e$^-$

r_A r_B

A   **R$_{AB}$ ≡R**   B

$\psi(\vec{r}, \vec{R}_A, \vec{R}_B)$

- **K.E. terms for nuclei A and B**

- **Terms corresponding to attractive Coulomb interaction between the nuclei and the electron**

$$\widehat{H} = -\frac{\hbar^2}{2M}(\nabla_A{}^2 + \nabla_B{}^2) - \frac{\hbar^2}{2m}\nabla_e{}^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \frac{e^2}{4\pi\varepsilon_0 R_{AB}}$$

- **K.E. term for the electron**

- **Term corresponding to repulsive Coulomb interaction between the nuclei A and B**

$$\widehat{H}\,\psi(\vec{r}, \vec{R}_A, \vec{R}_B) = E\psi(\vec{r}, \vec{R}_A, \vec{R}_B)$$

- Not practical to try to solve the Sch. eq. like this

- **Born-Oppenheimer Approximation:** Since the electron is much lighter than the nuclei, it will move much more rapidly than the nuclei. The Sch. Eqn. for the electronic motion can be studied for a fixed distance of "R" between the nuclei i.e. the two nuclei can be treated as stationary.

$$\psi(\vec{r}, \vec{R}_A, \vec{R}_B) = \psi_e(\vec{r}, R)\psi_N(\vec{R}_A, \vec{R}_B)$$

Wavefunction for electronic motion

Wavefunction for nuclear motion

- The Sch. Eqn. for the electronic motion is then

$$\hat{H}_e \psi_e(\vec{r}, R) = E_e(R) \psi_e(\vec{r}, R) \qquad (R \text{ constant})$$

$$\hat{H}_e = -\frac{\hbar^2}{2m} \nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r_A} - \frac{e^2}{4\pi\varepsilon_0 r_B} + \boxed{\frac{e^2}{4\pi\varepsilon_0 R}}$$

Constant

- For all R, we can solve the above eqn. to get $E_e(R)$ as function of R.

- **The Sch. Eqn. for the nuclear motion becomes**

$$\left[-\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) + E_e(R) \right] \psi_N(\vec{R}_A, \vec{R}_B) = E_N \psi_N(\vec{R}_A, \vec{R}_B)$$

The nuclei move in the potential energy $E_e(R)$ determined by the electronic motion

H_2^+ : Linear Combination of Atomic Orbitals (LCAO)

- If $\psi_{1s}(A)$ and $\psi_{1s}(B)$ are the atomic hydrogen orbitals (wavefunctions), on nuclei A and B, then we can write the trial wavefunctions

$$\psi_e = \psi_\pm = c_1\psi_{1s}(A) \pm c_2\psi_{1s}(B); \qquad c_1 \text{ and } c_1 \text{ are constants}$$

- Since the two nuclei are identical, $c_1 = c_2 = c$.

$$\psi_e = \psi_\pm = c[\psi_{1s}(A) \pm \psi_{1s}(B)]$$

- **Normalization of the molecular orbital (MO) with '+' sign requires**

$$\int_{\substack{All \\ space}} \psi_+{}^*\psi_+ d\tau = 1$$

$$c^2\left[\int_{\substack{All \\ space}} \psi_{1s}(A)^*\psi_{1s}(A)d\tau + \int_{\substack{All \\ space}} \psi_{1s}(B)^*\psi_{1s}(B)d\tau + \int_{\substack{All \\ space}} \psi_{1s}(A)^*\psi_{1s}(B)d\tau + \int_{\substack{All \\ space}} \psi_{1s}(B)^*\psi_{1s}(A)d\tau\right] = 1$$

