Review

H_2^+

→ electron

R

nucleus

guess a wave function → $\Psi(r, R)$

diff values of R, compute the energy

$\hat{H} \Psi(r, R) = E \Psi(r, R)$

R_{eq} ⇒ equilibrium internuclear distance

Molecular Orbital Theory

H_2^+

r_{1A}

r_{1B}

R

Ψ_A

Ψ_B

energy

E_-

E_+

2 4 6 8

$R / a_0 \longrightarrow$
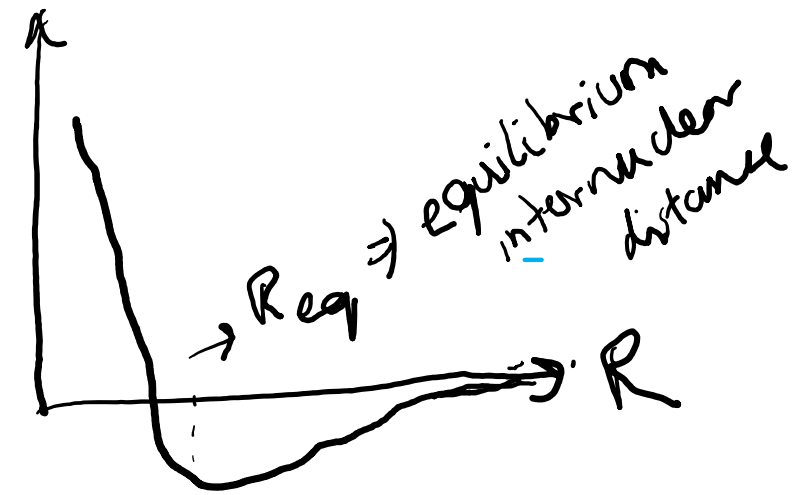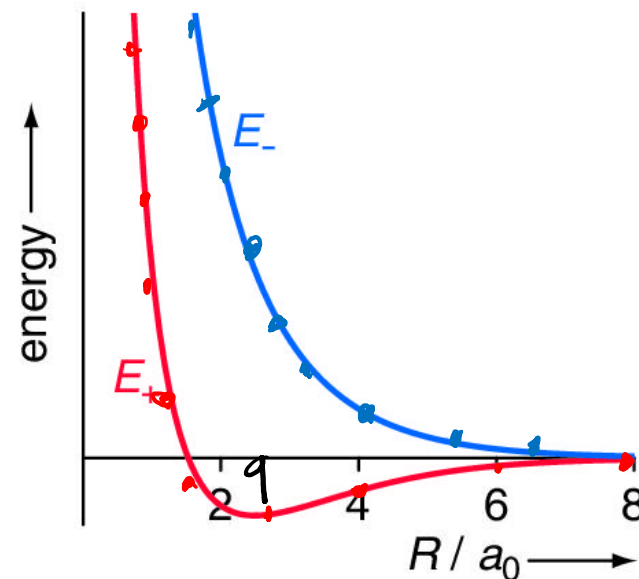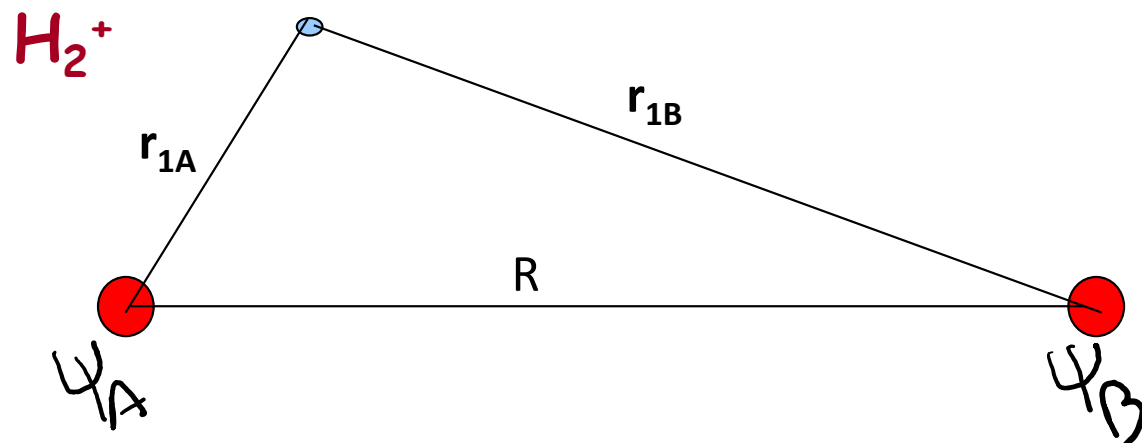
MO generated by **L**inear **C**ombination of **A**tomic **O**rbitals (**LCAO**)

$$\Psi_+ = c_A \Psi_A + c_B \Psi_B \qquad \text{Energy} = E_+$$

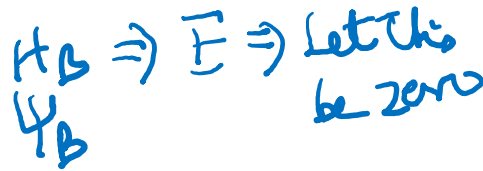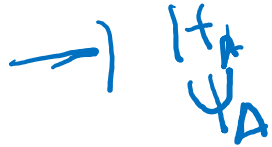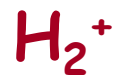$$\Psi_- = c_A \Psi_A - c_B \Psi_B \qquad \text{Energy} = E_-$$

For H_2^+: $c_A = c_B = 1$

Determine E_+ and E_- as a function of R

$\Psi_+ \Rightarrow E^+$ at $10 a_0$
E^+ at $8 a_0$
E^+ at $6 a_0$
E^+ at $4 a_0$
E^+ at $2, !$

