

HYDROGEN MOLECULE ION - DIFFERENT TRIAL FUNCTION

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We've seen a calculation of the ground state of the hydrogen molecule ion H_2^+ using the variational principle. In that example, the trial function is the sum of two hydrogen atom ground state functions. However, any trial function will serve in the variational principle, so we could have chosen the difference instead. Here we present a parallel derivation of the upper limit on the energy as determined by this trial function.

The hamiltonian for this system is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \quad (1)$$

where r_i is the distance from the electron to proton number i , and the operator ∇^2 takes derivatives with respect to the position \mathbf{r} of the electron. As a first attempt at the problem, we assume that the two protons are in fixed positions a distance R apart, and we place proton 1 at the origin (so that $\mathbf{r} = \mathbf{r}_1$) and proton 2 on the z axis so that $\mathbf{R} = R\hat{\mathbf{z}}$, and thus using the cosine rule for triangles:

$$r_2 = \sqrt{r^2 + R^2 - 2rR\cos\theta} \quad (2)$$

where θ is the usual spherical angular coordinate.

For our trial function ψ we can take the difference of two ground state hydrogen atom wave functions $\psi_0(\mathbf{r}_1)$ and $\psi_0(\mathbf{r}_2)$, where

$$\psi_0(\mathbf{r}_i) = \frac{1}{\sqrt{\pi a^3}} e^{-r_i/a} \quad (3)$$

Thus we start with

$$\psi = A(\psi_0(\mathbf{r}_1) - \psi_0(\mathbf{r}_2)) \quad (4)$$

where A is the normalization constant.

To find A we do the usual integral

$$\int |\psi|^2 d^3\mathbf{r} = 1 \quad (5)$$

$$= |A|^2 [\langle \psi_0(\mathbf{r}_1) | \psi_0(\mathbf{r}_1) \rangle + \langle \psi_0(\mathbf{r}_2) | \psi_0(\mathbf{r}_2) \rangle - 2 \langle \psi_0(\mathbf{r}_1) | \psi_0(\mathbf{r}_2) \rangle] \quad (6)$$

$$= 2|A|^2 [1 - I] \quad (7)$$

where we've used the normalization of the individual wave functions, and the definition:

$$I \equiv \langle \psi_0(\mathbf{r}_1) | \psi_0(\mathbf{r}_2) \rangle \quad (8)$$

$$= \frac{1}{\pi a^3} \int e^{-(r_1+r_2)/a} r^2 \sin\theta d\phi d\theta dr \quad (9)$$

Note that we *cannot* say that $I = 0$ by assuming that $\psi_0(\mathbf{r}_1)$ is orthogonal to $\psi_0(\mathbf{r}_2)$, since the two functions are actually the same function evaluated over different coordinates, rather than two orthogonal functions evaluated over the same coordinates, as would be required for the integral to be zero.

By using $r_1 = r$ and 2 we can do the integral using Maple (for the details of a manual calculation, see Griffiths, section 7.3), and get

$$I = e^{-R/a} \frac{3a^2 + 3aR + R^2}{3a^2} \quad (10)$$

$$|A|^2 = \frac{1}{2(1-I)} \quad (11)$$

Now we need to work out $\langle H \rangle$ for our trial function. We can do this by using the one-proton eigenvalue equation:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_i} \right] \psi_0(\mathbf{r}_i) = E_1 \psi_0(\mathbf{r}_i) \quad (12)$$

where E_1 is the ground state energy of the hydrogen atom (-13.6 eV). This equation is true for both position vectors \mathbf{r}_1 and \mathbf{r}_2 , even though the derivative ∇^2 is with respect to $r = r_1$. Therefore, we can write

$$H\psi = \left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \right] (\psi_0(\mathbf{r}_1) - \psi_0(\mathbf{r}_2)) \quad (13)$$

$$= E_1(\psi_0(\mathbf{r}_1) - \psi_0(\mathbf{r}_2)) - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_2}\psi_0(\mathbf{r}_1) - \frac{1}{r_1}\psi_0(\mathbf{r}_2) \right] \quad (14)$$

$$= E_1\psi - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_2}\psi_0(\mathbf{r}_1) - \frac{1}{r_1}\psi_0(\mathbf{r}_2) \right] \quad (15)$$

We thus have:

$$\langle H \rangle = E_1 - \frac{|A|^2 e^2}{4\pi\epsilon_0} \left\langle \psi_0(\mathbf{r}_1) \left| \frac{1}{r_2} \right| \psi_0(\mathbf{r}_1) \right\rangle - \frac{|A|^2 e^2}{4\pi\epsilon_0} \left\langle \psi_0(\mathbf{r}_2) \left| \frac{1}{r_1} \right| \psi_0(\mathbf{r}_2) \right\rangle \quad (16)$$

$$+ \frac{|A|^2 e^2}{4\pi\epsilon_0} \left\langle \psi_0(\mathbf{r}_2) \left| \frac{1}{r_2} \right| \psi_0(\mathbf{r}_1) \right\rangle + \frac{|A|^2 e^2}{4\pi\epsilon_0} \left\langle \psi_0(\mathbf{r}_1) \left| \frac{1}{r_1} \right| \psi_0(\mathbf{r}_2) \right\rangle \quad (17)$$

By the symmetry of the problem, the first two integrals are equal, as are the last two, so we have

$$\langle H \rangle = E_1 - \frac{2|A|^2 e^2}{4\pi\epsilon_0} \left[\left\langle \psi_0(\mathbf{r}_1) \left| \frac{1}{r_2} \right| \psi_0(\mathbf{r}_1) \right\rangle - \left\langle \psi_0(\mathbf{r}_1) \left| \frac{1}{r_1} \right| \psi_0(\mathbf{r}_2) \right\rangle \right] \quad (18)$$

