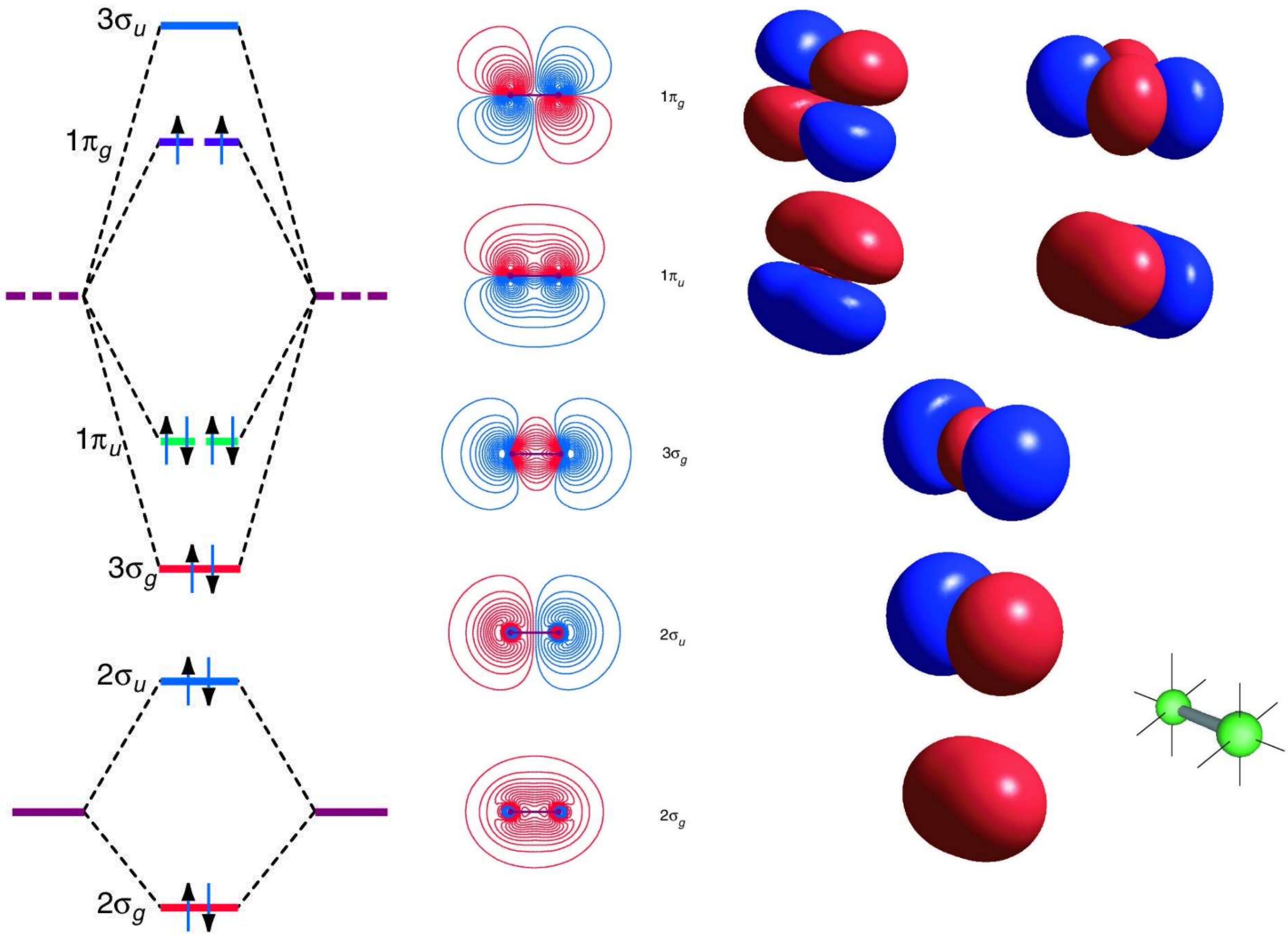
$H_2 + O_2 \longrightarrow H_2O$ $\Delta H = -460\ \text{kJ/mol}$

Idealized MO Diagrams: O_2, F_2, Ne_2



HOMO, LUMO and Bond Order

Idealized MO Diagrams: O_2



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

Photoelectron Spectroscopy of O_2

- Irradiate molecules with high-energy radiation and scan
- Determine the energies of the electrons ejected from the molecules

$$A + \text{photon} \rightarrow A^+ + e^-$$

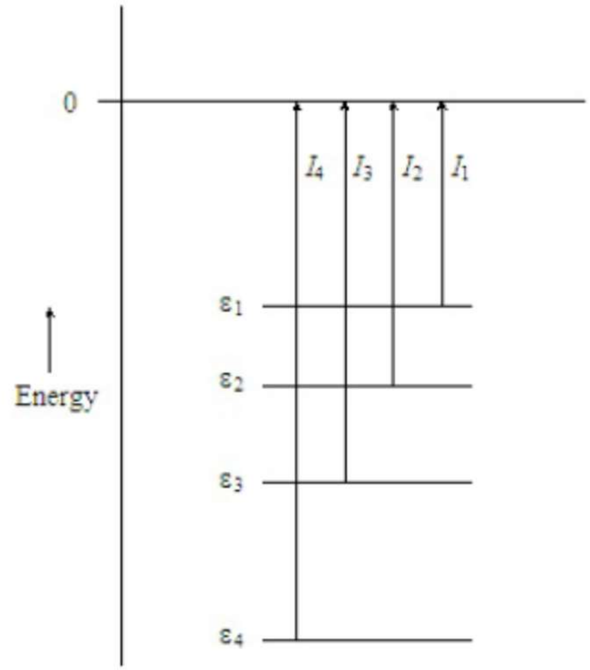
Conservation of energy then requires that $E(A) + h\nu = E(A^+) + E(e^-)$

Since the free electron's energy is present solely as kinetic energy (KE): $E(e^-) = KE$