$\Psi_- \Rightarrow E^-$ at $10 a_0$
E^- at $8 a_0$
E^- at $1 a_0$

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Molecular Orbital Theory

At $R = 2.5 a_0$

H_2^+

$Ψ_+ = c_A Ψ_A + c_B Ψ_B$ Energy $= E_+$

↳ atomic orbital

$Ψ_- = c_A Ψ_A - c_B Ψ_B$ Energy $= E_-$

molecular orbital

For H_2^+: $c_A = c_B = 1$

H_A $Ψ_A$ $H_B ⟹ E ⟹$ Let this be zero $Ψ_B$

$Ψ_-$ H_2^+ $Ψ_+$

R_{eq}
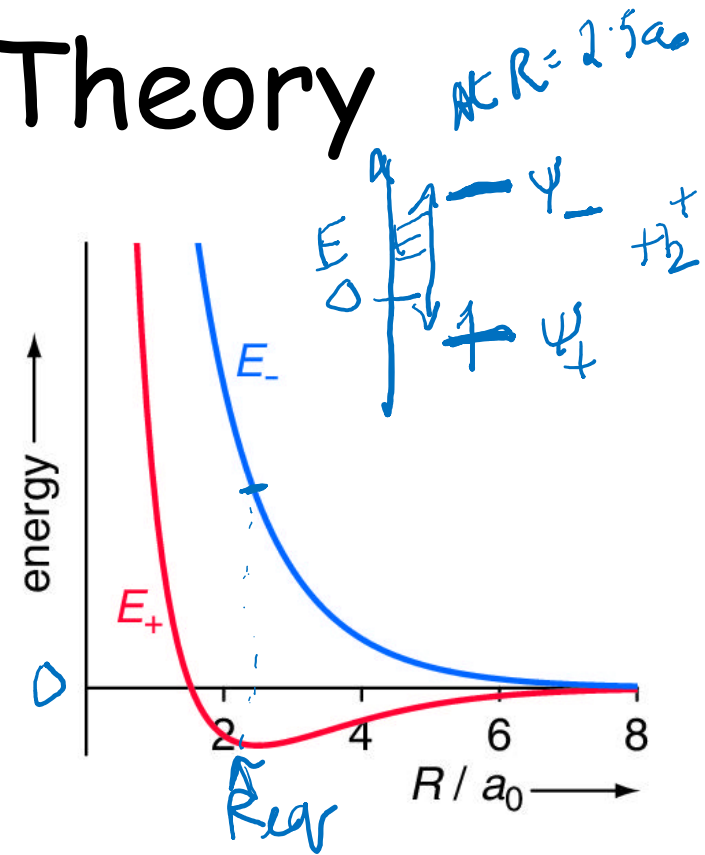
- As the atoms approach one another the energy of $Ψ_+$ falls at first, reaching a minimum at R $= 2.5$ a_0 (145 pm) before rising steeply
- If electron placed in this orbital, it is favorable for two atoms to come together until 2.5 a_0, at which point energy is minimum: called ***Bonding Orbital***
- As the atoms approach one another the energy of $Ψ_-$ simply rises
- If electrons were placed in this orbital it would be disadvantageous in energy terms: called ***Anti-Bonding Orbital***
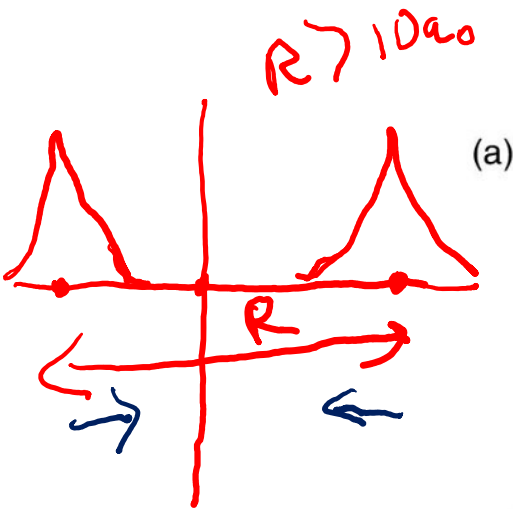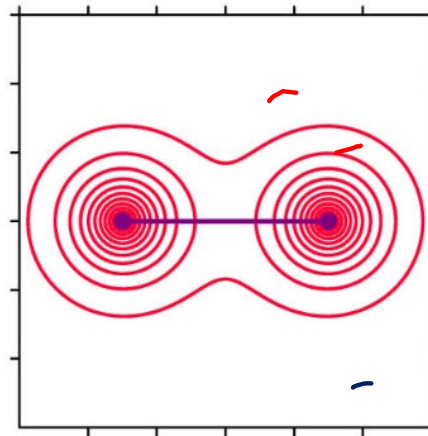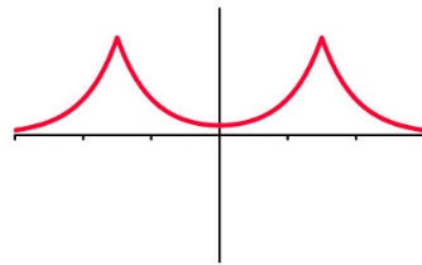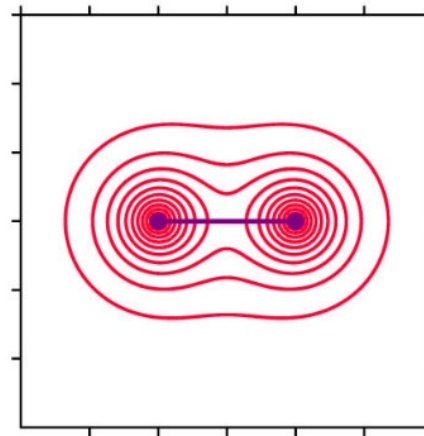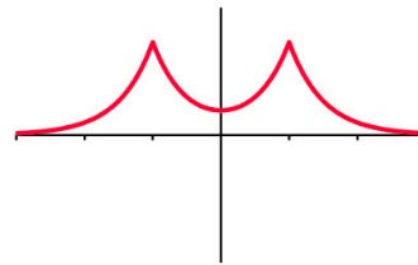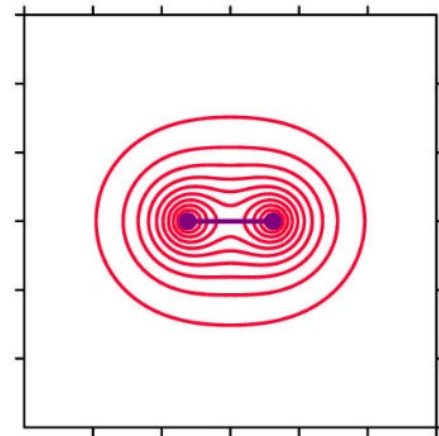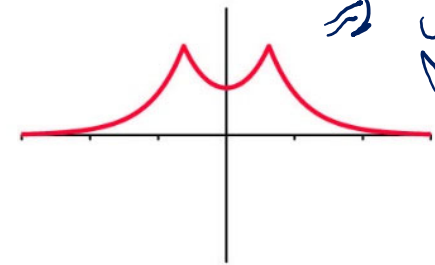
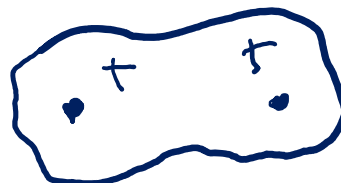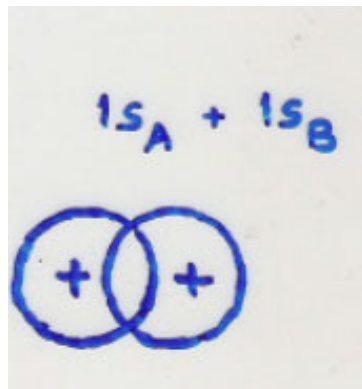13

Contour plots of bonding and anti-bonding MO's

(a)

