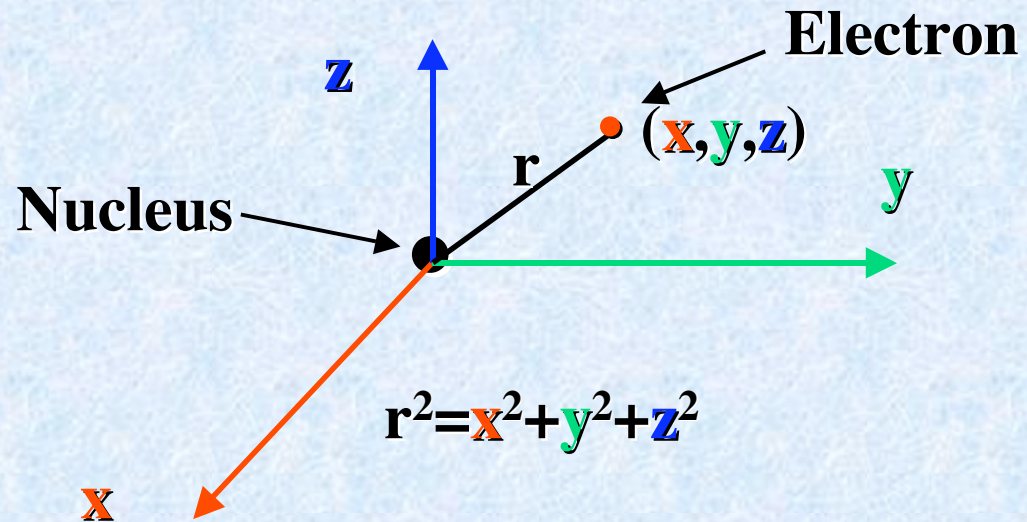


Chemical Bonding

Hydrogen atom based atomic **orbitals** a.k.a. hydrogen atom **wavefunctions**: 1s, 2s, 2p, 3s, 3p, 3d,

$$\psi_{1s} = 1/(\pi)^{1/2}(1/a_0)^{3/2} \exp[-r/a_0], a_0 = \text{Bohr Radius} = 0.529 \text{ Angstroms}$$



Orbitals, Wavefunctions and Probabilities

The orbital or wavefunction is just a mathematical function that can have a **magnitude** and **sign** (e.g. + 0.1 or -0.2) at a given point r in space.

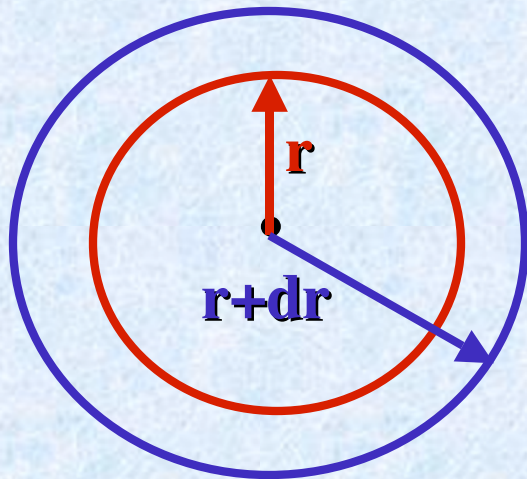
Probability of finding a 1s electron at a particular point in space is often not as interesting as finding the electron in a thin shell between r and $r+dr$.