We can define these two integrals as the *direct integral* D and the *exchange integral* X :

$$D \equiv a \left\langle \psi_0(\mathbf{r}_1) \left| \frac{1}{r_2} \right| \psi_0(\mathbf{r}_1) \right\rangle \quad (19)$$

$$X \equiv a \left\langle \psi_0(\mathbf{r}_1) \left| \frac{1}{r_1} \right| \psi_0(\mathbf{r}_2) \right\rangle \quad (20)$$

We can work them out using similar techniques to those in the evaluation of 9 or just use Maple:

$$D = \frac{a}{\pi a^3} \int \frac{e^{-2r/a}}{\sqrt{r^2 + R^2 - 2rR \cos \theta}} r^2 \sin \theta d\phi d\theta dr \quad (21)$$

$$= \frac{a}{R} - \left(1 + \frac{a}{R}\right) e^{-2R/a} \quad (22)$$

$$X = \frac{a}{\pi a^3} \int \frac{1}{r} e^{-r/a} e^{-\sqrt{r^2 + R^2 - 2rR \cos \theta}/a} r^2 \sin \theta d\phi d\theta dr \quad (23)$$

$$= \left(1 + \frac{R}{a}\right) e^{-R/a} \quad (24)$$

If we write the ground state energy of hydrogen as

$$E_1 = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2a} \quad (25)$$

we can combine these results to give

$$\langle H \rangle = E_1 \left(1 + 2 \frac{D - X}{1 - I}\right) \quad (26)$$

This represents the electron's energy, so we need to add the potential energy between the two protons, which is

$$V_{pp} = \frac{e^2}{4\pi\epsilon_0 R} = -\frac{2a}{R} E_1 \quad (27)$$

so the total energy (or rather the upper bound on the energy) is

$$E \leq \left(1 + 2 \frac{D - X}{1 - I} - \frac{2a}{R}\right) E_1 \quad (28)$$

In order for this to predict the existence of a bound state for the molecule ion, the quantity in parentheses needs to be greater than 1 (since $E_1 < 0$) in order for the upper bound on E to be less than E_1 . If we define $x \equiv R/a$, we can rewrite this formula as follows:

$$D = \frac{1}{x} - \left(1 + \frac{1}{x}\right) e^{-2x} \quad (29)$$

$$X = (1 + x) e^{-x} \quad (30)$$

$$I = e^{-x} \left(1 + x + \frac{x^2}{3}\right) \quad (31)$$

$$E \leq -F(x) E_1 \quad (32)$$

where

$$F(x) = -1 - 2 \frac{D-X}{1-I} + \frac{2}{x} \quad (33)$$

$$= -1 + \frac{2}{x} \left[\frac{-x(D-X) + 1 - I}{1-I} \right] \quad (34)$$

$$= -1 + \frac{2}{x} \left(1 - e^{-x} \left(1 + x + \frac{x^2}{3} \right) \right)^{-1} \times \\ \left(1 - e^{-x} \left(1 + x + \frac{x^2}{3} \right) - (1 - (x+1)e^{-2x}) + e^{-x}(x+x^2) \right) \quad (35)$$

$$= -1 + \frac{2}{x} \left(1 - e^{-x} \left(1 + x + \frac{x^2}{3} \right) \right)^{-1} \left[e^{-x} \left(-1 + \frac{2x^2}{3} \right) + (x+1)e^{-2x} \right] \quad (36)$$

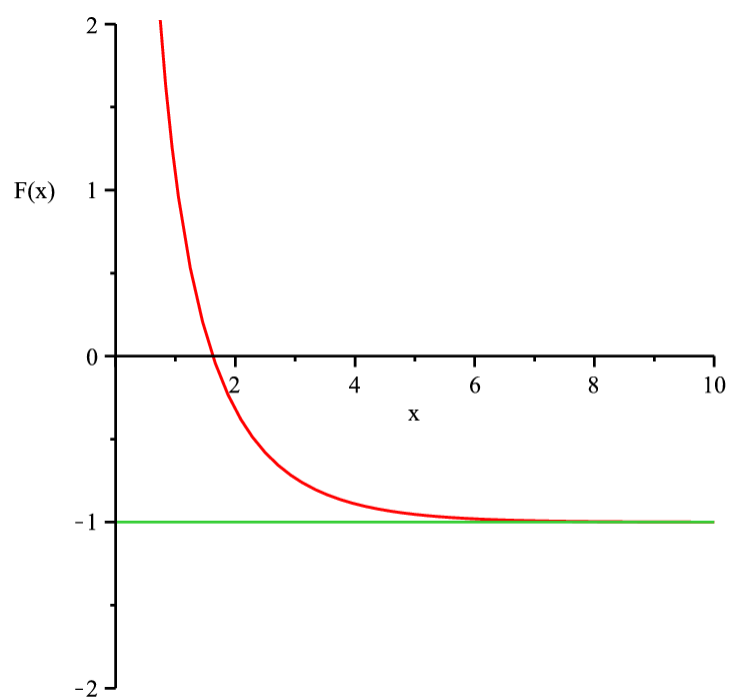
$$= -1 + \frac{2}{x} \left(-1 + e^{-x} \left(1 + x + \frac{x^2}{3} \right) \right)^{-1} \left[e^{-x} \left(1 - \frac{2x^2}{3} \right) - (x+1)e^{-2x} \right] \quad (37)$$

A plot of $F(x)$ (Fig. 1) shows that it never goes below -1 , although it does approach it asymptotically.

Since this is an upper bound on the energy it doesn't exclude a bound state, but it doesn't predict one either. Clearly the trial function that is the sum of two atomic functions is a better start.

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Trial function is difference

FIGURE 1.