Chem 6004
Problem Set 1

1. Consider an electron in a 1-D box of length $L = 1$ nm that has energy eigenstates given by:

$$\Psi_n(x) = \sqrt{2} \sin(n\pi x)$$

$x = nm$

After atomically precise hammer is used to deform bottom of box that e^- feels an effective potential given by:

$$V(x) = -2(x - 0.5)^3 + 0.5$$

a) Compute energy expectation value of electron described by $\Psi_1(x)$ after box is deformed.

$$\langle E \rangle = \Psi_1(x) \left| \hat{H} \right| \Psi_1(x) + \left\langle \Psi_{(x)} \left| V \right| \Psi_{(x)} \right\rangle$$

assume: $\hbar = 1$
$m = 1$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL} \quad , n = 1, 2,$$

$$E_1 = \frac{1^2 \pi 1^2}{2(1)(1)^2}$$

2.)
$$\hat{H} = \frac{-h^2}{2m} \frac{d^2}{dx} - 2(x-0.5)^3 + 0.5$$

$h=1$

$m=1$

3.) ✱ Hartree method's trial wavefunction:

$$\Psi_H = \phi_1(x_1)\, \phi_2(x_2)$$

✱ Hartree-Fock trial wavefunction:

$$\Psi_{HF} = \frac{1}{2} \phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\, \phi_2(x_1)$$

✱ Recall:
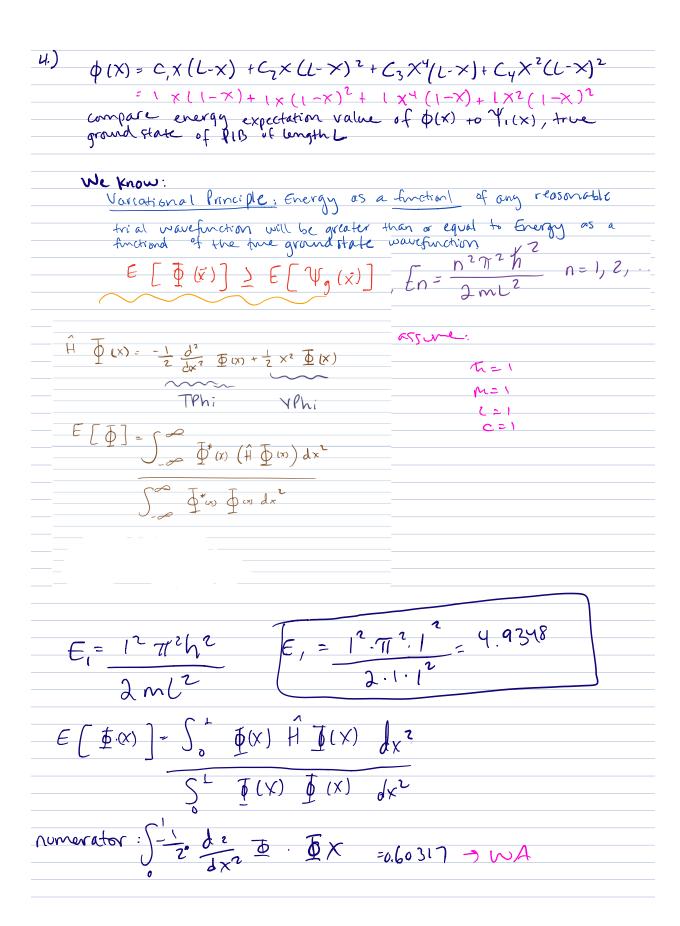
$$\hat{H} = \sum_i^N \hat{h}_i + \sum_{i>j}^N \hat{V}_{i,j},$$

$$\langle \Psi_{HF}|\hat{H}|\Psi_{HF}\rangle = \frac{1}{2}\langle \phi_1(x)\phi_2(x_2)[\hat{H}|\phi_1(x_1)(x_2)\rangle - \frac{1}{2}\langle \phi_1(x)\phi_2(x_2)[\hat{H}|\phi_1(x_2)\phi_2(x_1)\rangle$$
$$- \frac{1}{2}\langle \phi_1(x_2)\phi_2(x_1)|\hat{H}|\phi_1(x_1)\phi_2(x_2)\rangle + \frac{1}{2}\langle \phi(x)\phi_2(x)|\hat{H}|\phi_1(x_2)\phi(x)\rangle$$

$$\langle \Psi_H|\hat{H}|\Psi_H\rangle = \langle \phi_1 x_1\, \phi_2 x_2|\hat{H}|\phi_1(x_1)\phi_2(x_2)\rangle$$

$$\langle \Psi_H|\hat{H}|\Psi_H\rangle = \langle \phi x_1\, \phi_2 x_2[\hat{h}|\phi_1(x_1)(x_2)\rangle + \frac{1}{2}\langle \phi_1 x\phi x_2|\hat{V}_{ij}\, \phi_1(x_1)\phi_2(x_2)\rangle$$

