MEST - Assignment 3

Due date: 22/03/2022
(For each solution, show your work through a set of important steps.)

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

3. 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 β electrons. Assume that the orbitals (with indices 1, 2 , ..)are arranged according to 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.

4. 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)

5. (Taken from Szabo and Ostlund) Show that the energy required to remove an electron from χ_c and one from χ_d to produce the (N-2)-electron single determinant $|^{N-2}\Psi_{cd}\rangle$ is $-\epsilon_c - \epsilon_d + \langle cd|cd\rangle - \langle cd|dc\rangle$ where, ϵ_i denotes the Hartree-Fock orbital energy of obital i. (4 pts)

6. Derive the first order energy correction, using the fluctuation potential as a perturbation and the HF determinant as a zeroth order wavefunction for the many-electron HF operator. (3 pts)