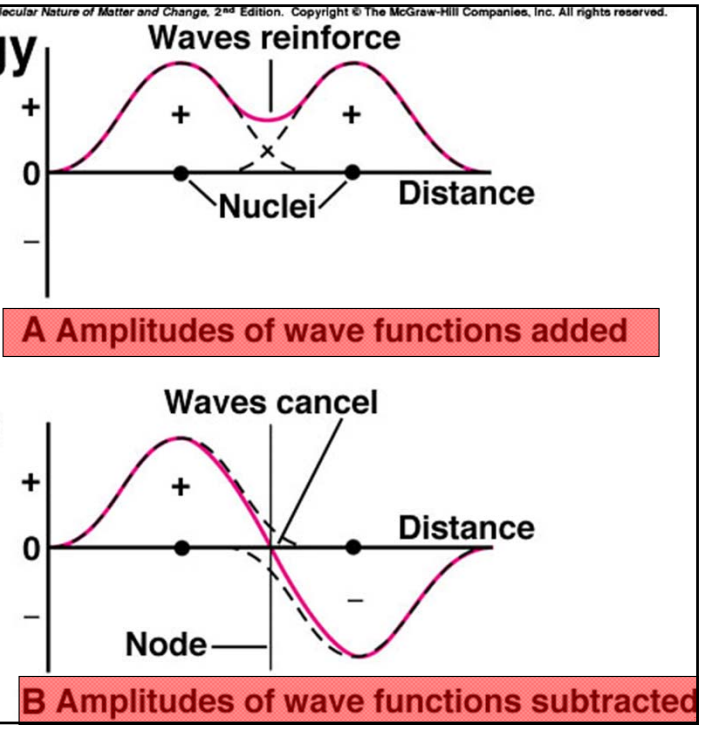
Molecular Orbital Theory

Reading: DeKock and Gray, Chap 4 (but not 4-8)
Chap 5 (through 5-8)

Miessler and Tarr, Chap 5

An Analogy between Light Waves and Atomic Wave Functions



Linear Combination of Atomic Orbitals (LCAO)

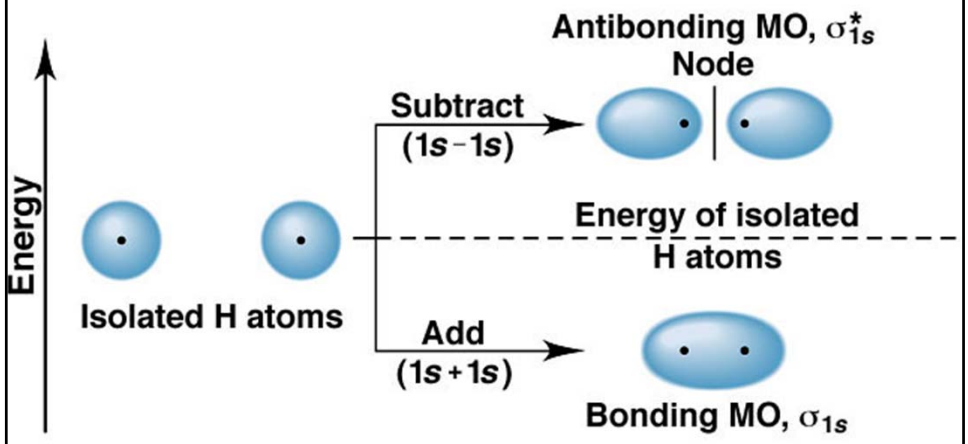
$$\psi_k = c_1\varphi_1 + c_2\varphi_2 + ... + c_n\varphi_n$$

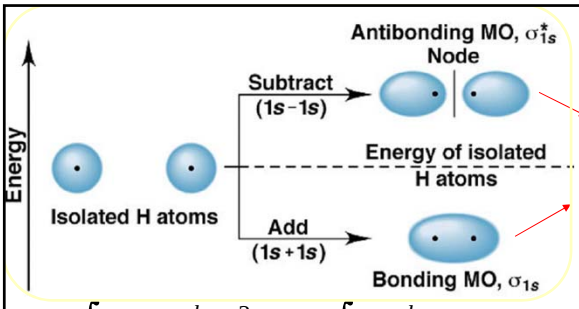
1. n atomic orbitals → n molecular orbitals.
2. Like atomic orbitals, MOs are ortho-normal

$$\int \psi_i \psi_j dv = 1 ... (i = j)$$

$$\int \psi_i \psi_j dv = 0 ... (i \neq j)$$

Contours and Energies of the Bonding and Antibonding Molecular Orbitals (MOs) in H_2





$$\psi(\sigma_u^*) = N^*(1s_A - 1s_B)$$

$$\psi(\sigma_g^b) = N^b(1s_A + 1s_B)$$

$$\int[\psi(\sigma_g^b)]^2 dv = \int[N^b(1s_A + 1s_B)]^2 dv = 1$$

$$(N^b)^2[\int(1s_A)^2 dv + 2\int(1s_A)(1s_B)dv + \int(1s_B)^2 dv] = 1$$

$$1 \qquad S_{AB} \qquad 1$$

$$N^b = \pm\sqrt{\frac{1}{2+2S_{AB}}}$$

$$N^* = \pm\sqrt{\frac{1}{2-2S_{AB}}}$$

Overlap integral

Degree of spatial overlap between any two AOs From different atoms in a molecule.