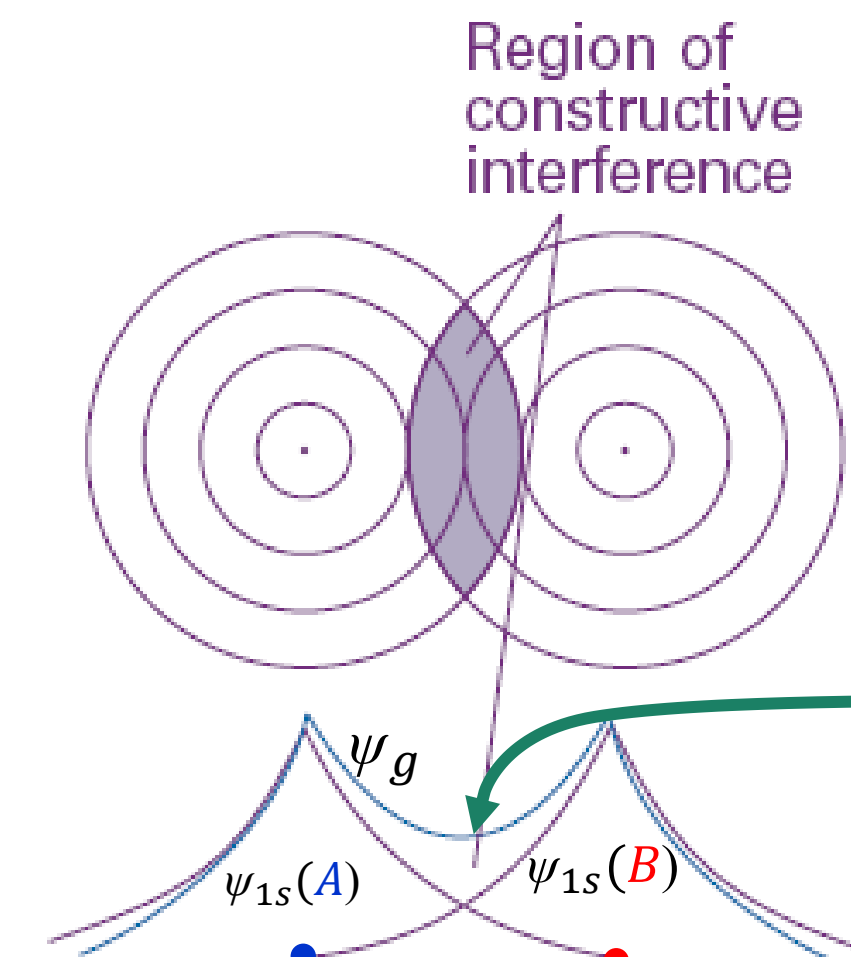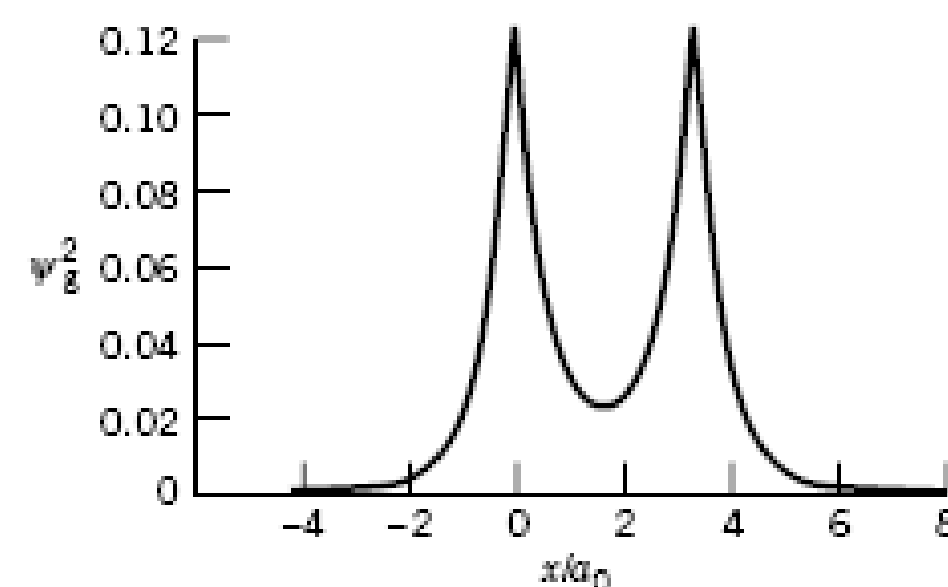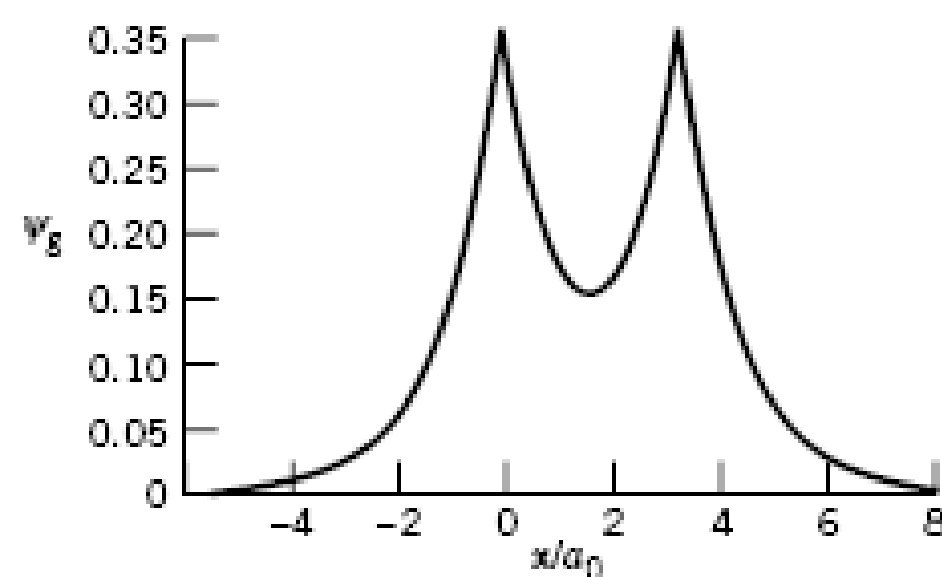**Since** $\psi_{1s}(A)$ and $\psi_{1s}(B)$ are real, the 3rd and 4th terms are same

