Chemical Bonding I

Cha Seoncheol

Department of Physics, Sogang University

H.Haken & H.C.Wolf, Molecular Physics and Elements of Quantum Chemistry
P.Atkins & R.Friedman, Molecular Quantum Mechanics

Proceedings of the National Academy of Sciences
Vol. 65, No. 4, pp. 823–830, April 1970

Failure of Energy Transfer between Identical Aromatic Molecules on Excitation at the Long Wave Edge of the Absorption Spectrum

Gregorio Weber and Meir Shinitzky

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS, URBANA

Proceedings of the National Academy of Sciences
Vol. 67, No. 3, pp. 1116–1121, November 1970

Role of Heterogeneity of the Solvation Site in Electronic Spectra in Solution*

William C. Galley and Robert M. Purkey

DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY, MONTREAL, CANADA

Communicated by Norman Davidson, August 3, 1970

Chemical Bonding

Heteropolar Bonding (Ionic Bonding)

Example : Na^+ Cl^-

Homopolar Bonding (Covalent Bonding, After Quantum Mechanics)

Example : H^2

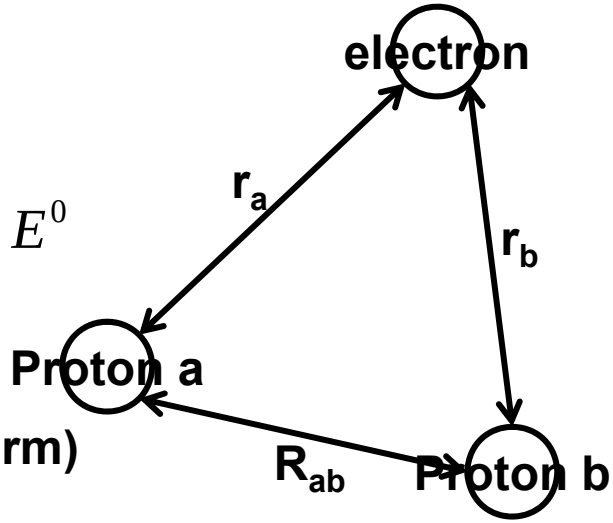
How could a hydrogen molecule be formed from two neutral H atoms?

The Hydrogen Molecule-Ion, H^+_2

The simplest case of chemical bonding

Starting from Hydrogen atom

$$(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a})\phi_a(r_a) = E_a^0\phi_a(r_a) \qquad E_a^0 = E_b^0 = E^0$$

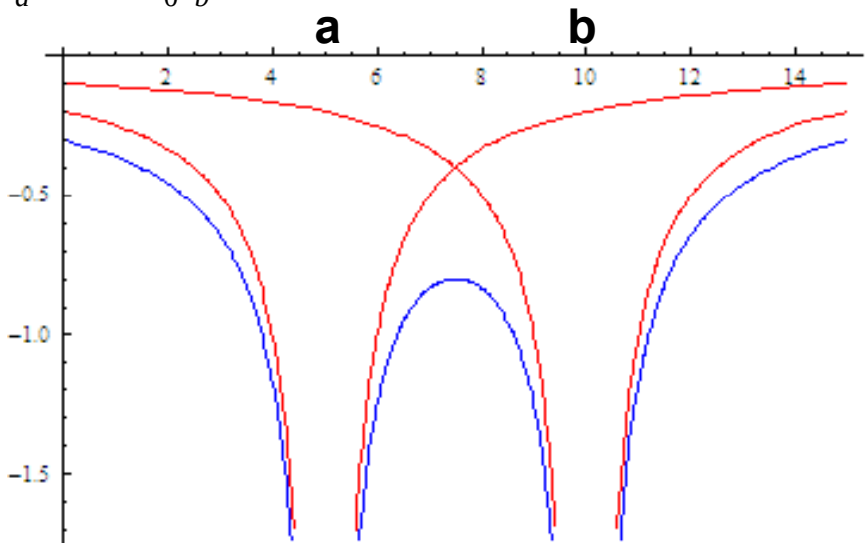


Adding a second proton

(Later, I consider electron interaction term)

$$(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} - \frac{e^2}{4\pi\varepsilon_0 r_b})\psi = E\psi$$

Potential Curve



Red : each wave fn.