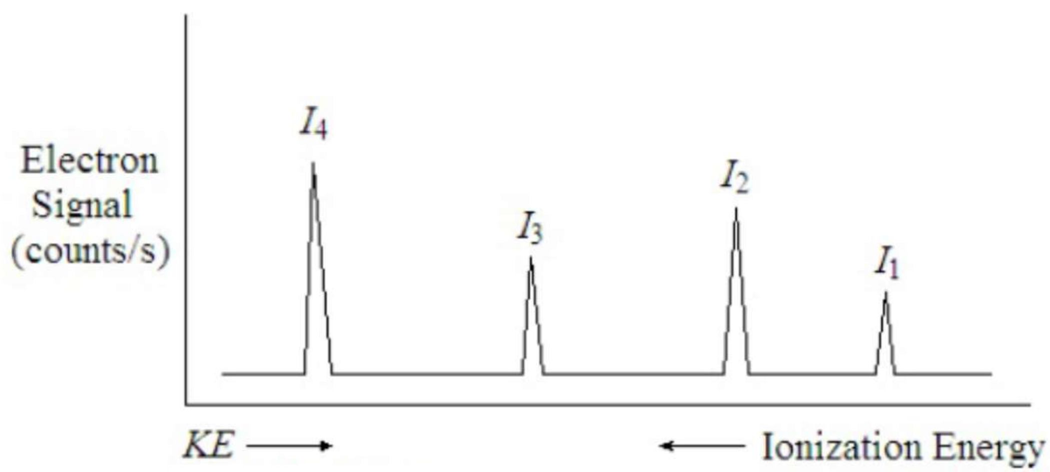
$$KE = h\nu - [E(A^+) - E(A)]$$

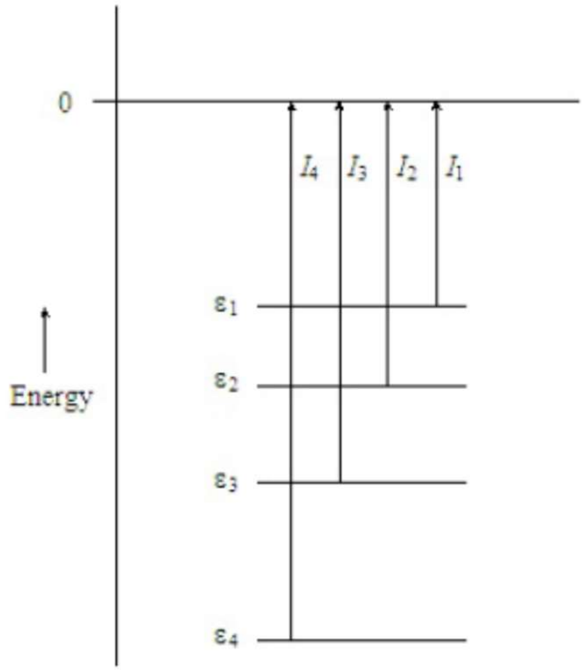
$$KE = h\nu - IE$$

$$IE = h\nu - KE$$

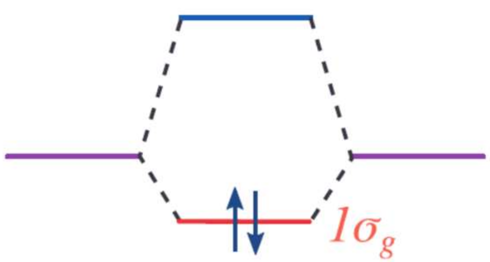


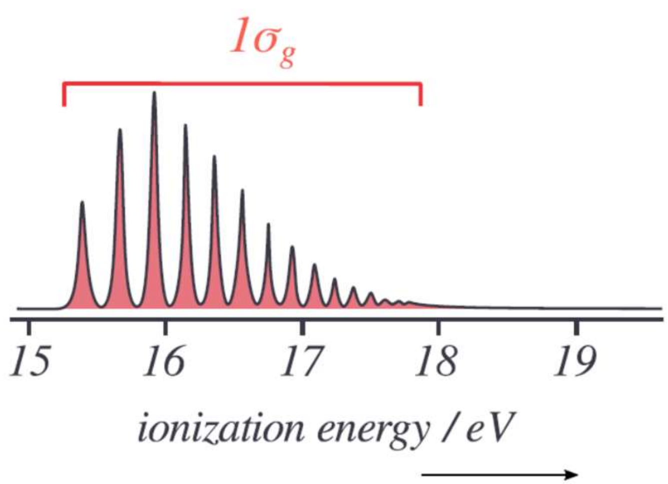
