

If we define $G_i = G^\circ (P_i = 1 \text{ atm})$ then

where P_f must be expressed in atmospheres.

In general for 1 mole ideal gas

Shows how G depends on P at fixed T if know $G^\circ(T)$.


To distinguish G for 1 mole, call it $\square (T, P) = \square^\circ (T) + RT \ln P$

μ is free energy/mole for an ideal gas at T and P. (Called chemical potential)

For n moles $n\mu = n\mu^\circ + nRT \ln P$

Consider now the Chemical reaction:

Free Energy for 1 mole
of ideal gas D at a partial
pressure of P_D



$$\Delta G = c[\mu_C^\circ + RT \ln P_C] + d[\mu_D^\circ + RT \ln P_D] - a[\mu_A^\circ + RT \ln P_A] - b[\mu_B^\circ + RT \ln P_B]$$

$$\Delta G = \Delta G^\circ + cRT \ln P_C + dRT \ln P_D - aRT \ln P_A - bRT \ln P_B$$

True for **arbitrary** values of P_C, P_D, P_A, P_B

Since initial and final states are in eq. ΔG is not neg for either direction. $\square \Delta G = 0 \square$

$$\text{But } K_p = \{(P_{Ceq})^c (P_{Deq})^d / (P_{Aeq})^a (P_{Beq})^b\}!$$

$$\Delta G^\circ = -RT \ln K_p$$

Remarkably important formula relates free energy and K_p .

$$K_p = e^{-\Delta G^\circ/RT} = 10^{-\Delta G^\circ/2.303RT}$$

$\Delta G^\circ > 0 \Rightarrow$ exponent < 0 $K_p < 1$

Bonus * Bonus * Bonus *
Bonus * Bonus * Bonus

Remember old rule for shift in eq. with T. Equilibrium shifts to left for an exothermic reaction and to right for an endothermic reaction.

Shift in Equilibrium with temperature:

$\Delta H^\circ < 0$ means heat released (exothermic)



$\Delta H^\circ < 0$ means heat released (exothermic)



Think of heat as a reagent that works like common ion effect:



$\Delta H^\circ > 0$ heat absorbed (endothermic)



$$K_p = e^{-\Delta H^\circ/RT} e^{\Delta S^\circ/R}$$

Increasing T causes $\Delta H^\circ/RT$ and hence $e^{+\Delta H^\circ/RT}$ to get smaller.

K_p increases and equilibrium shifts to right.

Connecting Kinetics and Equilibria

By definition, **kinetic processes** are not **equilibrium processes**. In fact, we may think of kinetic processes as the mechanism that nature uses to reach the equilibrium state.

$k_f[A]_e[B]_e = k_r[C]_e[D]_e$ (Equilibrium condition)

Where $[A]_e$ etc. are the equilibrium concentrations of $[A]$ etc.

Using the Arrhenius form for the rate constants k_f and k_r

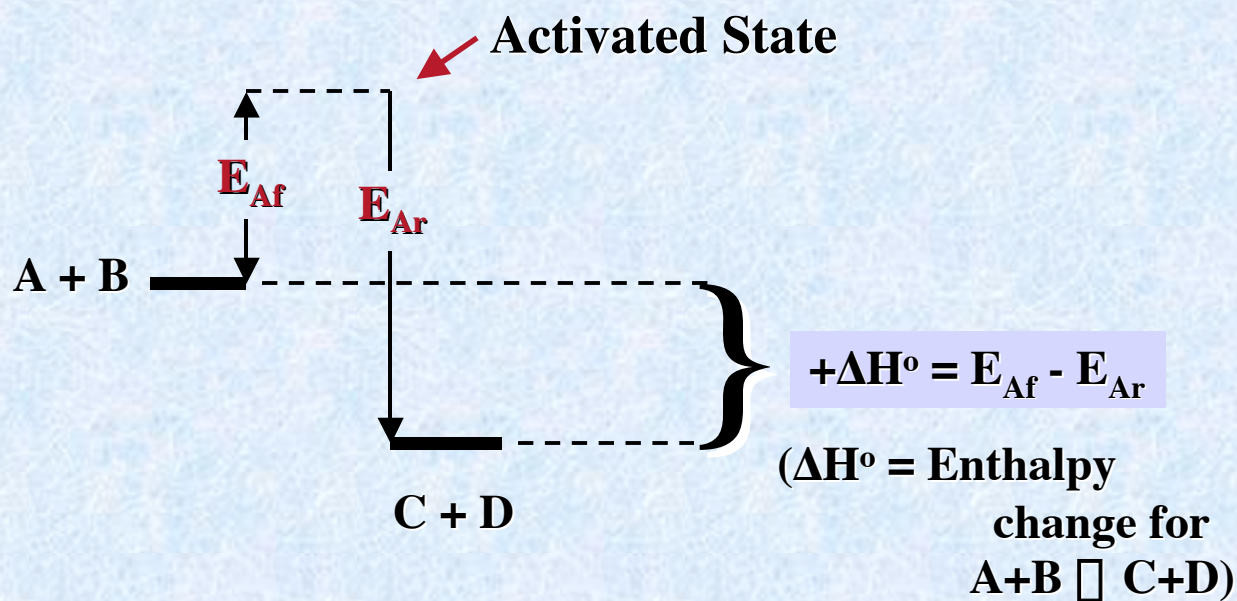
$$\mathbf{k_f = A_f e^{-E_{Af}/RT} \quad k_r = A_r e^{-E_{Ar}/RT}}$$