Blue : added wave fn.

SMOS
Soft-Matter Optical Spectroscopy

The Hydrogen Molecule-Ion, H^+_2

Determinating the wavefunction ψ

Assume wavefunction $\psi = c_1\phi_a + c_2\phi_b$

$$(\underbrace{-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a}}_{E^0} - \frac{e^2}{4\pi\varepsilon_0 r_b})c_1\phi_a + (\underbrace{-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_b}}_{E^0} - \frac{e^2}{4\pi\varepsilon_0 r_a})c_2\phi_b = E(c_1\phi_a + c_2\phi_b)$$

$$(\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_b})c_1\phi_a + (\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_a})c_2\phi_b = 0 \qquad E^0 - E = \Delta E$$

$$\int dV(\phi_a(\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_b})c_1\phi_a + \phi_a(\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_a})c_2\phi_b) = 0$$

$$\int dV(\phi_a\phi_a\Delta E - \underbrace{\phi_a \frac{e^2}{4\pi\varepsilon_0 r_b}\phi_a}_{\equiv C})c_1 + (\underbrace{\phi_a\phi_b\Delta E}_{\equiv S} - \underbrace{\phi_a \frac{e^2}{4\pi\varepsilon_0 r_a}\phi_b}_{\equiv D})c_2) = 0$$

$$(\Delta E + C)c_1 + (\Delta E S + D)c_2 = 0$$

The Hydrogen Molecule-Ion, H^+_2

$$\psi = c_1\phi_a + c_2\phi_b$$

$$\underbrace{(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a}}_{E^0} - \frac{e^2}{4\pi\varepsilon_0 r_b})c_1\phi_a + \underbrace{(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_b}}_{E^0} - \frac{e^2}{4\pi\varepsilon_0 r_a})c_2\phi_b = E(c_1\phi_a + c_2\phi_b)$$

$$(\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_b})c_1\phi_a + (\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_a})c_2\phi_b = 0 \qquad E^0 - E = \Delta E$$

$$\int dV(\phi_a(\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_b})c_1\phi_a + \phi_a(\Delta E - \frac{e^2}{4\pi\varepsilon_0 r_a})c_2\phi_b) = 0$$

$$\int dV(\underbrace{\phi_a\phi_a\Delta E - \phi_a\frac{e^2}{4\pi\varepsilon_0 r_b}\phi_a}_{\equiv C})c_1 + (\underbrace{\phi_a\phi_b\Delta E}_{\equiv S} - \underbrace{\phi_a\frac{e^2}{4\pi\varepsilon_0 r_a}\phi_b}_{\equiv D})c_2) = 0$$