Orbitals, Wavefunctions and Probabilities

Probability of finding a 1s electron in thin shell
between r and $r+dr$:

$$\text{Prob}(r, r+dr) \sim \psi_{1s}^2 [r^2] dr$$

Volume of shell of thickness dr :

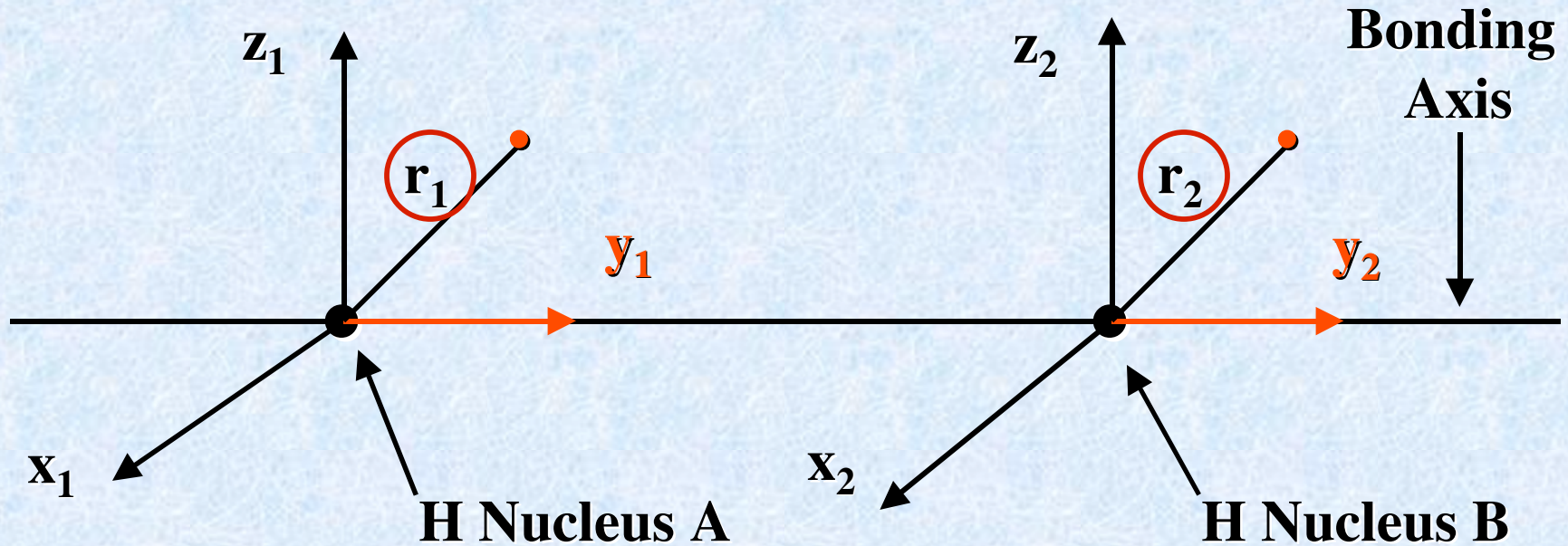


$$dV = (4/3)\pi [r^3 + 3r^2 dr + 3r(dr)^2 + (dr)^3 - r^3]$$

$$dV \approx (4\pi) [r^2 dr]$$

$$[r \gg dr \Rightarrow 3r^2 dr \gg 3r(dr)^2 + (dr)^3]$$

Bonding in Diatomic Molecules such as H₂



$$\psi_{1s}(A) = 1/(\pi)^{1/2}(1/a_0)^{3/2} \exp[-r_1/a_0], \text{ 1s orbital for atom A}$$



Note the two orbitals are centered at different points in space.

$\psi_{1s} = C_1[\psi_{1s}(A) + \psi_{1s}(B)]$, Sigma 1s **Bonding Molecular** orbital. C_1 is a constant.

Note that probabilities for finding electron at some position in space scale like $[\psi_{1s}]^2$ and $[\psi_{1s}^*]^2$:

$$[\psi_{1s}^*]^2 = \{C_2[\psi_{1s}(A) - \psi_{1s}(B)]\}^2 = \underbrace{(C_2)^2\{[\psi_{1s}(A)]^2 + [\psi_{1s}(B)]^2\}} - 2[\psi_{1s}(A)][\psi_{1s}(B)]\}$$

“Non-interacting” part is result for large separation between nucleus A and B

$$[\psi_{1s}]^2 = \{C_1[\psi_{1s}(A) + \psi_{1s}(B)]\}^2 = \underbrace{(C_1)^2\{[\psi_{1s}(A)]^2 + [\psi_{1s}(B)]^2\}} + 2[\psi_{1s}(A)][\psi_{1s}(B)]\}$$

