

Application of the variational method to H_2^+

H_2^+ is the simplest molecular ion, consisting only of a single electron and two nuclei (usually protons). The Hamiltonian of this system reads as follows

$$H = -\frac{\hbar^2}{2M} \vec{\nabla}_{R_1}^2 - \frac{\hbar^2}{2M} \vec{\nabla}_{R_2}^2 - \frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{R} \right)$$

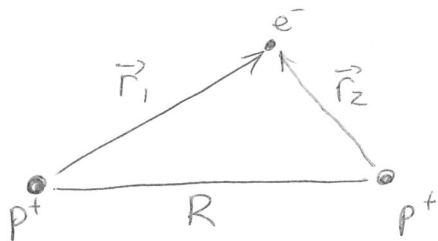
where \vec{R}_1 and \vec{R}_2 are the positions of nuclei, M are their masses, \vec{r}_1 and \vec{r}_2 are the distances of the electron respective to nuclei 1 and 2, m is the electron mass and $R = |\vec{R}_1 - \vec{R}_2|$.

Since $M \gg m$ we can try to solve for the wave function assuming that nuclei are fixed in space (or, equivalently, are infinitely heavy). This yields a simplified Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \underbrace{\frac{e^2}{4\pi\epsilon_0} \frac{1}{R}}_{\text{just an additive constant}}$$

Note that the dependence on R in this simplified Hamiltonian is parametric. R is no longer a variable, but rather a parameter, which H depends on. Hence, the energy and the wave function also depend on R parametrically, i.e. $E = E(R)$, $\psi = \psi(\vec{r}; R)$.

Our task is to solve for the ground state of H_2^+ using the variational method and find out whether bound states are allowed in this system. We also want to determine a qualitative dependence $E(R)$.



We will choose our trial function in the following form:

$$\psi = A [\psi_{100}(r_1) + \psi_{100}(r_2)] \quad \psi_{100}(r) = \frac{e^{-r/a}}{(\pi a^3)^{1/2}} \quad a = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

This form is motivated by two facts: 1) ψ must approach the hydrogenic wave function when two nuclei are separated by infinity 2) we do not want to discriminate between nuclei 1 and 2.

First let us compute the normalization factor, A :

$$1 = \int |\psi|^2 d\vec{r} = |A|^2 \left[\underbrace{\int |\psi_{100}(r_1)|^2 d\vec{r}}_1 + \underbrace{\int |\psi_{100}(r_2)|^2 d\vec{r}}_1 + 2 \int \psi_{100}(r_1) \psi_{100}(r_2) d\vec{r} \right]$$

$$I \equiv \langle \psi_{100}(r_1) | \psi_{100}(r_2) \rangle = \frac{1}{\pi a^3} \int e^{-(r_1+r_2)/a} d\vec{r}$$

Since the Hamiltonian contains only ∇_r^2 , $\frac{1}{r_1}$, and $\frac{1}{r_2}$, we can choose the origin for \vec{r} as we wish (it would not alter the Hamiltonian). Let us pick the origin at nucleus 1 and the second nucleus at distance R in the positive direction of the z -axis. Then

$$\vec{r}_1 = \vec{r} \quad r_2 = \sqrt{r^2 + R^2 - 2rR \cos\theta} \quad \text{where } \theta \text{ is the}$$

angle between \vec{r}_1 and \vec{R} . With that

$$I = \frac{1}{\pi a^3} \int e^{-\frac{r}{a}} e^{-\frac{1}{a}\sqrt{r^2 + R^2 - 2rR \cos\theta}} r^2 \sin\theta dr d\theta d\phi$$

The integration over ϕ yields 2π . The integral over

θ is:

$$\int_0^\pi e^{-\frac{\sqrt{r^2 + R^2 - 2rR \cos\theta}}{a}} \sin\theta d\theta = \left| \begin{array}{l} y^2 = r^2 + R^2 - 2rR \cos\theta \\ 2y dy = 2rR \sin\theta d\theta \end{array} \right| =$$

$$= \frac{1}{rR} \int_{|r-R|}^{r+R} e^{-\frac{y}{a}} y dy = \frac{1}{rR} \left(-\frac{\partial}{\partial \beta} \right) \int_{|r-R|}^{r+R} e^{-\beta y} dy \Bigg|_{\beta = \frac{1}{a}}$$

$$= \frac{1}{rR} \left(\frac{\partial}{\partial \beta} \right) \frac{1}{\beta} \left[e^{-\beta|r+R|} - e^{-\beta|r-R|} \right] \Big|_{\beta=\frac{1}{a}} = \frac{1}{rR} \left\{ -\frac{1}{\beta^2} \left[e^{-\beta|r+R|} - e^{-\beta|r-R|} \right] + \right.$$

$$\left. + \frac{1}{\beta} \left[-|r+R| e^{-\beta|r+R|} + |r-R| e^{-\beta|r-R|} \right] \right\} \Big|_{\beta=\frac{1}{a}} = \frac{1}{rR} \left\{ a^2 e^{-\frac{|r-R|}{a}} - a^2 e^{-\frac{|r+R|}{a}} \right.$$

$$\left. + a|r-R| e^{-\frac{|r-R|}{a}} - a|r+R| e^{-\frac{|r+R|}{a}} \right\} = \frac{a}{rR} \left\{ (a+|r-R|) e^{-\frac{|r-R|}{a}} - (a+|r+R|) e^{-\frac{|r+R|}{a}} \right\}$$