Gerade and Ungerade MO symmetry

$$\psi^+ = \frac{1s_a + 1s_b}{\sqrt{2(1+S_{ab})}} \Rightarrow \frac{1s_b + 1s_a}{\sqrt{2(1+S_{ab})}} = \psi^+$$

a, b, exchange position, MO does not change, inversion
Even parity, Gerade: German word for “even”.

$$\psi^- = \frac{1s_a - 1s_b}{\sqrt{2(1-S_{ab})}} \Rightarrow \frac{1s_b - 1s_a}{\sqrt{2(1-S_{ab})}} = -\psi^-$$

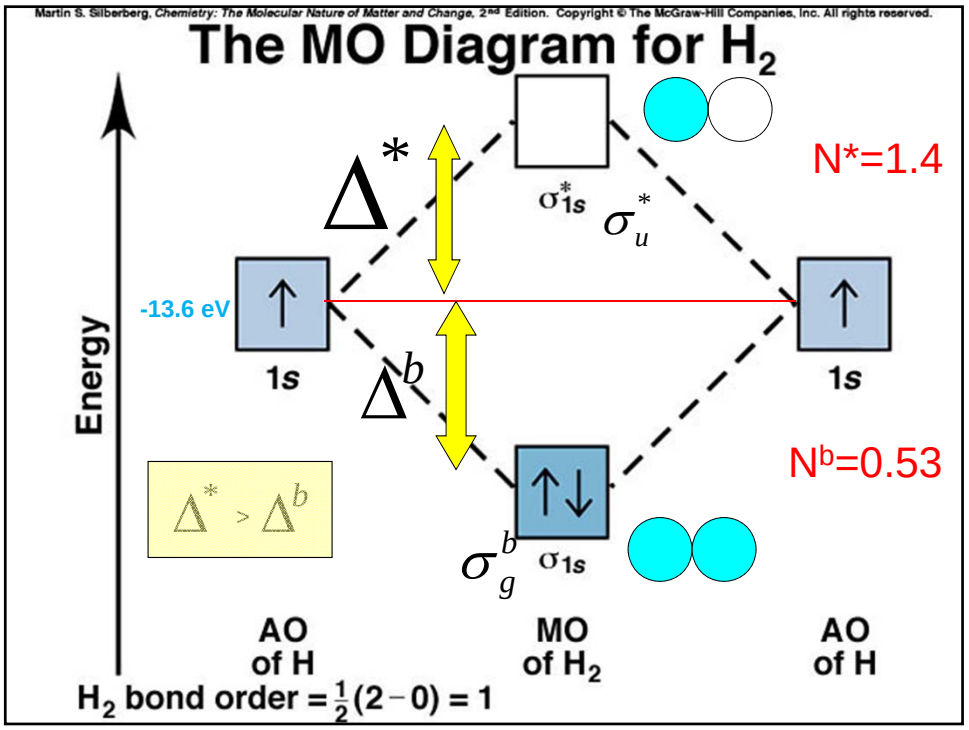
a, b, exchange position, MO does change, no inversion
odd parity, ungerade: German word for “odd”.

The energy of these two orbitals are obtained by applying Schrodinger Equation

Orbital Interaction Diagram

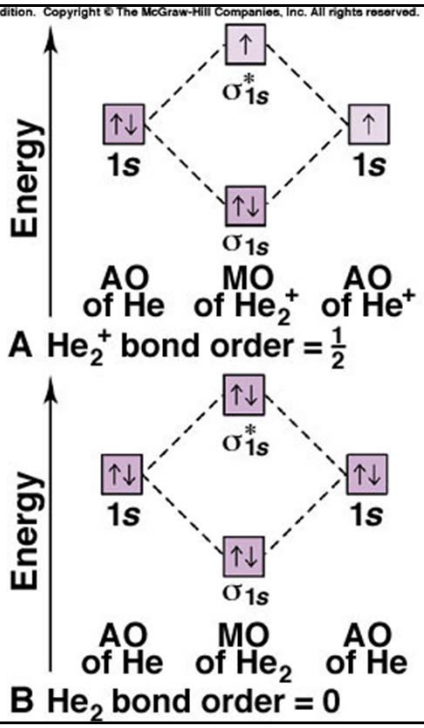
1. **Always draw axis**

2. **Fill in electron using Aufbau principle**



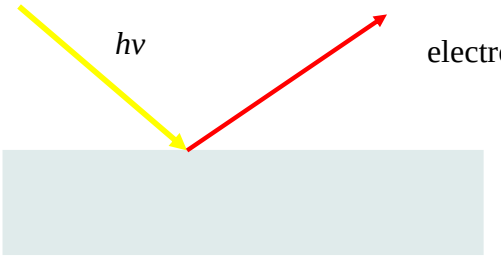
MO Diagrams of He_2^+ and He_2

- Bond order = ½ (#bonding e⁻s - #antibonding e⁻s)
- Bond order = 0 indicates the species will not exist.