Notational Detail

Oxtoby uses two different notations for orbitals in the 4th and 5th editions of the class text:

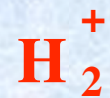
σ_{1s} in the 4th edition becomes σ_{g1s} in the 5th edition

σ_{1s}^* in the 4th edition becomes σ_{u1s}^* in the 5th edition

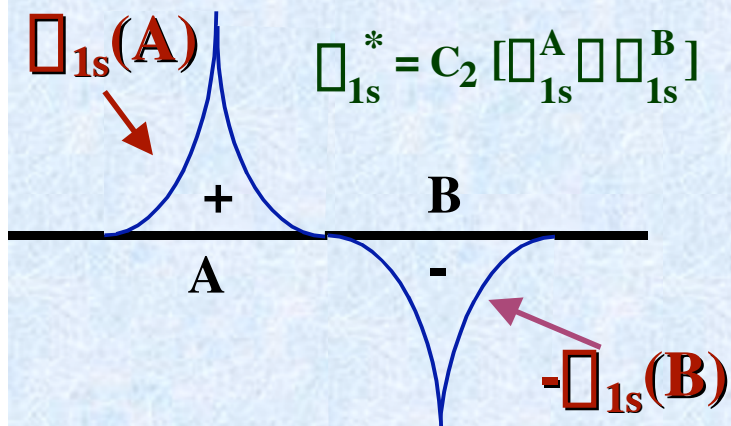
The addition of g and u provides some extra identification of the orbitals and is the one encountered in the professional literature.

g and u are from the German “gerade” and “ungerade”

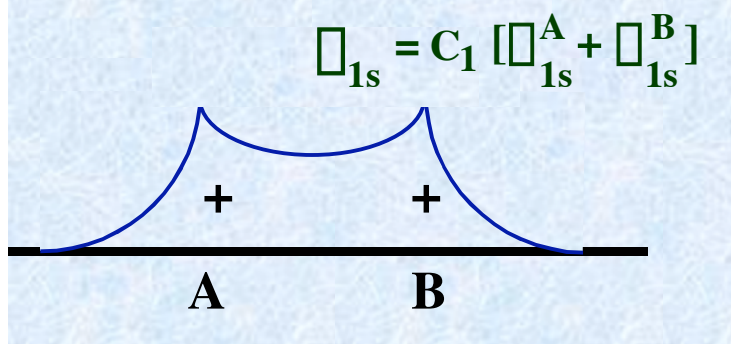
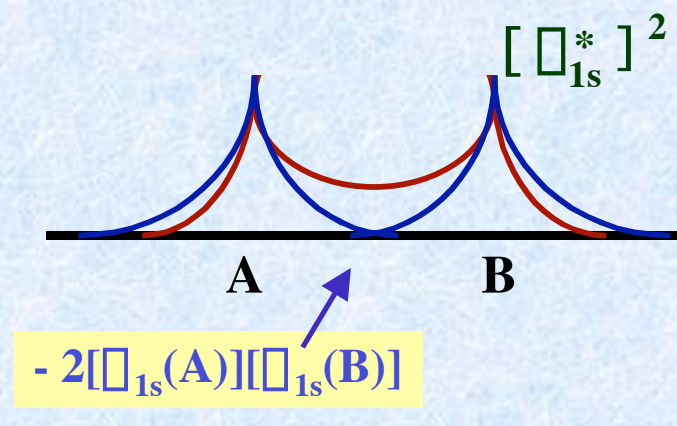
Wave Functions