$R = 6\,a_0$ $R = 4\,a_0$ $R = 2.5\,a_0$

$1s_A + 1s_B$

$+$ $+$

$\psi_+ \Rightarrow$ Bonding MO of H_2^+

energy

E_-

E_+

2   4   6   8

R / a_0

Contour plots of bonding and anti-bonding MO's

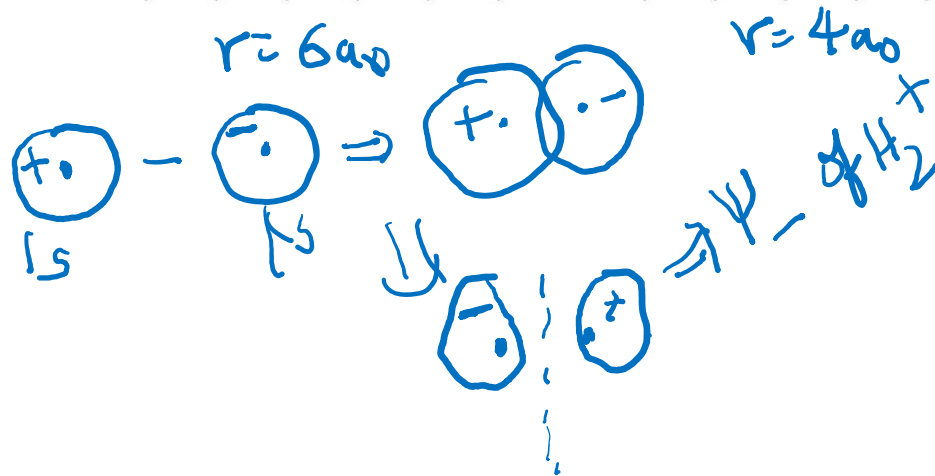$\Psi_- \Rightarrow \Psi_A - \Psi_B$, Ψ_A

$-\Psi_B + \Psi_A$

$o, -\Psi_B + \Psi_A$

$r > 10 a_0$

Ψ_A

Ψ_B

(b)

$r = 6 a_0$

$r = 4 a_0$

$v = 2.5 a_0$

$1s_A - 1s_B$

$+$ $-$

$+\cdot) - (\cdot) \Rightarrow (+\cdot \cdot)$

$1s$ $1s$ $\Downarrow$

$(\cdot) \ (\cdot) \Rightarrow \Psi_- \text{ of } H_2^+$

energy

E_-

E_+

2   4   6   8

R / a_0

Iso-surface representation of bonding and anti-bonding MO's

(a)