$$c^2\left[2 + 2\int_{All\ space} \psi_{1s}(A)^*\psi_{1s}(B)d\tau\right] = 1 \Rightarrow c^2[2 + 2S] = 1 \Rightarrow c = \frac{1}{\sqrt{2(1+S)}}$$

$$S: overlap\ integral$$

H$_2^+$: Linear Combination of Atomic Orbitals (LCAO)

- Thus, the normalized wavefunction with '+' sign (*gerade*) is given by

$$\psi_+ \equiv \psi_g = \frac{1}{\sqrt{2(1+S)}} [\psi_{1s}(A) + \psi_{1s}(B)]$$

Region of constructive interference

Buildup of electron density between the two nuclei, causing bonding. Hence, ψ_g is also referred to as bonding molecular orbital

- Similarly, the normalized wavefunction with '-' sign (*ungerade*) is given by

$$\psi_- \equiv \psi_u = \frac{1}{\sqrt{2(1-S)}} [\psi_{1s}(A) - \psi_{1s}(B)]$$

Region of destructive interference
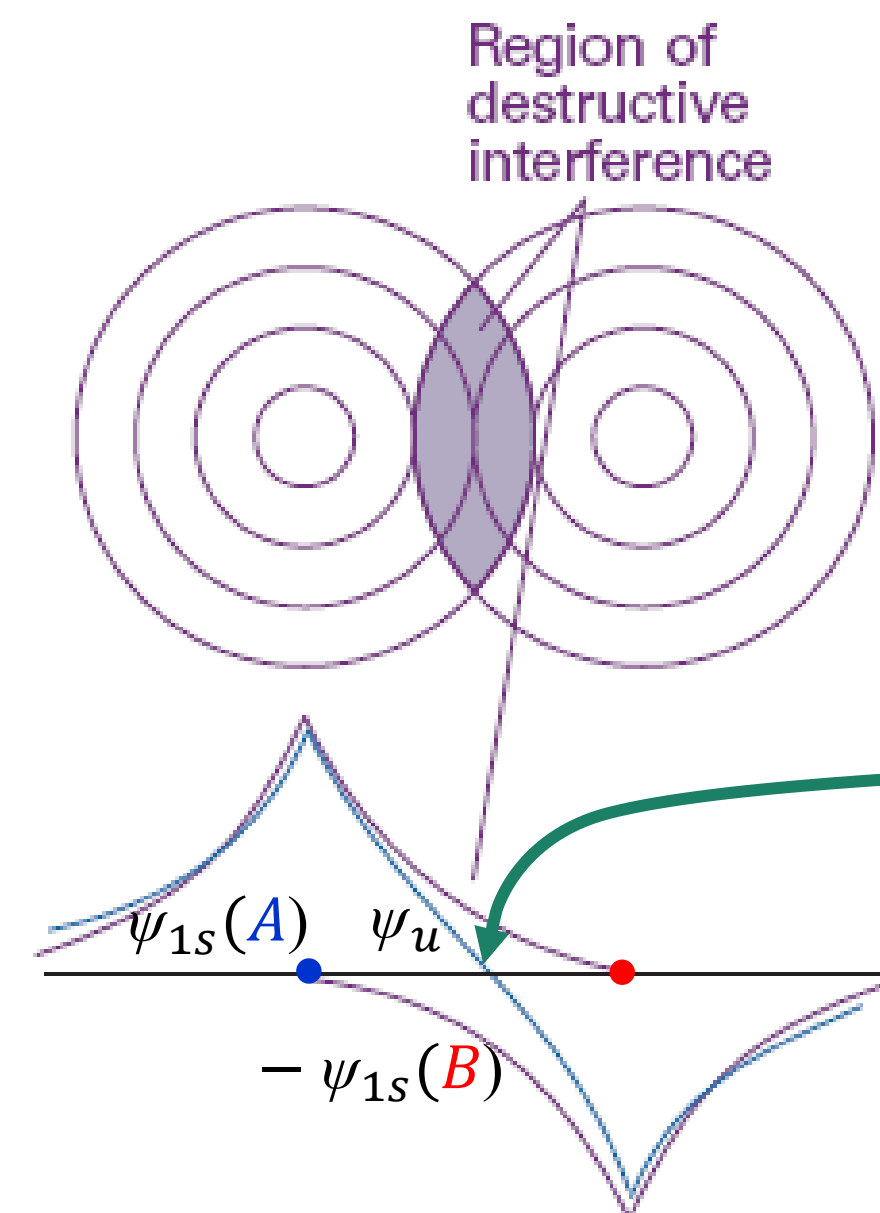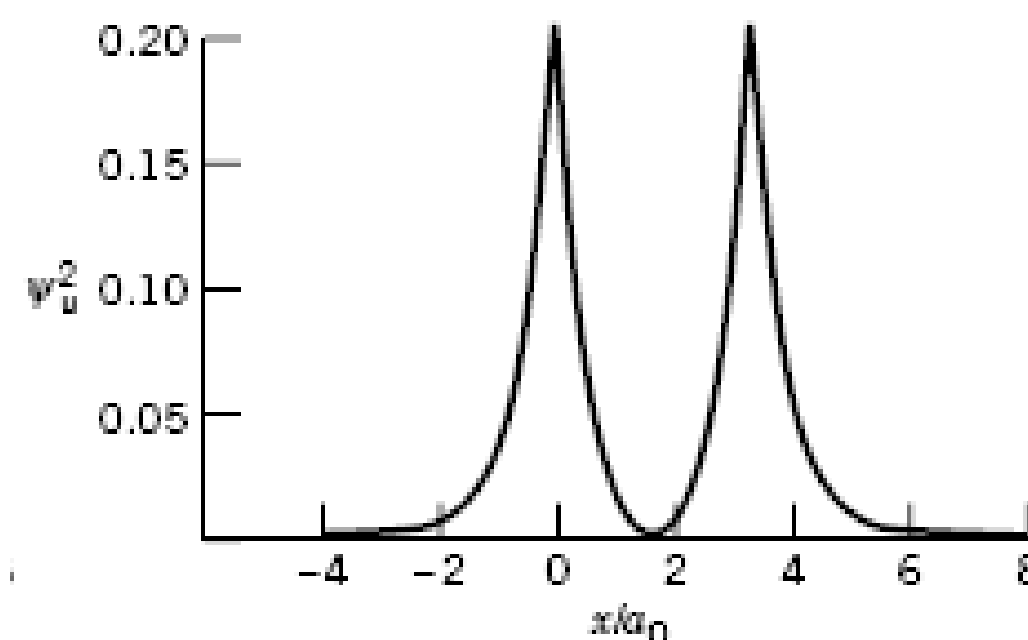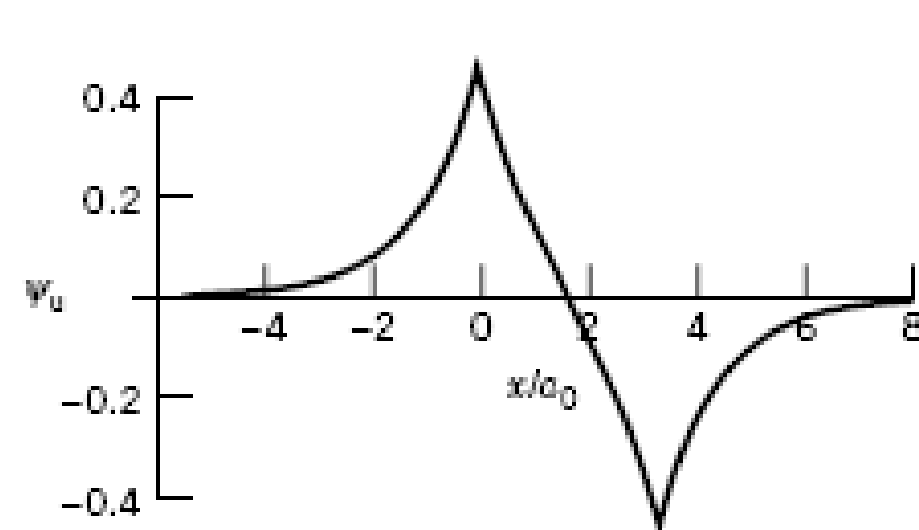
Reduction in electron density between the two nuclei, preventing bonding. Hence, ψ_u is also referred to as antibonding molecular orbital

