

VARIATIONAL PRINCIPLE AND THE HYDROGEN ION: TWO PARAMETERS

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 7.18.

An interesting variant on the variational principle used to calculate an upper bound on the ground state of the hydrogen ion is one proposed in 1944 by Chandrasekhar. It uses two adjustable parameters instead of the one we've used so far. The exact hamiltonian for the H^- ion is

$$(0.1) \quad H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0} \left[\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right]$$

Here we are using two independent spatial coordinates \mathbf{r}_1 and \mathbf{r}_2 , one for each electron. The terms in the square brackets are the interaction terms between the electrons and the nucleus and between the two electrons.

We use as a test function a combination of hydrogen ground states in the form

$$(0.2) \quad \psi = A [\psi_1(r_1) \psi_2(r_2) + \psi_1(r_2) \psi_2(r_1)]$$

where

$$(0.3) \quad \psi_i(r) = \sqrt{\frac{Z_i^3}{\pi a^3}} e^{-Z_i r/a}$$

is a normalized ground state hydrogen wave function and Z_1, Z_2 are the parameters. The idea is that each of the two electrons experiences a different amount of shielding due to differing distances from the nucleus. Equation 0.2 is written as a symmetric function of r_1 and r_2 implying that the spin state is antisymmetric in order to give the two electrons an overall antisymmetric function, as required by the Pauli exclusion principle.

To find the optimal values of the Z_i we can follow the usual procedure in the variational principle, although the calculations are quite tedious. One approach is simply to plug the equations as they stand into software such as

Maple and let it grind through the calculations. However, to get the answer in Griffiths's book requires a bit more work.

First, we observe that $\psi_i(r_j)$ is an eigenfunction of

$$(0.4) \quad H_{ij} \equiv -\frac{\hbar^2}{2m} \nabla_j^2 - \frac{e^2}{4\pi\epsilon_0} \frac{Z_i}{r_j}$$

with eigenvalue (energy) $Z_i^2 E_1$ where $E_1 = -13.6$ eV is the ground state energy of a hydrogen atom. Thus we can write the original hamiltonian 0.1 as

$$(0.5) \quad H = H_{11} + H_{22} + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_1 - 1}{r_1} + \frac{Z_2 - 1}{r_2} \right] + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$(0.6) \quad = H_{12} + H_{21} + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_2 - 1}{r_1} + \frac{Z_1 - 1}{r_2} \right] + \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

In calculating $H\psi$, we can use the fact that

$$(0.7) \quad (H_{11} + H_{22}) \psi_1(r_1) \psi_2(r_2) = E_1 (Z_1^2 + Z_2^2) \psi_1(r_1) \psi_2(r_2)$$

$$(0.8) \quad = (H_{12} + H_{21}) \psi_1(r_2) \psi_2(r_1)$$

To calculate $\langle H \rangle$ we therefore need to calculate the means of the remaining terms in 0.5 and 0.6.

First, however, we need to calculate the normalization constant A in 0.2. We get

$$(0.9) \quad A^2 \int \psi^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2 = 1$$

Doing the integrals with Maple, we get

$$(0.10) \quad 2A^2 \frac{Z_1^6 + 15Z_1^4Z_2^2 + 84Z_2^3Z_1^3 + 6Z_2^5Z_1 + 15Z_2^4Z_1^2 + Z_2^6 + 6Z_1^5Z_2}{Z_1^6 + 6Z_1^5Z_2 + 15Z_1^4Z_2^2 + 20Z_2^3Z_1^3 + 15Z_2^4Z_1^2 + 6Z_2^5Z_1 + Z_2^6} = 1$$

This rather frightening expression can be simplified by factoring the numerator and denominator. First, the numerator:

(0.11)

$$Z_1^6 + 15Z_1^4Z_2^2 + 84Z_2^3Z_1^3 + 6Z_2^5Z_1 + 15Z_2^4Z_1^2 + Z_2^6 + 6Z_1^5Z_2 = \dots$$

(0.12)

$$(Z_2^2 + 6Z_1Z_2 + Z_1^2)(Z_2^4 + 14Z_2^2Z_1^2 + Z_1^4) = \dots$$

(0.13)

$$\left[(Z_1 + Z_2)^2 + 4Z_1Z_2 \right] \left[(Z_1 + Z_2)^4 - 4Z_1^3Z_2 + 8Z_1^2Z_2^2 - 4Z_1Z_2^3 \right] = \dots$$

(0.14)

$$\left[(Z_1 + Z_2)^2 + 4Z_1Z_2 \right] \left[(Z_1 + Z_2)^4 + 16Z_1^2Z_2^2 - 4Z_1^3Z_2 - 8Z_1^2Z_2^2 - 4Z_1Z_2^3 \right] = \dots$$