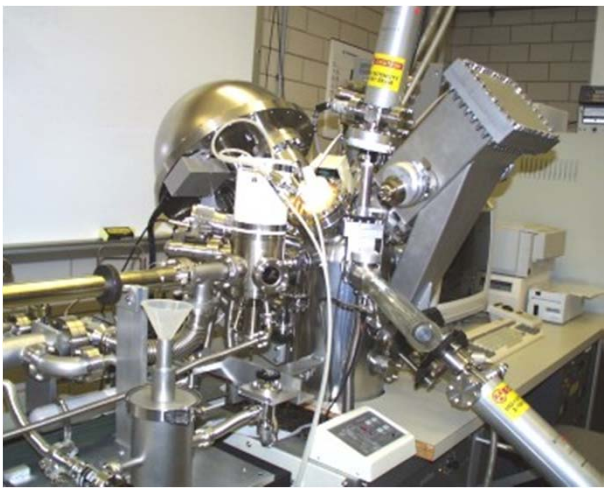
Photoelectron Spectroscopy

$$M + h\nu \rightarrow M^+ + e^-$$

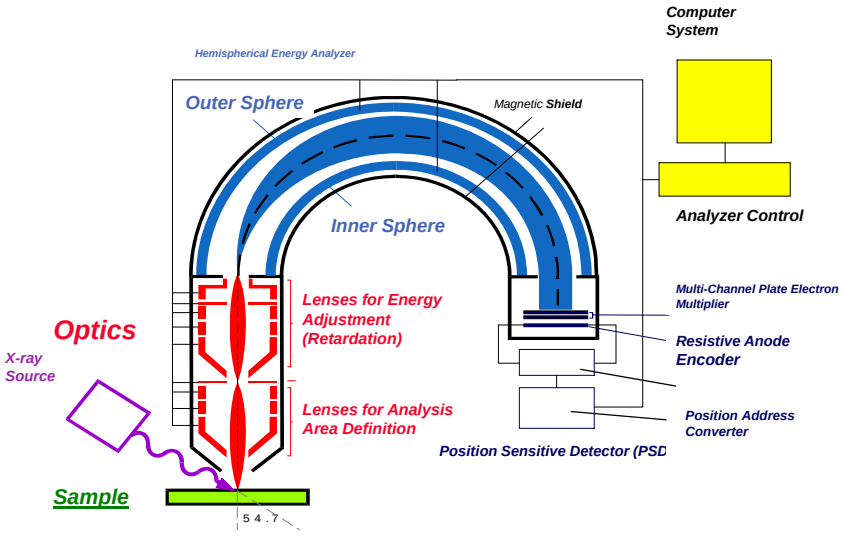


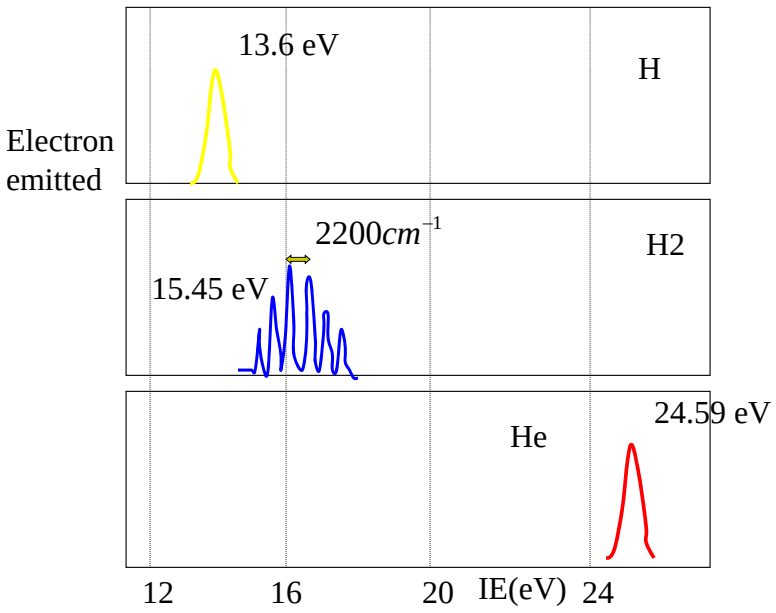
Photoelectric effect (Einstein)

$$h\nu = IE_M + \frac{1}{2}mv_e^2$$



PES instruments consist of an X-ray or UV source, an energy analyzer for the photoelectrons, and an electron detector.