Product ϕ_a

Product ϕ_b

$$(\Delta E + C)c_1 + (\Delta ES + D)c_2 = 0$$

$$(\Delta ES + D)c_1 + (\Delta E + C)c_2 = 0$$

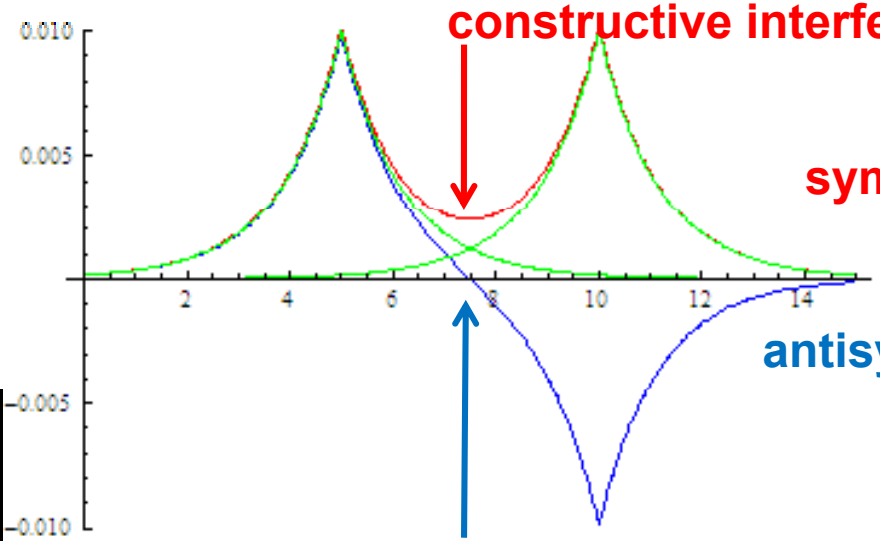
SMOS
Soft-Matter Optical Spectroscopy

The Hydrogen Molecule-Ion, H^+_2

$$\psi = c_1\phi_a + c_2\phi_b$$

c2 = -c1 ≡ -c

c2 = c1 ≡ c



constructive interference

symmetric

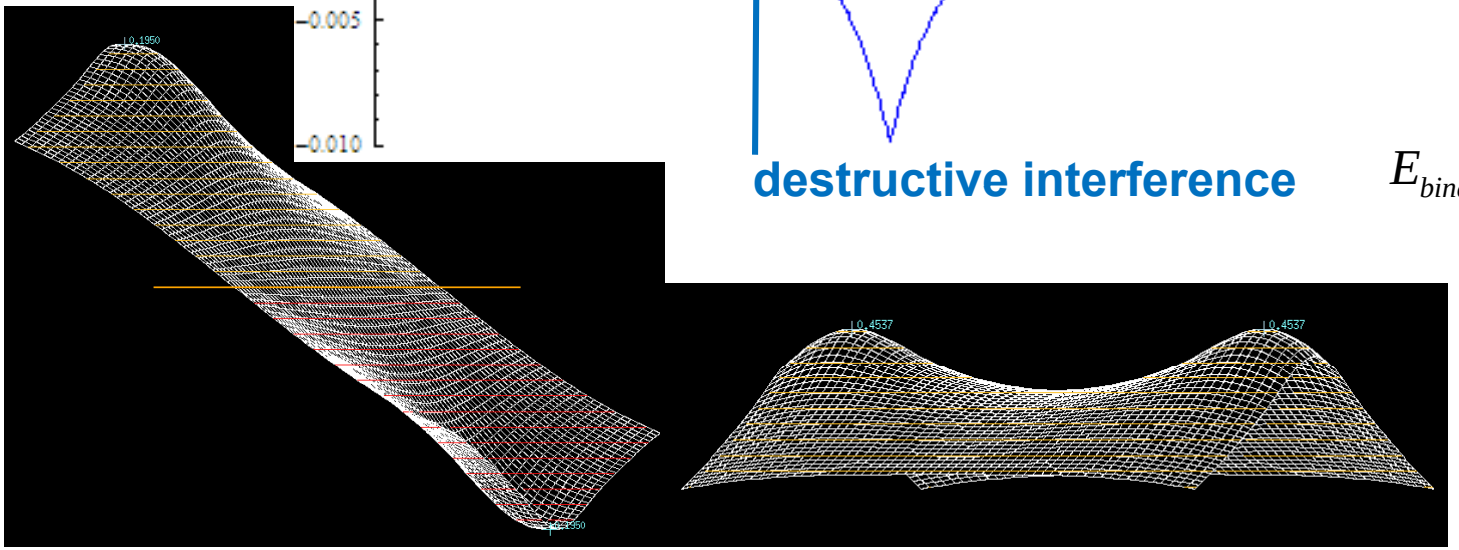
$$E = E^0 + \frac{C - D}{1 - S}$$

antisymmetric

$$E = E^0 + \frac{C + D}{1 + S}$$

destructive interference

$$E_{binding} = \frac{C \pm D}{1 \pm S} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}}$$