Even-odd (gerade-ungerade) Parity

- When the molecule has centre of symmetry, the wavefunction may or may

  not change the sign when it is inverted through the centre of symmetry

- When $\psi(x, y, z) = \psi(-x, -y, -z)$, the wavefunction is said to have even (*gerade*) parity.

- When $\psi(x, y, z) = -\psi(x, y, z)$, the wavefunction is said to have odd (*ungerade*) parity.
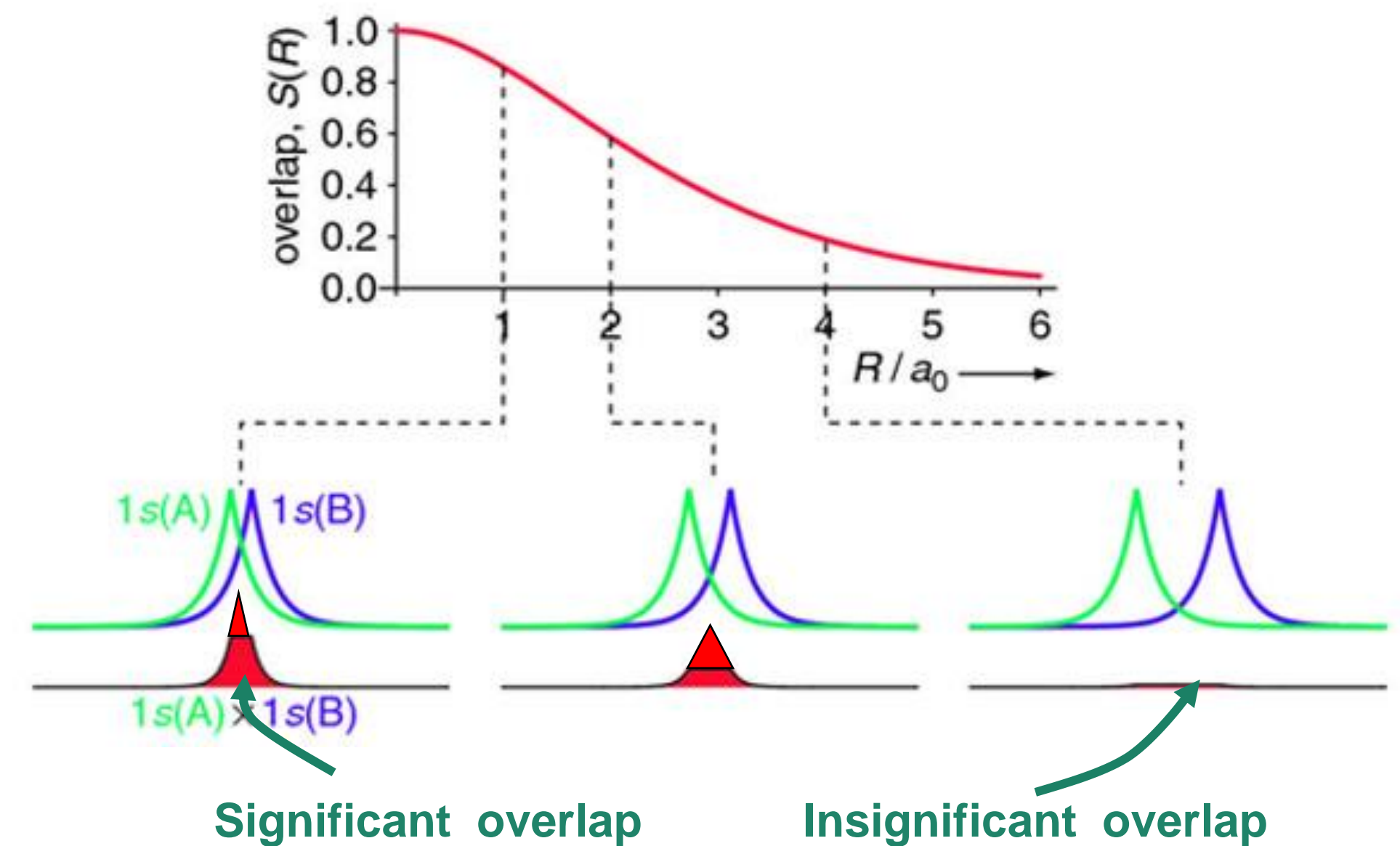
H_2^+ : The overlap integral $S(R)$

