MEST - Assignment 3

(For each solution, show your work through a set of important steps. Use Dirac Notation for all questions)

Linear algebra and Dirac notation

1. Write the following expressions in the Dirac formalism (1+1+2 pts):

   (a) $f(x) = \sum_n \phi_n(x) \int \phi_n^*(x^{'}) f(x^{'}) dx^{'}$

   (b) $\frac{\partial}{\partial x} f(x) = m(x) \int m^*(x^{'}) g(x^{'}) d(x^{'})$

   (c)
   $$E_0^{MP2} = \sum_{ij}^{occ} \sum_{ab}^{virt} \frac{|\int dx_1 dx_2 \chi_i^*(x_1) \chi_j^*(x_2) r_{12}^{-1} (1 - \hat{P}_{12}) \chi_a(x_1) \chi_b(x_2)|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

   ($\hat{P}_{12}$ is the permutation operator)

2. Prove that unitary transformation preserves the :

   (a) Hermiticity of a matrix (2 pts)

   (b) Trace of a matrix (2 pts)

3. In quantum computing a qubit is a two-state quantum mechanical system that corresponds to the basic unit of quantum information. Qubit states are generally represented by a superposition of two orthonormal basis states (say in basis X) denoted as $|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $|\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Suppose we have qubit states in basis Y represented by $|+\rangle = \frac{1}{\sqrt{2}}(|\alpha\rangle + |\beta\rangle), |-\rangle = \frac{1}{\sqrt{2}}(|\alpha\rangle - |\beta\rangle)$. (1 + 2 + 1 + 2 pts)

   (a) Write the qubit state $|\psi\rangle = a|-\rangle + b|+\rangle$ as linear combination of basis states of basis X ($|\alpha\rangle, |\beta\rangle$). What are the conditions on a and b for $|\psi\rangle$ to be normalized state vector

   (b) Find the unitary transformation matrix H that map the basis X ($|\alpha\rangle, |\beta\rangle$) to basis Y ($|+\rangle, |-\rangle$)

   (c) Write out the $H|\psi\rangle$ in terms of basis X and basis Y

   (d) What is the probability of obtaining the $|\alpha\rangle$ and $|\beta\rangle$ states when measuring the $H|\psi\rangle$

Langragian and Lagrange multiplier

1. Construct the Langrangian and find the maximum and minimum values of $f(x, y, z) = 6x - 3y - 2z$ subject to the constraint $g(x, y, z) = 4x^2 + 2y^2 + z^2 - 70 = 0$. (3 pts)

2. Using Lagrange multipliers, find the shortest distance from the point (x_0, y_0, z_0) to the plane ax+by+cz=d. (3 pts)

Hartree Fock Theory

1. Suppose in Lithium atom we have restricted Hartree-Fock spatial orbitals denoted by $\{\Psi_1, \Psi_2, \Psi_3, .., \Psi_n\}$ and each can accomodate an α and/or a β electron. Assume that the orbitals (with indices 1, 2 , ..)are arranged in increasing order of their energies. (4+3 pts)

   (a) Determine the Slater determinant and the Hartree fock energy in terms of h, K and J integrals for

      i. The "ground-state" of Lithium atom

      ii. The excited-state where one electron from Ψ_1 is excited to Ψ_2

      iii. The excited-state where one alpha electron from Ψ_1 is excited to Ψ_3

      iv. The excited-state where one beta electron from Ψ_1 is excited to Ψ_3

   (b) Derive the LUMO and LUMO+1 orbital energies.

2. Clementi and Roetti did Hartree-Fock calculations for ground and some excited states [E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (194)]. They consider the below Hartree-Fock ground state wave function for helium atom where they expressed the $1s$ orbital function f as combination of five $1s$ Slater-type orbitals.

$$\Psi_g = f(1)f(2) \cdot \left[\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt(2)}\right] \qquad \text{where, } f = \frac{1}{\sqrt{\pi}} \sum_{i=1}^{5} c_i (\frac{\xi_i}{a_0})^{3/2} e^{-\frac{\xi_i r}{a_0}}$$

   The expansion coefficient c_i are $c_1 = 0.76838, c_2 = 0.22346, c_3 = 0.04082, c_4 = -0.00994$, $c_5 = 0.00230$ and the orbital exponents ξ_i are $\xi_1 = 1.41714, \xi_2 = 2.37682, \xi_3 = 4.39628, \xi_4 = 6.52699, \xi_5 = 7.94252$. Calculate the total and first ionization energy of Helium using Hartree-Fock theory and compare it with experimental values. For solving the coloumb and exchange integrals express the electron repulsion term in spherical harmonics as done in Assignment 2 Q4. (10 pts)

3. From the literature, find two peer-reviewed articles which demonstrate physical significance of one electron orbitals (or spinors) with any experimentally observable quantity (other than ionization energies which has been discussed in the class). Justify why such a relationship is scientifically meaningful. (4 pts)