Chemistry 60649 — Fall 2008
Professor J. Daniel Gezelter — Due Monday 11/24/08

Problem Set 7

These problems will concentrate on approximate methods.

1. Perturbation Theory: The square well potential with infinite walls at $x = -a/2$ and $x = a/2$ has energy eigenvalues $E_n = n^2h^2/8ma^2$, and eigenfunctions

$$\langle x|n\rangle = \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi x}{a}\right)$$

if n is odd and

$$\langle x|n\rangle = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

if n is even.

Let the perturbing potential $V = kx^2/2$ be added to this square well, with

$$\frac{ka^2}{8} << \frac{\hbar}{8ma^2} - E_1.$$

a) Show that the first order correction to the energies of the states is

$$E_n^{(1)} = \frac{1}{2}ka^2\left(\frac{1}{12} - \frac{1}{2\pi^2 n^2}\right)$$

b) Suppose one were to calculate the first order correction to the ground state wave function $\langle x|1\rangle$. Which of the matrix elements $H_{j,1}^{(1)}$, if any, would vanish? Explain your answer

2. Variational Method: Using a Gaussian trial function $e^{-\alpha r^2}$ for the ground state of the hydrogen atom (and the Hamiltonian we used in class), show that

$$E(\alpha) = \frac{3\hbar^2\alpha}{2\mu} - \frac{e^2\alpha^{1/2}}{2^{1/2}\epsilon_0\pi^{3/2}}$$

and that

$$E_{min} = -\frac{4}{3\pi}\frac{\mu e^4}{16\pi^2\epsilon_0^2\hbar^2}$$

3. Consider a system whose Hamiltonian is

$$H = H_0 + V,$$

where V has the property that

$$\langle S|V|S\rangle > 0$$

for any state $|S\rangle$.

a) Prove, using the variational theorem, that if

$$H_0|0\rangle = \epsilon_0|0\rangle$$

and

$$H|\psi_0\rangle = E_0|\psi_0\rangle$$

are the ground states of the two Hamiltonians, respectively, then

$$E_0 \geq \epsilon_0$$

That is, ϵ_0 is a *lower bound* for E_0.

b) Now, let's put this idea to use on H^-. H^- has at least one bound state. In atomic units, what must the energy of H^- be less than? [This part of the problem involves no calculation.]

c) Use a trial wavefunction for the ground state, neglecting the spin, which is

$$\psi(\vec{r}_1, \vec{r}_2) \propto e^{-\alpha r_1} e^{-\alpha r_2}$$

where α is a variational parameter, to determine $\bar{E}$. Is a bound state obtained?

d) Now use part a) and obtain the average

$$\bar{E} = \frac{\bar{E} + \epsilon_0}{2}$$

Is this state bound? Compare your results c) and d) with the exact ground state energy.