

## HYDROGEN MOLECULE ION

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Another application of the variational principle is calculation of the ground state of the hydrogen molecule ion  $\text{H}_2^+$ , which consists of two protons and a single electron. In a sense, this is the inverse of the helium atom problem, since instead of two electrons and one nucleus, we have two nuclei and one electron. 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  $\nabla^2$  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  $\theta$  is the usual spherical angular coordinate.

For our trial function  $\psi$  we can take the sum 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  $\nabla^2$  is with respect to  $r = r_1$ . You can verify this by plugging in  $\psi_0(\mathbf{r}_2)$  and using 2, though it leads to a lot of messy algebra. 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 the variational principle, we need a parameter to vary to get the lowest upper bound on the energy. The only parameter we've introduced in this model is the proton-proton distance  $R$  so, in principle, we could take the derivative with respect to  $R$  and set the result to zero. This gives us a transcendental equation in  $R$  so we'd still need to solve it numerically or graphically. In order for the hydrogen molecule ion to be stable, we would need an energy  $E < E_1$ , and it turns out that if we graph the result, we do indeed find a minimum for  $E$  that is less than  $E_1$ , which indicates that the ion is stable. The value of  $R$  that gives this minimum is  $R = 2.4a$  and gives a binding energy of  $E = E_1 - 1.8$  eV. Experimentally, the value is actually  $E_1 - 2.8$  eV, but the variational principle always overestimates energies so this is expected. What is important is that the variational principle shows that a bound state does exist.

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