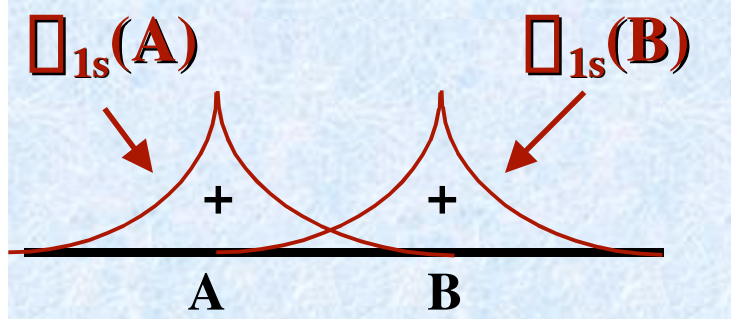
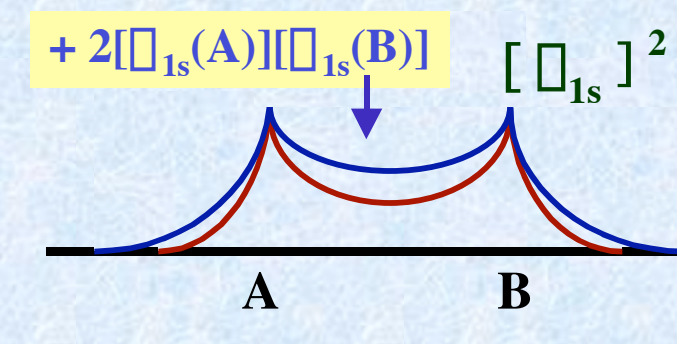
Electron Densities



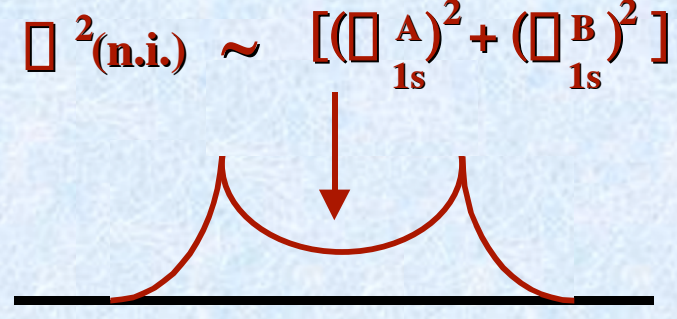
ANTIBONDING
Pushes e^- away from region between nuclei A and B