But as we just learned (or you already knew from high school):

Where ΔH^0 is the enthalpy change for the reaction and ΔS^0 is the entropy change for the reaction. ΔG^0 is the Free Energy

Equating these two forms for the equilibrium constant allows us to connect thermodynamics and kinetics!

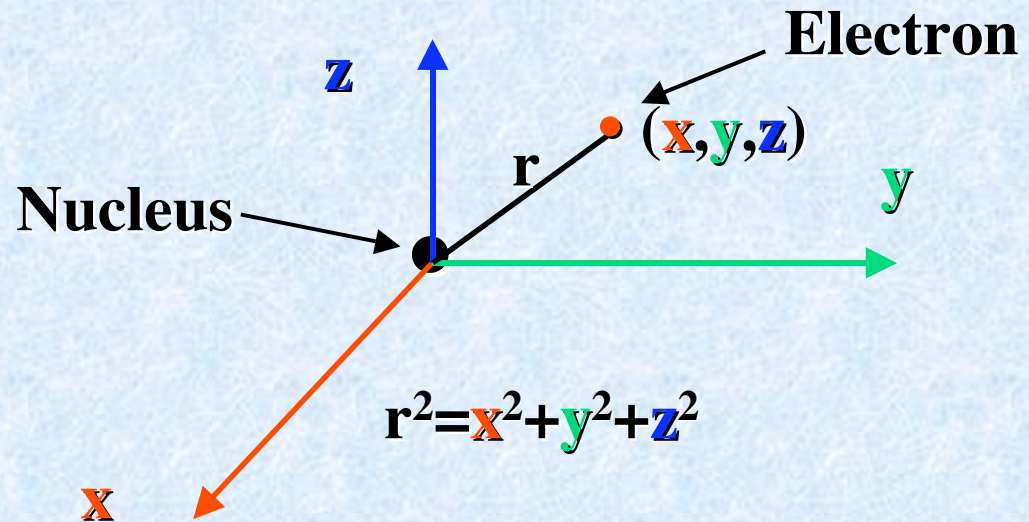
$$(A_f/A_r) \exp [-(E_{Af}-E_{Ar})/RT] = \{e^{(\Delta S^\circ/R)}\} \cdot \{e^{(-\Delta H^\circ/RT)}\}$$



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.

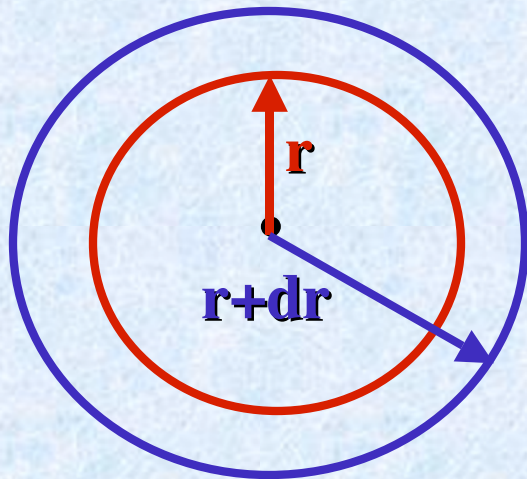
Probability of finding a 1s electron at a particular point in space is often not as interesting as finding the electron in a thin shell between r and $r+dr$.