The integral over r is then

$$I = 2\pi \cdot \frac{1}{\pi a^3} \cdot \frac{a}{R} \int_0^{\infty} e^{-\frac{r}{a}} \frac{1}{r} \left\{ (a+|r-R|) e^{-\frac{|r-R|}{a}} - (a+|r+R|) e^{-\frac{|r+R|}{a}} \right\} r^2 dr =$$

$$= \frac{2}{a^2 R} \left[\int_0^R e^{-\frac{r}{a}} e^{-\frac{R-r}{a}} (a+R-r) r dr + \int_R^{\infty} e^{-\frac{r}{a}} e^{-\frac{r-R}{a}} (a+r-R) r dr \right.$$

$$\left. - \int_0^{\infty} e^{-\frac{r}{a}} e^{-\frac{r+R}{a}} (a+r+R) r dr \right] = \frac{2}{a^2 R} \left[e^{-\frac{R}{a}} \int_0^R (a+R+r) r dr + e^{-\frac{R}{a}} \int_R^{\infty} (a+r-R) r dr \right.$$

$$\left. - e^{-\frac{R}{a}} \int_0^{\infty} (a+r+R) r dr \right]$$

After some careful algebraic manipulations (the remaining integrals are straightforward) we will obtain the following result:

$$I = e^{-\frac{R}{a}} \left[1 + \frac{R}{a} + \frac{1}{3} \left(\frac{R}{a} \right)^2 \right]$$

$$\text{and } A^2 = \frac{1}{2(1+I)}$$

Now we can proceed to the evaluation of $\langle H \rangle$.

$$H\psi = \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right] A [\psi_{100}(r_1) + \psi_{100}(r_2)]$$

$$= A E_1 \psi_{100}(r_1) - A \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_2} \psi_{100}(r_1) + A E_1 \psi_{100}(r_2) - A \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_1} \psi_{100}(r_2)$$

$$= E_1 \psi - A \frac{e^2}{4\pi\epsilon_0} \left[\frac{\psi_{100}(r_1)}{r_2} + \frac{\psi_{100}(r_2)}{r_1} \right]$$

$$\langle H \rangle_{\psi} = E_1 - |A|^2 \frac{e^2}{4\pi\epsilon_0} \langle A[\psi_{100}(r_1) + \psi_{100}(r_2)] \left| \frac{\psi_{100}(r_1)}{r_2} + \frac{\psi_{100}(r_2)}{r_1} \right\rangle =$$

$$= E_1 - 2|A|^2 \frac{e^2}{4\pi\epsilon_0} \left[\langle \psi_{100}(r_1) \left| \frac{1}{r_2} \right| \psi_{100}(r_1) \rangle + \langle \psi_{100}(r_1) \left| \frac{1}{r_1} \right| \psi_{100}(r_2) \rangle \right]$$

If we introduce notations (a is the Bohr radius)

$$D \equiv a \langle \psi_{100}(r_1) \left| \frac{1}{r_2} \right| \psi_{100}(r_1) \rangle$$

$$X \equiv a \langle \psi_{100}(r_1) \left| \frac{1}{r_1} \right| \psi_{100}(r_2) \rangle$$

then the expectation value

can be expressed as

$$\langle H \rangle = \left[1 + 2 \frac{D+X}{1+I} \right] E_1$$

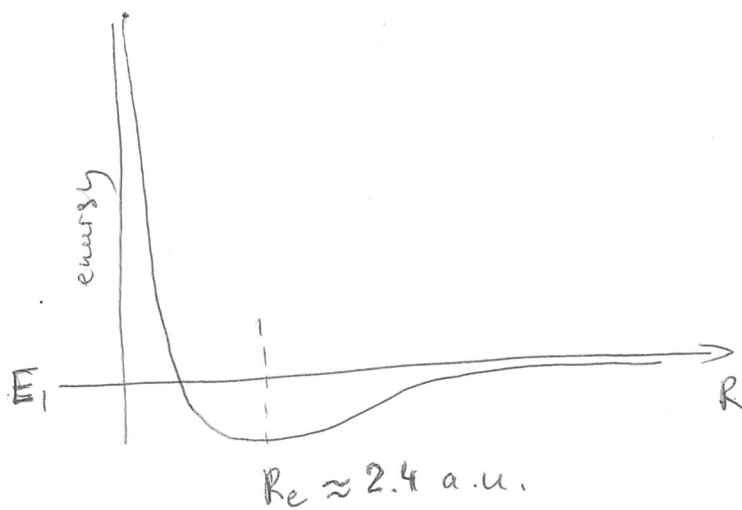
The evaluation of D and X can be done in a similar way as we did I. The results are as follows

$$D = \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-\frac{2R}{a}}$$

$$X = \left(1 + \frac{R}{a}\right) e^{-\frac{R}{a}}$$

The total energy of the system, in addition to $\langle H \rangle$, contains the proton-proton repulsion: $\frac{e^2}{4\pi\epsilon_0} \frac{1}{R}$

If we plot now $\langle H \rangle(R) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R}$ as a function of R we will get the following picture



We can see from this plot that the energy of the ground state of H_2^+ at $R = R_e$ is lower than the energy of a separate H atom and a proton. Thus, it is energetically favourable. Since

the variational method provides an upper bound, there is no doubt there are bound states of H_2^+ .