Schematic P.E.S. Spectrum



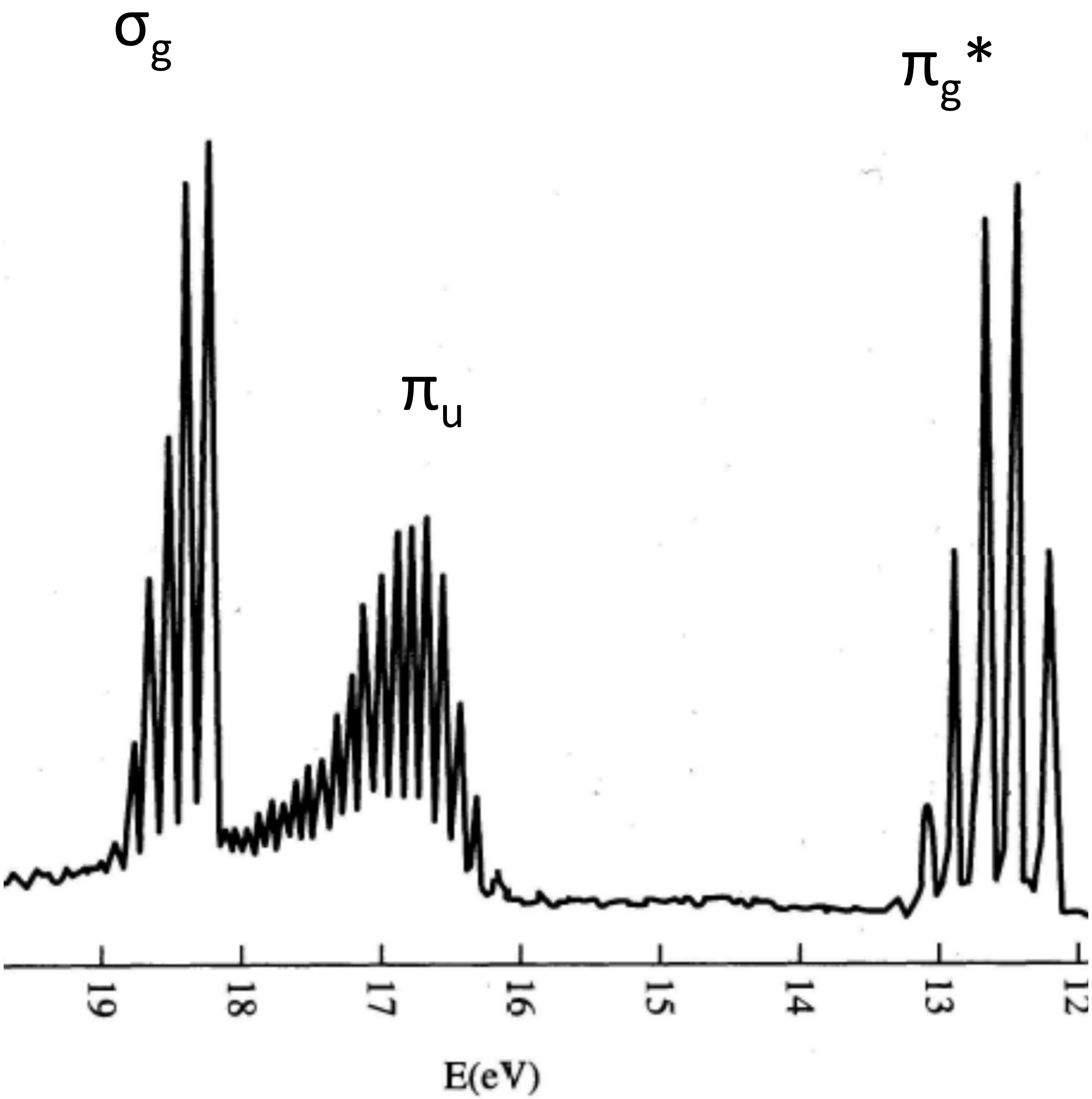


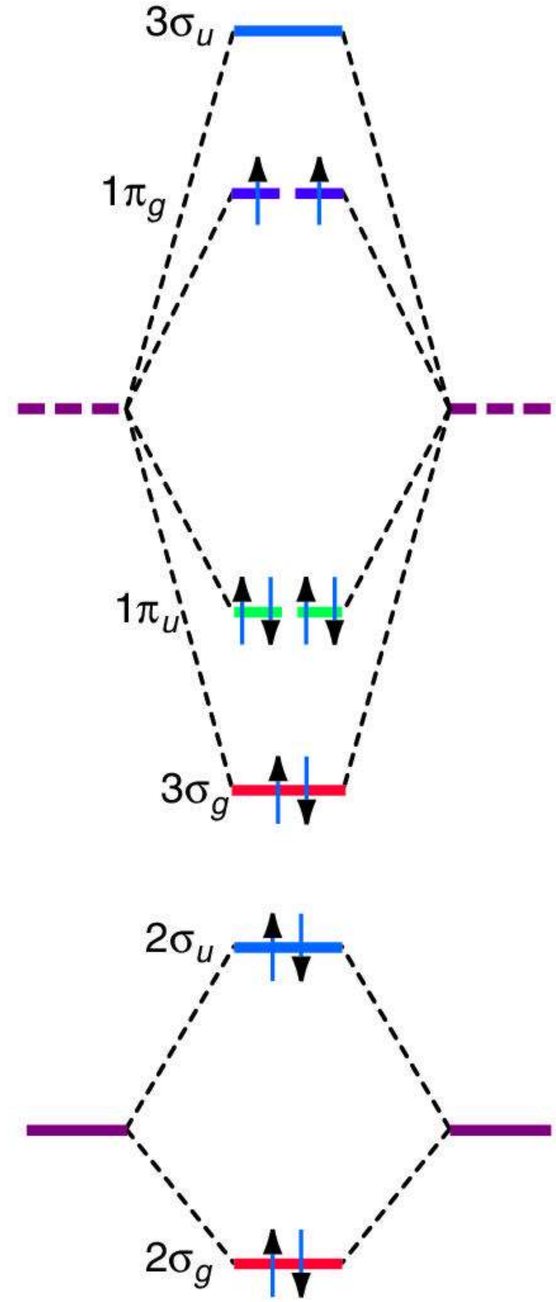
Schematic P.E.S. Spectrum



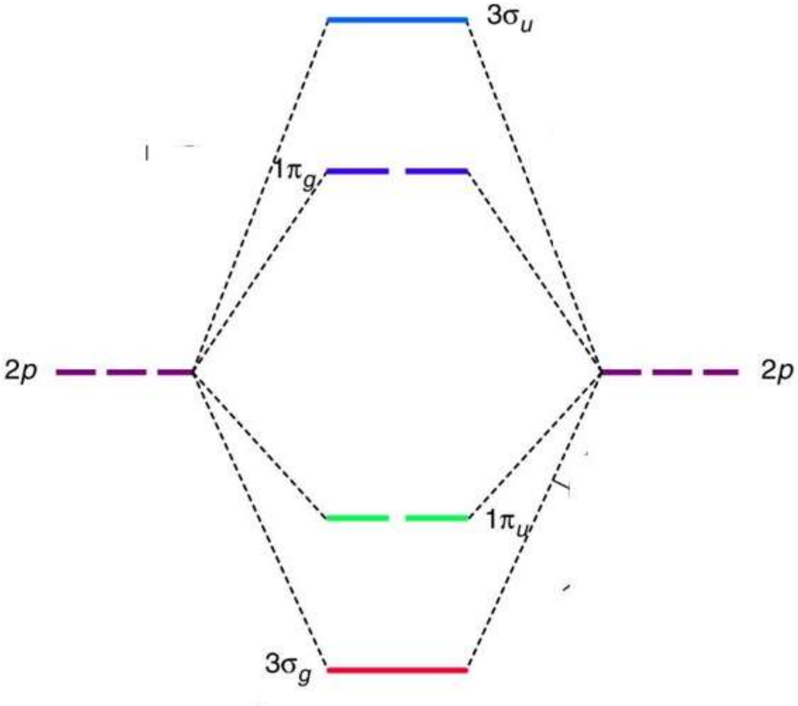


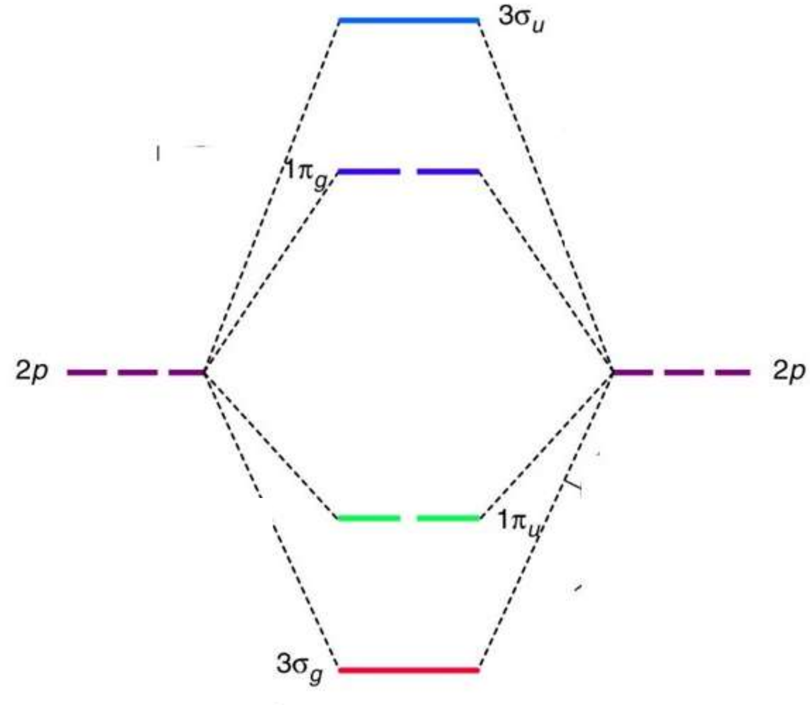
