

# PROBLEM SET #1

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Question #1:

a.) → Convert to SI units for calculations.

$$\begin{aligned} \textcircled{1} \quad \psi_n(x) &= \sqrt{\frac{2}{1 \times 10^{-9}}} \cdot \sin\left(\frac{n\pi x}{1 \times 10^{-9}}\right) \quad \xleftarrow{\text{E.E. Equation}} \\ \langle E \rangle &= \langle \psi_n(x) | -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} | \psi_n(x) \rangle + \langle \psi_n(x) | V(x) | \psi_n(x) \rangle \\ &= \underbrace{\langle \psi_n(x) | -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} | \psi_n(x) \rangle}_{E_1} + \langle \psi_n(x) | -2(x - (0.5 \times 10^{-9}))^3 + (0.5 \times 10^{-9}) | \psi_n(x) \rangle \end{aligned}$$

\* Use code to calculate this  $E_1$  equation to find KE part of equation.

\* Find PE part of equation after. (Use Wolfram Alpha for integration)

$$\begin{aligned} \text{PEpart} \quad \langle V \rangle &= \int_0^{1 \times 10^{-9}} \left( \frac{2}{1 \times 10^{-9}} \right) \sin^2\left(\frac{\pi x}{1 \times 10^{-9}}\right) \cdot \left[ -2(x - (0.5 \times 10^{-9}))^3 + (0.5 \times 10^{-9}) \right] \\ &= 5 \times 10^{-10} \text{ Joules (Wolfram Alpha answer)} \end{aligned}$$

$E_1$  is KE part =  $\langle K \rangle$

$$\boxed{\langle E \rangle = \langle K \rangle + \langle V \rangle} \quad \xleftarrow{\text{Sum used to find the Energy Expectation Value.}}$$

$$\langle K \rangle = 6.024658 \times 10^{-20} \text{ J}$$

$$\langle V \rangle = 5.00 \times 10^{-10} \text{ J}$$

$$\begin{aligned} \langle E \rangle &= 6.024658 \times 10^{-20} \text{ J} + 5.00 \times 10^{-10} \text{ J} \\ &= 5.00000001 \times 10^{-10} \\ &\approx 5.00 \times 10^{-10} \text{ Joules} \end{aligned}$$

b.) I do not believe that the original energy eigenstates,  $\psi_n(x)$ , would be stationary states of the deformed box. In order for the original energy eigenstates to be stationary states of the deformed box, they would have to also be eigenfunctions of the Hamiltonian Operator of the deformed box. We can see how the states change with time by perhaps using the time-dependent Schrodinger equation in the normal H. Stationary states consist of observables that are independent of time, so  $\psi_n(x)$  can be an energy eigenstate of the normal Hamiltonian, but not for the deformed box Hamiltonian in Question 1.

## Question #2

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

- \* Problem asks to write  $\hat{H}$ .
- \* Use LVM (first 3 energy eigenstates)

Remember

SI Units

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} - 2(x - (0.5 \times 10^{-9}))^3 + (0.5 \times 10^{-9})$$

\* First 3 Energy Eigenfunctions

(diagonalize like before)

$$H_{ij} = \langle \Psi_i(x) | \hat{H} | \Psi_j(x) \rangle$$

$$H_{ii} = E_i + \langle \Psi_i(x) | \hat{V} | \Psi_i(x) \rangle$$

$$\rightarrow H_{ij} = \langle \Psi_i(x) | \hat{V} | \Psi_j(x) \rangle$$

\* NOTE = Integrals coded on Jupyter Notebook

↳ Estimated Ground state Energy =  $4.999 e^{-10}$  Joules

## Question #3

Hartree Method  $\rightarrow$  Hartree-Fock theory

- Hartree-Fock Method = Includes anti-symmetry in trial wavefunction (Slater Det.)
- Hartree Method = uses simple product wavefunction (no anti-symmetry)

$$HM \rightarrow \Psi_H = \phi_1(x_1) \phi_2(x_2)$$

$$HFM \rightarrow \Psi_{HF} = \phi_1(x_1) \phi_2(x_2) - \phi_1(x_2) \phi_2(x_1)$$

$\phi_1$  and  $\phi_2$  = molecular orbitals

$x_1$  and  $x_2$  = coordinates of electron 1 and electron 2

$$\hat{H} = \sum_i^N \hat{h}_i + \sum_{i>j}^N \hat{V}_{ij} \quad \leftarrow \text{Given Equation}$$

$$\rightarrow \Psi_H(x_1, x_2) = \phi_1(x_1) \phi_2(x_2) \quad \leftarrow HM \text{ for } H_2$$

$$\rightarrow \Psi_{HF}(x_1, x_2) = 0.5 [\phi_1(x_1) \phi_2(x_2) - \phi_1(x_2) \phi_2(x_1)]$$

$$\hat{H} = \underbrace{\hat{h}_1 + \hat{h}_2}_{\substack{\text{individual} \\ \text{operators}}} + \underbrace{\hat{V}_{1,2}}_{\substack{\text{2-electron operator}}}$$

$$\begin{matrix} i=1 \\ j=2 \end{matrix}$$

Energy Expectation Values:

$$\langle \phi_1(x_1) \phi_2(x_2) | \hat{H} | \phi_1(x_1) \phi_2(x_2) \rangle = \langle \phi_1(x_1) | \hat{h}_1 | \phi_1(x_1) \rangle + \langle \phi_1(x_2) | \hat{h}_2 | \phi_1(x_2) \rangle + \langle \phi_1(x_1) \phi_2(x_2) | \hat{V}_{1,2} | \phi_1(x_1) \phi_2(x_2) \rangle$$