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 :

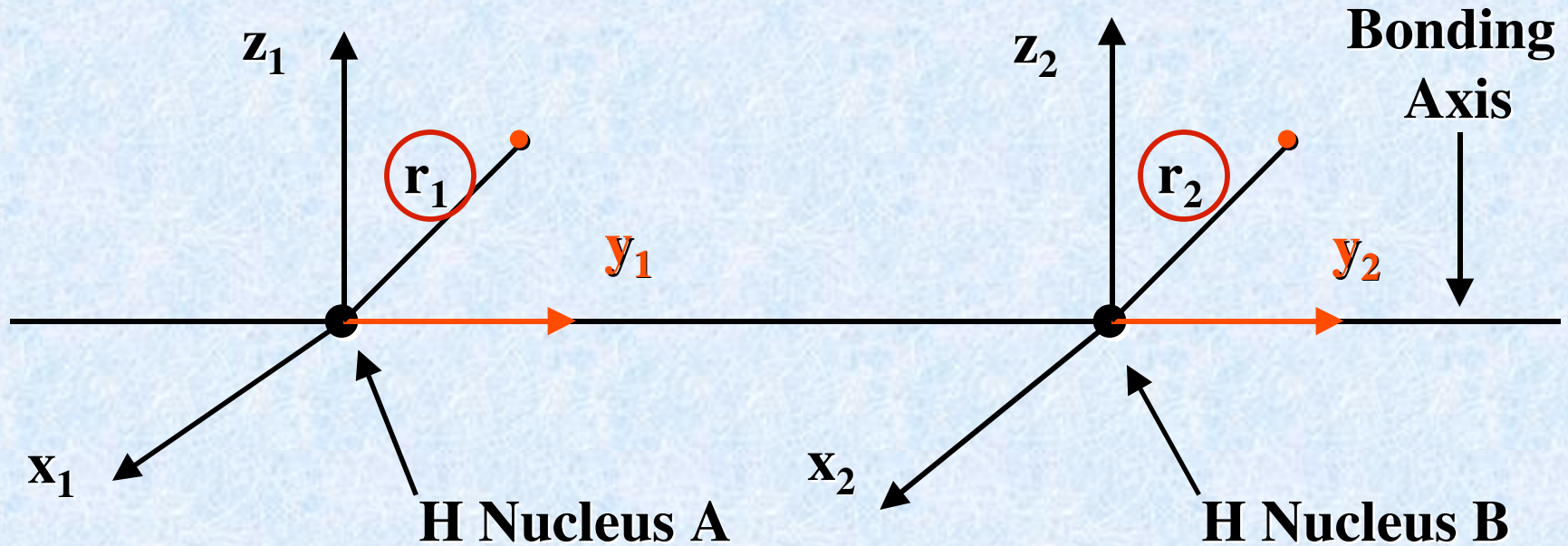


$$dV = (4/3)\pi [(r+dr)^3 - r^3]$$

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

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

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:

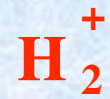
σ_{1s} in the 4th edition becomes σ_{g1s} in the 5th edition

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

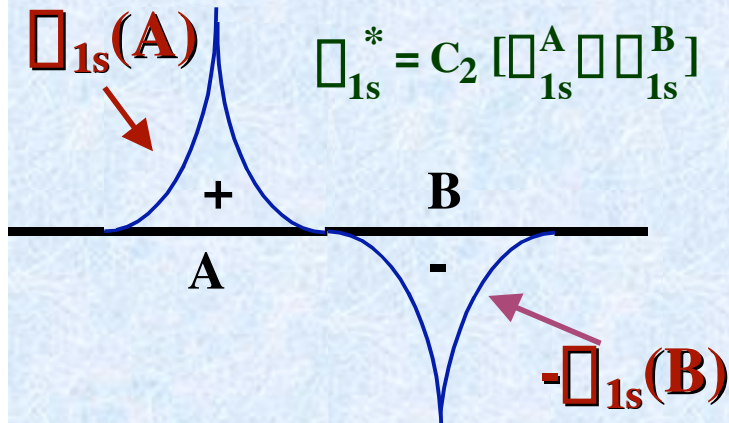
The addition of g and u provides some extra identification of the orbitals and is the one encountered in the professional literature.