I believe Hartree's wavelength will yield higher energy. I'm assuming this because the quantities in Hartree's wavelength are being added together. Where in the HF, they are being subtracted.

✱ For this problem, I used chapter 4 in Cramer, my notes and physics.metu.edu.tr/~sturgut/hf.pdf

4.)

$$\phi(x) = C_1 x(L-x) + C_2 x(L-x)^2 + C_3 x^4(L-x) + C_4 x^2(L-x)^2$$
$$= 1 \cdot x(1-x) + 1 \cdot x(1-x)^2 + 1 \cdot x^4(1-x) + 1 \cdot x^2(1-x)^2$$

compare energy expectation value of $\phi(x)$ to $\psi_1(x)$, true ground state of PIB of length L.

We know:

Variational Principle: Energy as a functional of any reasonable trial wavefunction will be greater than or equal to Energy as a functional of the true ground state wavefunction

$$E[\phi(\bar{x})] \geq E[\psi_g(\bar{x})] \quad , \quad E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \quad n = 1, 2, \dots$$

assume:

$$\hbar = 1$$
$$m = 1$$
$$L = 1$$
$$C = 1$$

$$\hat{H} \, \Phi(x) = -\frac{1}{2} \frac{d^2}{dx^2} \Phi(x) + \frac{1}{2} x^2 \Phi(x)$$

$\underbrace{\hspace{2cm}}_{T\Phi} \quad \underbrace{\hspace{2cm}}_{V\Phi}$

$$E[\Phi] = \frac{\int_{-\infty}^{\infty} \Phi^*(x) \left(\hat{H} \Phi(x)\right) dx^2}{\int_{-\infty}^{\infty} \Phi^*(x) \Phi(x) dx^2}$$

$$E_1 = \frac{1^2 \pi^2 \hbar^2}{2mL^2}$$

$$\boxed{E_1 = \frac{1^2 \cdot \pi^2 \cdot 1^2}{2 \cdot 1 \cdot 1^2} = 4.9348}$$

$$E[\phi(x)] = \frac{\int_0^L \phi(x) \, \hat{H} \, \phi(x) \, dx^2}{\int_0^L \phi(x) \, \phi(x) \, dx^2}$$

numerator: $\int_0^1 -\frac{1}{2} \cdot \frac{d^2}{dx^2} \Phi \cdot \Phi x \quad = 0.60317 \rightarrow WA$

denominator: $\int_0^1 \bar{\Phi}X \bar{\Phi}X = 0.11948 \rightarrow WA$

$$\frac{0.60317}{0.11948} = 5.0483$$

$\boxed{E[\Phi x] = 5.0483}$

$E[\Phi x]$ is greater than the g.s. $\wedge$ energy, so it is consistent with the variational principle.

★ for this problem, I used my notes and WA.

5.)

$$E_{MP_2} = 2 \sum_{i,j,a,b}^{N} \frac{\langle ij|V|ab\rangle \langle ab|V|ij\rangle}{\varepsilon_i + \varepsilon_j + \varepsilon_a + \varepsilon_b} - 2 \sum_{i,j,a,b}^{N} \frac{\langle ij|V|ab\rangle \langle ab|V|ij\rangle}{\varepsilon_i + \varepsilon_j + \varepsilon_a + \varepsilon_b}$$

Comes from the second order corrections. The numerator is simplified by the orthogonality of ground state and excited slater determinants, then using codon-slater rules, we only consider doubly and singly excited determinants. The singly excited will = 0 (due to Brillows Theory).

The denominator for each doubly excited determinant will differ from the g.s. by including the sum of energies of the unoccupied orbitals into which excitation occured and excluding the energies of the orbitals from which excitation occured, giving us the second order energy correction. All the energy corrections sum up to E_{MP_2}.

★ for this problem, I used chapter 7 in Cramer