Photoelectron Spectra of O_2

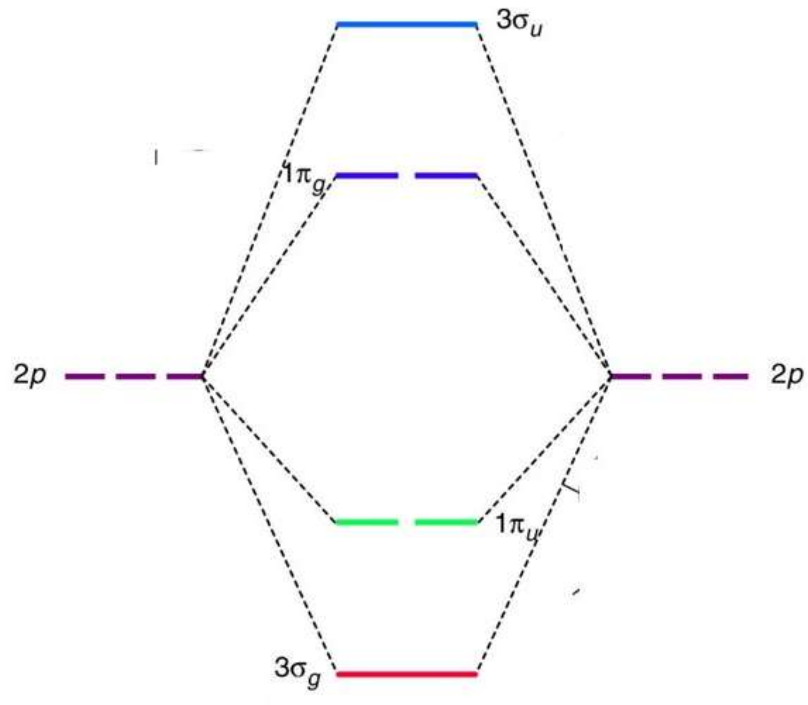




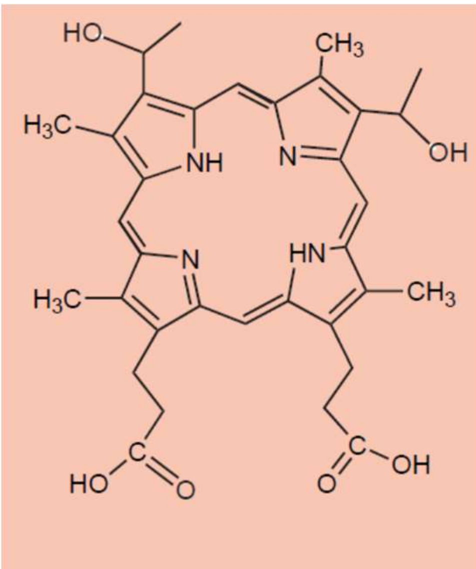
Possible Excited States of O_2

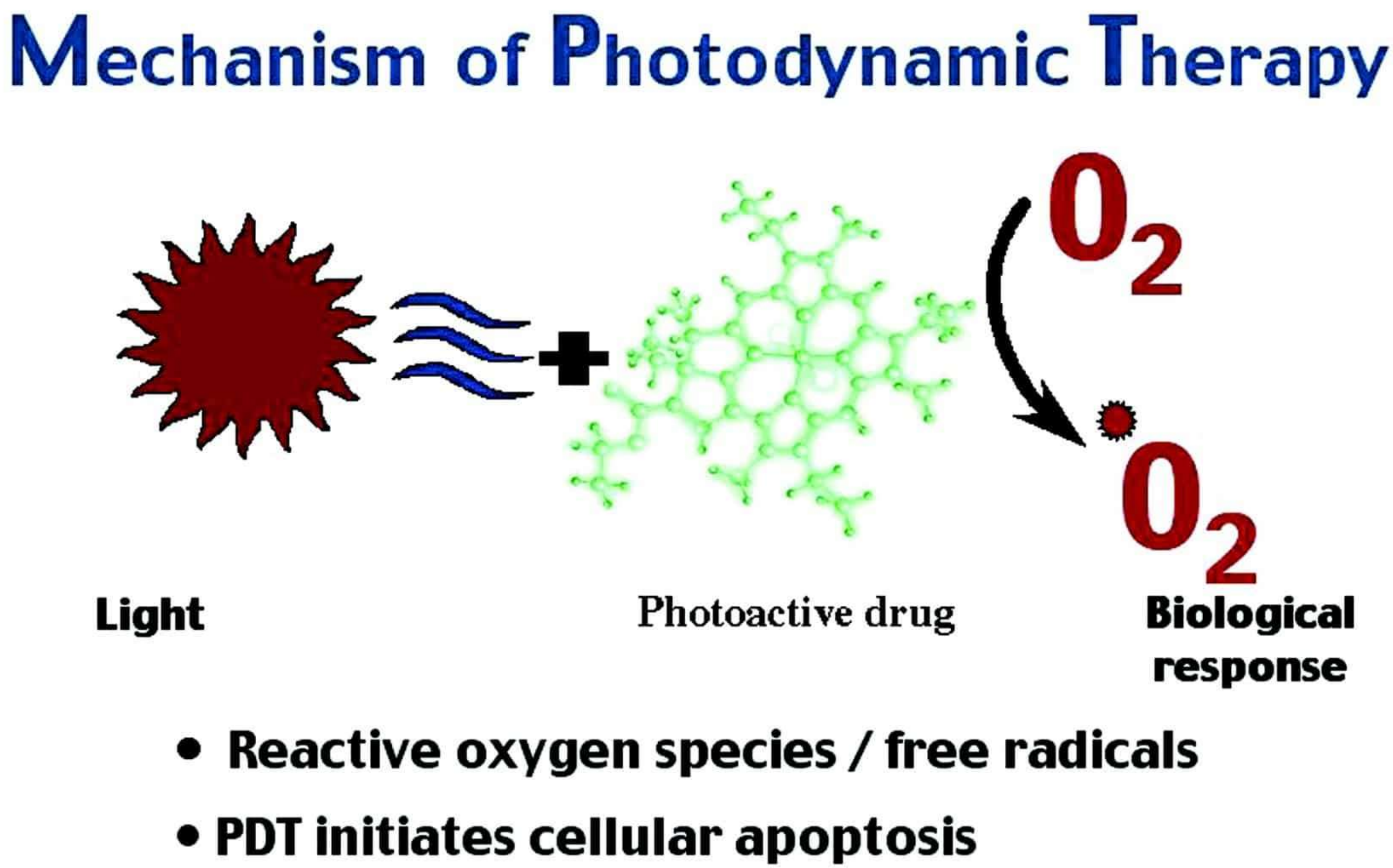




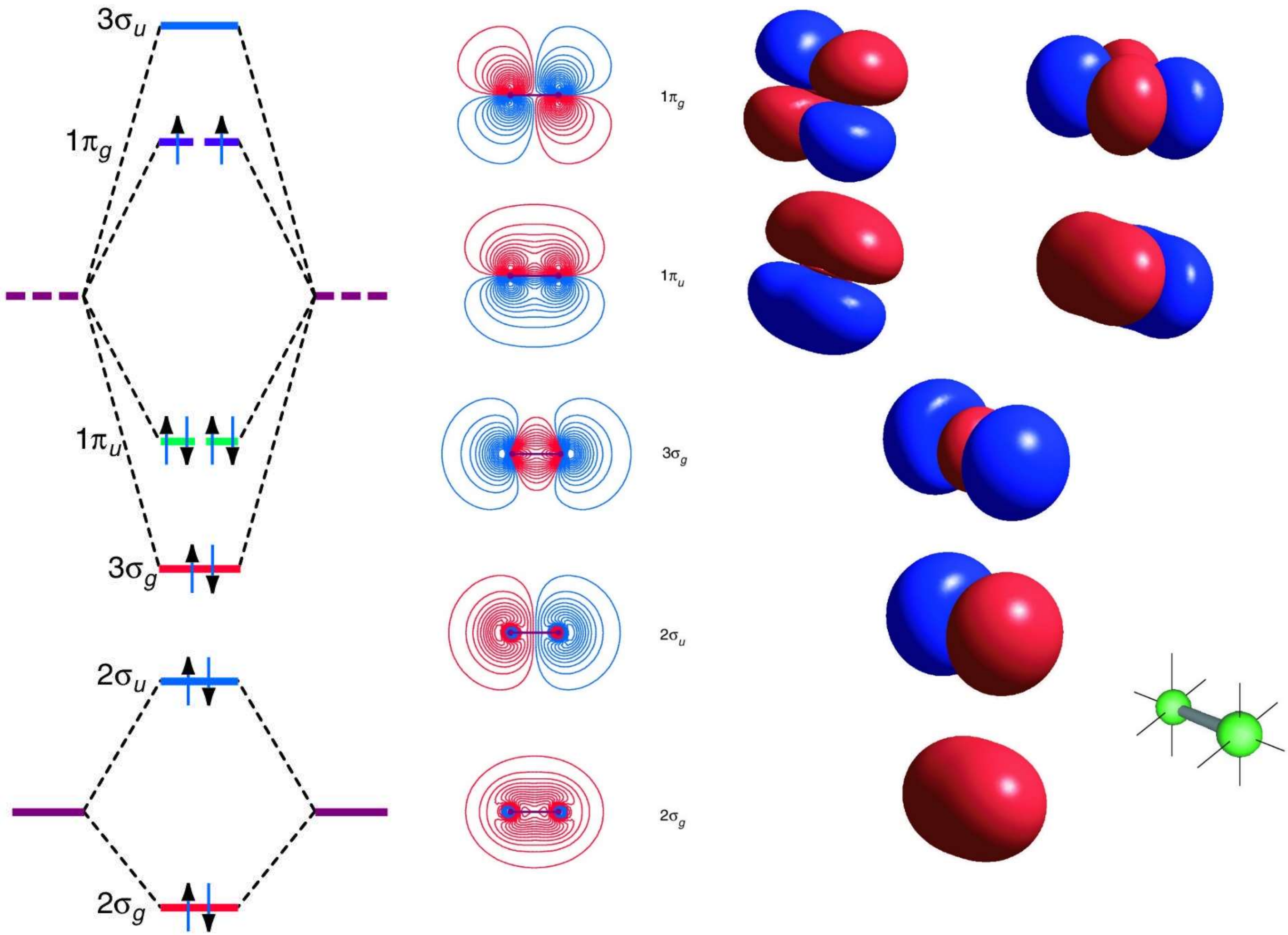