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

Wave Functions

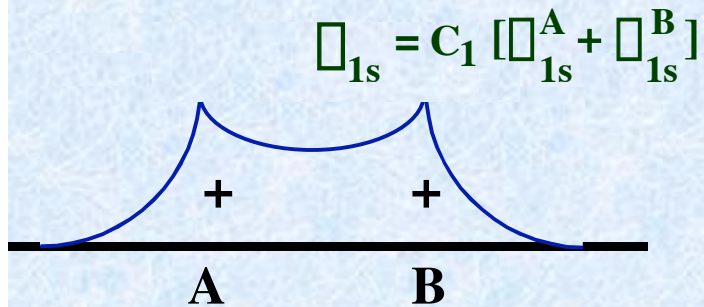
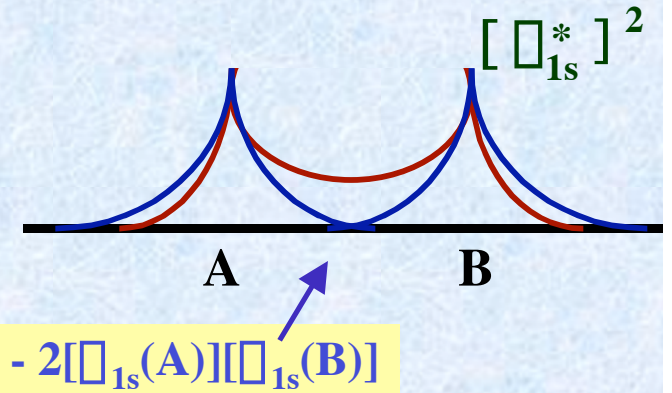


Electron Densities



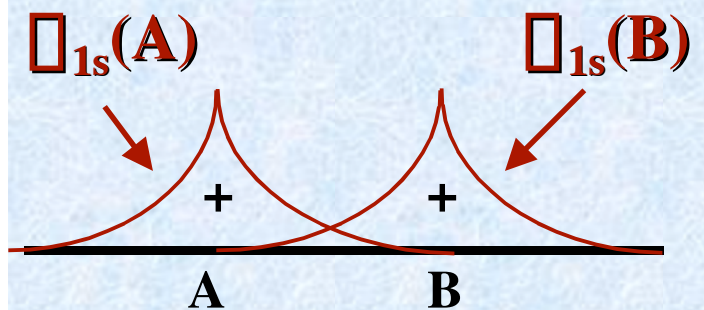
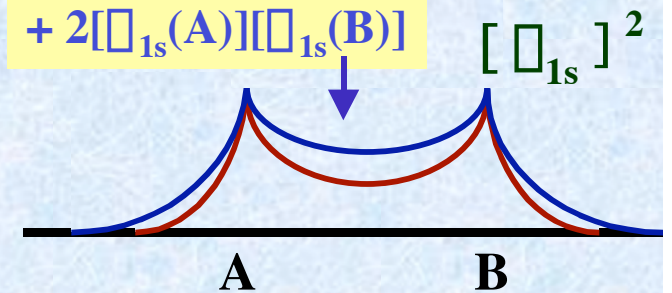
ANTIBONDING