(0.15)

$$\left[(Z_1 + Z_2)^2 + 4Z_1Z_2 \right] \left[(Z_1 + Z_2)^4 + 16Z_1^2Z_2^2 - 4Z_1Z_2(Z_1^2 + 2Z_1Z_2 + Z_2^2) \right] = \dots$$

(0.16)

$$\left[(Z_1 + Z_2)^2 + 4Z_1Z_2 \right] \left[(Z_1 + Z_2)^4 + 16Z_1^2Z_2^2 - 4Z_1Z_2(Z_1 + Z_2)^2 \right] = \dots$$

(0.17)

$$(x^2 + y^2) [x^4 + y^4 - x^2y^2] = x^6 + y^6$$

where we've defined

(0.18)

$$x \equiv Z_1 + Z_2$$

(0.19)

$$y \equiv 2\sqrt{Z_1Z_2}$$

The denominator comes out to

(0.20)

$$Z_1^6 + 6Z_1^5Z_2 + 15Z_1^4Z_2^2 + 20Z_2^3Z_1^3 + 15Z_2^4Z_1^2 + 6Z_2^5Z_1 + Z_2^6 = x^6$$

so

(0.21)

$$A^2 = \frac{x^6}{2(x^6 + y^6)}$$

Now we need to grind through the calculations for the terms in 0.5 and 0.6. First, we'll do the electron-electron interaction term:

(0.22)

$$\langle V_{ee} \rangle = \frac{e^2 A^2}{4\pi\epsilon_0} \int [\psi_1(r_1)\psi_2(r_2) + \psi_1(r_2)\psi_2(r_1)]^2 \frac{d^3\mathbf{r}_1 d^3\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

(0.23)

$$= \frac{e^2 A^2}{4\pi\epsilon_0} \int [\psi_1(r_1)\psi_2(r_2) + \psi_1(r_2)\psi_2(r_1)]^2 \frac{d^3\mathbf{r}_1 d^3\mathbf{r}_2}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2}}$$

(0.24)

$$= \frac{e^2 A^2}{2 \times 4\pi\epsilon_0 a} \frac{y^2 (5Z_2^3 Z_1 + 5Z_1^3 Z_2 + 28Z_2^2 Z_1^2 + Z_1^4 + Z_2^4)}{(Z_1^5 + 5Z_1^4 Z_2 + 10Z_1^3 Z_2^2 + 10Z_1^2 Z_2^3 + 5Z_2^4 Z_1 + Z_2^5)}$$

(0.25)

$$= -E_1 A^2 \frac{y^2 (5Z_2^3 Z_1 + 5Z_1^3 Z_2 + 28Z_2^2 Z_1^2 + Z_1^4 + Z_2^4)}{x^5}$$

To reduce the numerator:

$$(0.26) \quad 5Z_2^3 Z_1 + 5Z_1^3 Z_2 + 28Z_2^2 Z_1^2 + Z_1^4 + Z_2^4 = \dots$$

$$(0.27) \quad x^4 + Z_2^3 Z_1 + Z_1^3 Z_2 + 22Z_2^2 Z_1^2 = \dots$$

$$(0.28) \quad x^4 + Z_1 Z_2 (Z_1^2 + Z_2^2 + 2Z_1 Z_2 + 20Z_1 Z_2) = x^4 + \frac{y^2}{4} (x^2 + 5y^2)$$

Therefore

$$(0.29) \quad \langle V_{ee} \rangle = -E_1 A^2 y^2 \frac{4x^4 + y^2 (x^2 + 5y^2)}{4x^5}$$

$$(0.30) \quad = -\frac{1}{8} \frac{E_1 x y^2 (4x^4 + 5y^4 + x^2 y^2)}{x^6 + y^6}$$

Now for the electron-nucleus terms in 0.5 and 0.6.

$$(0.31) \quad I_1 = \frac{e^2}{4\pi\epsilon_0} \int \psi \left[\frac{Z_1 - 1}{r_1} + \frac{Z_2 - 1}{r_2} \right] \psi_1(r_1) \psi_2(r_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

$$(0.32) \quad = -2E_1 A^2 \frac{N}{x^5}$$

The numerator is

$$\begin{aligned}
 N &= Z_2^7 + 5Z_1^6Z_2 - 84Z_2^3Z_1^3 + 11Z_1^2Z_2^5 - 6Z_1^5Z_2 + 47Z_1^4Z_2^3 - Z_1^6 + 11Z_1^5Z_2^2 \\
 (0.33) \quad &- 15Z_1^4Z_2^2 - Z_2^6 - 6Z_2^5Z_1 + 47Z_1^3Z_2^4 + 5Z_1Z_2^6 + Z_1^7 - 15Z_2^4Z_1^2
 \end{aligned}$$

We can break this down by picking out the terms where the exponents sum to 6 (denoted by N_6) and then the terms where they sum to 7 (N_7). The terms summing to 6 are:

$$\begin{aligned}
 (0.34) \quad N_6 &= -Z_2^6 - 6Z_1^5Z_2 - Z_1^6 - 15Z_1^4Z_2^2 - 6Z_2^5Z_1 - 84Z_2^3Z_1^3 - 15Z_2^4Z_1^2 \\
 (0.35) \quad &= -(Z_2^2 + 6Z_1Z_2 + Z_1^2)(Z_2^4 + 14Z_2^2Z_1^2 + Z_1^4)
 \end{aligned}$$

$$\begin{aligned}
 (0.36) \quad &= -x^6 - y^6
 \end{aligned}$$

using 0.17.