Photodynamic Therapy





Expected MO Diagrams of N_2



Actual MO and Energy Diagram for N_2

Nature 2004 vol 432 867

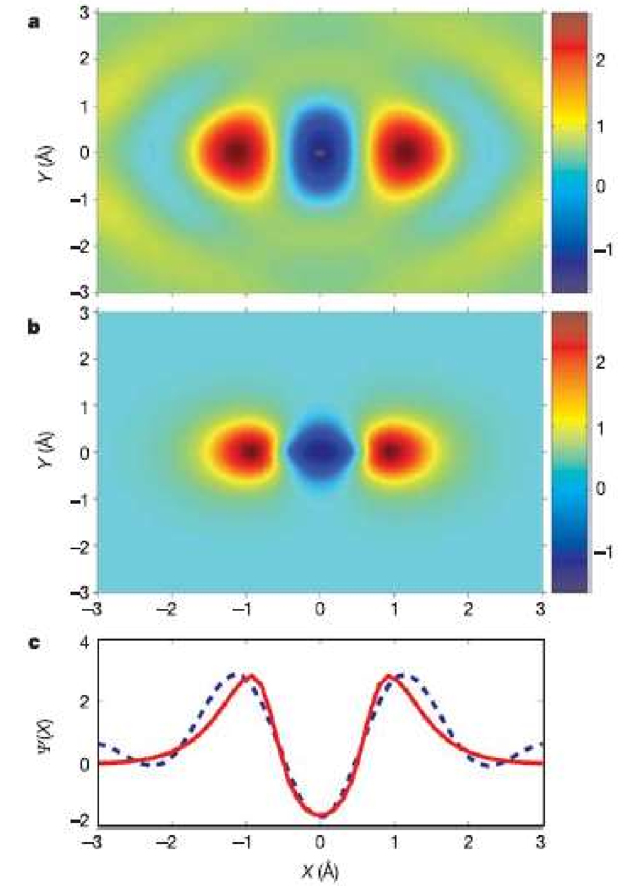
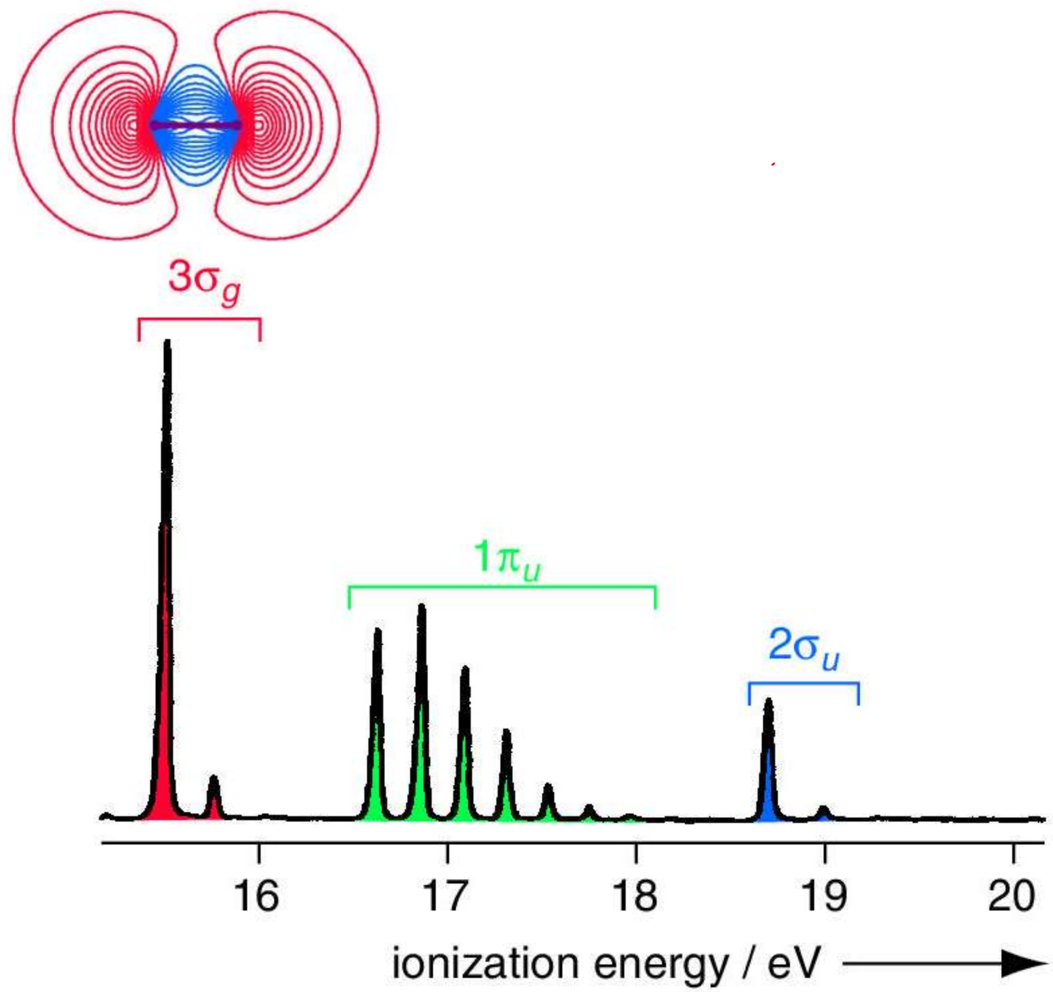
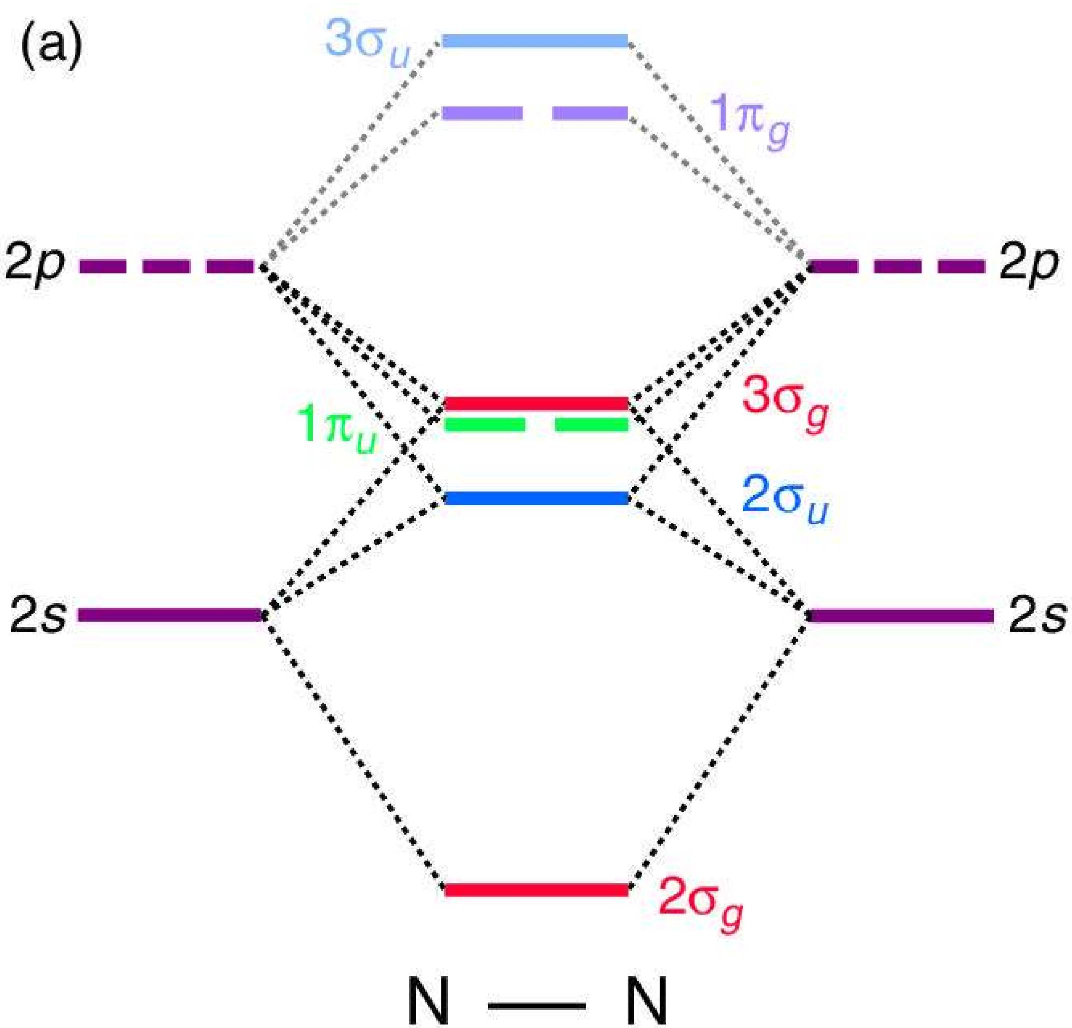