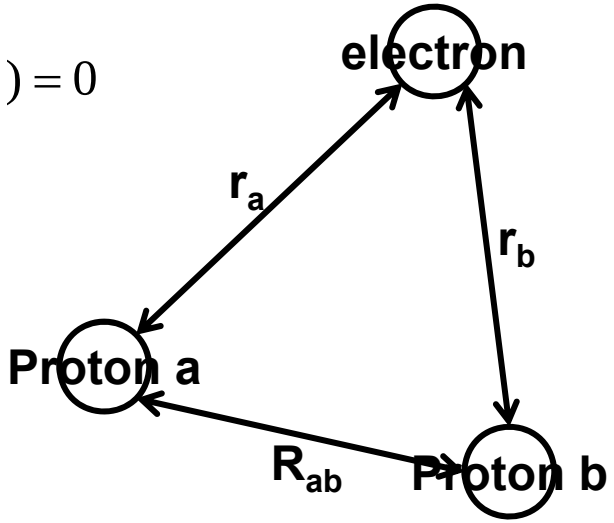


Soft-Matter Optical Spectroscopy

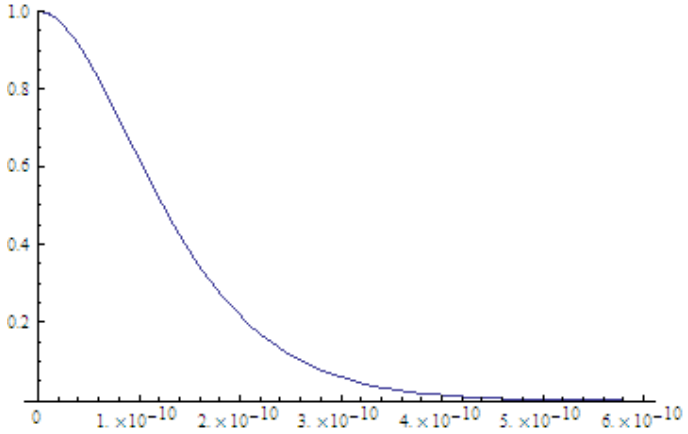
The Hydrogen Molecule-Ion, H^+_2

$$\int dV(\phi_a\phi_a\Delta E - \phi_a \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_b}}_{\equiv C}\phi_a)c_1 + (\phi_a\phi_b\Delta E - \phi_a \underbrace{\frac{e^2}{4\pi\varepsilon_0 r_a}}_{\equiv D}\phi_b)c_2) = 0 \qquad \equiv S$$

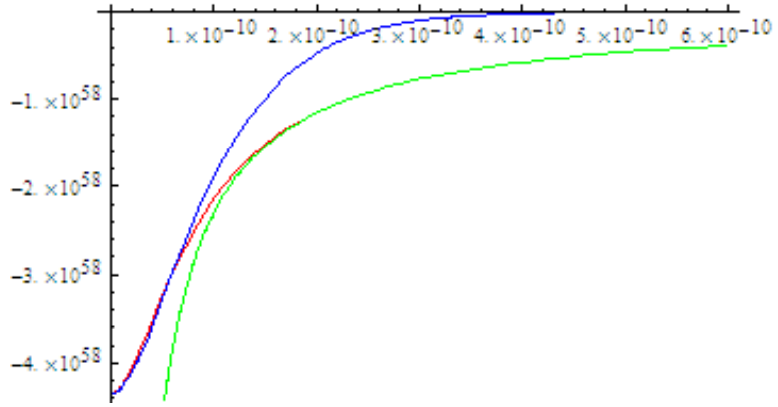
$$E_{binding} = \frac{C \pm D}{1 \pm S} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}}$$



For Ground State (1s state)