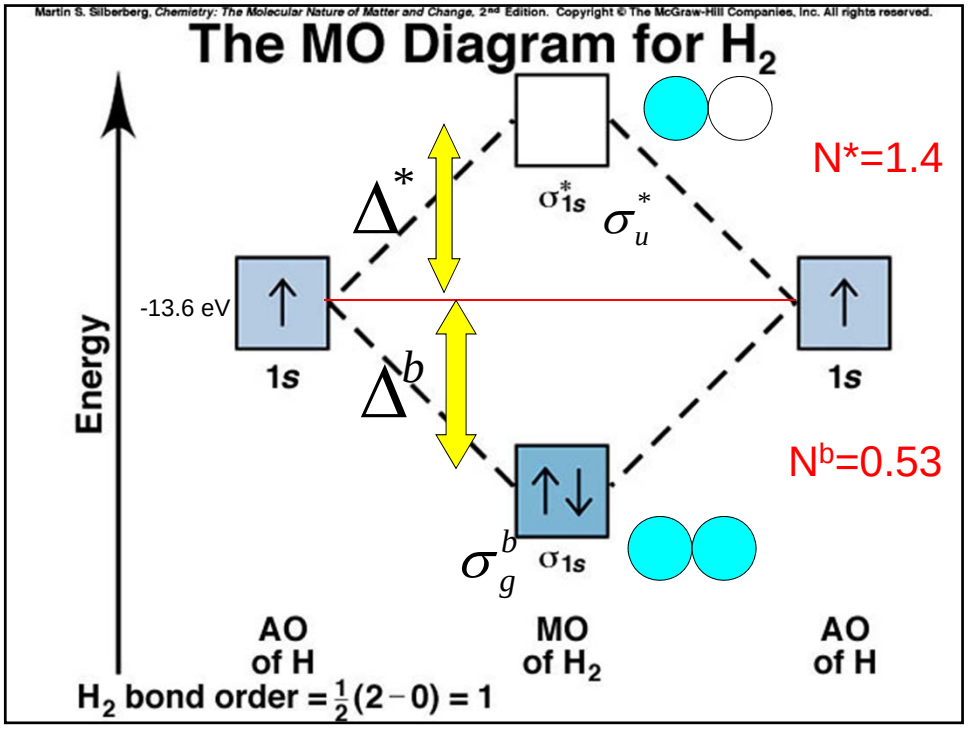


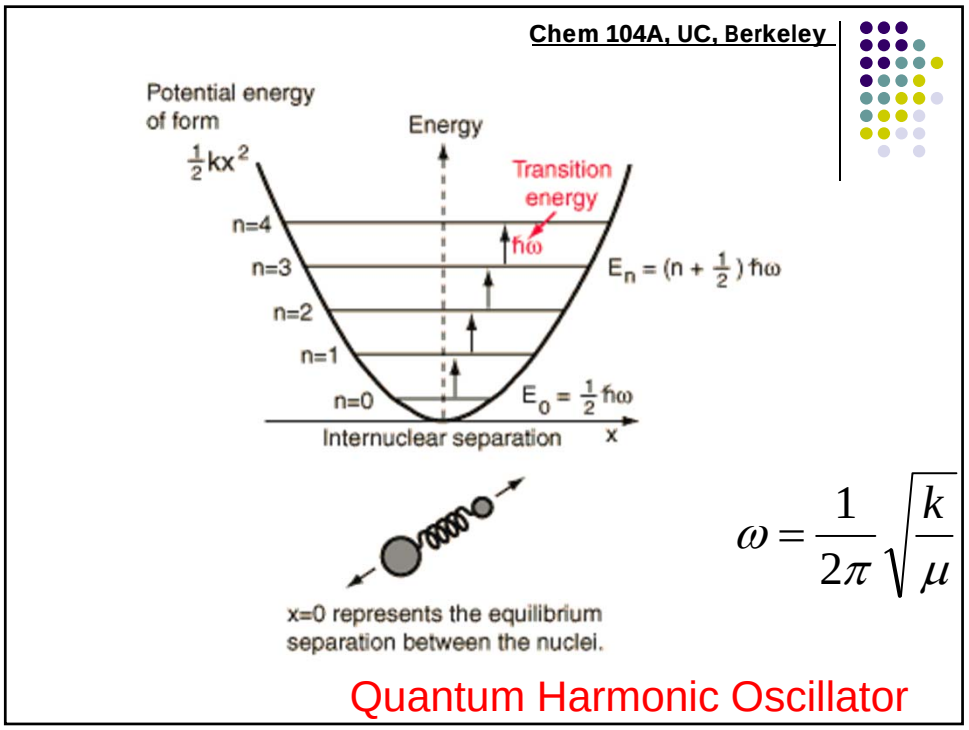
Koopman's Theorem

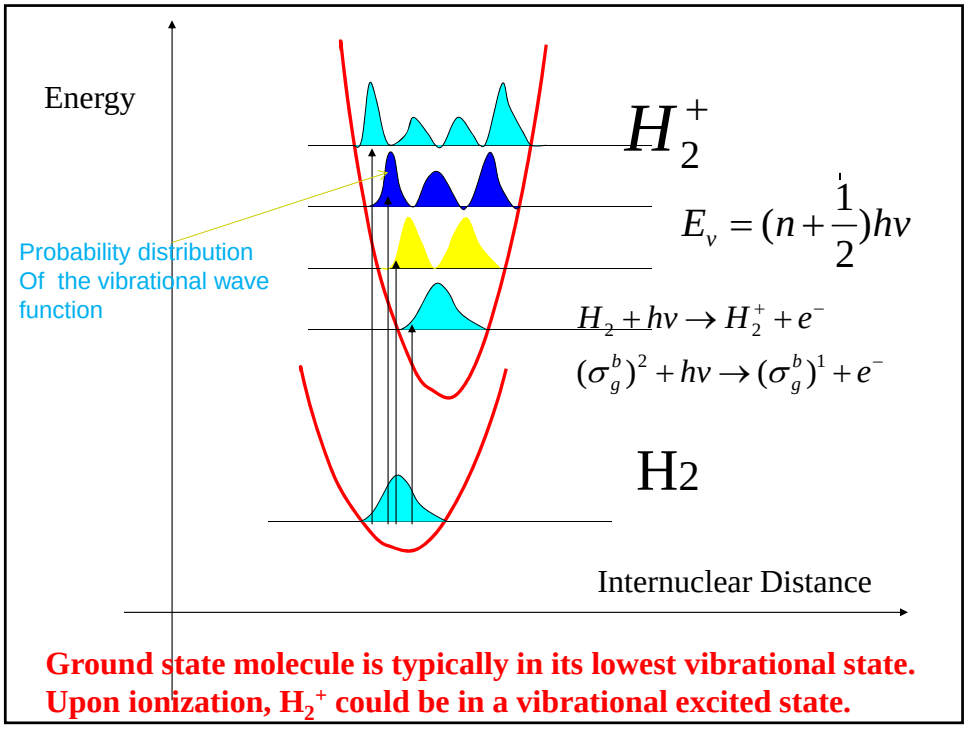
$IE\ (n) = -\ E_n$

The ionization energy of electron n is equal to the negative of its Orbital energy.

