Homework 1

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In this homework, we need to do practical calculations on HeH^+ system. This system consists of two atoms and two electrons. To describe the interactions between the two electrons, we use the Hartree-Fock method to solve this problem. After completing this homework, you could have a better feeling about what *ab initio* calculations are. Below I will give you some necessary formulation and my calculation results. For more details please refer to the classical book written by Szabo and Ostlund[1]. Hartree units are used by default.

As we learn from the first lecture of Prof. Li, the single-particle Hartree-Fock equation is

$$f(1)|\chi_a >= \epsilon_a|\chi_a > \tag{1}$$

with the Fock operator being

$$f(1) = h(1) + \sum_{b=1}^{N}(J_b(1) - K_b(1)) \tag{2}$$

Here, $1 = \mathbf{x_1}$ represents the spatial and spin coordinate of electron 1, and N is the number of electrons. χ_a is the spin orbital. That means,

$$\chi_a(\mathbf{x}) = \psi_a(\mathbf{r})\alpha(\omega) \tag{3}$$

$\psi_a(r)$ is called the spatial orbital. h(1) includes the kinetic energy and the attraction energy from the nuclei,

$$h(1) = -\frac{1}{2}\nabla_1^2 - \sum_I \frac{Z_I}{r_{1I}} \tag{4}$$

$J_b(1)$ and $K_b(1)$ are the so-called Coulomb and exchange operator, respectively.

$$J_b(1)\chi_a(1) = [\int d\mathbf{x}_2\chi_b^*(2)1/r_{12}\chi_b(2)]\chi_b(1) \tag{5}$$

$$K_b(1)\chi_a(1) = [\int d\mathbf{x}_2\chi_b^*(2)1/r_{12}\chi_a(2)]\chi_b(1) \tag{6}$$

J is a local operator, while K is non-local because you need to know the value of χ_a in the whole space. The total energy is written as

$$E = \sum_{a=1}^{N} < \chi_a|h|\chi_a > + \frac{1}{2}\sum_{a,b=1}^{N} < \chi_a\chi_b|v|\chi_b\chi_a > \tag{7}$$

It should be noted that $|\chi_a\chi_b >$ is a 2×2 determinant, that is,

$$|\chi_b\chi_a >= \frac{1}{\sqrt{2}}\begin{vmatrix}\chi_a(1) & \chi_b(1)\\ \chi_b(2) & \chi_b(2)\end{vmatrix} \tag{8}$$

Substituting (8) to (7) gives

$$E = \sum_{a=1}^{N}[a|h|a] > + \frac{1}{2}\sum_{a,b=1}^{N}[aa|bb > -[ab|ba] \tag{9}$$

where $[a|h|a]$ and $[ij|kl]$ are convenient notations used in chemical community for one-electron and two-electron integrals over spin orbitals, respectively.

$$[i|h|j] = \int d\mathbf{x}_1\chi_i^*(\mathbf{x}_1)h(\mathbf{r}_1)\chi_j(\mathbf{x}_1) \tag{10}$$

$$[ij|kl] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1)\chi_j(\mathbf{x}_1)1/r_{12}\chi_k^*(\mathbf{x}_2)\chi_l(\mathbf{x}_2) \tag{11}$$

For our system, the ground state is a closed-shell state. In other words, the two electrons occupy the same spatial orbital but have opposite spin. So to simplify the problem, we can make the orbital doubly occupied. That is, one spatial orbital can form two spin orbitals. In so doing, we will obtain the restricted Hartree-Fock equation,

$$f(1)\psi_a(1) = \epsilon_a \psi_a(1) \tag{12}$$

The Fock operator becomes

$$f(1) = h(1) + \sum_{a=1}^{N/2} 2J_a(1) - K_a(1) \tag{13}$$

Now the Coulomb operator and exchange operator are

$$J_b(1)\psi_a(1) = [\int d\mathbf{r}_2 \psi_b^*(2)1/r_{12}\psi_b(2)]\psi_a(1) \tag{14}$$

$$K_b(1)\psi_a(1) = [\int d\mathbf{r}_2 \psi_b^*(2)1/r_{12}\psi_a(2)]\psi_b(1) \tag{15}$$

The total energy is written as

$$E = 2\sum_{a=1}^{N/2}(a|h|a) + \sum_{ab}^{N/2} 2(aa|bb) - (ab|ba) \tag{16}$$

Here, the notaions $(a|h|a)$ and $(ij|kl)$ are similar to (10) and (11) but integrate over spatial orbitals.

