

Practice Session 3

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Introduction

In this practice session a general program to do RHF calculations for simple two-electron diatomic molecules is developed. In this case a STO-3G basis set is used and the molecular integrals are parametrized.

With only two electron, $n = 2$, the Slater determinant describing the systems ground state will take the form of Equation 1, with $n/2$ spatial MO.

$$\Phi = \frac{1}{\sqrt{2!}} |\psi_1(r_1)\alpha \psi_1(r_2)\beta| \quad (1)$$

The ψ_1 spatial orbital is an eigenfunction of the one-electron Fock operator, and in some cases, it can be expressed as a linear combination of atomic orbitals (LCAO). Two 1s AO (represented by a STO-3G) centered in each atom are used to describe the system, so the number of basis functions used, m , will be two, with 3 primitive gaussians each. The Roothan-Hall equations will yield 2 orbitals, one for each basis function, 1 occupied by the two electrons, and one virtual. The Roothan-Hall equations consist of:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\epsilon} \quad (2)$$

where \mathbf{F} is the Fock matrix, \mathbf{S} the overlap matrix between basis functions, \mathbf{C} the matrix containing the MO coefficients, and $\boldsymbol{\epsilon}$ the diagonal matrix containing the orbital energies. All this matrices are $m \times m$ symmetric matrices (2×2 in our case with 2 basis functions).

The Fock matrix is constructed with the mono-electronic core Hamiltonian, \mathbf{H} , and bi-electronic matrix, \mathbf{G} :

$$\mathbf{F} = \mathbf{H} + \mathbf{G} \quad (3)$$

where \mathbf{H} includes the kinetic energy and electron-nucleus attraction terms:

$$\mathbf{H} = \mathbf{T} + \mathbf{V} \quad (4)$$

and \mathbf{G} is computed with the bi-electronic integrals, $(ij|kl)$ and the density matrix, $\mathbf{P} = 2\mathbf{CC}^T$:

$$\mathbf{G}_{\mu\nu} = \sum_{\lambda}^m \sum_{\sigma}^m \mathbf{P}_{\lambda\sigma} \left[(\mu\nu|\sigma\lambda) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right] \quad (5)$$

Depending on the atoms, since the matrices are symmetric, some integrals are repeated, and only a few need to be considered. As for example in the H_2 , where $\mathbf{T}_{11} = \mathbf{T}_{22}$.

To simplify the solution of the Roothan-Hall equations, an additional step for orthonormalize the basis set is conducted. Here, a transformation matrix, \mathbf{X} , such that $\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{1}$ is used, using the canonical transformation $\mathbf{X} = \mathbf{U} \mathbf{s}^{-1/2}$, where \mathbf{U} is a unitary matrix (can be obtained from the eigenvectors of \mathbf{S}) and \mathbf{s} the diagonalized matrix of \mathbf{S} .

With all this information, the standard procedure to solve the RHF equation will follow the scheme in Figure 1. Which is used in the problems below and in the code developed for this practice session.

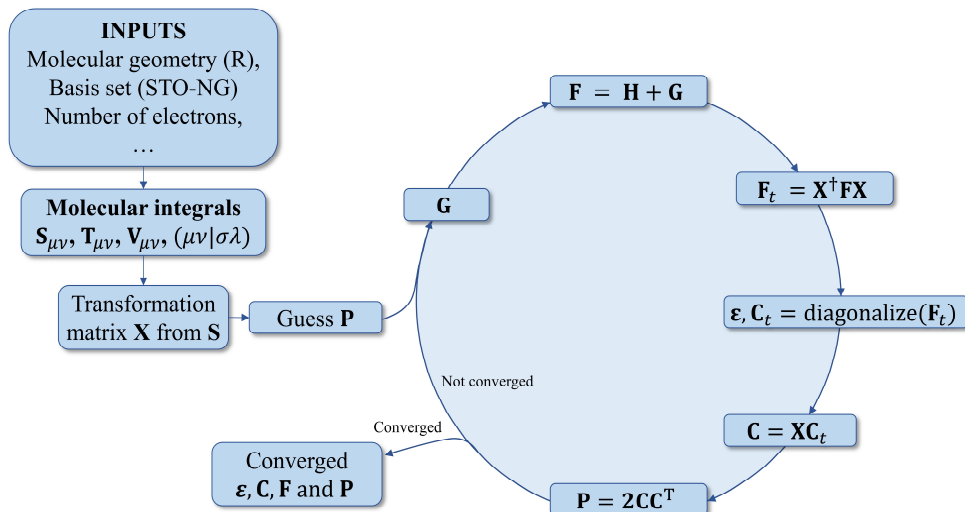


Figure 1. Main scheme for the RHF calculations with the SCF loop.

