

## HYDROGEN MOLECULE ION – OSCILLATION OF THE PROTONS

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 7.10.

We've estimated the ground state energy of the hydrogen molecule ion  $\text{H}_2^+$  using the variational principle. If we take the trial function to be the sum of two ground-state hydrogen atom wave functions, we can use similar techniques to those in the derivation where the trial function was the difference of two atomic wave functions to write the energy upper bound, including the Coulomb repulsion of the two protons, as

(0.1)

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

(0.2)

$$= -F(x) E_1$$

(0.3)

$$F(x) \equiv -1 + \frac{2}{x} \left( 1 + e^{-x} \left( 1 + x + \frac{x^2}{3} \right) \right)^{-1} \left[ e^{-x} \left( 1 - \frac{2x^2}{3} \right) + (x+1)e^{-2x} \right]$$

where  $x = R/a$  and  $R$  is the distance between the protons.

Since  $F$  is the upper limit on the ground state energy as a function of the proton-proton distance, we can interpret it as an effective harmonic oscillator potential for values of  $R$  very close to the value  $R_{min}$  which minimizes  $F$ . Think of  $F(x)$  expanded in a Taylor series about  $R_{min}$  and keep up to terms in  $\Delta R^2$ . The potential for a pure harmonic oscillator is

$$(0.4) \quad V(R) = \frac{1}{2} m \omega^2 R^2$$

so the second derivative can be used to find the oscillation frequency  $\omega$ :

$$(0.5) \quad \omega = \sqrt{\frac{V''}{m}}$$

In terms of  $F$ , we have

$$(0.6) \quad \frac{dF}{dR} = \frac{dF}{dx} \frac{dx}{dR}$$

$$(0.7) \quad = \frac{1}{a} F'$$

$$(0.8) \quad \frac{d^2F}{dR^2} = \frac{1}{a^2} F''$$

In terms of energy, we get

$$(0.9) \quad V'' = -\frac{E_1}{a^2} F''$$

In order to do the calculation, we need to evaluate the second derivative  $F''$  at  $R = R_{min}$ , so we need to solve  $F'(x) = 0$ . Taking the derivative of 0.3 is messy, but it would give a transcendental equation in any case, so we need to solve it numerically. We find that

$$(0.10) \quad x_{min} = 2.49283$$

at which the minimum value of  $F$  is

$$(0.11) \quad F_{min} = -1.12966$$

Similarly, we can take the second derivative and evaluate it at  $x_{min}$ , getting

$$(0.12) \quad F''(x_{min}) = 0.12567$$

The  $m$  in 0.5 is the reduced mass of the two protons, which is  $m = m_p/2 = 916.575m_e$ , where  $m_e$  is the mass of the electron. We also have the ground state energy of hydrogen:

$$(0.13) \quad E_1 = -\frac{\hbar^2}{2m_e a^2}$$

so

$$(0.14) \quad \omega = \sqrt{\frac{0.12567\hbar^2}{2 \times 916.575m_e^2 a^4}}$$

$$(0.15) \quad = 0.00828 \frac{\hbar}{m_e a^2}$$

The ground state of the harmonic oscillator is

$$(0.16) \quad E_0 = \frac{1}{2}\hbar\omega$$

$$(0.17) \quad = 0.00828 \frac{\hbar^2}{2m_e a^2}$$

$$(0.18) \quad = -0.00828E_1$$

The upper bound on the ground state of the hydrogen ion is

$$(0.19) \quad -F_{min}E_1 = 1.12966E_1$$

The binding energy is  $0.12966E_1$ , since  $E_1$  of the energy comes from the atomic wave function applied to the trial function.

Note that  $E_0 > 0$  (since  $E_1 < 0$ ) and that  $-F_{min}E_1 < 0$ . However, the ground state energy of the harmonic oscillator is considerably smaller in magnitude ( $0.00828 \ll 0.12966$ ) than the binding energy, so the oscillation is not sufficient to break up the molecule.

In fact, the molecule should be stable up to the value of  $n$  such that  $(n + \frac{1}{2})\hbar\omega < -0.12966E_1$ . Taking this as an equality, we have

$$(0.20) \quad \left(n + \frac{1}{2}\right)\hbar\omega = -0.12966E_1$$

$$(0.21) \quad 2\left(n + \frac{1}{2}\right)\frac{1}{2}\hbar\omega = -0.12966E_1$$

$$(0.22) \quad -\left(n + \frac{1}{2}\right)0.016559E_1 = -0.12966E_1$$

$$(0.23) \quad n = 7.33$$

Thus the highest stable oscillator state is  $n = 7$ , giving a total of 8 states (since the lowest is at  $n = 0$ ).