CHEMISTRY 3BB3 1999/2000

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SOLUTIONS TO ASSIGNMENT 3

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

Since this function depends only on the radius, we need only do the radial integral. However, we must check the normalization, since the normalization includes the angular parts. We can either say that

$$\int_0^{\pi} \int_0^{2\pi} \sin\theta \; d\theta \, d\phi = 4\pi$$

so that

$$\int_0^{\infty} \psi_{1s}^2 r^2 dr = \frac{1}{4\pi}$$

or we could do the normalization integral directly, using the formula

$$\int_0^{\infty} r^n e^{-ar} dr = \frac{n!}{a^{n+1}}$$

The expectation value of $1/r$ is given by

$$\left\langle \frac{1}{r} \right\rangle = \frac{\int_0^{\infty} \frac{1}{r} \psi_{1s}^2 \, r^2 dr}{\int_0^{\infty} \psi_{1s}^2 \, r^2 dr}$$

$$= \frac{\frac{1}{\pi a_0^3} \int_0^{\infty} r \, e^{-2r/a_0} dr}{\frac{1}{4\pi}}$$

$$= \frac{\frac{1}{\pi a_0^3} \frac{1}{(2/a_0)^2}}{\frac{1}{4\pi}}$$

$$= \frac{1}{a_0}$$

Similarly, the expectation value of r is given by

$$\langle r \rangle = \frac{\int_0^\infty r y_{1s}^2 \, r^2 dr}{\int_0^\infty y_{1s}^2 \, r^2 dr}$$

$$= \frac{\dfrac{1}{p a_0^3} \displaystyle\int_0^\infty r^3 \, e^{-2r/a_0} dr}{\dfrac{1}{4p}}$$

$$= \frac{\dfrac{1}{p a_0^3} \dfrac{3!}{\left(2/a_0\right)^4}}{\dfrac{1}{4p}}$$

$$= \frac{3}{2} a_0$$

Because this is a distribution, with the electron spread out, the two averages are not reciprocals of each other.

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.

The variation principle states that the expectation value of the Hamiltonian over the trial wavefunction must be higher than the true energy. For the particle in a box, the true ground state energy is $\frac{h^2}{8mL^2}$. For the particle in a box, the Hamiltonian is $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$. The expectation value of the Hamiltonian is given by

$$\langle H\rangle = \frac{\int_0^L \sin^2\left(\frac{p\,x}{L}\right)\left(-\frac{\hbar^2}{2m}\right)\frac{d^2}{dx^2}\sin^2\left(\frac{p\,x}{L}\right)dx}{\int_0^L \sin^4\left(\frac{p\,x}{L}\right)dx}$$

$$= \frac{-\frac{\hbar^2}{2m}\left(\frac{p}{L}\right)^2\int_0^L \sin^2\left(\frac{p\,x}{L}\right)2\left[\cos^2\left(\frac{p\,x}{L}\right)-\sin^2\left(\frac{p\,x}{L}\right)\right]dx}{\frac{L}{p}\frac{3p}{8}}$$

$$= \frac{-\frac{\hbar^2}{m}\left(\frac{p}{L}\right)^2\left[\int_0^L \sin^2\left(\frac{p\,x}{L}\right)\cos^2\left(\frac{p\,x}{L}\right)dx-\int_0^L \sin^4\left(\frac{p\,x}{L}\right)dx\right]}{\frac{3L}{8}}$$

$$= \frac{-\frac{\hbar^2}{m}\left(\frac{p}{L}\right)^2\left[\frac{L}{8}-\frac{3L}{8}\right]}{\frac{3L}{8}}$$

$$= \frac{2\hbar^2 p^2}{3mL^2}$$

$$= \frac{h^2}{6mL^2} \quad \left(\text{remember } \hbar = \frac{h}{2p}\right)$$

This satisfies 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 $R = \infty$

The plot is given here. The minimum is at about 2.5 atomic units (=1.32 Angstroms) and has the value of about -0.54683 atomic units. Therefore, the binding energy is 0.04683 a.u., which equals 170 kJ mol^{-1}, a fairly reasonable number for a weak chemical bond.