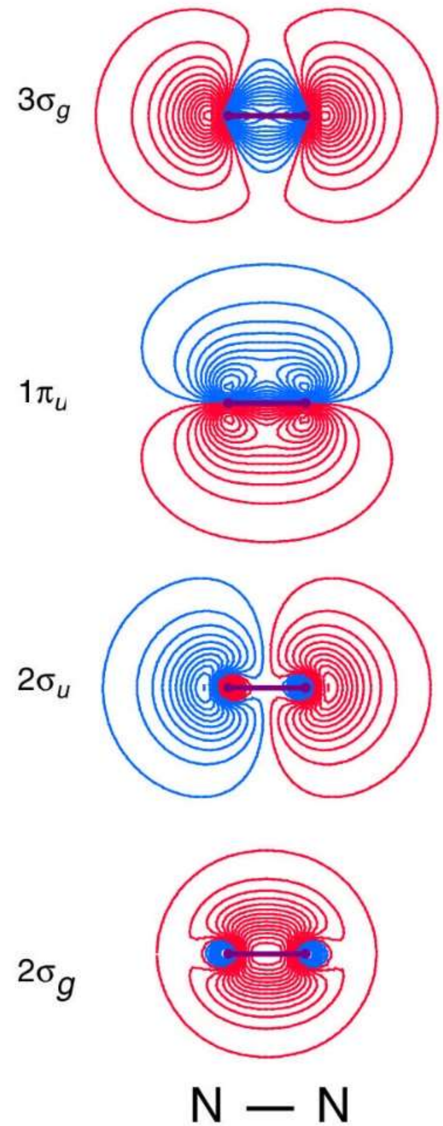
Figure 4 Molecular orbital wavefunction of N_2. **a**, Reconstructed wavefunction of the HOMO of N_2. The reconstruction is from a tomographic inversion of the high harmonic