S : overlap integral



C : Coulomb integral

D: Resonance integral

(-) Proton Coulomb interaction

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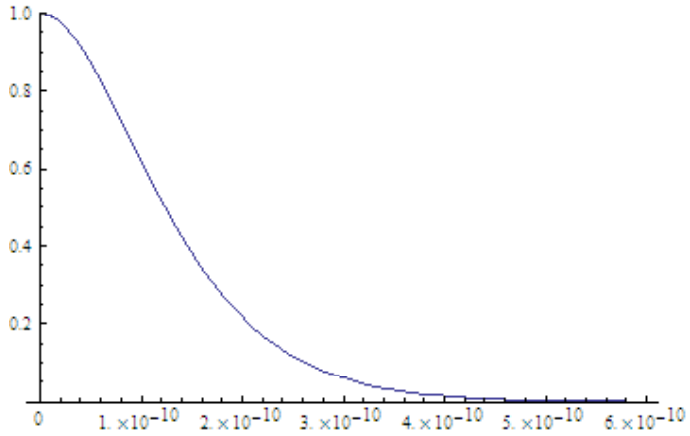
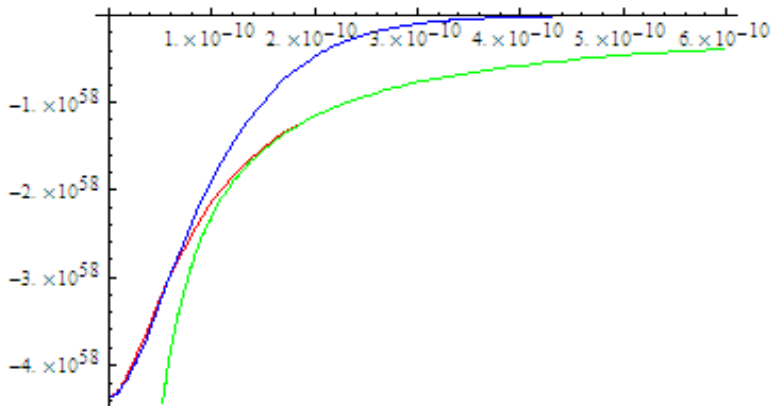
The Hydrogen Molecule-Ion, H^+_2

For Ground State (1s state)

$$E_{binding} = \frac{C \pm D}{1 \pm S} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}}$$



S : overlap integral



C : Coulomb integral

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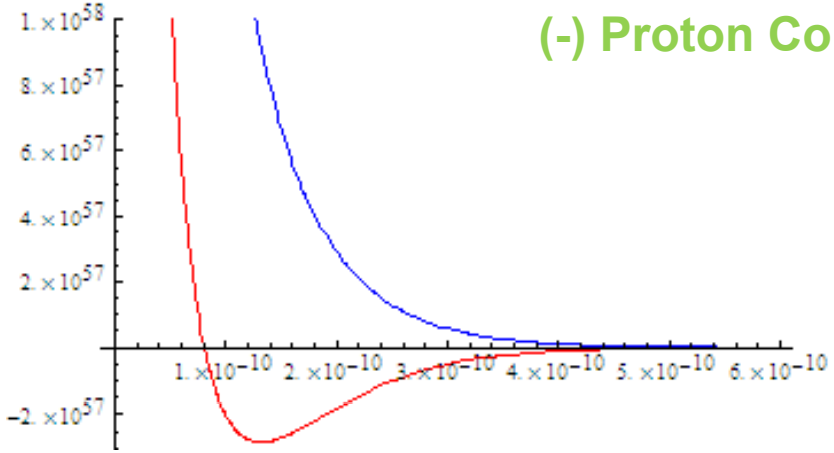
(-) Proton Coulomb interaction



Bonding State (Symmetric wavefn)