$R = 6\,a_0$ $R = 4\,a_0$ $R = 2.5\,a_0$

(a)
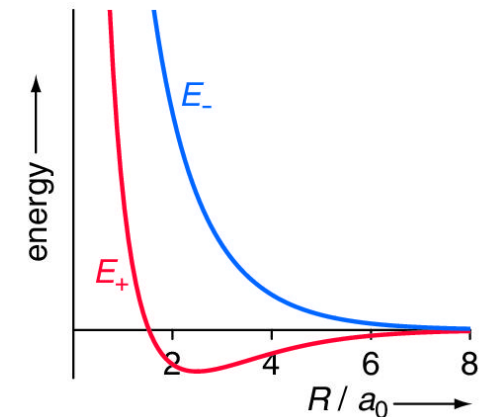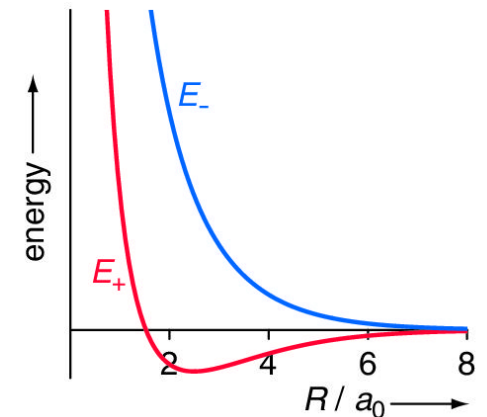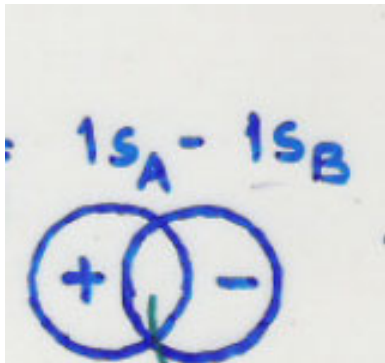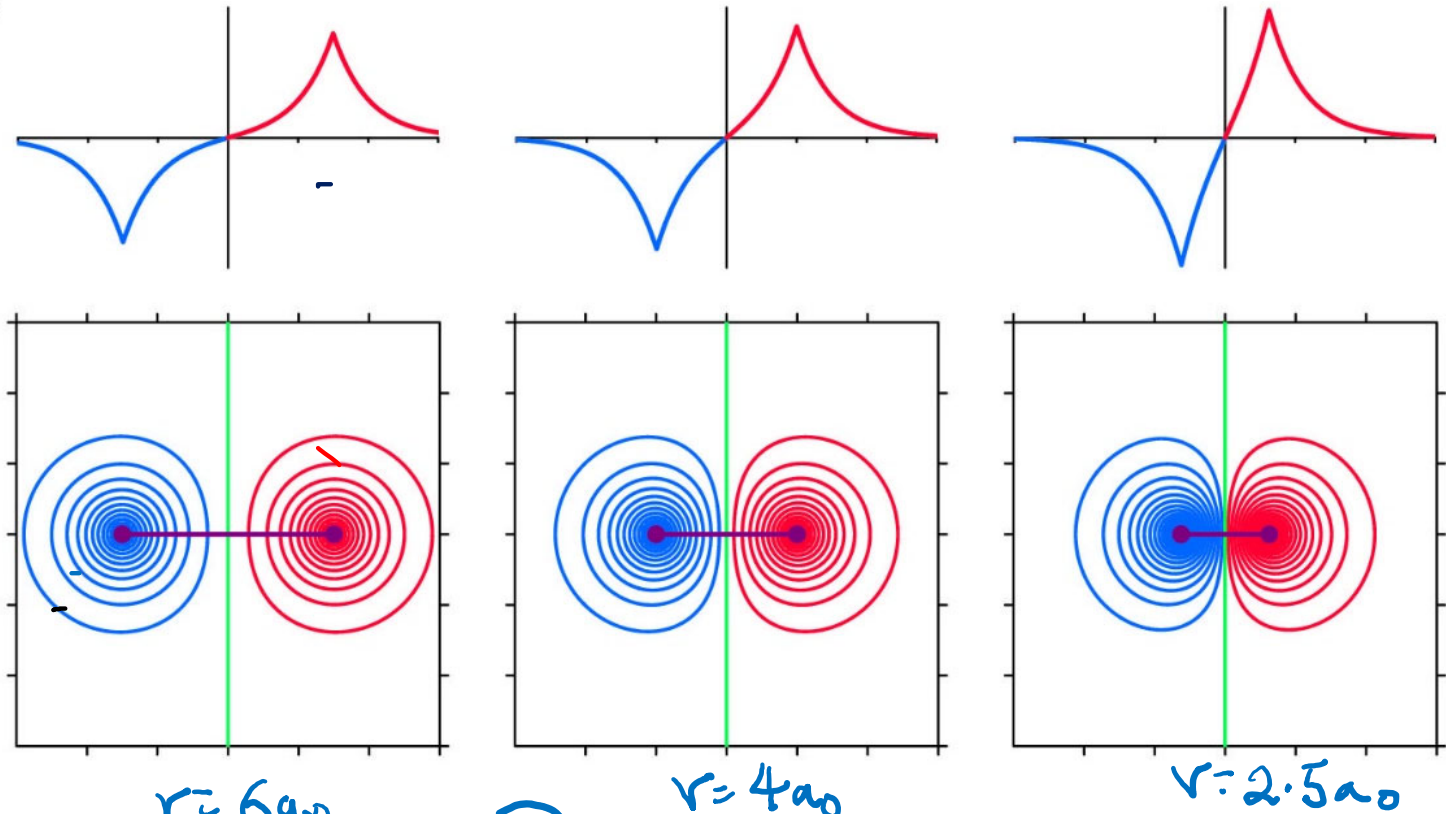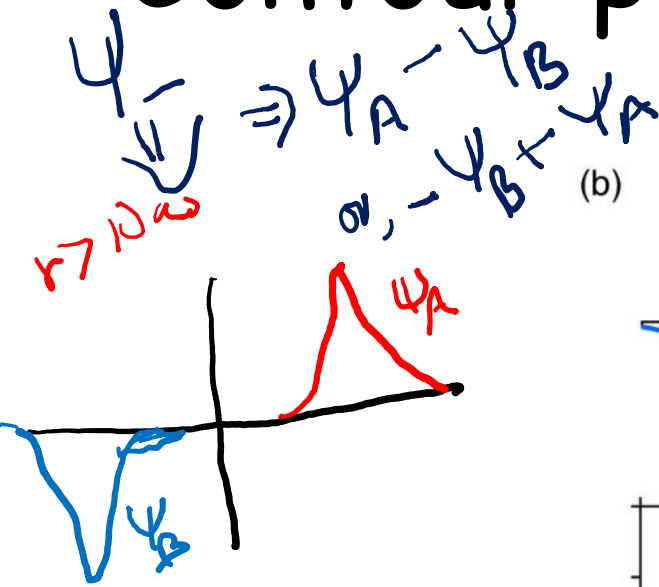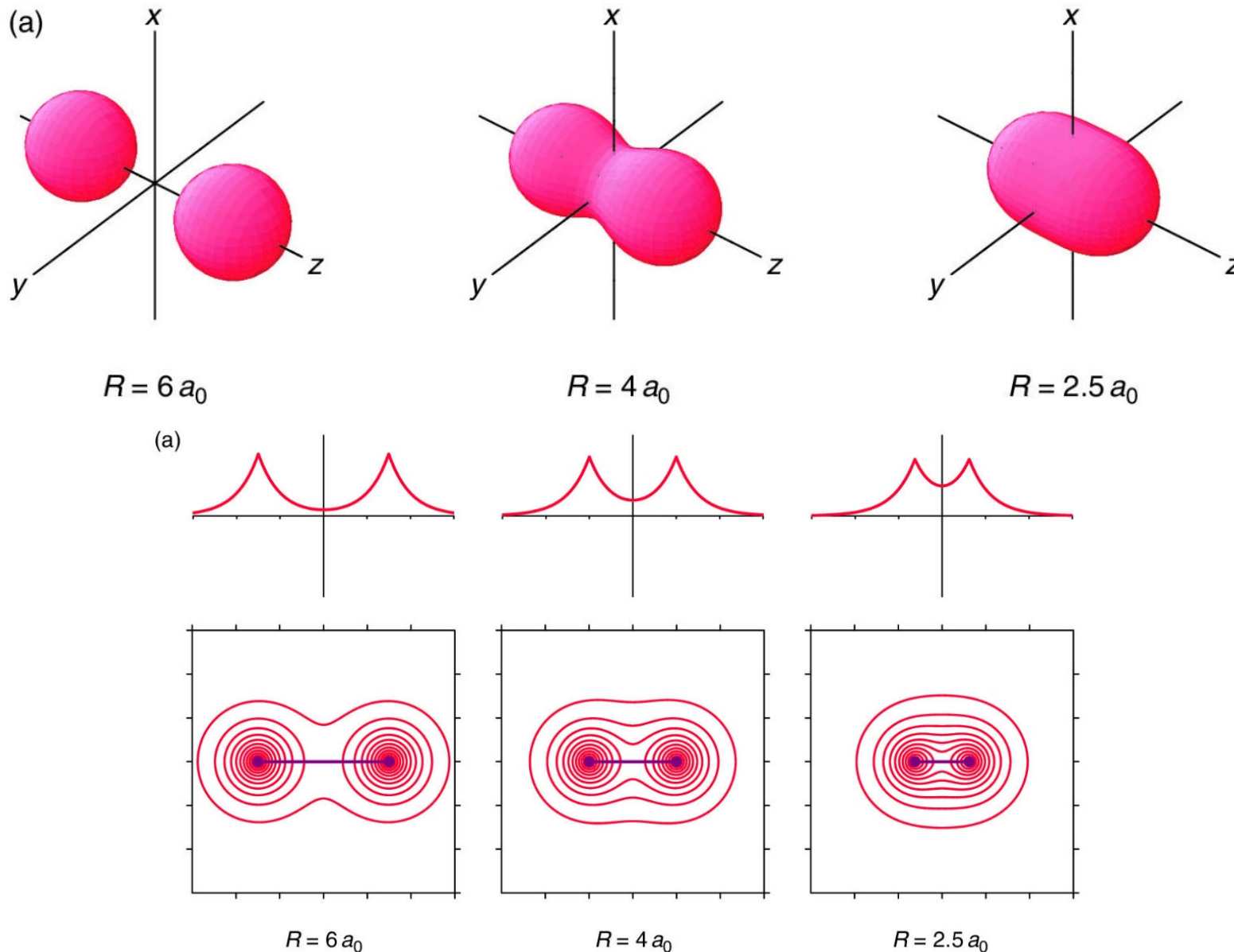
$R = 6\,a_0$ $R = 4\,a_0$ $R = 2.5\,a_0$