- Mixing of 2S and $2P_z$ orbital → due to small energy gap
  - 2s and $2p_z$ electrons feels not so different Z_{eff}

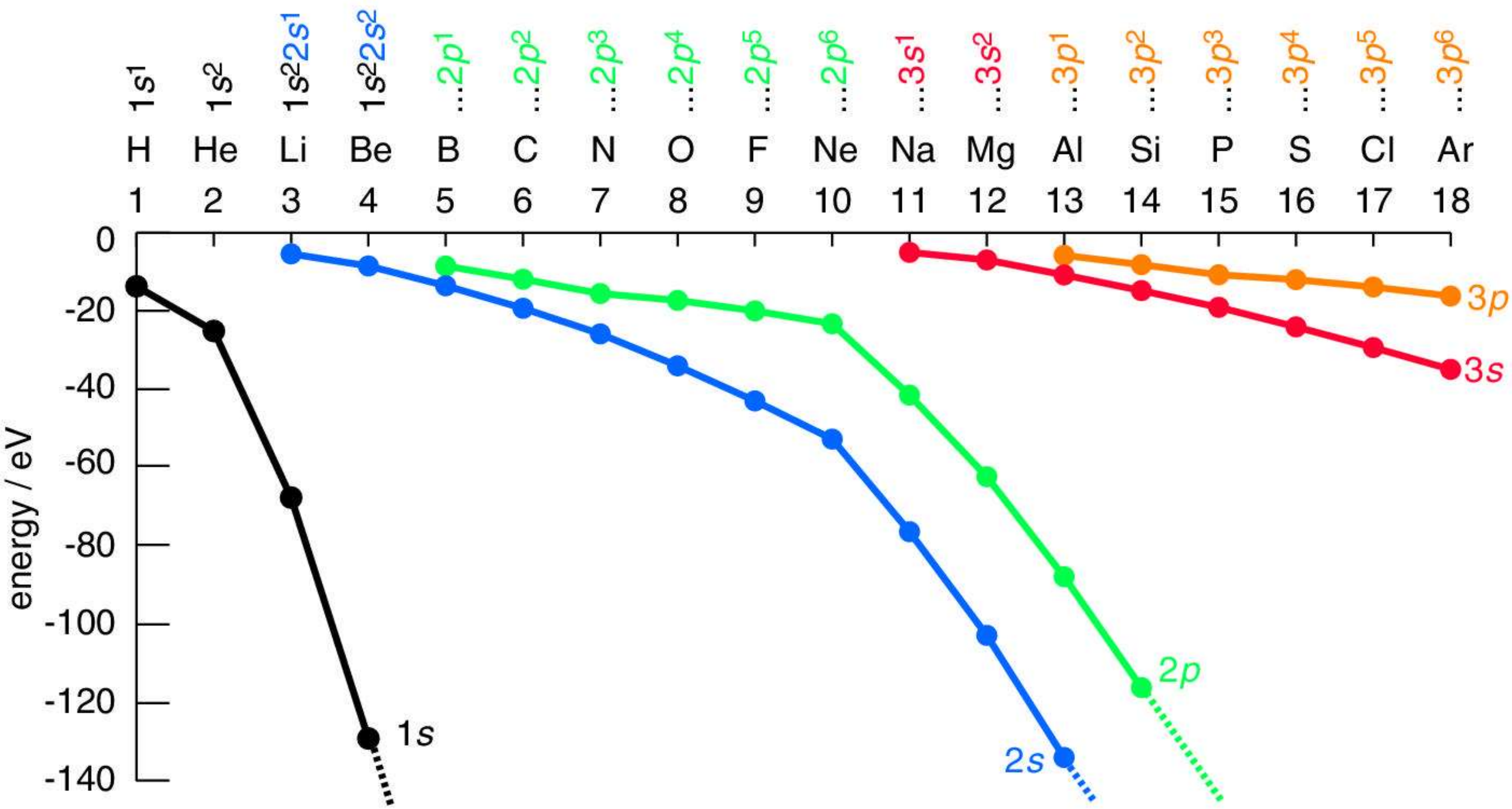
Actual MO and Energy Diagram for N_2



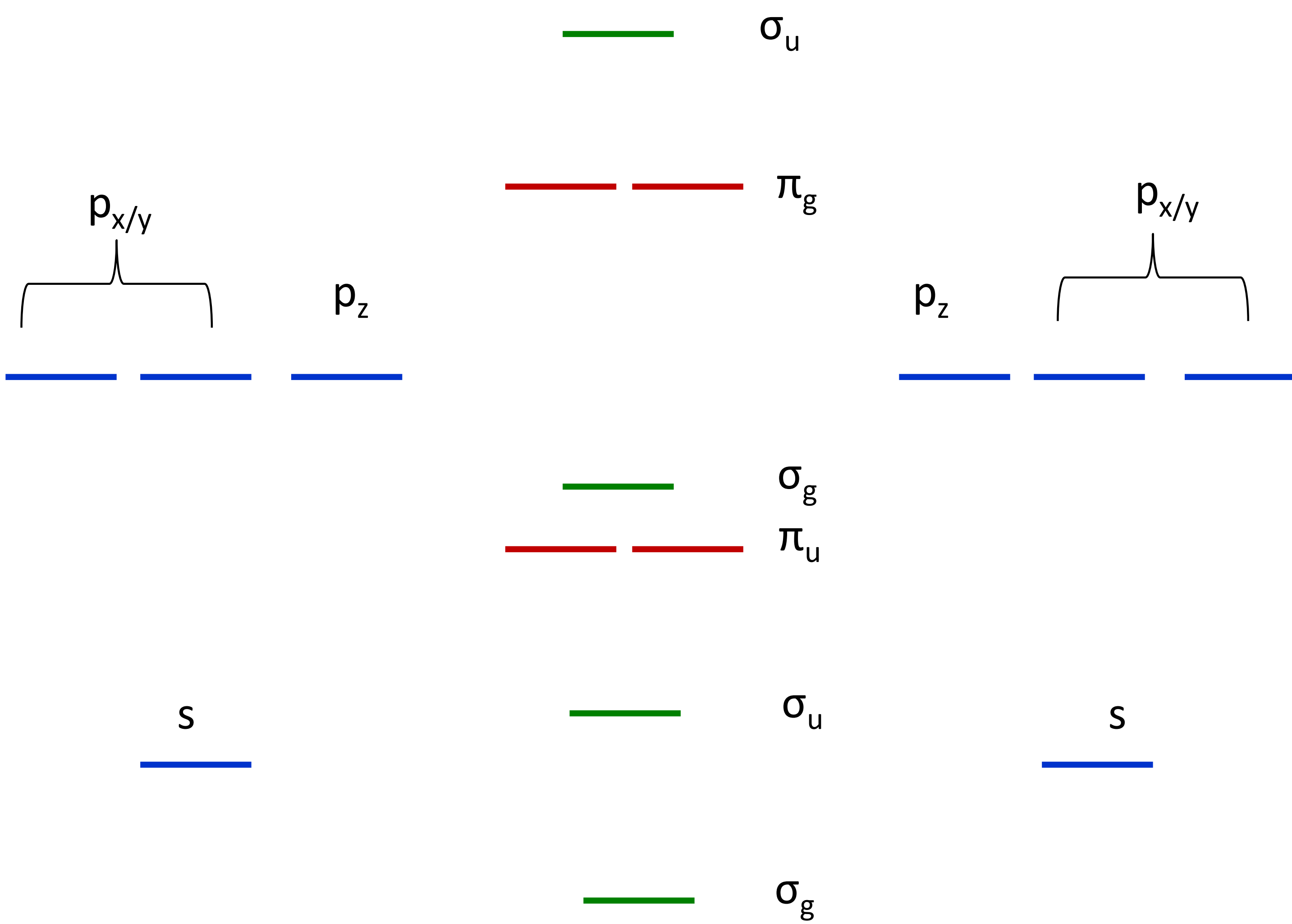


S-P Mixing in Atomic Orbitals

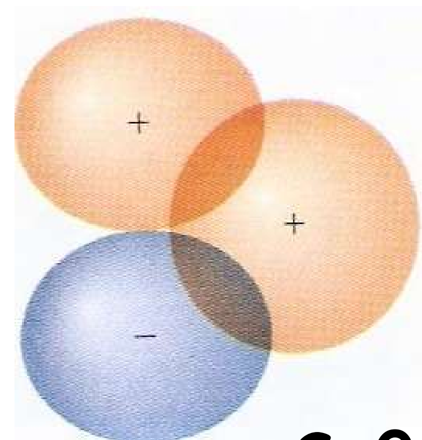
Recall:



MO of N_2

