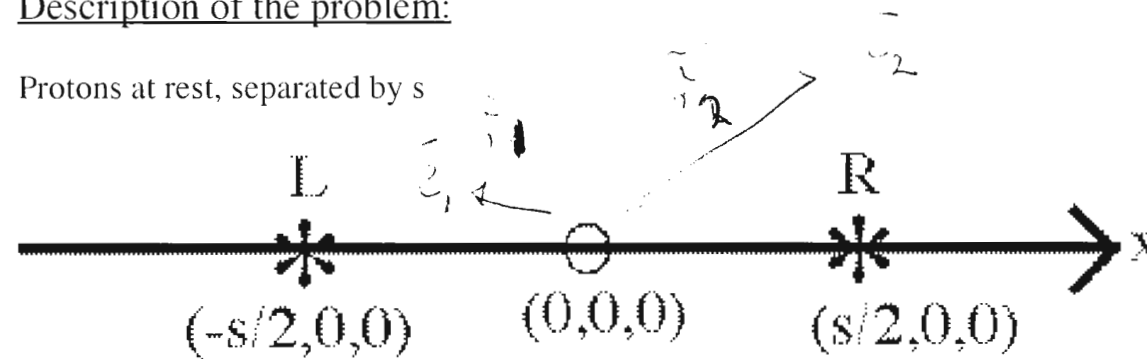# HYDROGEN MOLECULE - VARIATIONAL CALCULATION

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Description of the problem:

Protons at rest, separated by s

* represents a proton and o is the origin. Note that the protons are on the x-axis.
L&R represent protons; 1 and 2 stand for electrons.
Initial conditions

- Electrons in spin antisymmeric state
- Spatial part of the wave function is symmetric
- Without loss of generality, one can take the spatial part of the wave function to be positive everywhere

Recall that

$$H\Psi(\vec{r}_1,\vec{r}_2,s) = E_o(s)\Psi(\vec{r}_1,\vec{r}_2,s) \tag{1}$$

The Hamiltonian for the system is

$$H = -\frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} - \frac{e^2}{r_{1L}} - \frac{e^2}{r_{1R}} - \frac{e^2}{r_{2L}} - \frac{e^2}{r_{2R}} + \frac{e^2}{r_{12}} \tag{2}$$

where

- $\vec{r}_{1L} = \left|\vec{r}_1 + \frac{s}{2}\hat{x}\right|$ (3a)

- $\vec{r}_{2L} = \left|\vec{r}_2 + \frac{s}{2}\hat{x}\right|$ (3b)

- $\vec{r}_{1R} = \left|\vec{r}_1 - \frac{s}{2}\hat{x}\right|$ (3c)

- $\vec{r}_{2R} = \left| \vec{r}_2 - \dfrac{s}{2} \hat{x} \right|$ (3d)

- $\vec{r}_{12} = \left| \vec{r}_1 - \vec{r}_2 \right|$ (3e)

Multiply eq. (1) by $\Psi(\vec{r}_1, \vec{r}_2, s)$ and integrate over $\vec{r}_1$ and $\vec{r}_2$

$$\int d\vec{r}_1 \int d\vec{r}_2 \Psi(\vec{r}_1, \vec{r}_2, s) H \Psi(\vec{r}_1, \vec{r}_2, s) = E_o(s) \int d\vec{r}_1 \int d\vec{r}_2 \Psi^2(\vec{r}_1, \vec{r}_2, s)$$

or

$$E_o(s) = \frac{\int d\vec{r}_1 \int d\vec{r}_2 \Psi(\vec{r}_1, \vec{r}_2, s) H \Psi(\vec{r}_1, \vec{r}_2, s)}{\int d\vec{r}_1 \int d\vec{r}_2 \Psi^2(\vec{r}_1, \vec{r}_2, s)} .$$

Now let

$$\omega(\vec{r}_1, \vec{r}_2, s) = \frac{\Psi^2(\vec{r}_1, \vec{r}_2, s)}{\int d\vec{r}_1 \int d\vec{r}_2 \Psi^2(\vec{r}_1, \vec{r}_2, s)} = \text{probability density function} \qquad (4)$$

and

$$\varepsilon(\vec{r}_1, \vec{r}_2, s) = \frac{H \Psi(\vec{r}_1, \vec{r}_2, s)}{\Psi(\vec{r}_1, \vec{r}_2, s)} \qquad (5)$$

giving the following

$$E_o(s) = \int dr_1 \int dr_2 \omega(\vec{r}_1, \vec{r}_2, s) \varepsilon(\vec{r}_1, \vec{r}_2, s). \qquad (6)$$

Choice of the wave function:

Suppose the electron - electron interaction is zero. In that case, let us find out what the wave function will be. To the non-interacting wave function, we will add terms that bring in the effects of electron-electron interaction (e⁻ - e⁻) corrections.