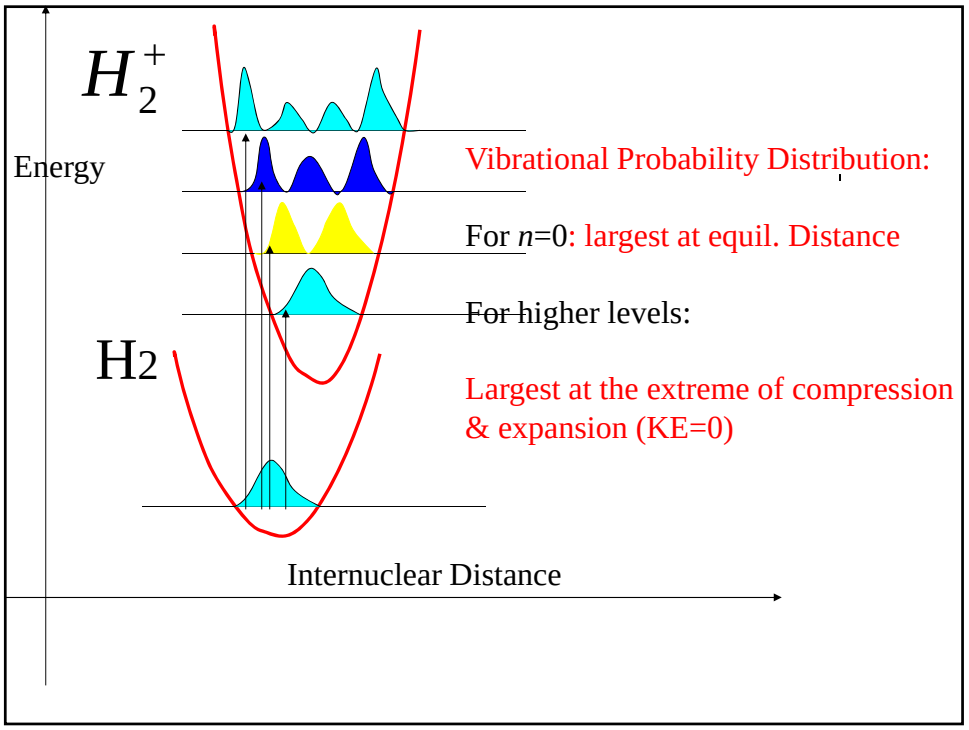
We can obtain orbital energies via PES!







Ground state molecule is typically in its lowest vibrational state. Upon ionization, H_2^+ could be in a vibrational excited state.

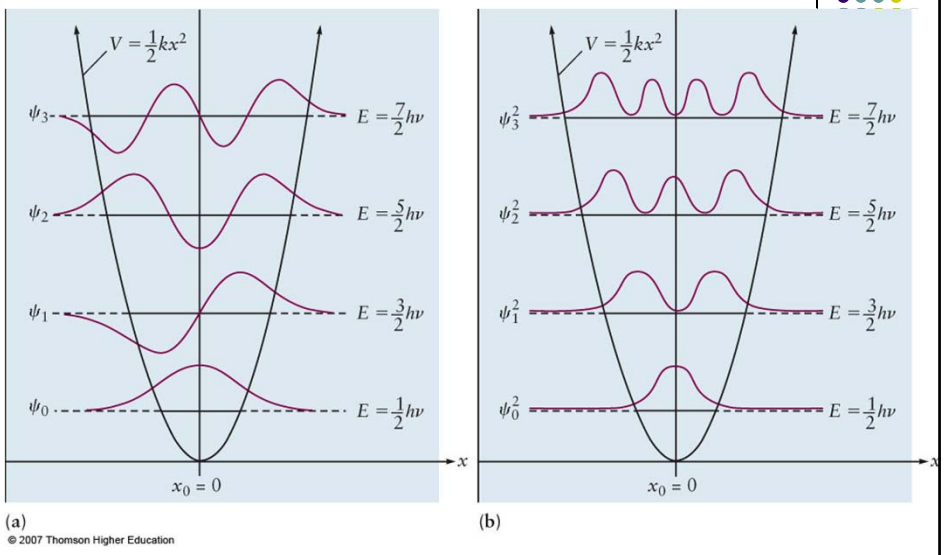


Vibrational Probability Distribution:

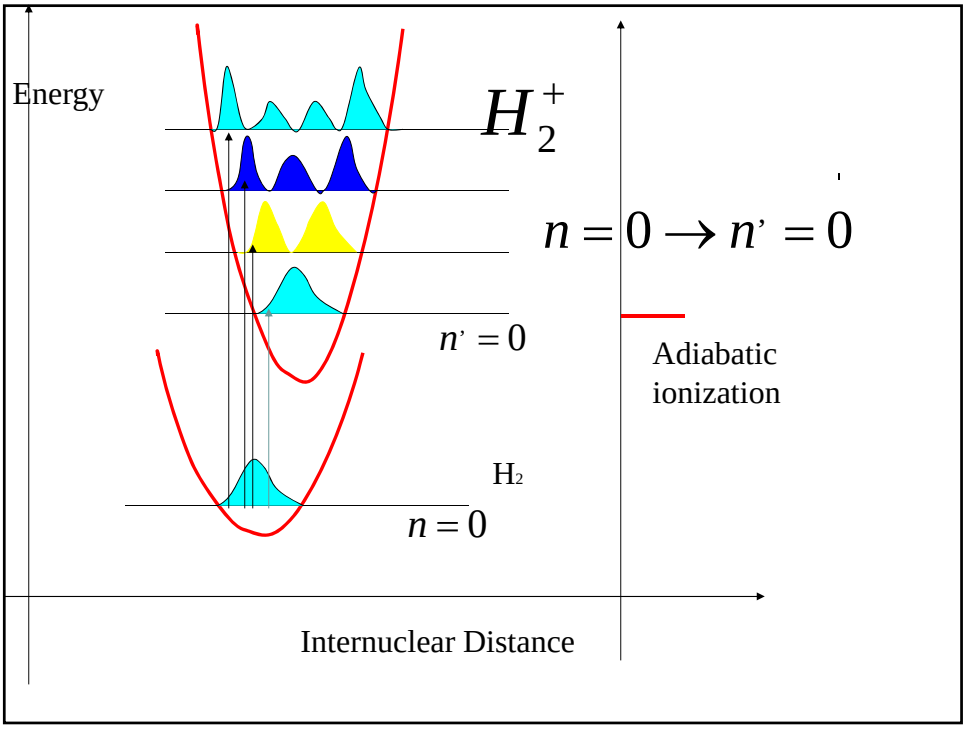
For n=0: largest at equil. Distance

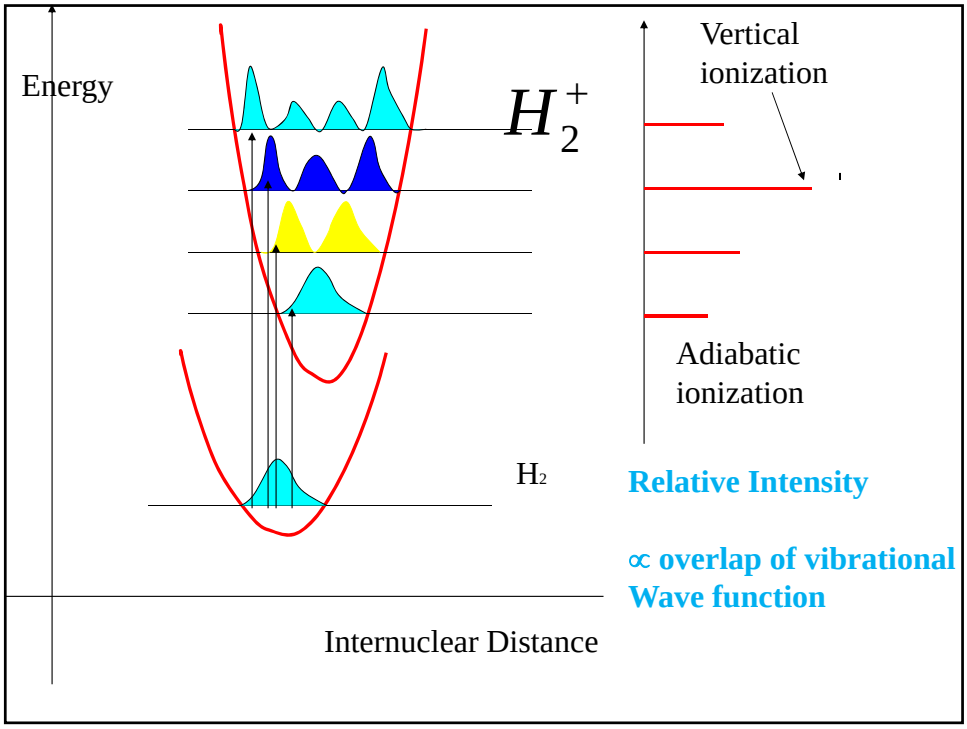
~~For~~ higher levels:

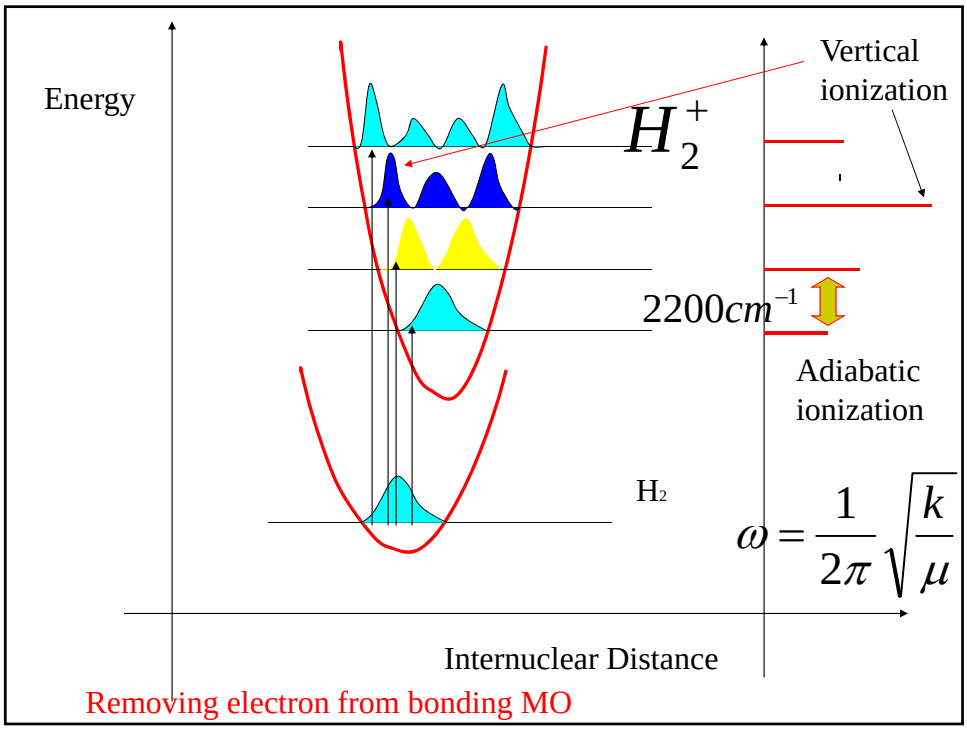
Largest at the extreme of compression & expansion (KE=0)

