CHEMISTRY 3BB3 1999/2000

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ASSIGNMENT 3

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1. In atomic units, the 1s orbital for the hydrogen atom is $y_{1s} = \sqrt{\frac{1}{p\, a_0^3}}\, e^{-r/a_0}$, where a_0 is the Bohr radius. For this function, calculate the expectation value of the distance from the nucleus,*r*, and *1/r*.

2. For a particle in a box (length L), calculate the expectation value of the Hamiltonian for the trial wavefunction $\sin^2(\pi x/L)$, and show that it obeys the variation principle.

3. For the hydrogen molecular ion, H_2^+, the energy integrals (in atomic units) as a function of internuclear distance, *R*, are given below (these integrals are done by trained professionals - don't do this at home, kids).

$$S_{12} = e^{-R}\left[1 + R + R^2/3\right]$$

$$H_{11} = -\frac{1}{2} - \frac{1}{R}\left(1 - e^{-2R}\left[1 + R\right]\right)$$

$$H_{12} = -\frac{S_{12}}{2} - e^{-R}\left[1 + R\right]$$

The total energy of the system is given by

$$W = \frac{H_{11} + H_{12}}{1 + S_{12}} + \frac{1}{R}$$

where the last term represents the internuclear repulsion. Plot this function from $R = 1$ to 15, and determine the R value that gives the minimum energy. Also, calculate the binding energy (in kJ mol^{-1}). Recall the binding energy is the energy at the minimum, relative to the value at $R = \infty$