CHEM 6472: Quantum Chem and Spectroscopy

Problem Set VIII

For practice only, not to be handed in

1. Compute the average radius $< r >$ for a hydrogen atom in its ground state, Ψ_{100}. How does this compare to the radius with the highest probability, which we computed in class?

2. Calculate the first-order correction to the ground-state energy of an anharmonic oscillator with potential energy
$$V(x) = \frac{1}{2}kx^2 + \frac{1}{6}\gamma x^3 + \frac{1}{24}bx^4. \tag{1}$$

3. Use the variational method to calculate the ground-state energy of a particle in a box ($0 \leq x \leq a$) with a potential given by
$$\begin{aligned} V(x) &= V_1 x & 0 \leq x \leq \frac{a}{2} \\ &= V_1(a-x) & \frac{a}{2} \leq x \leq a. \end{aligned} \tag{2}$$
As a trial function, use a linear combination of the first two particle-in-a-box functions,
$$\Phi(x) = c_1\sqrt{\frac{2}{a}}sin\left(\frac{\pi x}{a}\right) + c_2\sqrt{\frac{2}{a}}sin\left(\frac{2\pi x}{a}\right). \tag{3}$$
Do this by constructing the appropriate 2x2 Hamiltonian matrix and diagonalizing. You should find that, for this particular problem, life is easy because the Hamiltonian is *already* diagonal in this basis (why?) and the eigenvalues should work out to be
$$E = \frac{\hbar^2\pi^2}{2ma^2} + V_1 a\left(\frac{1}{4} + \frac{1}{\pi^2}\right), \tag{4}$$
and
$$E = \frac{2\hbar^2\pi^2}{ma^2} + \frac{V_1 a}{4}. \tag{5}$$
The lower one of these energies will represent the ground state, and the larger one will represent the first excited state. Which one is actually lower depends on the size of V_1.