The terms summing to 7 give:

$$\begin{aligned}
 (0.37) \quad N_7 &= Z_1^7 + 47Z_1^3Z_2^4 + 5Z_1Z_2^6 + Z_2^7 + 11Z_1^5Z_2^2 + 47Z_1^4Z_2^3 + 11Z_1^2Z_2^5 + 5Z_1^6Z_2 \\
 (0.38) \quad &= (Z_2 + Z_1) \left(Z_2^6 + 4Z_2^5Z_1 + 7Z_2^4Z_1^2 + 40Z_2^3Z_1^3 + 7Z_1^4Z_2^2 + 4Z_1^5Z_2 + Z_1^6 \right)
 \end{aligned}$$

We can write the sixth degree polynomial as

$$\begin{aligned}
 (0.39) \quad Z_2^6 + 4Z_2^5Z_1 + 7Z_2^4Z_1^2 + 40Z_2^3Z_1^3 + 7Z_1^4Z_2^2 + 4Z_1^5Z_2 + Z_1^6 &= \dots
 \end{aligned}$$

$$\begin{aligned}
 (0.40) \quad (Z_1 + Z_2)^6 - 2Z_1^5Z_2 - 2Z_1Z_2^5 - 8Z_1^4Z_2^2 - 8Z_1^2Z_2^4 + 20Z_1^3Z_2^3 &= \dots \\
 (0.41) \quad &
 \end{aligned}$$

$$\begin{aligned}
 (0.42) \quad x^6 - \frac{y^2}{2} (Z_1^4 + Z_2^4 + 4Z_1^3Z_2 + 4Z_1Z_2^3 - 10Z_1^2Z_2^2) &= x^6 - \frac{y^2}{2} (x^4 - y^4) \\
 N_7 &= x \left[x^6 - \frac{y^2}{2} (x^4 - y^4) \right]
 \end{aligned}$$

Putting it together:

$$(0.43) \quad I_1 = -2E_1A^2 \frac{x \left[x^6 - \frac{y^2}{2} (x^4 - y^4) \right] - x^6 - y^6}{x^5}$$

$$(0.44) \quad = -E_1x \frac{x \left[x^6 - \frac{y^2}{2} (x^4 - y^4) \right] - x^6 - y^6}{x^6 + y^6}$$

The other integral is

$$(0.45) \quad I_2 = \frac{e^2}{4\pi\epsilon_0} \int \psi \left[\frac{Z_2 - 1}{r_1} + \frac{Z_1 - 1}{r_2} \right] \psi_1(r_2) \psi_2(r_1) d^3\mathbf{r}_1 d^3\mathbf{r}_2$$

which turns out to be equal to I_1 . So finally

$$(0.46)$$

$$\langle H \rangle = E_1 (Z_1^2 + Z_2^2) + I_1 + I_2 + \langle V_{ee} \rangle$$

$$(0.47)$$

$$= E_1 (Z_1^2 + Z_2^2) - 2E_1x \frac{x \left[x^6 - \frac{y^2}{2} (x^4 - y^4) \right] - x^6 - y^6}{x^6 + y^6} - \frac{1}{8} \frac{E_1xy^2 (4x^4 + 5y^4 + x^2y^2)}{x^6 + y^6}$$

Using $Z_1^2 + Z_2^2 = x^2 - y^2/2$, we can put everything over a common denominator and cancel terms to get

$$(0.48)$$

$$\langle H \rangle = \frac{E_1}{x^6 + y^6} \left[-x^8 + 2x^7 + \frac{1}{2}x^6y^2 - \frac{1}{2}x^5y^2 - \frac{1}{8}x^3y^4 + \frac{11}{8}xy^6 - \frac{1}{2}y^8 \right]$$

To find the minimum of this, we can find the maximum of $\langle H \rangle / E_1$ (since $E_1 < 0$) and we can use Maple's Maximize function to do this numerically. We find

$$(0.49) \quad x_{min} = 1.32245$$

$$(0.50) \quad y_{min} = 1.08505$$

$$(0.51) \quad \langle H \rangle_{min} = 1.0266E_1$$

These values of x_{min} and y_{min} correspond to

$$(0.52) \quad Z_{1-min} = 1.03923$$

$$(0.53) \quad Z_{2-min} = 0.28322$$

Thus the upper bound on the energy is slightly lower than E_1 indicating that the H^- ion is stable.