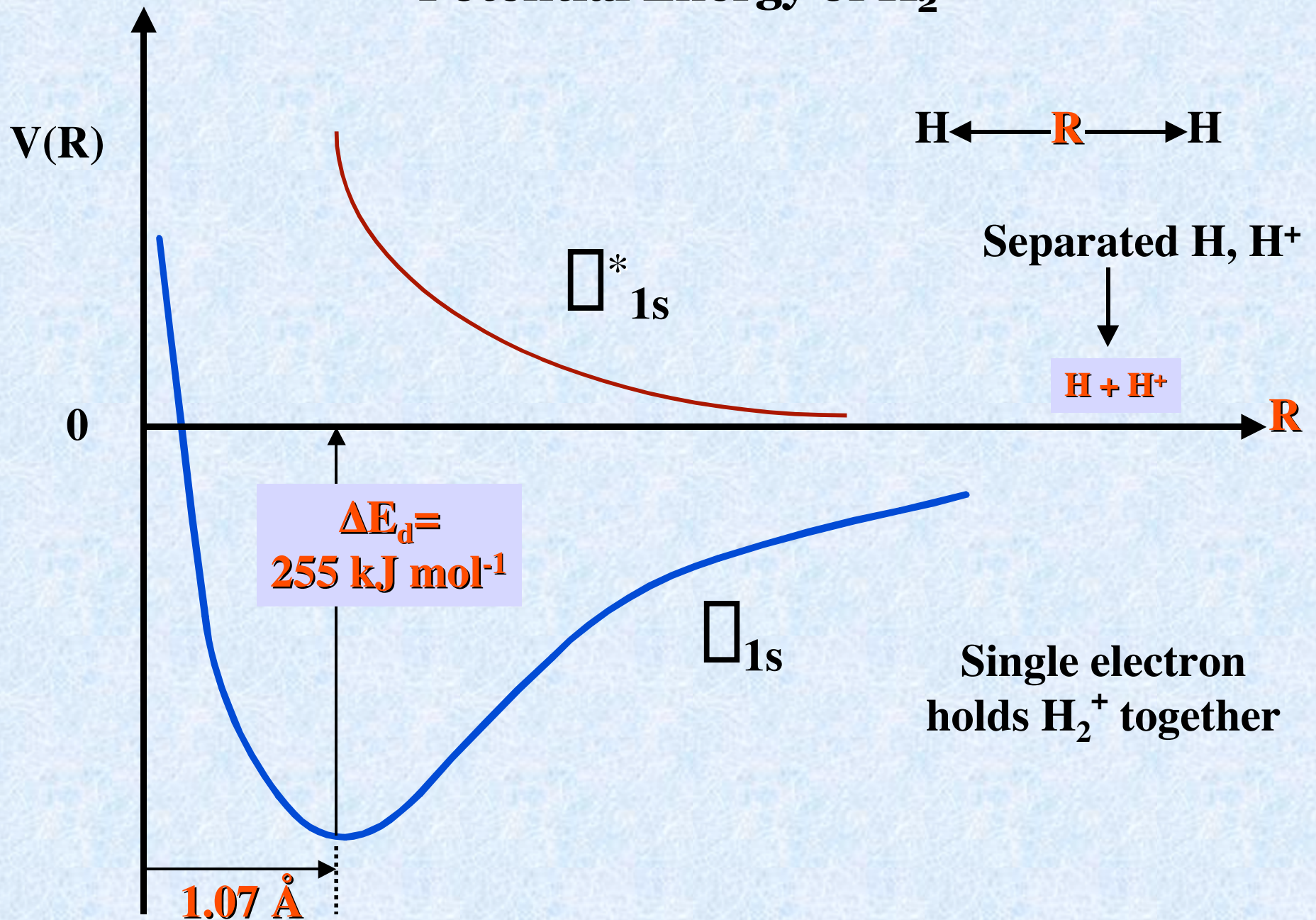
BONDING
Pushes e^- between nuclei A and B



NON-INTERACTING

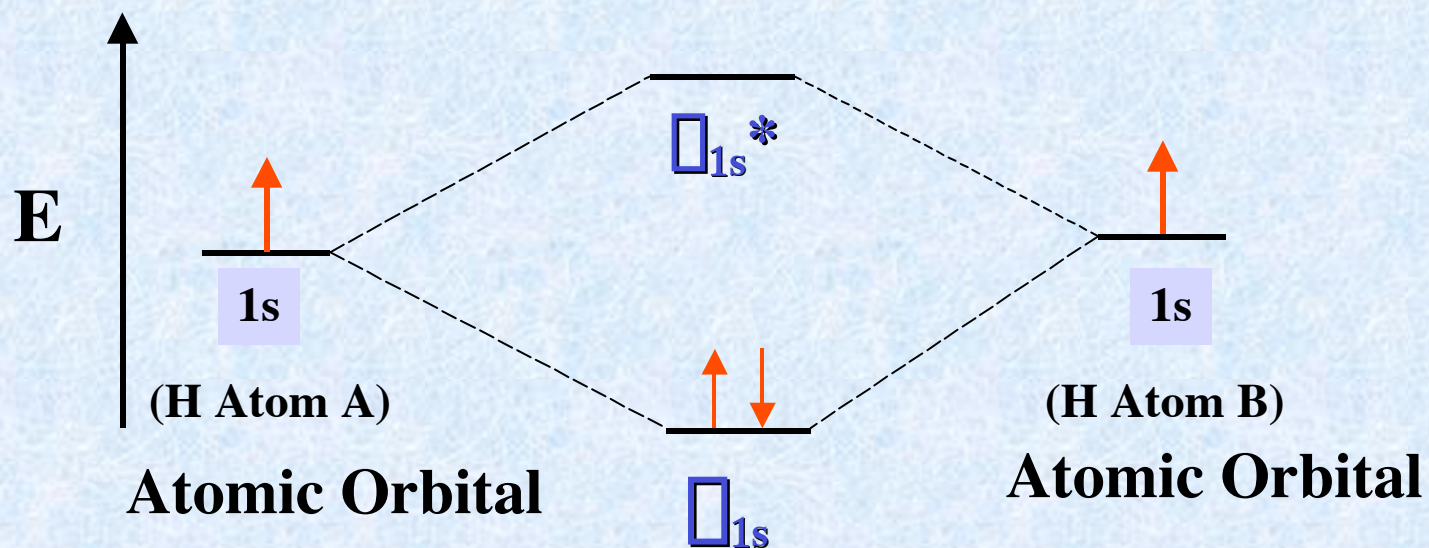
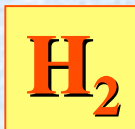