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

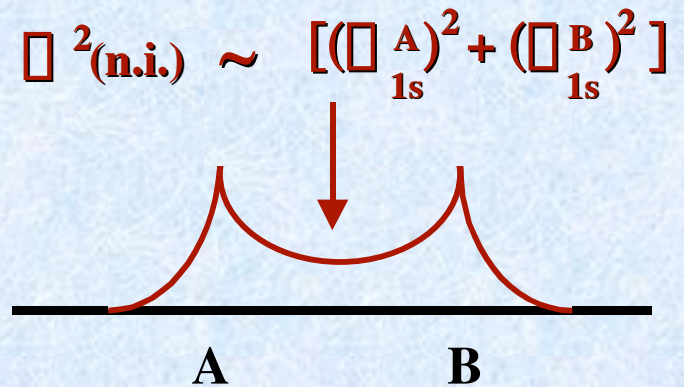


BONDING

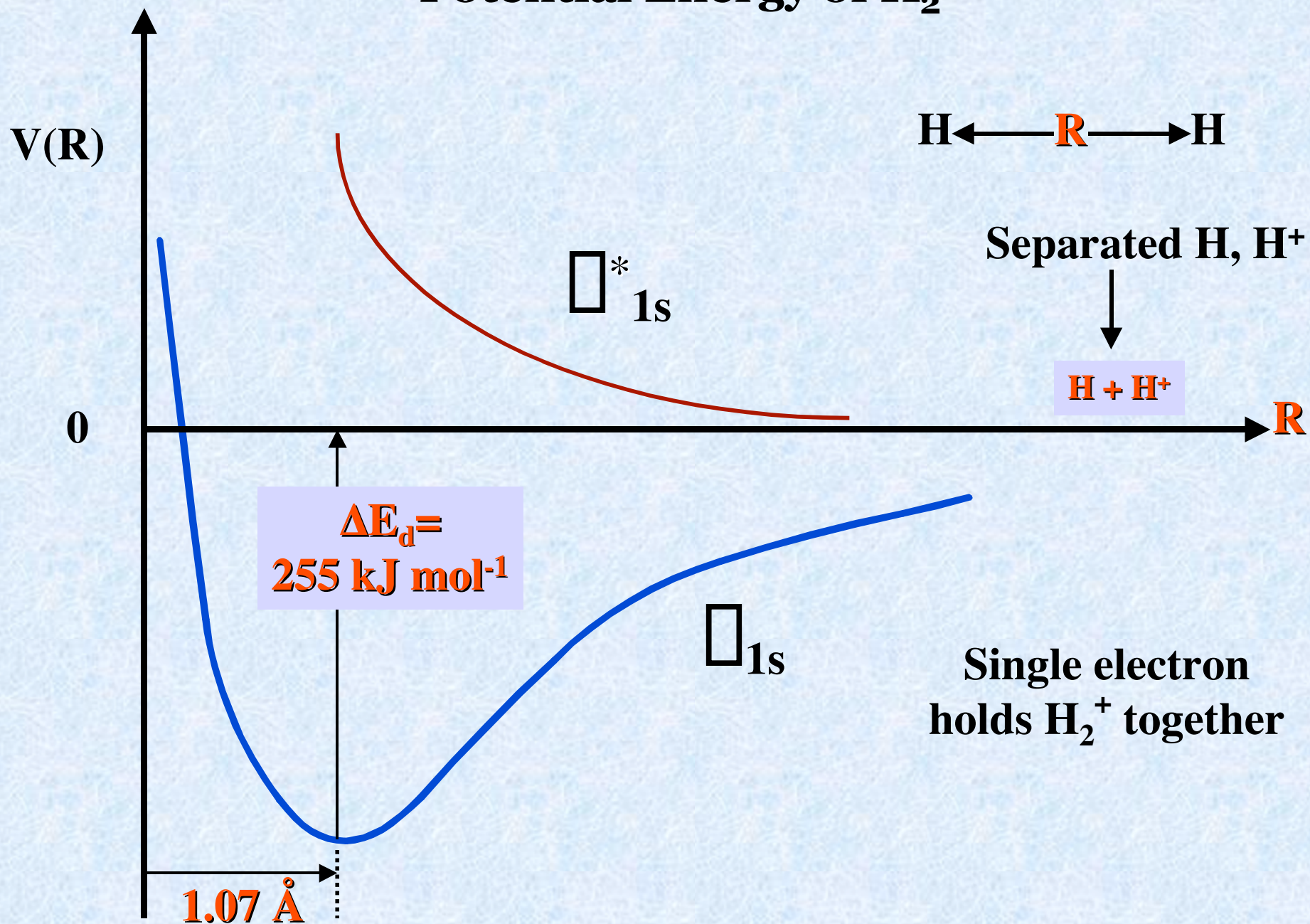
Pushes e^- between nuclei A and B



NON-INTERACTING

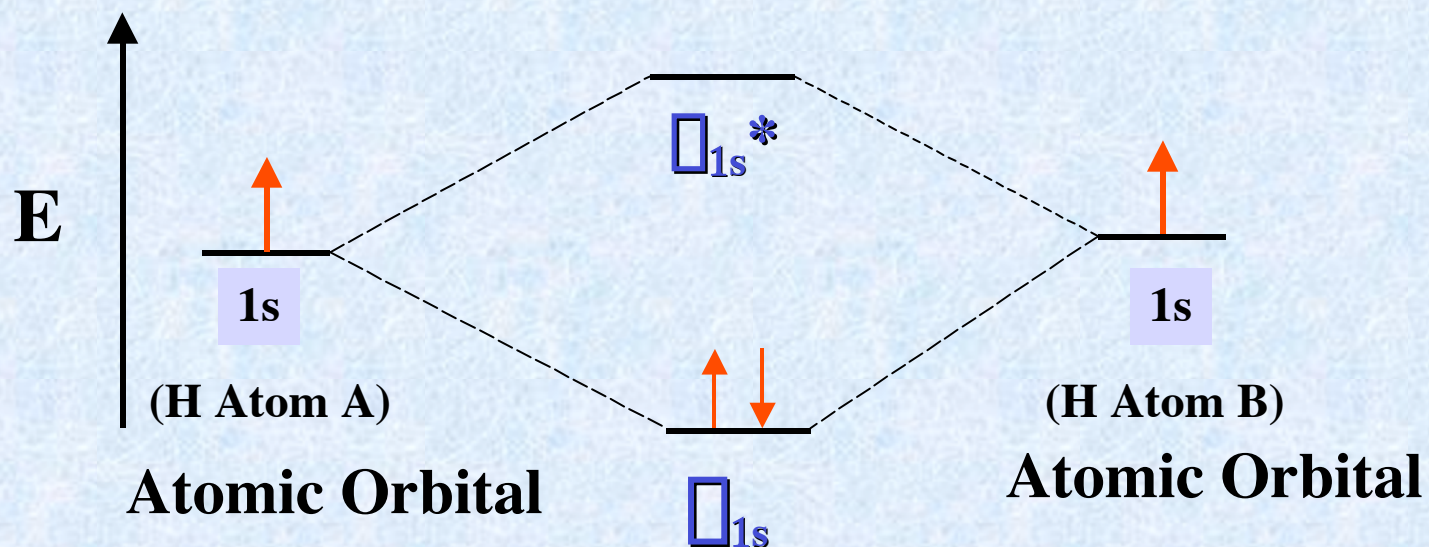
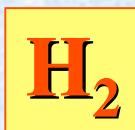


