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

$$H = -\frac{\hbar^2}{2M}\vec{\nabla}^2_{R_1} - \frac{\hbar^2}{2M}\vec{\nabla}^2_{R_2} - \frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{R}\right)$$

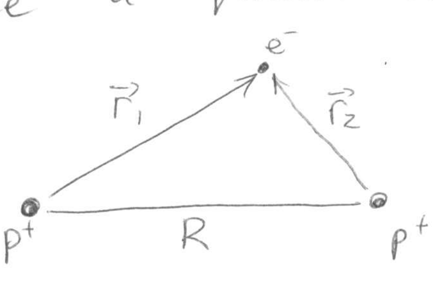
where $\vec{R}_1$ and $\vec{R}_2$ are the positions of nuclei, M are their masses, $\vec{r}_1$ and $\vec{r}_2$ are the distances of the electron respective to nuclei 1 and 2, m is the electron mass and $R = |\vec{R}_1 - \vec{R}_2|$.

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

$$H = -\frac{\hbar^2}{2m}\nabla - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{R}}_{\text{just an additive constant}}$$

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:

$$\psi = A\left[\psi_{100}(r_1) + \psi_{100}(r_2)\right] \qquad \psi_{100}(r) = \frac{1}{(\pi a^3)^{1/2}} e^{-\frac{r}{a}}$$

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:

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

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

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

$$\vec{r}_1 = \vec{r} \qquad r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta}$$

where θ 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:

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

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

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

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

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

The integral over r is then

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

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

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

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

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

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

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

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

$$H\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right] A\left[\psi_{100}(r_1) + \psi_{100}(r_2)\right]$$

$$= AE_1\psi_{100}(r_1) - A\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_2}\psi_{100}(r_1) + AE_1\psi_{100}(r_2) - A\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_1}\psi_{100}(r_2)$$

$$= E_1\psi - A\frac{e^2}{4\pi\varepsilon_0}\left[\frac{\psi_{100}(r_1)}{r_2} + \frac{\psi_{100}(r_2)}{r_1}\right]$$

$$\langle H\rangle_\psi = E_1 - |A|^2 \frac{e^2}{4\pi\varepsilon_0}\left\langle A[\psi_{100}(r_1)+\psi_{100}(r_2)] \middle| \frac{\psi_{100}(r_1)}{r_2} + \frac{\psi_{100}(r_2)}{r_1}\right\rangle =$$

$$= E_1 - 2|A|^2 \frac{e^2}{4\pi\varepsilon_0}\left[\left\langle\psi_{100}(r_1)\middle|\frac{1}{r_2}\middle|\psi_{100}(r_1)\right\rangle + \left\langle\psi_{100}(r_1)\middle|\frac{1}{r_1}\middle|\psi_{100}(r_2)\right\rangle\right]$$

If we introduce notations (a is the Bohr radius)

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

then the expectation value can be expressed as

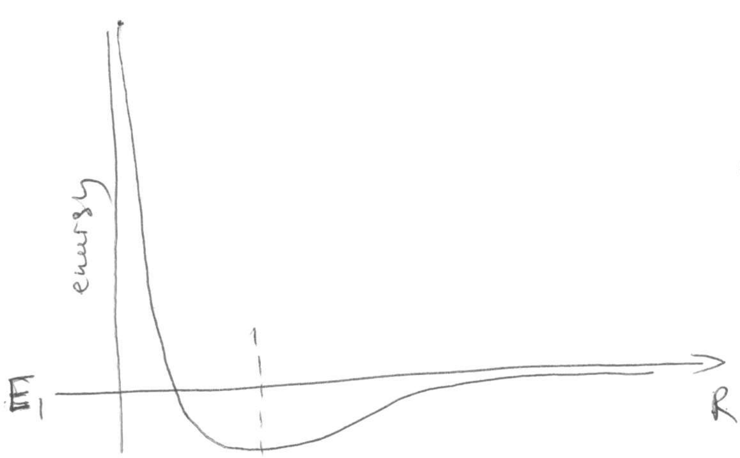
$$\langle H\rangle = \left[1 + 2\frac{D+X}{1+I}\right]E_1$$

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

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

The total energy of the system, in addition to $\langle H\rangle$, contains the proton-proton repulsion: $\frac{e^2}{4\pi\varepsilon_0}\frac{1}{R}$

If we plot now $\langle H\rangle(R) + \frac{e^2}{4\pi\varepsilon_0}\frac{1}{R}$ as a function of R we will get the following picture



$R_e \approx 2.4$ a.u.

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^+.