Non-interacting simulation:

For the non-interacting system, let

$$H_0 \tilde{\Psi}_0(\vec{r}_1, \vec{r}_2, s) = \tilde{E}_0(s)\tilde{\Psi}_0(\vec{r}_1, \vec{r}_2, s).$$

where the Hamiltonian is

$$H_o = -\frac{\nabla_1^2}{2m} - \frac{\nabla_2^2}{2m} - \frac{e^2}{r_{1L}} - \frac{e^2}{r_{1R}} - \frac{e^2}{r_{2L}} - \frac{e^2}{r_{2R}} = H_{01} + H_{02}. \tag{7}$$

In equation (7)

$$H_{01} = -\frac{\nabla_1^2}{2m} - \frac{e^2}{r_{1L}} - \frac{e^2}{r_{1R}} \tag{8}$$

and

$$H_{02} = -\frac{\nabla_2^2}{2m} - \frac{e^2}{r_{2L}} - \frac{e^2}{r_{2R}}. \tag{9}$$

Substitute (7) in (1)

$$\left(H_{01} + H_{02}\right)\tilde{\Psi}_0(\vec{r}_1, \vec{r}_2) = \tilde{E}_0 \tilde{\Psi}_0(\vec{r}_1, \vec{r}_2) \tag{10}$$

Let

$$\Psi_0(\vec{r}_1, \vec{r}_2, s) = \varphi_1(\vec{r}_1)\varphi_2(\vec{r}_2). \tag{11}$$

Plugging (11) into (10), one finds

$$\tilde{E}_o(s) = \tilde{E}_1 + \tilde{E}_2 \tag{12}$$

where

$$H_{o1}\varphi(\vec{r}_1) = \tilde{E}_1\varphi(\vec{r}_1) \tag{13}$$

and

$$H_{o2}\varphi(\vec{r}_2) = \tilde{E}_1\varphi(\vec{r}_2) \tag{14}$$

$\varphi(\vec{r}_1, s)$ is the independent particle wave function shared equally between the 2 protons,

$$\Psi(r_1,s) = e^{-r_{1L}/a} + e^{-r_{1R}/a} \tag{15}$$

$$\Psi(r_2,s) = e^{-r_{2L}/a} + e^{-r_{2R}/a} \tag{16}$$

In the presence of electron-electron interation, let

$$\Psi(r_1,r_2,s) = \varphi(r_1,s) \bullet \varphi(r_2,s) \bullet f(r_{12}) \tag{17}$$

which is the correlated wave function. In the above equation, $f(r_{12})$ is

$$f(r_{12}) = \exp\left(\frac{r_{12}}{\alpha(1+\beta r_{12})}\right) \tag{18}$$

For large distances r_{12}, $e^2/r_{12} \to 0$

$$f(r_{12}) \to \text{constant}$$

and

$$\Psi(\vec{r}_1,\vec{r}_2,s)) \to \varphi_1(\vec{r}_1,s)\varphi_2(\vec{r}_2,s) \tag{19}$$

Coulomb-Cusp condition:

The Schordinger equation for 1 hydrogen aton is

$$H\varphi = \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r}\right)\varphi = E\varphi \tag{20}$$

Let us examine the kinetic energy term as electron 1 approaches proton L. Then

$$\frac{1}{\varphi}\nabla_i^2\varphi \to -\frac{2}{ar_{iL}}\left[\frac{1}{1+e^{-s/a}}\right] \tag{21}$$

Mutipling the above equation by $-\dfrac{\hbar^2}{2m}$, one obtains

$$-\frac{\hbar^2}{2m}\frac{1}{\varphi}\nabla^2\varphi \to \frac{\hbar^2}{m}\frac{1}{ar_{iL}}\frac{1}{1+e^{-s/a}}. \tag{22}$$

The singularity as $r_{iL} \to 0$ is offset by the singularity from the coulomb attraction. This yields the condtion

$$\frac{\hbar^2}{ma}\frac{1}{1+e^{-s/a}} = e^2 \tag{23}$$

Recall that $\dfrac{\hbar^2}{me^2} = a_0$, Bohr Radius. Pluging a_0 into the above equation one finds

$$a = \frac{a_0}{1+e^{-s/a}} \tag{24}$$

Similarly, one can show that $\alpha = 2a_0$.

Start with

$$f(r_{12}) = \exp\left(\frac{r_{12}}{\alpha(1+\beta r_{12})}\right) \tag{25}$$

$$\nabla_1^2 f(r_{12}) = f\frac{1}{\alpha^2(1+\beta r_{12})^4} + \frac{3f}{\alpha r_{12}(1+\beta r_{12})^2} + \frac{f}{\alpha}\left[-\frac{1}{r_{12}}\frac{1}{(1+\beta r_{12})^2} - \frac{2\beta}{(1+\beta r_{12})^3}\right] \tag{26}$$

For $r_{12} \to 0$

$$\nabla_1^2 f(r_{21}) \to \frac{2f}{\alpha r_{21}(1+\beta r_{12})^2} \tag{27}$$

Similarly, we can arrive at $\nabla_2^2 f(r_{21}) \to \dfrac{2f}{\alpha r_{21}(1+\beta r_{12})^2}$ as $r_{12} \to 0$.

For small r_{12}, we arrive at the condition

$$-\frac{\hbar^2}{2m}\left[\frac{2f}{\alpha}+\frac{2f}{\alpha}\right]+e^2=0 \tag{28}$$

or $\alpha = \dfrac{2\hbar^2}{me^2} = 2a_0$ \hfill (29)

Outline of program:

The Monte Carlo simulation will be performed on equation (6) with $\Psi(\vec{r}_1,\vec{r}_2,s)$ from equation (16). Fix s and β and vary the positions of the electrons one at a time until the minimum energy is found. (Note: s can be looked up.) Every time that you move an electron, if $\omega_{new} > \omega_{old}$ accept the new position. If $\omega_{new} < \omega_{old}$ then generate a random number, γ, between 0 and 1. Find $\dfrac{\omega_{new}}{\omega_{old}}$ if this is greater than γ then accept the new position and calculate ε, but if it is less than γ retain the old position. After obtaining a reliable estimate of energy $E_0(s)$, choose another β and find the minimum value of the energy.