To do the above integrals, we need to know what the spatial orbital is. Usually, we expand the orbital with known functions such as Gaussian functions, atomic orbitals and plane waves, etc.

$$\psi_i = \sum_{\mu}^{K} C_{\mu i}\phi_\mu, \quad i = 1, 2, \cdots, K \tag{17}$$

Substituting (17) to (12), we have

$$f(1)\sum_\nu C_{\nu i}\phi_\nu(1) = \epsilon_i \sum_\nu C_{\nu i}\phi_\nu(1) \tag{18}$$

After multiplying by $\phi_\mu^*(1)$ on the left and integrating, we get the following matrix equation,

$$\mathbf{FC} = \mathbf{SC}\epsilon \tag{19}$$

$\mathbf{S}$ is the so-called overlap matrix,

$$S_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1)\phi_\nu(1) \tag{20}$$

$\mathbf{F}$ is the Fock matrix and has elements,

$$F_{\mu\nu} = \int d\mathbf{r}_1 \phi_\mu^*(1) f(1) \phi_\nu(1) \tag{21}$$

Substituting the expression of Fock operator, (13), to (21), we have

$$F_{\mu\nu} = H_{\mu\nu}^{core} + \sum_{a}^{N/2} 2(\mu\nu|aa) - (\mu a|a\nu) \tag{22}$$

The first part on the rhs of (22) is the so-called core-Hamiltonian matrix, which includes the kinetic energy matrix and the matrix due to nuclear attraction,

$$H^{core}_{\mu\nu} = T_{\mu\nu} + V^{ne}_{\mu\nu} \tag{23}$$

with

$$T_{\mu\nu} = \int d\mathbf{r}_1 \phi^*_\mu(1)[-\frac{1}{2}\nabla^2_1]\phi_\nu(1) \tag{24}$$

$$V^{ne}_{\mu\nu} = \int d\mathbf{r}_1 \phi^*_\mu(1)[-\sum_I \frac{Z_I}{|\mathbf{r}_1 - \mathbf{R}_I|}]\phi_\nu(1) \tag{25}$$

The second part on the rhs of (23) has spatial orbitals which are needed to be represented by the basis function further. In so doing, we have the final expression for the Fock matrix,

$$F_{\mu\nu} = H^{core}_{\mu\nu} + \sum^K_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)] \tag{26}$$

Here, we have defined a density matrix,

$$P_{\lambda\sigma} = 2\sum^{N/2}_a C_{\lambda a} C^*_{\sigma a} \tag{27}$$

It should be noted that the summation is over the expansion coefficients of N/2 occupied spatial orbitals. The electron density is connected with the density matrix by

$$\rho(\mathbf{r}) = 2\sum^{N/2}_a \psi^*_a(\mathbf{r})\psi_a(\mathbf{r}) = \sum_{\mu\nu} P_{\mu\nu}\phi_\mu(\mathbf{r})\phi^*_\nu(\mathbf{r}) \tag{28}$$

In the later, we will use this formula to plot the distribution of electron density in real space.

Looking at the matrix equation (19), if the overlap matrix $\mathbf{S}$ is a unit matrix, it will be a usual eigenvalue problem. Unfortunately, the basis set used in practical calculations may not be orthonormal. So we need to find a transformation matrix that makes the basis set ϕ_μ orthogonalized, i.e.

$$\phi^{'}_\mu = \sum_\nu X_{\nu\mu}\phi_\nu, \quad \mu = 1, 2, \cdots, K \tag{29}$$

with the matrix $\mathbf{X}$ satisfying

$$\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1} \tag{30}$$

Since $\mathbf{S}$ is Hermitian, it's always possible to find a unitary matrix which diagonalizes $\mathbf{S}$,

$$\mathbf{U}^\dagger \mathbf{S} \mathbf{U} = \mathbf{s} \tag{31}$$

Combine (30) and (31), we can obtain

$$\mathbf{X} = \mathbf{U}\mathbf{s}^{-1/2} \tag{32}$$

Correspondingly, the coefficient matrix $\mathbf{C}'$ in the new basis is related to the old one by

$$\mathbf{C}' = \mathbf{X}^{-1}\mathbf{C} \tag{33}$$

Substituting (33) to (19) and multiplying on the left by $\mathbf{X}^\dagger$ give the following eigenvalue equation,

$$\mathbf{F}'\mathbf{C}' = \mathbf{C}'\epsilon \tag{34}$$

where

$$\mathbf{F}' = \mathbf{X}^{\dagger}\mathbf{F}\mathbf{X} \tag{35}$$

Before beginning to do the SCF procedure, we need to choose the basis set. In quantum chemistry calculations, the most popular basis is the Gaussian basis. In our case, we also choose the Gaussian basis set. Particularly, we chose 1s STO-3G minimal basis set. It means that we use 3 different primitive Gaussian functions (3G) to fit a 1s-type Slater orbital (STO) and give each atom one basis (minimal basis). For example, the normalized 1s Slater function has the form