Problem 1. H₂

For the case of the H₂ molecule, both nucleus are the same, therefore, the symmetry makes a lot of the bi-electronic integrals the same, from the total 16, only 4 need to be calculated. In fact, we can group the integrals by the special indexation of each ij or kl , where if $i = j$, we index it as i and else as the sum $i + j$. So, for example, the case (11|12) has indices [1,3]. With that indices, we can group the integrals by symmetry, so that if they have the same sorted indices, will present the same integral value.

The overlapping, kinetic and potential integrals will also present symmetries. in all cases the element $M_{11} = M_{22}$, so we only need to account for the elements M_{11} and M_{12} . The integrals used are found in Figure 2.

$S_{12} = 0.6593$	$(11 11) = 0.7746$	[1,1] & [2,2]
$t_{11} = 0.7600$	$(11 22) = 0.5697$	[1,2]
$t_{12} = 0.2365$	$(21 11) = 0.4441$	[1,3] & [2,3]
$v^1_{11} = -1.2266$	$(21 21) = 0.2970$	[3,3]
$v^1_{12} = -0.5974$		
$v^1_{22} = -0.6538$		

Figure 2. Molecular integrals(left) and bi-electronic integrals (right) with the correspondent general sorted indices they correspond.

With the parametrised integrals, the Hamiltonian matrix \mathbf{H} and transformation matrix \mathbf{X} can be constructed. An initial null density matrix is used, and then the SCF loop is conducted. The HH distance used is 1.4 a.u.

After 2 iterations the SCF converges with the following results:

Electronic Energy:	$E_{elec} = -1.83091812$
Nuclear Repulsion:	$V_{nn} = 0.71428571$
Total Energy:	$E = -1.11663241$

$$\boldsymbol{\varepsilon} = \begin{pmatrix} -0.578160 & 0 \\ 0 & 0.670196 \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} 0.548937 & -1.211431 \\ 0.548937 & 1.211431 \end{pmatrix}$$

• Python Script available at: [GitHub](#) or attached to the task as p1.py.

Problem 2. HeH⁺

For the case of the HeH⁺ molecule, no such symmetry is achieved since both nucleus are not the same. Nevertheless, there are some integrals that will be repeated. From the total 16, only 6 need to be calculated, since now $11 \neq 22$. Still, we can group the integrals as before by the special indexation of each ij or kl . With that indices, we can group the integrals by symmetry, so that if they have the same sorted indices, will present the same integral value.

The overlapping matrix will still present symmetries, since $S_{11} = S_{22} = 1$, but kinetic and potential integrals will present different diagonal elements. The integrals used are found in Figure 2.

$S_{12} = 0.4508$	$(11 11) = 1.3072$ [1,1]
$t_{11} = 2.1643$	$(22 22) = 0.7746$ [2,2]
$t_{22} = 0.7600$	$(22 11) = 0.6057$ [1,2]
$t_{12} = 0.1617$	$(21 11) = 0.4373$ [1,3]
$v_{11}^1 = -4.1398$	$(22 21) = 0.3118$ [2,3]
$v_{12}^1 = -1.1029$	$(21 21) = 0.1773$ [3,3]
$v_{22}^1 = -1.2652$	
$v_{11}^2 = -0.6772$	
$v_{12}^2 = -0.4113$	
$v_{22}^2 = -1.2266$	

Figure 3. Molecular integrals(left) and bi-electronic integrals (right) with the correspondent general sorted indices they correspond.

With the parametrised integrals, the Hamiltonian matrix **H** and transformation matrix **X** can be constructed. An initial null density matrix is used, and then the SCF loop is conducted. The H-He distance used is 1.4632 a.u.

After 6 iterations the SCF converges with the following results:

Electronic Energy:	$E_{elec} = -4.2331007$
Nuclear Repulsion:	$V_{nn} = 1.3668671$
Total Energy:	$E = -2.86623360$

$$\boldsymbol{\epsilon} = \begin{pmatrix} -1.601286 & 0 \\ 0 & -0.052931 \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} 0.800198 & 0.784050 \\ 0.339133 & -1.067727 \end{pmatrix}$$

- Python Script available at: [GitHub](#) or attached to the task as `p2.py`.