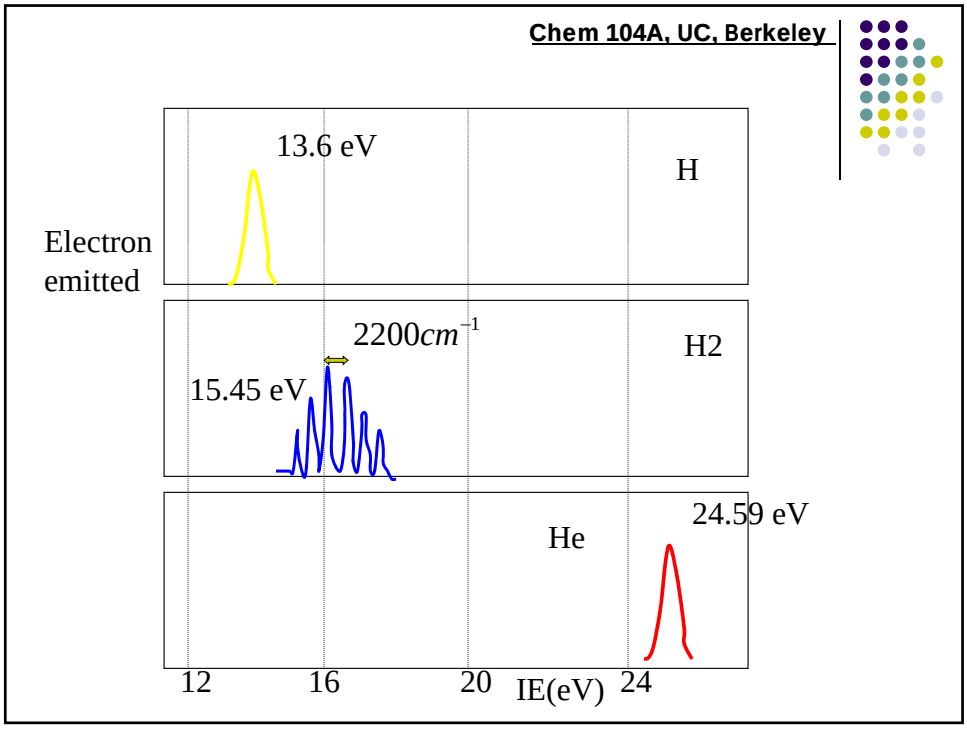


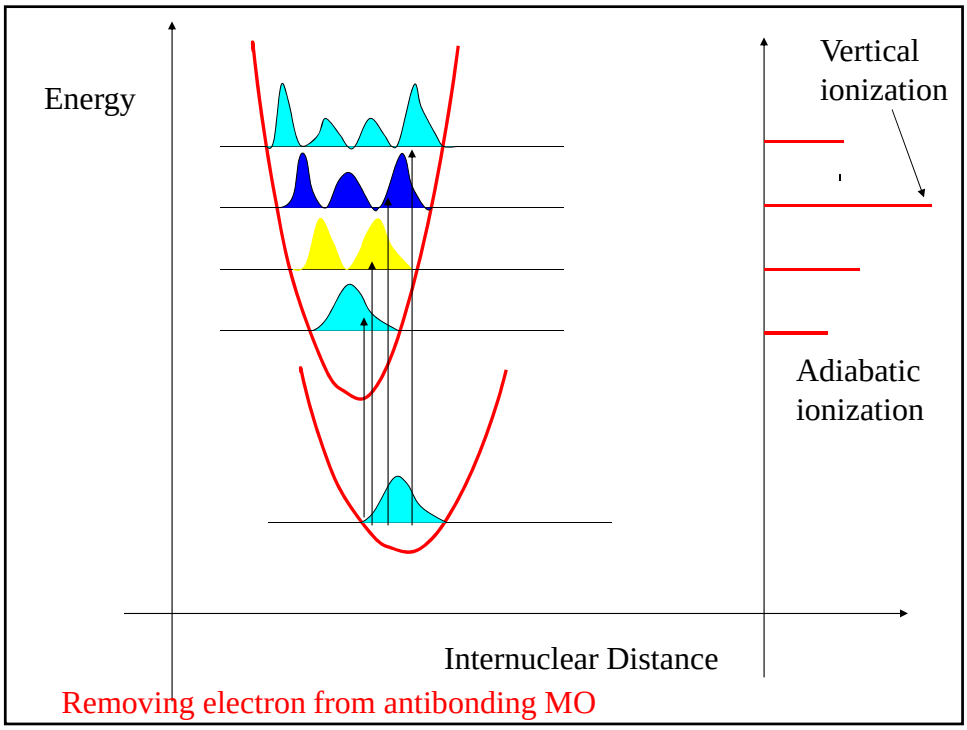
Wave functions, allowed energies, and corresponding probability densities for the harmonic oscillator