$$\phi_{1s}^{SF}(\zeta, \mathbf{r} - \mathbf{R}_I) = (\zeta^3/\pi)^{1/2} e^{-\zeta|\mathbf{r}-\mathbf{R}_I|} \tag{36}$$

and for the hydrogen atom we can represent it by three Gaussian functions,

$$\begin{gathered}\phi_{1s}^{CGF}(\zeta = 1.24, STO - 3G) = 0.444635\phi_{1s}^{GF}(0.168856) + \\ 0.535328\phi_{1s}^{GF}(0.623913) + 0.154329\phi_{1s}^{GF}(3.42525)\end{gathered} \tag{37}$$

Keep in mind that the centers of these primitive Gaussian functions are located on the same nuclei. CGF means contracted Gaussian functions. The numbers in the brackets on the rhs of (37) are the exponents of Gaussian functions. Note that the value of ζ is larger than one which is the exact value for the hydrogen atom. This is because atomic orbitals will change when atoms form chemical bonds. STO-3G basis set can be downloaded form `https://bse.pnl.gov/bse/portal`. The Gaussian basis set is convenient for the integral mentioned above because the product of two Gaussian functions is another Gaussian function. Using this property, the above matrices (24)-(28) have analytic forms.

For the overlap matrix $\mathbf{S}$,

$$S_{\mu\nu} = \sum_{p,q=1}^{L} d_{p\mu}^{*} d_{q\nu} S_{pq} \tag{38}$$

with

$$S_{pq} = (\frac{4\alpha\beta}{(\alpha+\beta)^2})^{3/4} e^{-\frac{\alpha\beta}{\alpha+\beta}|\mathbf{R}_\mu - \mathbf{R}_\nu|^2}$$

Here, L is the number of primitive Gaussian function for each CGF. α and β are the exponents of Gaussian functions.

$$\alpha = \alpha_{p\mu}, \beta = \alpha_{q\nu} \tag{39}$$

R_μ and R_ν are the center of basis ϕ_μ and ϕ_ν, respectively. Similarly, for $T_{\mu\nu}$,

$$T_{pq} = [\frac{3\alpha\beta}{\alpha+\beta} - 2(\frac{\alpha\beta}{\alpha+\beta})^2 |\mathbf{R}_\mu - \mathbf{R}_\nu|^2] S_{pq} \tag{40}$$

For $V_{\mu\nu}^{ne}$,

$$V_{pq}^{ne} = \begin{cases} -Z_I \frac{erf(\sqrt{\alpha+\beta}|\mathbf{R}_P - \mathbf{R}_I|)}{|\mathbf{R}_P - \mathbf{R}_I|} S_{pq}, & \mathbf{R}_P \neq \mathbf{R}_I \\ \\ -2Z_I S_{pq}\sqrt{\frac{\alpha+\beta}{\pi}}, & \mathbf{R}_P = \mathbf{R}_I \end{cases} \tag{41}$$

where

$$\mathbf{R}_P = \frac{\alpha\mathbf{R}_\mu + \beta\mathbf{R}_\nu}{\alpha+\beta} \tag{42}$$

For $(\mu\nu|\sigma\lambda)$,

$$(pq|rs) = \begin{cases} S_{pq}S_{rs}\frac{erf(\sqrt{\alpha_t}|\mathbf{R}_P - \mathbf{R}_Q|)}{\mathbf{R}_P - \mathbf{R}_Q}, & \mathbf{R}_P \neq \mathbf{R}_Q \\ \\ 2S_{pq}S_{rs}\sqrt{\frac{\alpha_t}{\pi}}, & \mathbf{R}_P = \mathbf{R}_Q \end{cases} \tag{43}$$

where

$$\begin{cases} \gamma = \alpha_{r\sigma}, \\ \delta = \alpha_{s\lambda}, \\ \\ \alpha_t = \frac{(\alpha+\beta)(\gamma+\delta)}{\alpha+\beta+\gamma+\delta} \end{cases} \tag{44}$$

and

$$\mathbf{R}_Q = \frac{\gamma\mathbf{R}_\sigma + \delta\mathbf{R}_\lambda}{\gamma+\delta} \tag{45}$$

For the sake of simplicity, I didn't write down the summation over coefficients d like in (38) for (40),(41) and (43). You should take care of this point.