$$S(R) = \int_{All\ space} \psi_{1s}(A)^* \psi_{1s}(B)d\tau$$

- **The overlap integral S for the H_2^+ molecule can be** evaluated analytically as function of internuclear distance R

$$S(R) = e^{-R/a_0}\left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right)$$

- When two 1s orbitals overlap completely, $R = 0 \Rightarrow S = 1$

- When two 1s orbitals are infinitely apart, $R \longrightarrow \infty \Rightarrow S \longrightarrow 0$

At R_{eq}=106 pm, $S = 0.409694$

1s(A)   1s(B)

1s(A) × 1s(B)

Significant overlap   **Insignificant overlap**

H_2^+ : Molecular Orbital (MO) Energy

$$E_g = \frac{\int_{All\ space} \psi_g^* \widehat{H}_e \psi_g d\tau}{\int_{All\ space} \psi_g^* \psi_g d\tau} \qquad \text{where } \psi_g = c_1 \psi_{1s}(A) + c_2 \psi_{1s}(B)$$

$$E_g = \frac{\int_{All\ space}[c_1\psi_{1s}(A) + c_2\psi_{1s}(B)]^* \widehat{H}_e [c_1\psi_{1s}(A) + c_2\psi_{1s}(B)]d\tau}{\int_{All\ space}[c_1\psi_{1s}(A) + c_2\psi_{1s}(B)]^*[c_1\psi_{1s}(A) + c_2\psi_{1s}(B)]d\tau}$$

$$E_g = \frac{c_1^2 H_{AA} + 2c_1 c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 S_{AA} + 2c_1 c_2 S_{AB} + c_2^2 S_{BB}} = \frac{c_1^2 H_{AA} + 2c_1 c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 + 2c_1 c_2 S_{AB} + c_2^2}$$

Note that ψ_{1s} is real

$$H_{AA} = \int_{All\ space} \psi_{1s}(A)\widehat{H}_e \psi_{1s}(A)d\tau = \int_{All\ space} \psi_{1s}(B)\widehat{H}_e \psi_{1s}(B)d\tau = H_{BB}$$

$$H_{AB} = \int_{All\ space} \psi_{1s}(A)\widehat{H}_e \psi_{1s}(B)d\tau = \int_{All\ space} \psi_{1s}(B)\widehat{H}_e \psi_{1s}(A)d\tau = H_{BA}$$

$$S_{AA} = \int_{All\ space} \psi_{1s}(A)\psi_{1s}(A)d\tau = \int_{All\ space} \psi_{1s}(B)\psi_{1s}(B)d\tau = S_{BB} = 1$$

$$S_{AB} = \int_{All\ space} \psi_{1s}(A)\psi_{1s}(B)d\tau = \int_{All\ space} \psi_{1s}(B)\psi_{1s}(A)d\tau = S_{BA} = S$$