HFM Energy Expectation Values:

$$\begin{aligned} & \rightarrow \frac{1}{2} \langle \phi_1(x_1) \phi_2(x_2) | \hat{H} | \phi_1(x_1) \phi_2(x_2) \rangle - \frac{1}{2} \langle \phi_1(x_2) \phi_2(x_1) | \hat{H} | \phi_1(x_1) \phi_2(x_2) \rangle - \frac{1}{2} \langle \phi_1(x_1) \phi_2(x_2) | \hat{H} | \phi_1(x_2) \phi_2(x_1) \rangle \dots \\ & \quad \text{*this is the simplified equation...} \quad \dots + \frac{1}{2} \langle \phi_1(x_2) \phi_2(x_1) | \hat{H} | \phi_1(x_2) \phi_2(x_1) \rangle \end{aligned}$$

$$\rightarrow \langle \phi_1(x_1) | \hat{h}_1 | \phi_1(x_1) \rangle + \langle \phi_1(x_2) | \hat{h}_2 | \phi_1(x_2) \rangle + \langle \phi_1(x_1) \phi_2(x_2) | \hat{V}_{12} | \phi_1(x_1) \phi_2(x_2) \rangle - \langle \phi_1(x_1) \phi_2(x_2) | \hat{V}_{21} | \phi_1(x_1) \phi_2(x_2) \rangle$$

\* I believe that the HFM will yield a lower total energy in comparison to the HM because it lowers the energy expectation value by including the subtraction (neg. component) in the equation, whereas the HM does not. Hartree-Fock Theory seeks the best Energy of a single Slater Determinant, based on Variational Principle, the lowest is the best.

#### Question #4

$$\phi(x) = c_1 x (L-x) + c_2 x (L-x)^2 + c_3 x^4 (L-x) + c_4 x^2 (L-x)^2 \quad (\text{Given})$$

- Compare Energy Expectation Value  $\rightarrow \langle \phi(x) | \hat{H} | \phi(x) \rangle$  to  $\psi_1(x)$  ?
- Consistent with the Variational Principle?

$$\begin{aligned} \langle E \rangle &= \frac{\langle \phi(x) | \hat{H} | \phi(x) \rangle}{\langle \phi(x) | \phi(x) \rangle} \quad L = 1 \text{ atomic unit} \\ \hat{H} &= -\frac{1}{2} \cdot \frac{d^2}{dx^2} \quad c_1 = 1 \quad c_2 = 1 \quad c_3 = 1 \quad c_4 = 1 \end{aligned}$$

$$\rightarrow \frac{d^2}{dx^2} (x(1-x) + x(1-x)^2 + x^4(1-x) + x^2(1-x)^2) = -20x^3 + 24x^2 - 6x - 4 \quad (\text{Wolfram Alpha})$$

$$\rightarrow \text{Numerator: } \int_0^{L=1} -\frac{1}{2} (-20x^3 + 24x^2 - 6x - 4) \cdot [x(1-x) + x(1-x)^2 + x^4(1-x) + x^2(1-x)^2] dx$$

$\rightarrow$  Wolfram Alpha answer =  $\frac{38}{63} \approx 0.60317$

$$\rightarrow \text{Denominator: } \int_0^{L=1} [x(1-x) + x(1-x)^2 + x^4(1-x) + x^2(1-x)^2]^2 dx$$

$\rightarrow$  Wolfram Alpha answer =  $\frac{46}{385} \approx 0.11948$

$$\langle E \rangle = \frac{\langle \phi(x) | \hat{H} | \phi(x) \rangle}{\langle \phi(x) | \phi(x) \rangle} = \frac{0.60317}{0.11948} = 5.048292601 \text{ atomic units}$$

\* In order for this to follow the Variational principle, the true ground state energy must be lower than the energy of the wavefunction.

$\hookrightarrow$  Ground State Energy =  $E_1$ , (first/lowest energy level)

$$\rightarrow E_1 = \frac{12\pi^2}{2} = 4.934802201 \text{ atomic units}$$

\* Since the ground state energy calculated above is lower than that of the wavefunction, we can say it is consistent with the Variational Principle.

## Question #5

Energy Expression 2<sup>nd</sup> order Moller-Plesset Perturbation Theory:

$$E_{MP2} = 2 \sum_{i,j,a,b}^N \frac{\langle ij|v|ab\rangle \langle ab|v|ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} - \sum_{i,j,a,b}^N \frac{\langle ij|v|ab\rangle \langle ab|v|ij\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

N = # molecular orbitals

$\epsilon_p$  = molecular orbital energy of orbital p.

$\langle pq|V|rs\rangle$  is the 2-electron integral involving orbitals  $\phi_p, \phi_q, \phi_r$ , and  $\phi_s$ .

\* I believe that because there are 4 variable orbitals being involved in the sum (i,j,a,b), that there will be a computational cost scaling to the fourth order of the function. The Computational cost to evaluate the MP2 energy will scale with the amount of molecular orbitals. Comp. Cost will increase because you would most likely have to create individual loops for i,j,a, and b molecular orbitals.