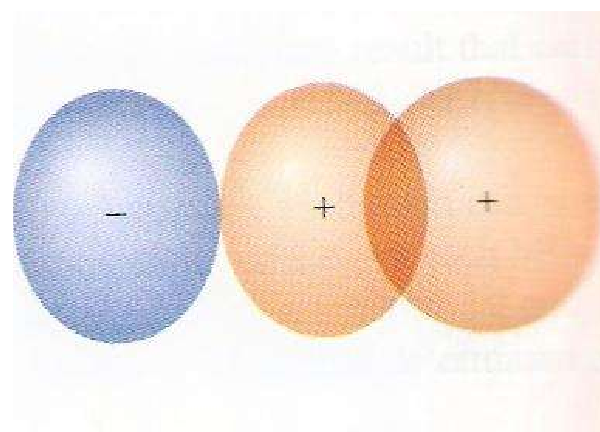


$P_{X/Y}$ +s



S=0

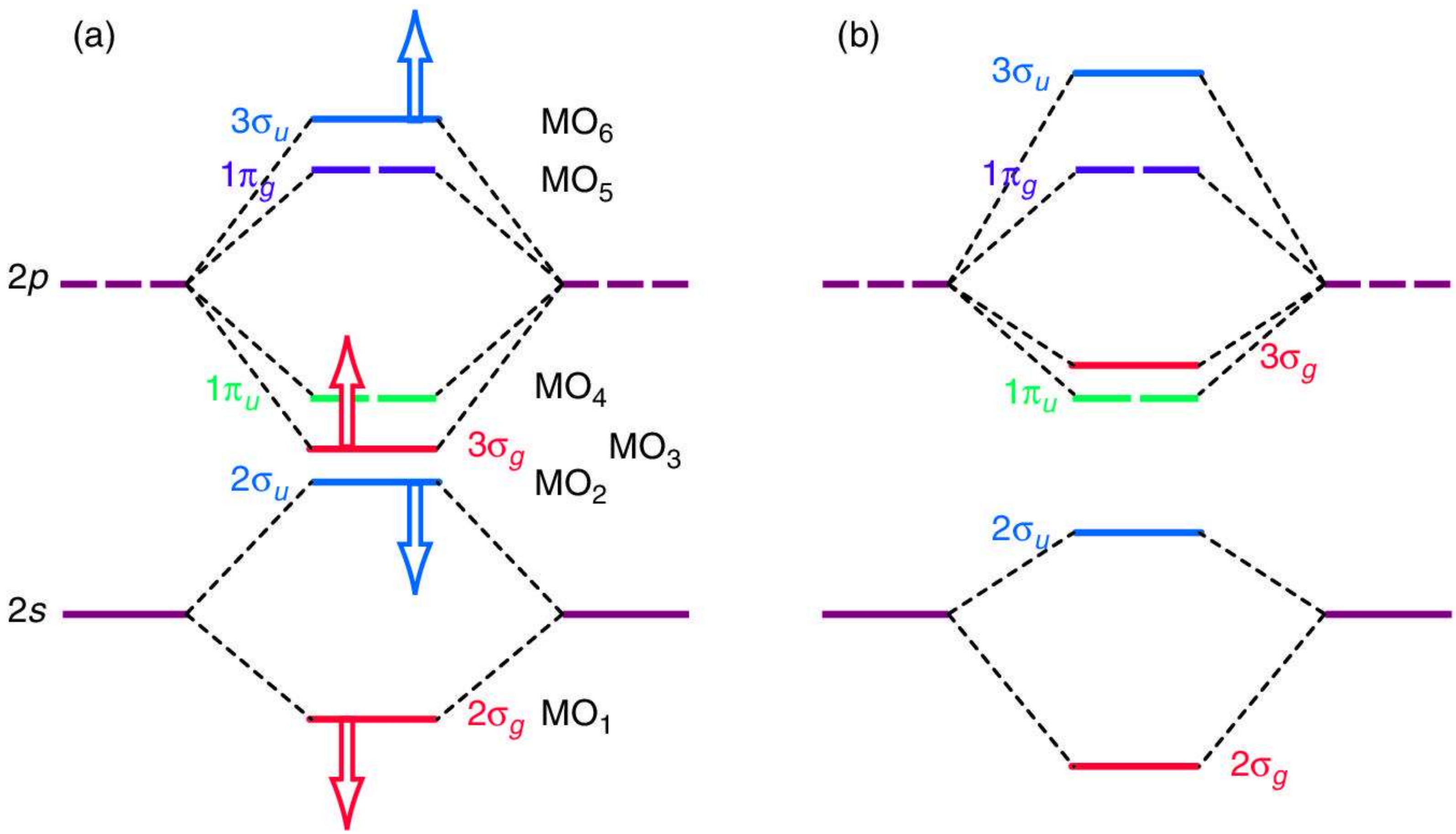
P_Z + s



S>0 or <0?

4 MO's can be constructed from 2s (two) and $2p_z$ (two)
Example one MO can be $c_1*(2s) + c_2*(2s) + c_3*(2p_z) + c_4*(2p_z)$

S-P Mixing in Atomic Orbitals



Mixing of 2s and 2p

Actual MO and Energy Diagram for N_2