The Simplest Molecule: H_2^+ (Worksheet)

Name: KEY

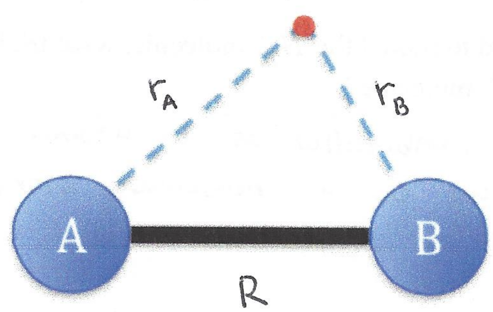
Section: ______________________

Student ID#: ______________________

Work in groups on these problems. You should try to answer the questions without referring to your textbook. If you get stuck, try asking another group for help.

Q1

The absolutely simplest molecule consists of two nuclei with one proton each and one electron.



Using atomic units..

- What is the kinetic energy of the electron in the H_2^+ Hamiltonian, $\hat{T}$?

$$\hat{T}_{el} = \frac{-1}{2} \nabla^2_{el}$$

- What is the potential energy of the electron interacting with nucleus A of the Hamiltonian?

$$\hat{V}_{el-A} = \frac{-1}{r_A}$$

- What is the potential energy of the electron interacting with nucleus B of the Hamiltonian?

$$\hat{V}_{el-B} = \frac{-1}{r_B}$$

Q2

Because electrons move so much faster than nuclei, we can assume that on the timescale of electron motion, the nuclei are not moving. This separation of electron and nuclear coordinates is called the *Born-Oppenheimer approximation*.

What is the potential energy of nucleus A interacting with nucleus B?

$$\hat{V}_{A-B} = \frac{1}{R}$$

To describe the complete Hamiltonian for the electron, do we need to include kinetic energy of the nuclei? Do we need to include the potential energy for the nuclei?

Do not include the kinetic energy of the nuclei, but include the potential energy for the nuclei.

If we want to use variation method to model the H_2^+ molecule, what trial wavefunction do you think would be reasonable to guess for the H_2^+ molecule?

A linear combination of 1s atomic orbital wavefunctions may be a reasonable starting point.

Q3

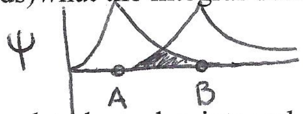
Using $\phi = c_1\psi_{1s_A} + c_2\psi_{1s_B} = c_1|1s_A\rangle + c_2|1s_B\rangle$ and $E_\phi = \dfrac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$ we can find an energy for the system. Substituting the trial wavefunction into the denominator, $\langle\phi|\phi\rangle$, leads to $\langle\phi|\phi\rangle = \langle c_1 1s_A + c_1 1s_B | c_1 1s_A + c_1 1s_B\rangle$. By multiplying the terms in the integral, what are the four terms that arise? (integrals or brackets)

$$\frac{\langle c_1 1s_A|\hat{H}|c_1 1s_A\rangle}{\langle c_1 1s_A|c_1 1s_A\rangle} = \frac{H_{AA}}{S_{AA}} \qquad \frac{H_{AB}}{S_{AB}} \qquad \frac{H_{BA}}{S_{BA}} \qquad \frac{H_{BB}}{S_{BB}}$$

The first integral in the sum is $\langle c_1 1s_A | c_1 1s_A\rangle$. What is the value of this integral?

$$\langle c_1 1s_A | c_1 1s_A\rangle = S_{AA} = c_1^2$$

We also get terms in $\langle\phi|\phi\rangle$ that look like $\langle c_1 1s_A | c_1 1s_B\rangle$. We call this an overlap integral. Explain (in words)what the integral describes.

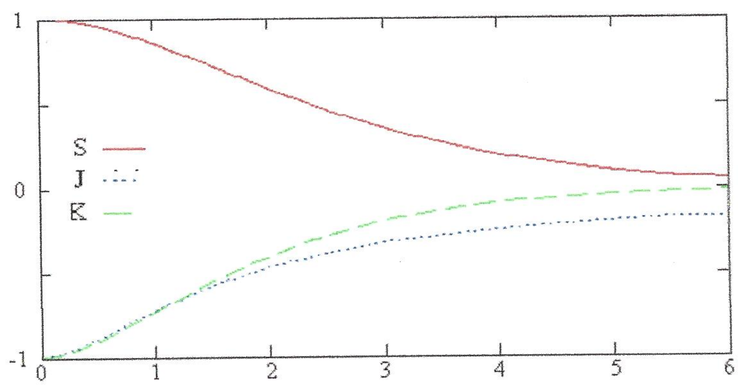


The integral S_{AB} describes the overlap of atomic orbital wavefunctions in a molecule.

The related overlap integral (just missing the constants) is commonly called $\langle 1s_A | 1s_B\rangle = S$.

Use your expression for $\langle c_1 1s_A | c_1 1s_A\rangle$ and the definition $\langle 1s_A | 1s_B\rangle = S$ to write a simple form for $\langle\phi|\phi\rangle$

The Figure below plots the overlap integral (solid red curve) as a function of internuclear distance. Based on this graph, what happens to the overlap integral as the internuclear bond stretches?



The numerator for $E_\phi = \dfrac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle}$ is $\langle\phi|\hat{H}|\phi\rangle$. Substituting the trial wavefunction into the numerator yields $\langle\phi|\hat{H}|\phi\rangle = \langle c_1 1s_A + c_1 1s_B|\hat{H}|c_1 1s_A + c_1 1s_B\rangle$. What four terms arise from this expression?

① $\langle c_1 1s_A|\hat{H}|c_1 1s_A\rangle = \langle c_1 A|H|c_1 A\rangle$ ② $\langle c_1 A|H|c_2 B\rangle$ ③ $\langle c_2 B|H|c_1 A\rangle$ ④ $\langle c_2 B|\hat{H}|c_2 B\rangle$

The first term in the $\langle\phi|\hat{H}|\phi\rangle$ integral is $\langle c_1 1s_A|\hat{H}|c_1 1s_A\rangle$. Substitute the Hamiltonian into this expression. How can you simplify this term?

If $\hat{H} = \frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$ distrube and collect terms and simplify by using K and J integral notation

The second term in $\langle\phi|\hat{H}|\phi\rangle$ is $\langle c_1 1s_A|\hat{H}|c_1 1s_B\rangle$. Substitute the Hamiltonian into this expression. How can you simplify this term?

$\langle c_1 A|\hat{H}|c_2 B\rangle = \langle c_2 B|\hat{H}|c_1 A\rangle$ due to symmetry of H_2^+

$$\langle E\rangle = \frac{c_1^2 H_{AA} + 2c_1c_2 H_{AB} + c_2^2 H_{BB}}{c_1^2 \underbrace{S_{AA}}_{=1} + 2c_1c_2 S_{AB} + c_2^2 \underbrace{S_{BB}}_{=1}} = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$$

We define the Coulomb integral as $J = \langle c_1 1s_A | \frac{1}{r_B} | c_1 1s_A \rangle$.

We define the exchange integral as $K = \langle c_1 1s_A | \frac{1}{r_A} | c_1 1s_B \rangle$.

Using these expressions, what is the total expression for $\langle \phi | \hat{H} | \phi \rangle$?

$$\langle \phi | \hat{H} | \phi \rangle = E_{1s} + \frac{J \pm K}{1 \pm S}$$