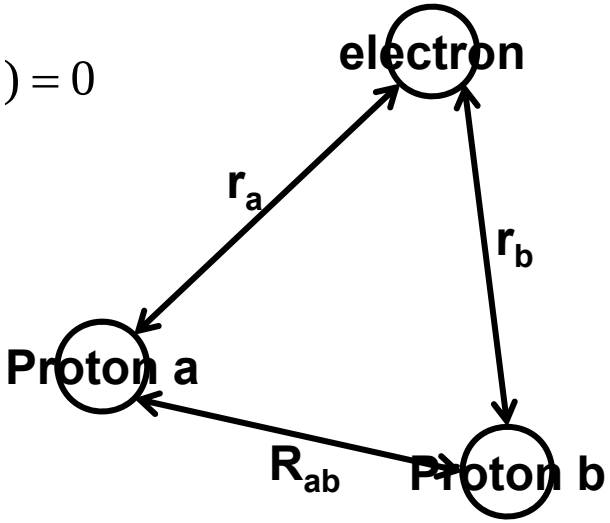
Antibonding State (Antisymmetric wavefn)

Soft-Matter Optical Spectroscopy

The Hydrogen Molecule-Ion, H^+_2

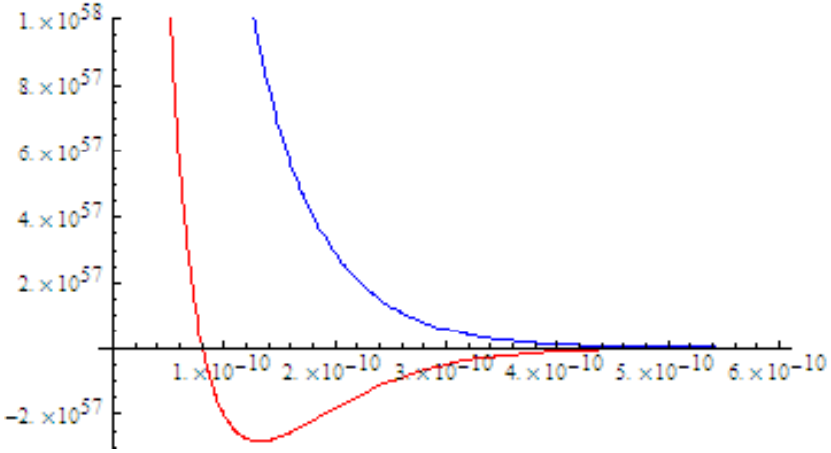
$$\int dV(\phi_a\phi_a\Delta E - \phi_a \frac{e^2}{4\pi\varepsilon_0 r_b}\phi_a)c_1 + (\phi_a\phi_b\Delta E - \phi_a \frac{e^2}{4\pi\varepsilon_0 r_a}\phi_b)c_2) = 0$$

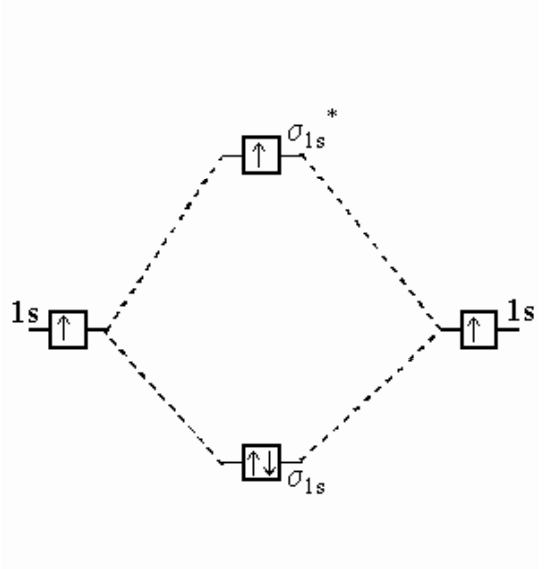
$\equiv C$ $\equiv S$ $\equiv D$



$$E_{binding} = \frac{C \pm D}{1 \pm S} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}}$$

For Ground State (1s state)