Potential Energy of H_2^+



Energy Ordering: CORRELATION DIAGRAM

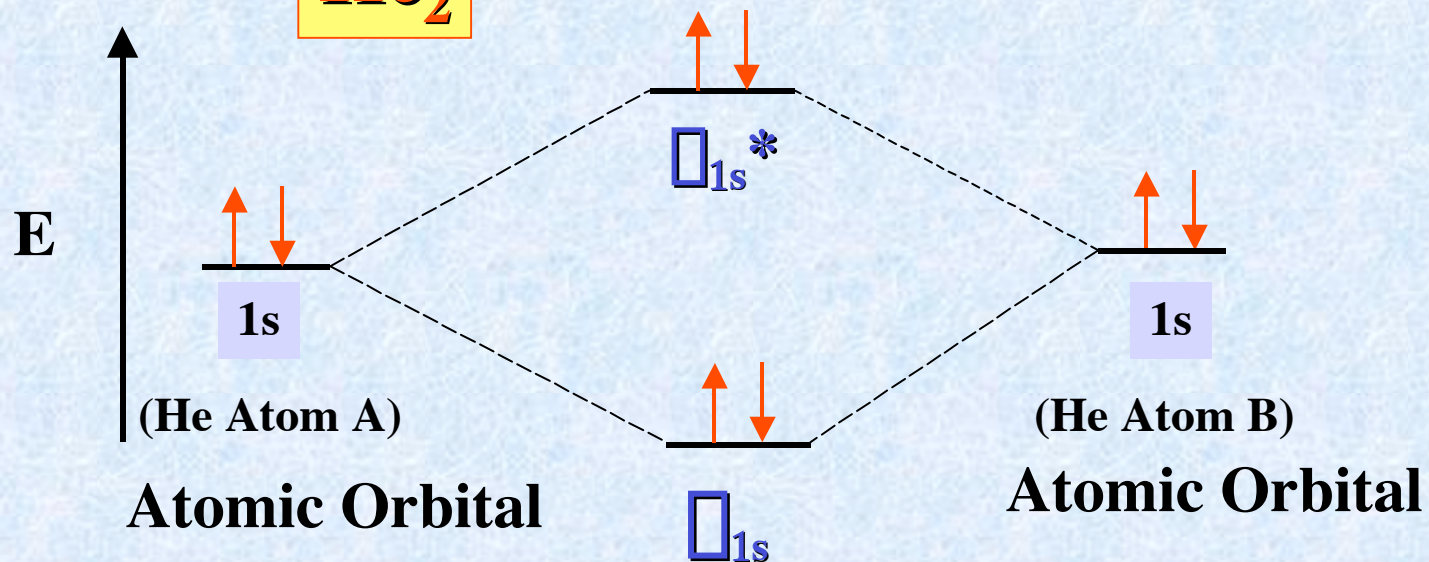
$$\sigma_{1s} < 1s < \sigma_{1s}^*$$



H₂ Molecular Orbitals

CORRELATION DIAGRAM

Z for He = 2



Atomic Orbital

Atomic Orbital

He₂ Molecular Orbitals

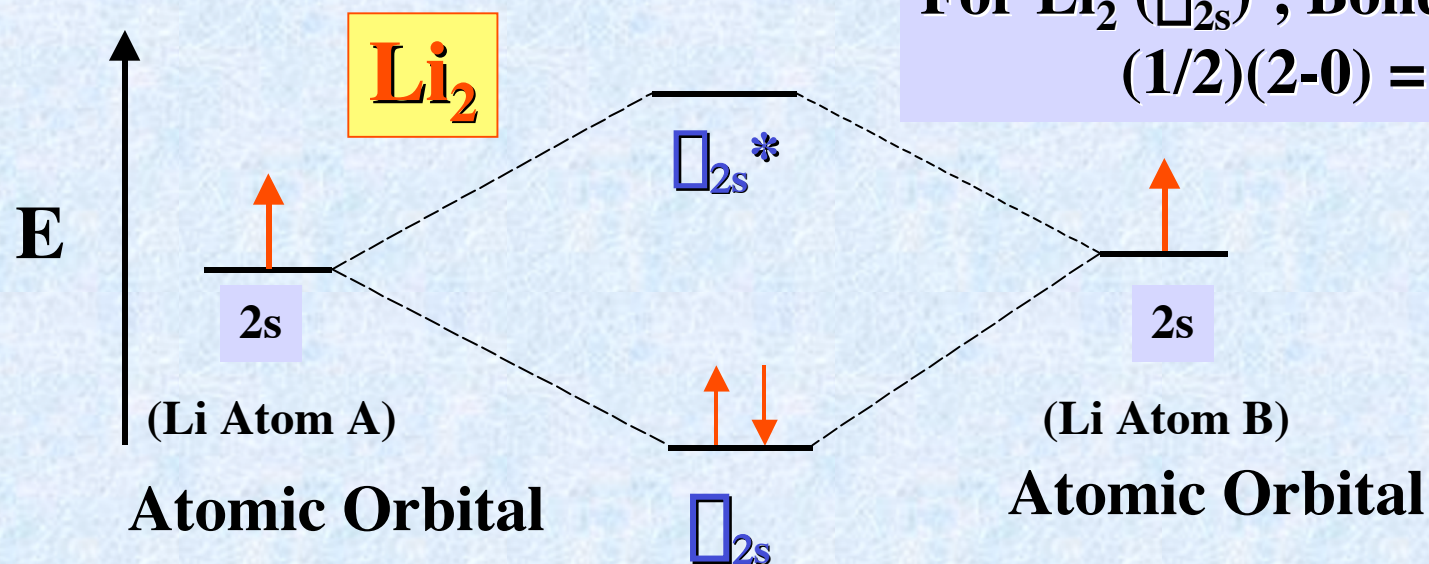
Bonding for Second Row Diatomics Involves the n=2 Atomic Shell

Lithium atomic configuration is $1s^2 2s^1$

(Only the 2s electron is a valence electron.)

Li_2 dimer has the configuration: $[(\sigma_{1s})^2(\sigma_{1s}^*)^2] (\sigma_{2s})^2 = [\text{KK}](\sigma_{2s})^2$

CORRELATION DIAGRAM



For $\text{Li}_2 (\sigma_{2s})^2$, Bond order = $(1/2)(2-0) = 1$

Li_2 Molecular Orbitals

Bonding for Second Row Diatomics: the Role of 2p Orbitals

Once the σ_{2s} , σ_{2s}^* molecular orbitals formed from the 2s atomic orbitals on each atom are filled (4 electrons, Be_2), we must consider the role of the 2p electrons (B_2 is first diatomic using 2p electrons).

There are 3 different sets of p orbitals ($2p_x$, $2p_y$, and $2p_z$), all mutually perpendicular. If we choose the molecular diatomic axis to be the z axis (this is arbitrary), we have a picture like this:



