22.6.4: iii. Problems

Q1

This problem will be concerned with carrying out an SCF calculation for the HeH$^+$ molecule in the $^1\sum_g^+(1\sigma^2)$ ground state. The one- and two-electron integrals (in atomic units) needed to carry out this SCF calculation at R = 1.4 a.u. using Slater type orbitals with orbital exponents of 1.6875 and 1.0 for the He and H, respectively are:

$$S_{11} = 1.0, \qquad S_{22} = 1.0, \qquad S_{12} = 0.5784 \qquad (22.6.4.1)$$
$$h_{11} = -2.6442, \qquad h_{22} = -1.7201, \qquad h_{12} = -1.5113, \qquad (22.6.4.2)$$
$$g_{1111} = 1.0547, \qquad g_{1121} = 0.4744, \qquad g_{1212} = 0.5664, \qquad (22.6.4.3)$$
$$g_{2211} = 0.2469, \qquad g_{2221} = 0.3504, \qquad g_{2222} = 0.6250, \qquad (22.6.4.4)$$

where 1 refers to $1s_{He}$ and 2 to $1s_H$. Note that the two-electrons integrals are given in Dirac notation. Parts a. - d. should be done by hand. Any subsequent parts can make use of the QMIC software provided.

a. Using $\phi_1 \approx 1s_{He}$ for the initial guess of the occupied molecular orbital, form a 2x2 Fock matrix. Use the equation derived above in question 1 for $F_{\mu\nu}$.

b. SOlve the Fock matrix eigenvalue equations given above to obtain the orbital energies and an improved occupied molecular orbital. In so doing, note that $\langle\phi_1|\phi_1\rangle = 1 = C_1^T S C_1$ gives the needed normalization condition for the expansion coefficients of the ϕ_1 in the atomic orbital basis.

c. Determine the total SCF energy using the result of exercise 3 above at this step of the iterative procedure. When will this energy agree with that obtained by using the alternative expression for E(SCF) given in exercise 2?

d. Obtain the new molecular orbital, ϕ_1, from the solution of the matrix eigenvalue problem (part b).

e. A new Fock matrix and related total energy can be obtained with this improved choice of molecular orbital, $\phi1$. This process can be continued until a convergence criterion has been satisfied. Typical convergence criteria include: no significant change in the molecular orbitals or the total energy (or both) from one iteration to the next. Perform this iterative procedure for the HeH$^+$ system until the difference in total energy between two successive iterations is less than 10^{-5} a.u.

f. Show, by comparing the difference between the SCF total energy at one iteration and the converged SCF total energy, that the convergence of the above SCF approach is primarily linear (or first order).

g. Is the SCF total energy calculated at each iteration of the above SCF procedure (via exercise 3) an upper bound to the exact ground-state total energy?

h. Using the converged self-consistent set of molecular orbitals, $\phi1$ and $\phi2$, calculate the one- and two-electron integrals in the molecular orbital basis. Using the equations for E(SCF) in exercises 2 and 3 calculate the converged values of the orbital energies making use of these integrals in the mo basis.

i. Does this SCF wavefunction give rise (at R $\rightarrow \infty$) to proper dissociation products?

Q2

This problem will continue to address the same HeH$^+$ molecular system as above, extending the analysis to include "correlation effects." We will use the one- and two-electron integrals (same geometry) in the converged (to 10^{-5} au) SCF molecular orbital basis which we would have obtained after 7 iterations above. The **converged** mos you would have obtained in problem 1 are:

$$\phi_1 = \begin{bmatrix} -0.89997792 \\ -0.15843012 \end{bmatrix} \phi_2 = \begin{bmatrix} -0.83233180 \\ 1.21558030 \end{bmatrix}$$

a. Carry out a two configuration CI calculation using the $1\sigma^2$ and $2\sigma^2$ configurations first by obtaining an expression for the CI matrix elements $H_{ij}(i, j = 1\sigma^2, 2\sigma^2)$ in terms of one- and two-electron integrals, and secondly by showing that the resultant CI matrix is (ignoring the nuclear repulsion term):

$$\begin{bmatrix} -4.2720 & 0.1261 \\ 0.1261 & -2.0149 \end{bmatrix}$$

b. Obtain the two CI energies and eigenvectors for the matrix found in a part a.

c. Show that the lowest energy CI wavefunction is equivalent to the following two-determinant (single configuration) wavefunction:

$$\frac{1}{2}\left[\left| \left(a^{\frac{1}{2}}\phi_1 + b^{\frac{1}{2}}\phi_2 \right) \alpha \left(a^{\frac{1}{2}}\phi_1 - b^{\frac{1}{2}}\phi_2 \right) \beta \right| + \left| \left(a^{\frac{1}{2}}\phi_1 - b^{\frac{1}{2}}\phi_2 \right) \alpha \left(a^{\frac{1}{2}}\phi_1 + b^{\frac{1}{2}}\phi_2 \right) \beta \right| \right]$$

involving the polarized orbitals: $a^{\frac{1}{2}}\phi_1 \pm b^{\frac{1}{2}}\phi_2$, where a = 0.9984 and b = 0.0556.

d. Expanding the CI list to 3 configurations by adding the $1\sigma 2\sigma$ to the original $1\sigma^2$ and $2\sigma^2$ configurations of part a above. First, express the proper singlet spin-coupled $1\sigma 2\sigma$ configuration as a combination of Slater determinants and then computer all elements of this 3x3 matrix.

e. Obtain all eigenenergies and corresponding normalized eigenvectors for this CI problem.

f. Determine the excitation energies and transition moments for HeH$^+$ using the full CI result of part e above. The nonvanishing matrix elements of the dipole operator **r**(x,y,z) in the atomic basis are:

$$\langle 1_{SH} | z | 1_{SHe} \rangle = 0.2854 \text{ and } \langle 1_{SH} | z | 1_{SH} \rangle = 1.4$$

First determine the matrix elements of r in the SCF orbital basis then determine the excitation energies and transition moments from the ground state to the two excited singlet states of HeH$^+$.

g. Now turning to perturbation theory, carry out a RSPT calculation of the first-order wavefunction $|1\sigma^2\rangle^{(1)}$ for the case in which the zeroth-order wavefunction is taken to be the $1\sigma^2$ Slater determinant. Show that the first-order wavefunction is given by:

$$|1\sigma^2\rangle^{(1)} = -0.0442 |2\sigma^2\rangle.$$

h. Why does the $|1\sigma 2\sigma\rangle$ configuration not enter into the first-order wavefuncion?

i. Normalize the resultant wavefunction that contains zeroth- plus first-order parts and compare it to the wavefunction obtained in the two-configuration CI study of part b.

j. Show that the second-order RSPT correlation energy, $E^{(2)}$, of HeH$^+$ is -0.0056 a.u. How does this compare with the correlation energy obtained from the two- configuration CI study of part b?

Q3

Using the QMIC programs, calculate the SCF energy of HeH^+ using the same geometry as in problem 1 and the STO3G basis set provided in the QMIC basis set library. How does this energy compare to that found in problem 1? Run the calculation again with the 3- 21G basis basis provided. How does this energy compare to the STO3G and the energy found using STOs in problem 1?

Q4

Generate SCF potential energy surfaces for HeH^+ and H_2 using the QMIC software provided. Use the 3-21G basis set and generate points for geometries of R = 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, and 10.0. Plot the energies vs. geometry for each system. Which system dissociates properly?

Q5

Generate CI potential energy surfaces for the 4 states of H_2 resulting from a CAS calculation with 2 electrons in the lowest 2 SCF orbitals $(1\sigma_g$ and $1\sigma_u)$. Use the same geometries and basis set as in problem 4. Plot the energies vs. geometry for each system. Properly label and characterize each of the states (e.g., repulsive, dissociate properly, etc.).