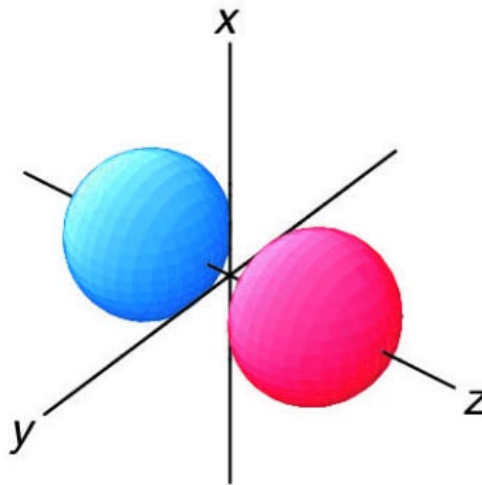
Iso-surface representation of bonding and anti-bonding MO's
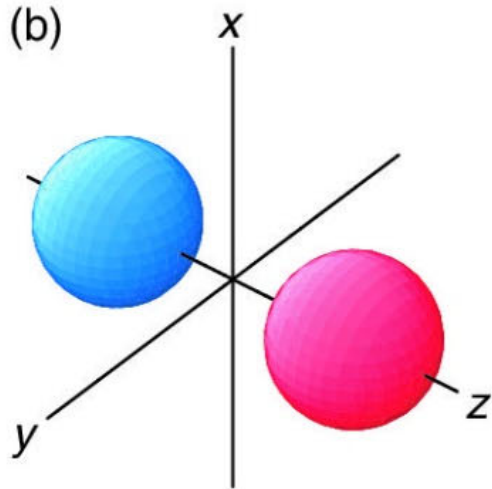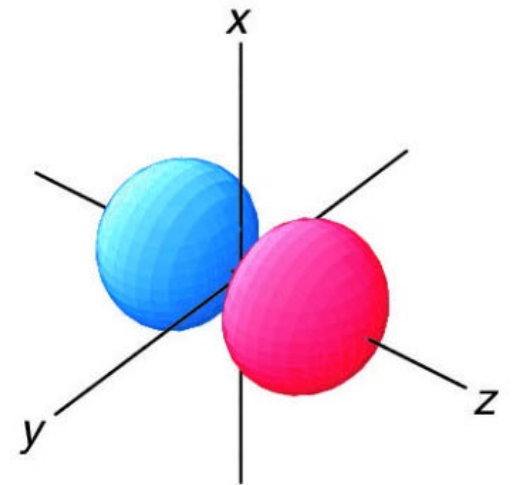
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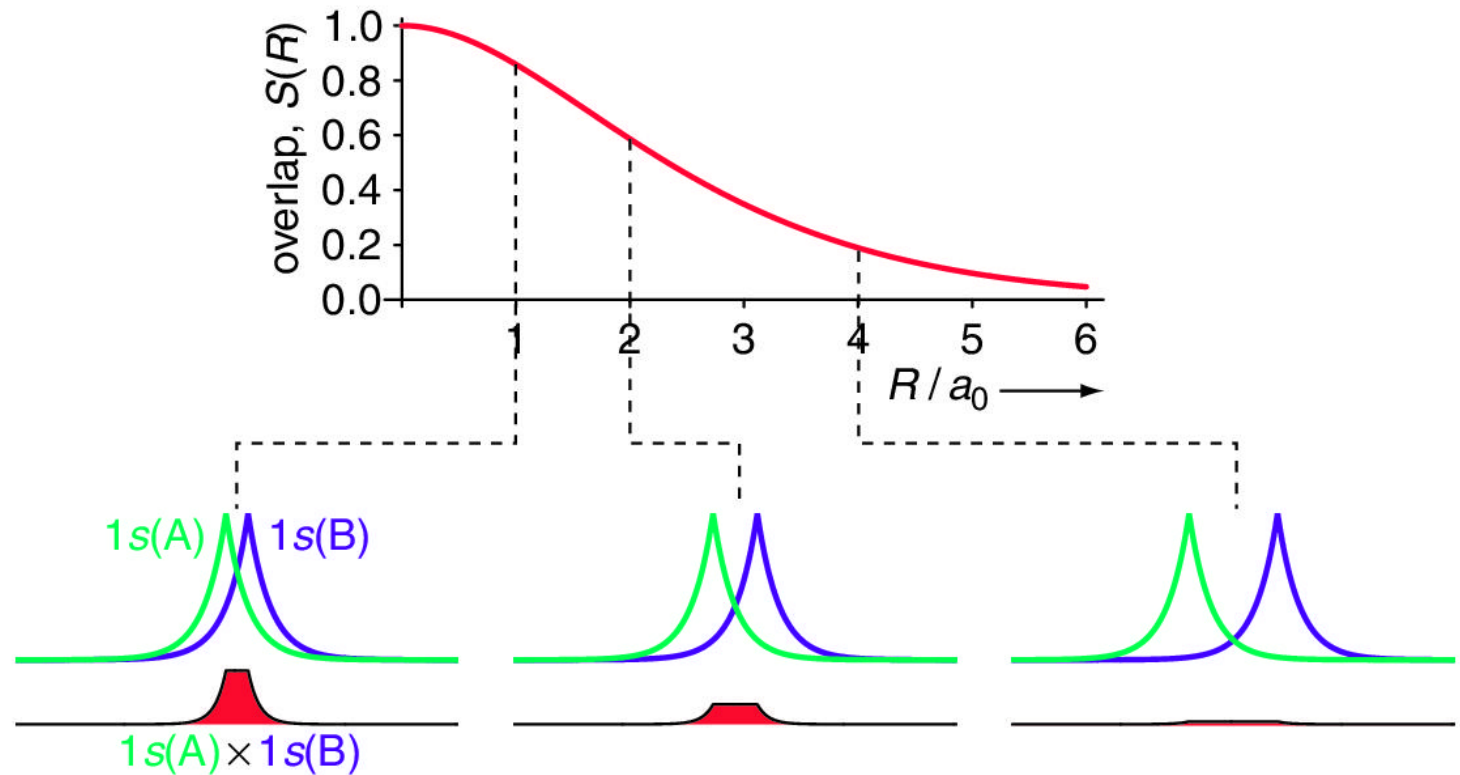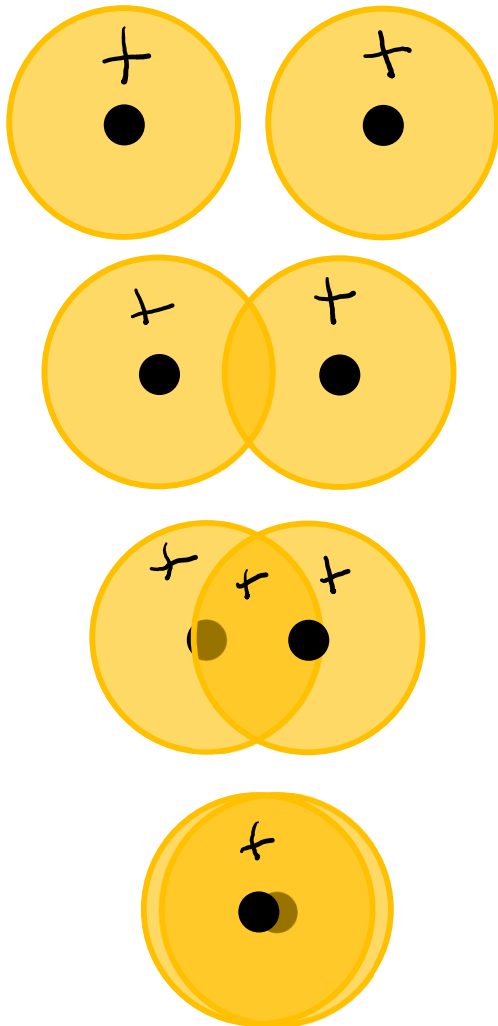
Overlap and Overlap Integral

- As R decreases, MO's shift in energy further away from energy of AO's

- Calculations complicated- useful guide to the strength of the interaction of AO's (hence energy shift of MO's) can be obtained by looking at **overlap integral (S)**

- Overlap integral between two AO's is determined by multiplying together two AO wavefunctions, and then taking the integral of the products

- *Recall: Integral of a function is the area under the curve of the function*
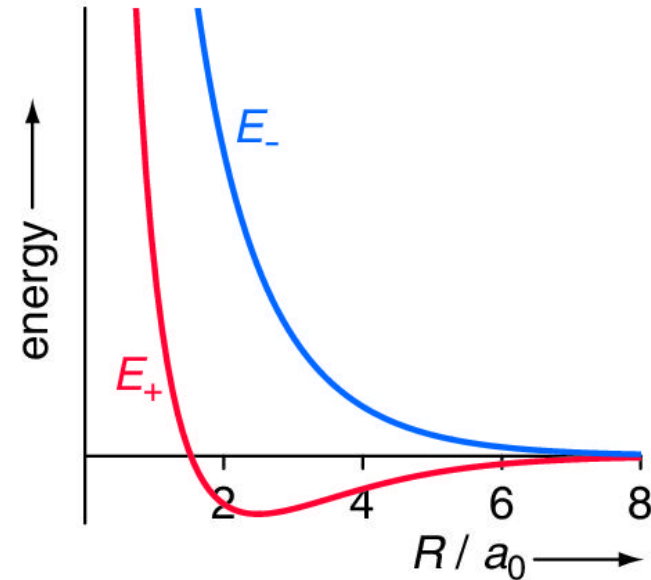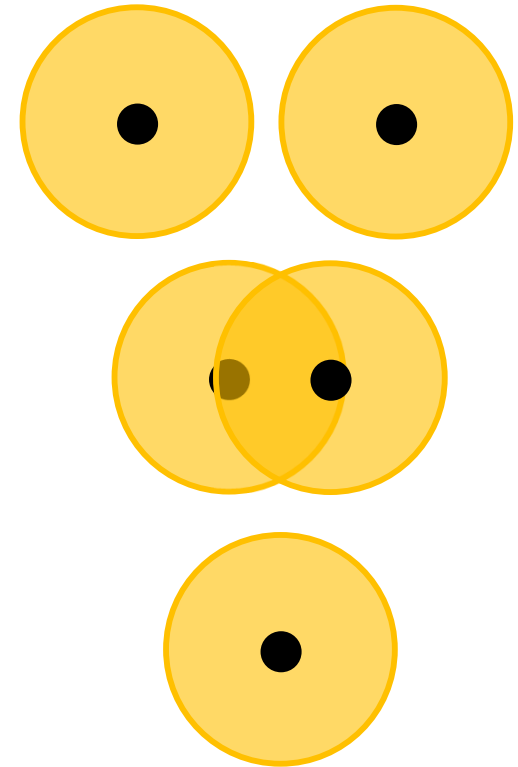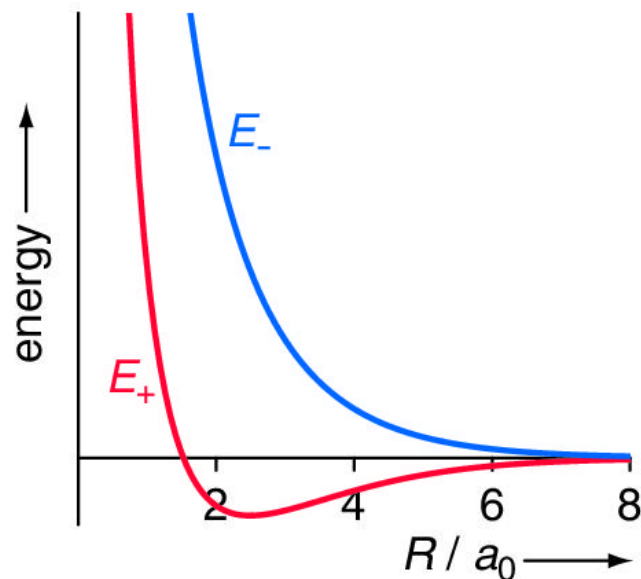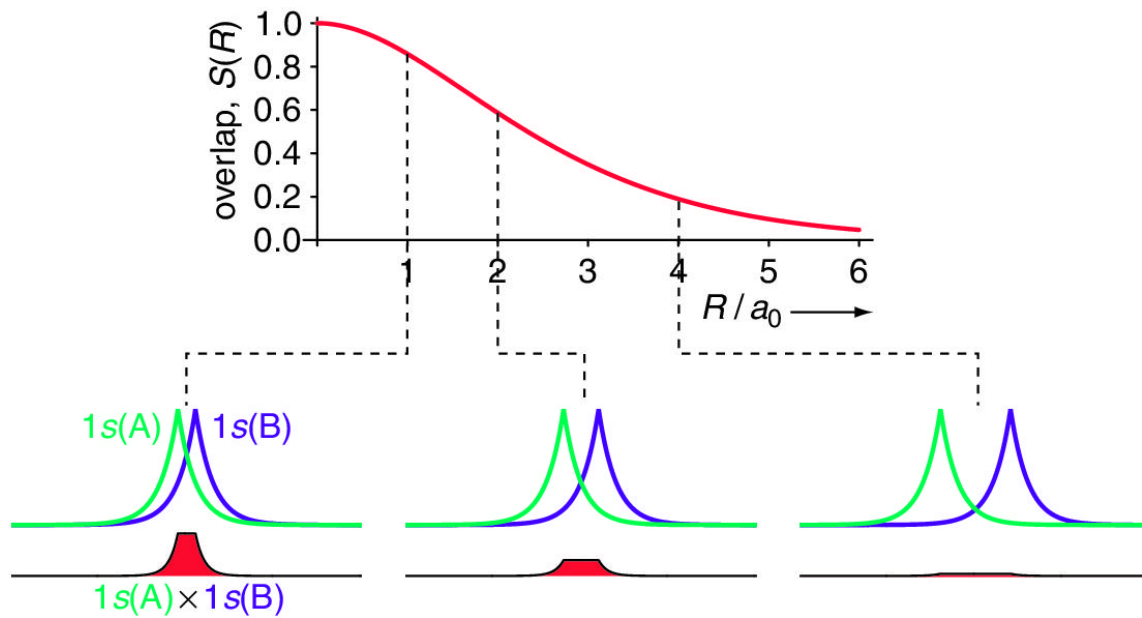
Overlap Integral depends on R_{AB}