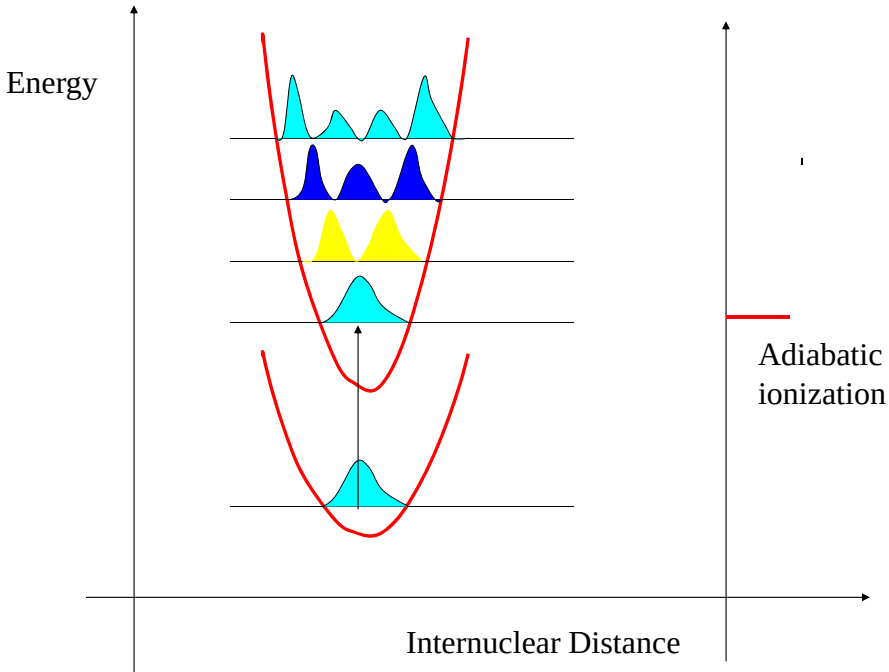

Energy
H_2^+
Vertical
ionization
Adiabatic
ionization
H_2
Relative Intensity
∝ overlap of vibrational
Wave function
Internuclear Distance


Energy
H_2^+
Vertical
ionization
$2200cm^{-1}$
Adiabatic
ionization
H_2
$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$
Internuclear Distance
Removing electron from bonding MO

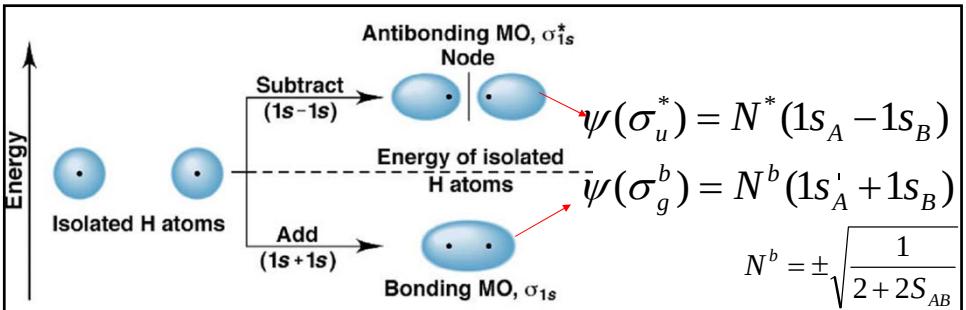




Removing electron from antibonding MO



Removing electron from nonbonding MO



$$\psi(\sigma_u^*) = N^*(1s_A - 1s_B)$$

$$\psi(\sigma_g^b) = N^b(1s_A' + 1s_B)$$

$$N^b = \pm\sqrt{\frac{1}{2+2S_{AB}}}$$

$$N^* = \pm\sqrt{\frac{1}{2-2S_{AB}}}$$

Overlap integral
Degree of spatial overlap between any two AOs
From different atoms in a molecule.

Degree of AO interaction is closely related to their overlap

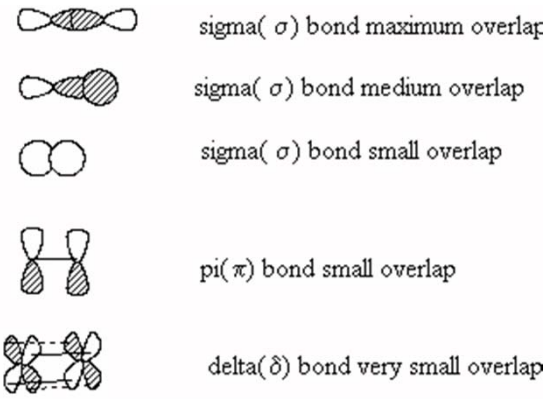
Functions of distance, symmetry.

S_{AB} >0, bonding interaction, E stabilized

σ

π

δ



S_{AB} <0, antibonding interaction, E destabilized

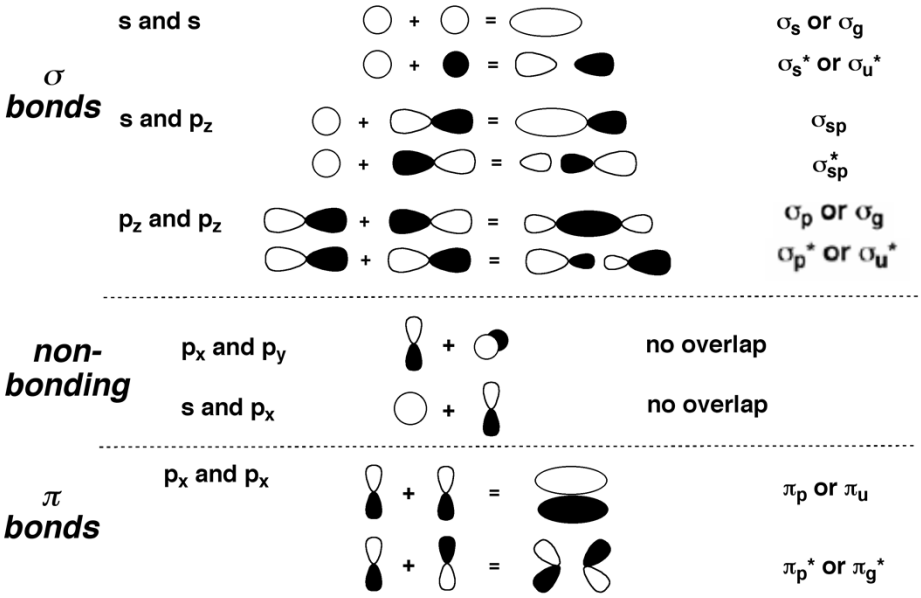
σ^*

π^*

δ^*

S_{AB} =0, nonbonding, no orbital interaction.

MO Theory: Bonding Types



MO Theory: Bonding Types (continued)