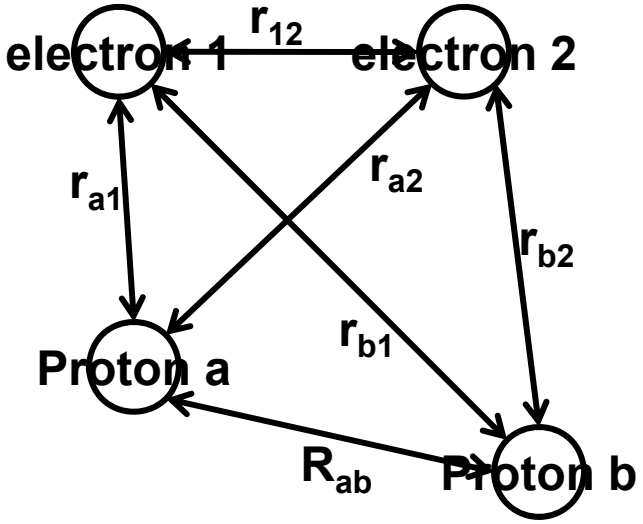
Bonding State (Symmetric wavefn)

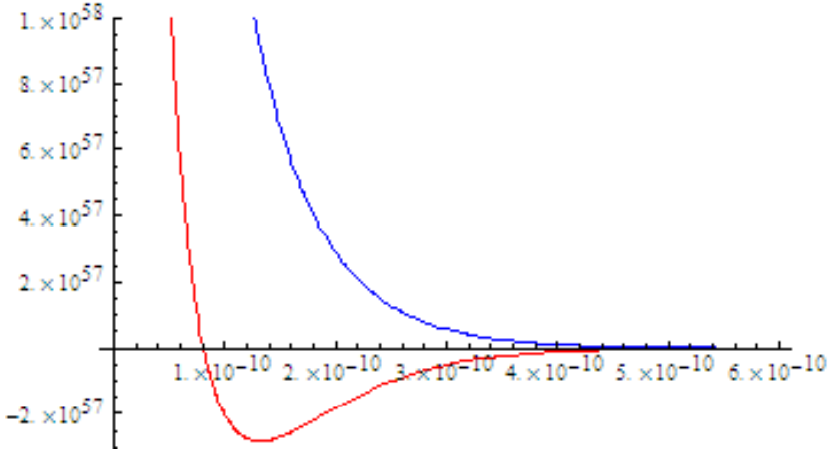
Antibonding State (Antisymmetric wavefn)

SMOS
Soft-Matter Optical Spectroscopy

The Hydrogen Molecule, H_2

$$H = -\frac{\hbar^2}{2m_0}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0 r_{a1}} - \frac{\hbar^2}{2m_0}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_{b2}} - \frac{e^2}{4\pi\varepsilon_0 r_{b1}} - \frac{e^2}{4\pi\varepsilon_0 r_{a2}} - \frac{e^2}{4\pi\varepsilon_0 R_{ab}} - \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$





Soft-Matter Optical Spectroscopy

The Hydrogen Molecule, H_2

We can get wavefunction from variational principle

If we in fact do not use a true eigenfunction of the ground state of the system for ψ, but rather some other wavefunction, ten its corresponding energy expectation value will always be larger than the eigenvalue of a solution of a true eigenfunction

$$E_{trial} = \frac{\int dV \psi^*_{trial} H \psi_{trial}}{\int dV \psi^*_{trial} \psi_{trial}} \qquad E_{true} = \frac{\int dV \psi^*_{true} H \psi_{true}}{\int dV \psi^*_{true} \psi_{true}}$$

$$E_{trial} \geq E_{true}$$

Approaching Methods

Molecular Orbitals will be built up using LCAO
(LCAO : Linear Combination of Atomic Orbitals)

$$\psi = \sum_r c_r \phi_r$$

Pauli Exclusion Principle

Hund's Rule

Results

The central symmetry of the Coulomb potential is removed

-> the angular momentum quantum number l is no longer a good quantum number. So a new quantization condition is introduced in molecular physics, characterised by the quantity λ.

The electrons are associated with both atoms at the same time

The electronic terms which were originally degenerate are split.

Next Stories…

Electronic Structure of Diatomic Molecule

Electronic Structure of Polyatomic molecules
(Especially, Conjugated π-sytems)

Electronic Structure of Larger Molecules