Homework 7, Due March 25

1. In a 1D infinite square well in $[0, L]$, a small potential perturbation is placed at the center of the well:

$$\hat{H}' = \begin{cases} \varepsilon, & \text{if } (L-a)/2 \le x \le (L+a)/2 \\ 0, & \text{elsewhere in the well} \end{cases}$$

Use the perturbation theory to determine the energy correction to the first order. Compute the energy correction for the first and second levels if a=L/10.

2. Use the first-order perturbation theory to determine the ground state energy of the quartic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \chi x^4$$

Assume the harmonic oscillator in defining the zeroth-order Hamiltonian and use the ladder operators.

3. Use variation theory to determine the energy of an H-like atom with a trial wave function of the following form:

$$\psi = e^{-kr}, \qquad k \text{ is the variational parameter}$$

(Hints: treat the atom in 3D spherical coordinates where the Hamiltonian has the following from:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{l}^2}{2\mu r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}.$$

The following integration formula might be useful:

$$\int_0^\infty e^{-ax}x^n dx = \frac{n!}{a^{n+1}})$$

4. The MO energies of a diatomic molecule can be obtained using the variational theory and LCAO. Assuming each atom provides one AO, the MO wave function can in general be written as

$$\Psi_{MO} = c_A\phi_A + c_B\phi_B,$$

where ϕ_A and ϕ_B are the AO wave functions located on atoms A and B. Use the variational principle to prove that the variational parameters can be found as the solution of the following secular equations:

$$(\alpha_A - E)c_A + (\beta - ES)c_B = 0$$
$$(\beta - ES)c_A + (\alpha_B - E)c_B = 0,$$

where

$$S = \int \phi_A \phi_B d\tau$$
$$\alpha_A = \int \phi_A \hat{H} \phi_A d\tau, \alpha_B = \int \phi_B \hat{H} \phi_B d\tau$$
$$\beta = \int \phi_A \hat{H} \phi_B d\tau$$

Generalize the method to MOs made of N AOs, namely $\Psi_{MO} = \sum_{n=1,N} c_n \phi_n$. Suggest a way to solve the above coupled linear equations.