H_2^+ : MO Energy

Homonuclear Case: $c_1 = c_2 = c$

$$E_g = \frac{H_{AA} + 2H_{AB} + H_{BB}}{(2 + 2S)}$$
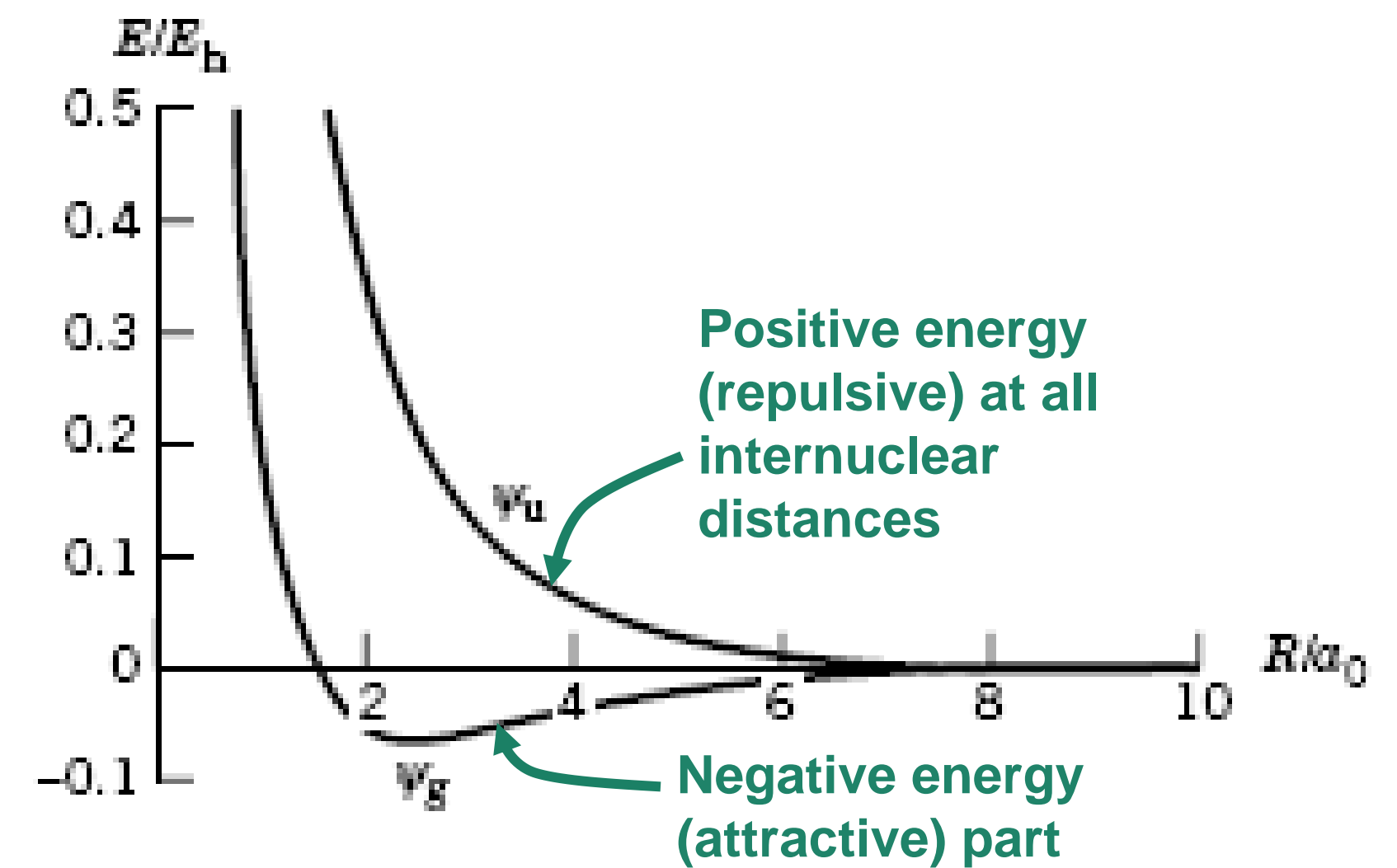
$$E_g = E_{1s} + \frac{J + K}{(1 + S)}$$

J(R): Coulomb Integral

K(R): Exchange Integral

Similarly,

$$E_u = \frac{H_{AA} - 2H_{AB} + H_{BB}}{(2 - 2S)}$$

$$E_u = E_{1s} + \frac{J - K}{(1 - S)}$$

Positive energy (repulsive) at all internuclear distances

Negative energy (attractive) part

	LCAO Theory	Experiment
Equilibrium bond length (R_e)	$2.5a_0$=132 pm	$2.0a_0$=106 pm
Binding Energy	170 kJ mol^{-1}	258 kJ mol^{-1}

H$_2^+$: MO Energy

MO Energy Diagram

$$\Delta E_g = (E_g - E_{1s}) = \frac{J + K}{(1 + S)}$$

$$\Delta E_u = (E_u - E_{1s}) = \frac{J - K}{(1 - S)}$$