Potential Energy of H_2^+



Energy Ordering: CORRELATION DIAGRAM

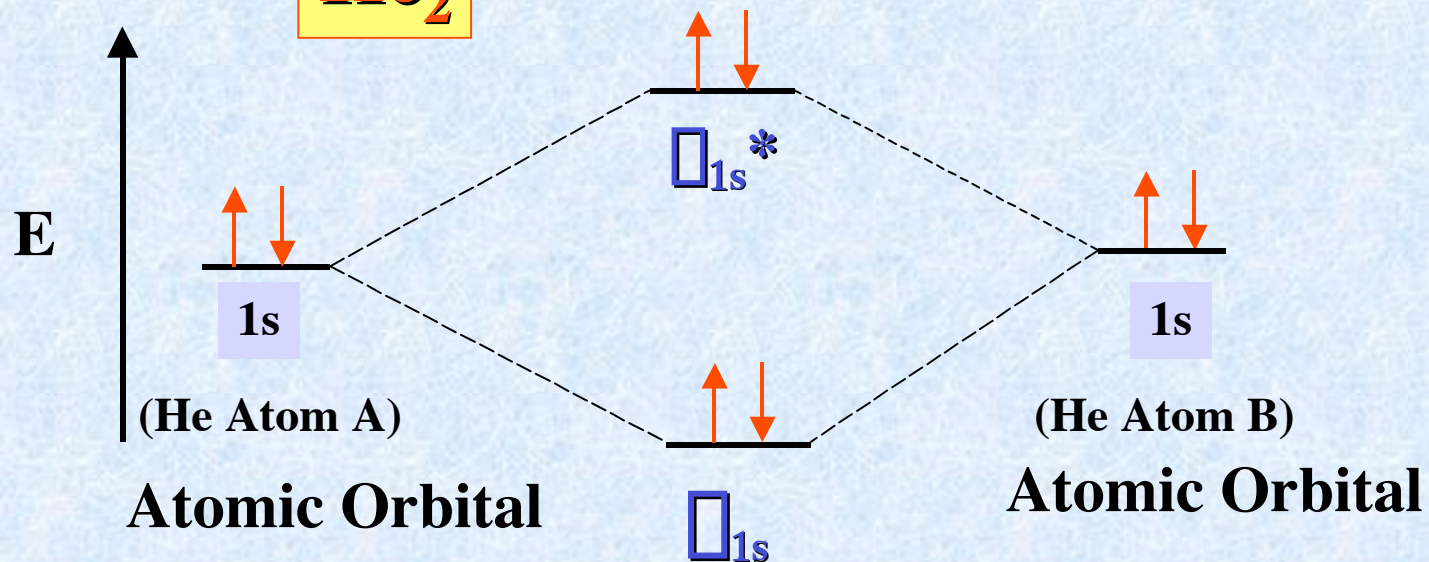
$$\sigma_{1s} < 1s < \sigma_{1s}^*$$



H₂ Molecular Orbitals

CORRELATION DIAGRAM

Z for He = 2



Atomic Orbital

Atomic Orbital

He₂ Molecular Orbitals