The Effect of Lepton Mass on the Energy and Bond Length of the Hydrogen Molecule Ion

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There are many in the chemical education community who believe that chemical bonding is simply an electrostatic phenomenon. I and several others have argued against this incorrect, simplistic view on many occasions (most of my critiques can be found in this section of my tutorials). In this tutorial the simplistic electrostatic model is shown to be inadequate by consideration of the effect of lepton mass on the equilibrium geometry (bond length) and energy of the hydrogen molecule ion. The electron has several heavy weight cousins and in this analysis we will look at the effect of replacing the electron with the muon (207 m_e).

The molecular orbital for the hydrogen molecule ion is formed as a linear combination of scaled hydrogenic 1s orbitals centered on the nuclei, **a** and **b**.

$$\Psi = \frac{a+b}{\sqrt{2+2\cdot S}} \quad \text{where} \quad a = \sqrt{\frac{\alpha^3}{\pi}}\cdot\exp(-\alpha\cdot r_a) \qquad b = \sqrt{\frac{\alpha^3}{\pi}}\cdot\exp(-\alpha\cdot r_b) \qquad S = \int a\cdot b\, d\tau$$

The molecular energy operator in atomic units:

$$H = \frac{-1}{2}\cdot\left[\frac{d}{dr}\left(r^2\cdot\frac{d}{dr}\blacksquare\right)\right] - \frac{1}{r_a} - \frac{1}{r_b} + \frac{1}{R}$$

The energy integral to be minimized by the variation method:

$$E = \frac{\int (a+b)\cdot H\cdot(a+b)\, d\tau}{2+2\cdot S}$$

When this integral is evaluated the following expression for the energy is obtained.

$$E(\alpha, m, R) := \frac{-\alpha^2}{2\cdot m} + \frac{\frac{\alpha^2}{m} - \alpha - \frac{1}{R} + \frac{1}{R}\cdot(1+\alpha\cdot R)\cdot\exp(-2\cdot\alpha\cdot R) + \alpha\cdot\left(\frac{\alpha}{m} - 2\right)\cdot(1+\alpha\cdot R)\cdot\exp(-\alpha\cdot R)}{1+\exp(-\alpha\cdot R)\cdot\left(1+\alpha\cdot R+\frac{\alpha^2\cdot R^2}{3}\right)} + \frac{1}{R}$$

Minimization of the energy of the hydrogen molecule ion for the electron follows. There are two variational parameters, the orbital scale factor and internuclear distance.

Electron mass: $m := 1$ Seed values for the variational parameter and internuclear separation: $\alpha := 1$ $R := .1$

$$\text{Given} \quad \frac{d}{d\alpha}E(\alpha, m, R) = 0 \quad \frac{d}{dR}E(\alpha, m, R) = 0 \quad \begin{pmatrix}\alpha \\ R\end{pmatrix} := \text{Find}(\alpha, R) \quad \begin{pmatrix}\alpha \\ R\end{pmatrix} = \begin{pmatrix}1.238 \\ 2.0033\end{pmatrix} \quad E(\alpha, m, R) = -0.5865$$

This result is well-known and can be found in any comprehensive quantum chemistry text. Next we replace the electron with the more massive muon and recalculate the ground-state energy.

Muon mass: $m := 207$ Seed values for the variational parameter and internuclear separation: $\alpha := 200$ $R := .012$

$$\text{Given} \quad \frac{d}{d\alpha}E(\alpha, m, R) = 0 \quad \frac{d}{dR}E(\alpha, m, R) = 0 \quad \begin{pmatrix}\alpha \\ R\end{pmatrix} := \text{Find}(\alpha, R) \quad \begin{pmatrix}\alpha \\ R\end{pmatrix} = \begin{pmatrix}256.2721 \\ 0.0097\end{pmatrix} \quad E(\alpha, m, R) = -121.4068$$

The results of the calculations are summarized in the following table.

Lepton	$\frac{E}{E_h}$	$\frac{R}{a_o}$
Electron	−0.5865	2.0033
Muon	−121.41	0.0097

Now imagine that you have a regular hydrogen molecule ion in its ground state and the electron is suddenly by some mechanism replaced by a muon. Nothing has changed from an electrostatic perspective, but the changes in energy and internuclear distance (bond length) of the molecule are very large as is shown in the table. For example, in the muonium molecule the bond length decreases sharply bringing the nuclei 207 times closer than they are in the electron version of the molecule.

This mass effect provides a challenge for those who think chemical bond can be explained in terms of electrostatic potential energy effects. The mass change is important because quantum mechanical kinetic energy is inversely proportional to mass. By comparison classical kinetic energy is directly proportional to mass.*

Of course, there is an even bigger problem for the potential energy aficionados, and that is the fundamental issue of atomic and molecular stability. Quantum mechanical kinetic energy is required to explain the stability of matter and the physical nature of the chemical bond.

* The mass effect in the harmonic oscillator (kinetic isotope effect) is also a quantum kinetic energy phenomenon. See http://www.users.csbsju.edu/~frioux/sho/Uncertainty-SHO.pdf for calculations on the effect of mass in the harmonic oscillator.