Overlap Integral $S_{AB}(R) = \langle \psi_1 | \psi_2 \rangle = \int \psi_1 \psi_2 \, d\tau$
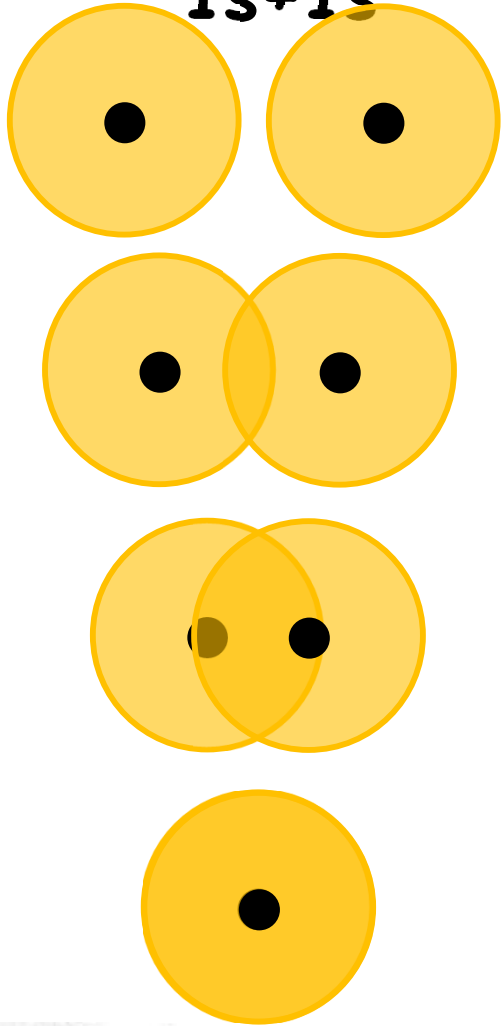
1s+1s

1s(A) 1s(B)

1s(A) × 1s(B)