Now we can construct the SCF procedure,
1)Provide the system geometry, nuclear charge Z_I, number of electrons N and basis set ϕ_μ.
2)Calculate $S_{\mu\nu}$, $H_{\mu\nu}^{core}$ and $(\mu\nu|\sigma\lambda)$.
3)Diagonalize $\mathbf{S}$ using (31) and obtain $\mathbf{X}$ from (32).
4)Guess a density matrix $\mathbf{P}$ like zero matrix.
5)Calculate $\mathbf{F}$ from (26).
6)Calculate the transformed Fock matrix $\mathbf{F}'$ from (35).
7)Solve Eq. (34) to obtain $\mathbf{C}'$ and ϵ.
8)Calculate $\mathbf{C}$.
9)Form a new density matrix $\mathbf{P}$ form $\mathbf{C}$ using (27).
10)Determine whether the procedure has converged, i.e. the total energy change is less than a threshold value like 1e-8 Ha. If not converged, return to step (5) using the new $\mathbf{P}$. If converged, calculate the quantities like the total energy, orbital energy and electron density.

The following stuff are my results.

TABLE I. Output

Step	E	dE
1	0.0	-1000.0
2	-4.164617162819847	-4.164617162819847
3	-4.207215151050275	-0.04259798823042793
4	-4.208666169654602	-0.001451018604327281
5	-4.208702748225332	-3.657857072969506e-05
6	-4.20870361877731	-8.705519780605186e-07
7	-4.2087036393062425	-2.0528932331842498e-08
8	-4.208703639789659	-4.834168620959645e-10

It can be seen that after 8 iterations the energy change is less than 1e-8 Ha. Plus the nuclei-nuclei exclusive energy E_{nn},

$$E_{nn} = \sum_I \sum_{J>I} \frac{Z_I Z_J}{R_{IJ}} \tag{46}$$

the system's total energy is -2.8418364987923006 Ha. The two lowest orbital energy are -1.63279763 and -0.17248458 Ha. Overlap matrix $\mathbf{S}$,

$$\mathbf{S} = \begin{pmatrix} 0.99999999 & 0.53681935 \\ 0.53681935 & 0.99999999 \end{pmatrix} \tag{47}$$

Kinetic matrix $\mathbf{T}$,

$$\mathbf{T} = \begin{pmatrix} 0.76003188 & 0.19744319 \\ 0.19744319 & 1.41176317 \end{pmatrix} \tag{48}$$

Electron-nuclei attraction energy matrix $\mathbf{V}^{ne}$,

$$\mathbf{V}^{ne} = \begin{pmatrix} -2.49185753 & -1.62927168 \\ -1.62927168 & -4.01004617 \end{pmatrix} \tag{49}$$

The two-electron integral matrix $(\mu\nu|\sigma\lambda)$ is four-dimensional. I only show six unique elements,

$$\begin{aligned} (11|11) &= 0.7746059298062676 \\ (11|22) &= 0.5908072996142457 \\ (11|12) &= 0.3674101510433870 \\ (12|12) &= 0.2243193354528469 \\ (12|22) &= 0.4439649815206948 \\ (22|22) &= 1.0557129304699766 \end{aligned} \tag{50}$$

We can use (28) to obtain the electron density as shown in Fig.1. It can be seen that the density is higher near Helium atom than Hydrogen atom. And the two atoms form the s-type bond.

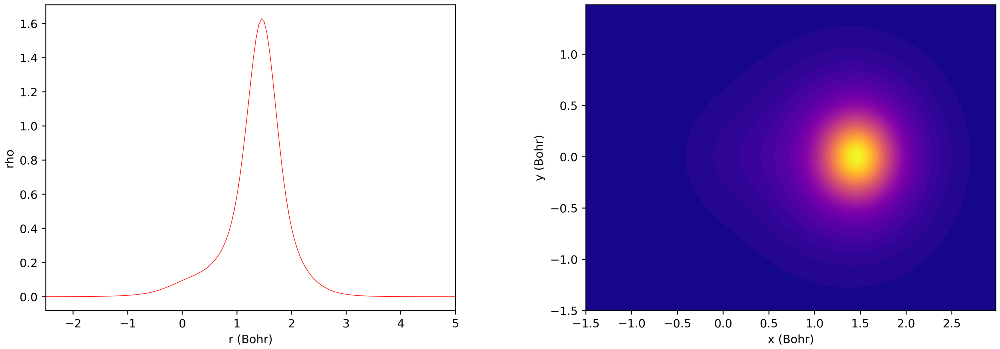

FIG. 1. The electron density distribution in real space. Hydrogen atom is located at (0,0,0) and Helium atom is located at (1.4632,0,0).

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[1] Attila Szabo and Neil S Ostlund. *Modern quantum chemistry: introduction to advanced electronic structure theory*. Courier Corporation, 2012.