- Plot of overlap integral S(R) for two 1s orbitals as a function of R

- S(R) is the integral of the product of the two wavefunctions, which in this case is the area under the graph of this product
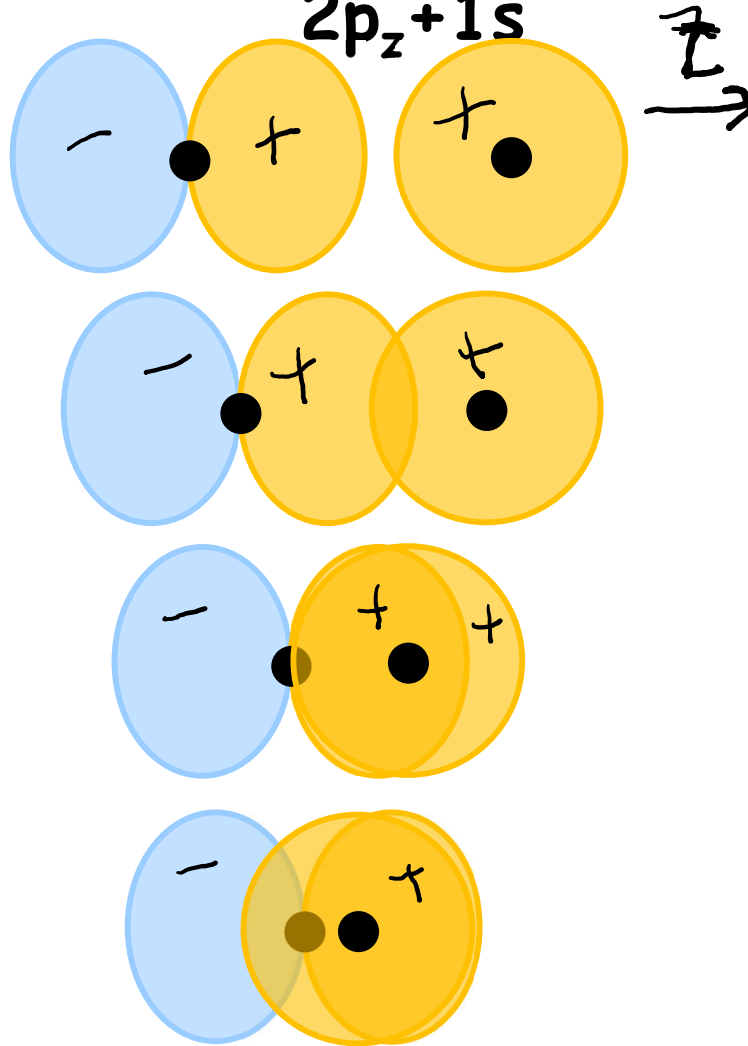
Overlap Integral and Bond Length
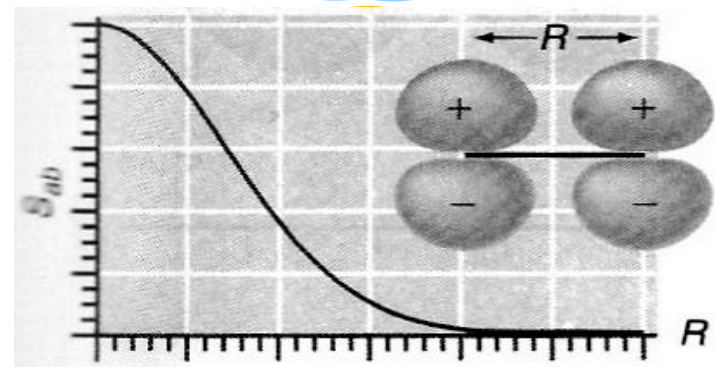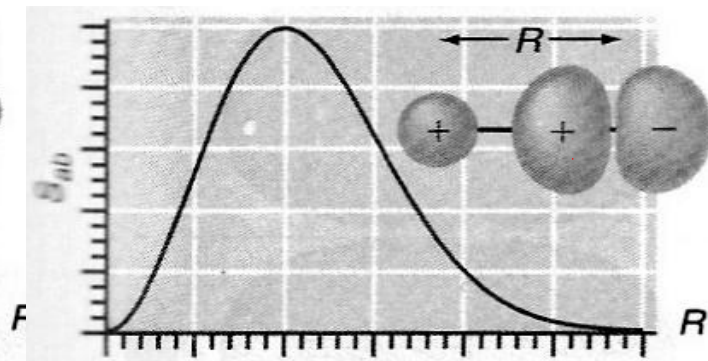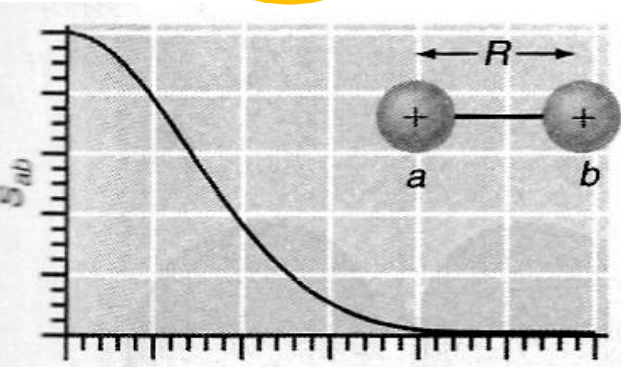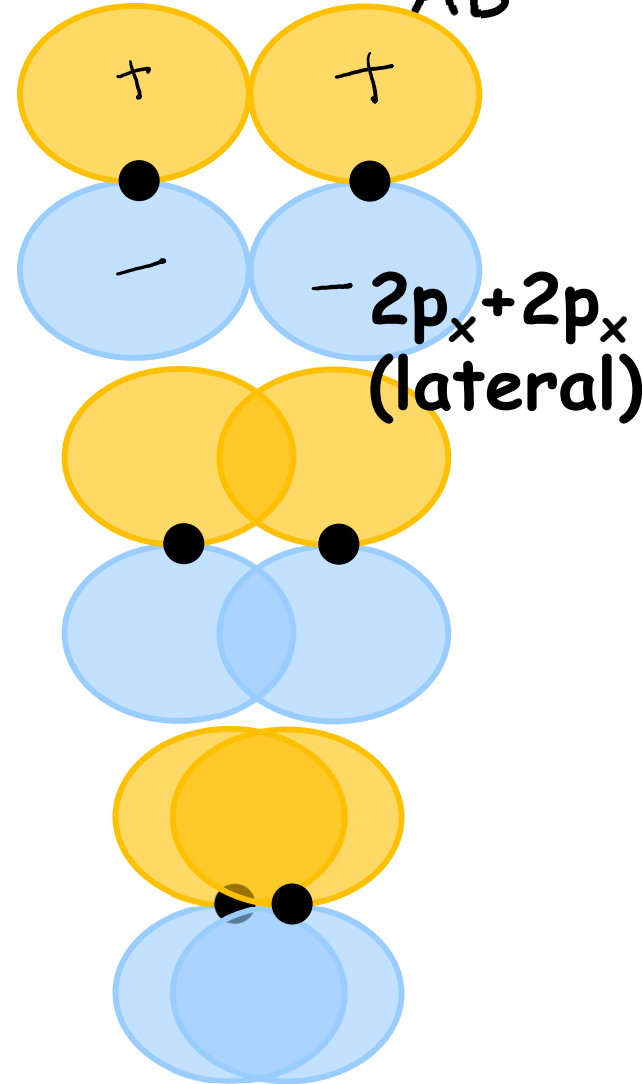
Overlap Integral depends on R_{AB}
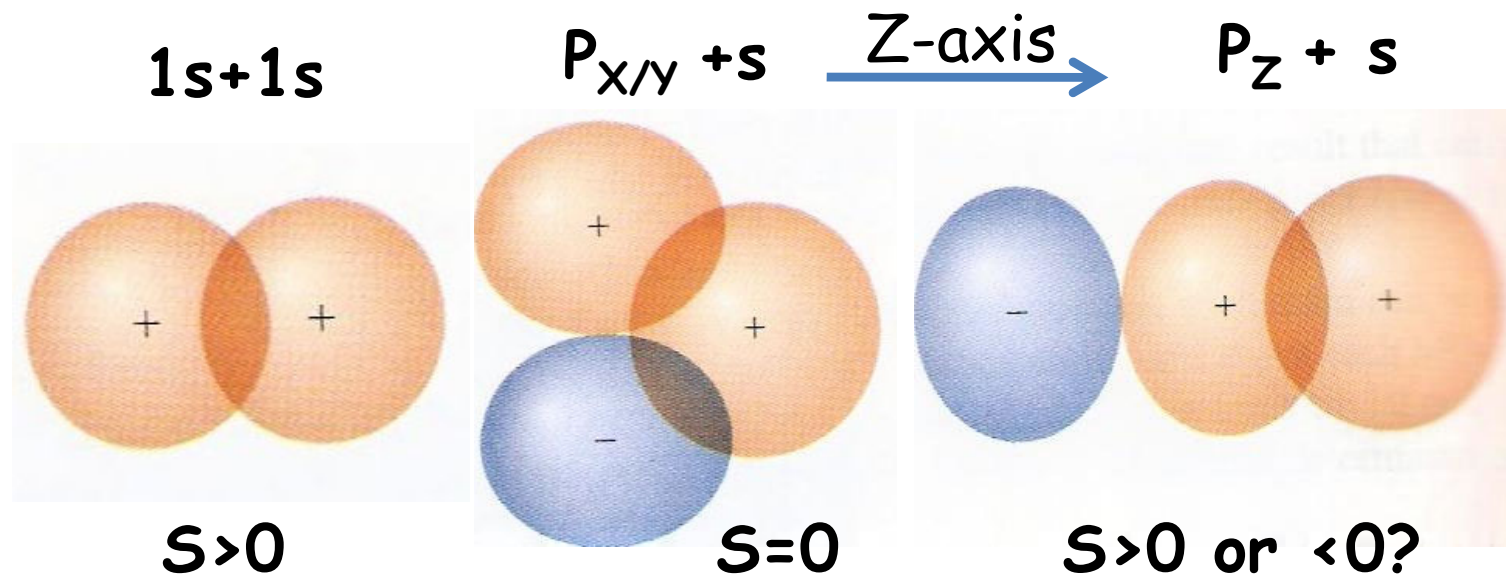

1s+1s

$2p_z$+1s

$2p_x$+$2p_x$ (lateral)

Overlap Integral: Symmetry

$$Overlap\ Integral\ S_{AB}(R) = \langle \psi_1 | \psi_2 \rangle = \int \psi_1 \psi_2 d\tau$$

Overlapped area of 2 Wave-functions (can have +/- values)

Have to consider extent (amount) of both positive and negative contributions!

1s+1s

$P_{X/Y}$ +s

Z-axis

P_Z + s

+

+

+

+

−

−

+

+

S>0

S=0

S>0 or <0?

→S is a qualitative measure of bond strength
→If S>>0; electron delocalized over molecule
→S(R) = 0 → bond formation cannot occur

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