Practice Session 4

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Introduction

In this practice session a general program to do RHF calculations for simple two-electron diatomic molecules using the STO-NG basis set is developed. Now, all the integrals are calculated and then the SCF is used to calculate the energy of the molecule, its MO coefficients and energies, etc. This is a mixture of the scripts developed in practice session two, where the monoelectronic molecular integrals were calculated, and practice session 3, where the general SCF procedure was developed for parametrized integrals.

Again, since we are using a STO-NG basis set with one basis function for each atom, the molecular integrals matrices (**M**) (overlap, **S**, kinetic, **T**, and nucleus-electron potential, **V**) are calculated as in Equation 1, taking into account the N primitive gaussians functions used.

$$\mathbf{M}_{ab} = \sum_{p=1}^{N} \sum_{q=1}^{N} d_{pa} d_{qb} M_{pq} \tag{1}$$

where M_{pq} are the integrals between individual primitive GTO and d the coefficients of the gaussian.

The individual overlap integrals, are calculated with:

$$S_{pq} = \langle A|B \rangle = \left(\frac{\pi}{\alpha + \beta}\right)^{\frac{3}{2}} \exp\left(-\frac{\alpha\beta}{\alpha + \beta}|R_A - R_B|^2\right) \tag{2}$$

The individual kinetic integrals with:

$$T_{pq} = \left\langle A \left| -\frac{1}{2}\nabla^2 \right| B \right\rangle = \frac{\alpha\beta}{\alpha + \beta}\left(3 - 2\frac{\alpha\beta}{\alpha + \beta}|R_A - R_B|^2\right)\langle A|B \rangle \tag{3}$$

And the individual electron-nucleus attraction with:

$$V_{pq}^C = \left\langle A \left| -\frac{Z_C}{r_{1C}} \right| B \right\rangle = \frac{-2\pi}{\alpha + \beta} Z_C \exp\left(\frac{-\alpha\beta}{\alpha + \beta}|R_A - R_B|^2\right) F_o\big((\alpha + \beta)|R_P - R_C|^2\big) \tag{4}$$

where Z_C and R_C are the nuclear charge and position of the C atom, respectively, R_p the intermediate point between two gaussians, calculated with $R_p = (\alpha R_A + \beta R_B)/(\alpha + \beta)$, and F_o an auxiliary function related to the error function, $F_o(t) = 1/2\sqrt{\pi/t}\,\text{erf}(\sqrt{t})$. For small values of t ($t < 10^{-6}$), the approximation $F_o(t) \approx 1 - t/3$ is used to avoid division by zero.

In the case of diatomic molecules, the nuclear-electron retraction term is obtained by summing all contributions for each atom:

$$V_{pq} = \langle A|V|B \rangle = \left\langle A \left| -\frac{Z_A}{r_{1A}} \right| B \right\rangle + \left\langle A \left| -\frac{Z_B}{r_{1B}} \right| B \right\rangle \tag{5}$$

In all the equation above, the normalization constant $N(\alpha, \beta) = [(2\alpha/\pi)(2\beta/\pi)]^{3/4}$ must be taken into account.

Now, the bi-electronic integrals, $(ij|kl)$ also have to be computed. To accomplish that, a $m \times m \times m \times m$ tensor (**B**) is built with the following equation:

$$\mathbf{B}_{ijkl} = \sum_{p=1}^{N} \sum_{q=1}^{N} \sum_{r=1}^{N} \sum_{s=1}^{N} d_{pi} d_{qj} d_{rk} d_{sl} B_{pqrs} \tag{6}$$

with B_{pqrs} being the individual bi-electronic integral, calculated as:

$$B_{pqrs} = (AB|CD) =$$

$$\frac{2\pi^{\frac{5}{2}}}{(\alpha+\beta)(\gamma+\delta)\sqrt{\alpha+\beta+\gamma+\delta}} \exp\left(\frac{-\alpha\beta}{\alpha+\beta}|R_A - R_B|^2 - \frac{-\gamma\delta}{\gamma+\delta}|R_C - R_D|^2\right) \tag{7}$$

$$\times F_o\left(\frac{(\alpha+\beta)(\gamma+\delta)}{\alpha+\beta+\gamma+\delta}|R_P - R_Q|^2\right)$$

Now, with all the molecular matrices calculated, we can diagonalise **S** to find the transformation matrix, such that $\mathbf{X}^\dagger \mathbf{S} \mathbf{X} = \mathbf{I}$, construct a guess density matrix $\mathbf{P}^0$ (0 in our case), and start the SCF loop. We start by computing the bi-electronic matrix **G** from the density matrix **P** and bi-electronic integrals $(ij|kl)$:

$$\mathbf{G}_{\mu\nu} = \sum_{\lambda}^{m} \sum_{\sigma}^{m} \mathbf{P}_{\lambda\sigma}\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right] \tag{8}$$

Then, the Fock matrix is constructed with the core Hamiltonian, **H**, and bi-electronic matrix, **G**, where **H** includes the kinetic energy and electron-nucleus attraction terms:

$$\mathbf{F} = \mathbf{H} + \mathbf{G} \qquad \mathbf{H} = \mathbf{T} + \mathbf{V} \tag{9}$$

The Fock matrix is transformed with **X** and diagonalized to obtain the transformed MO coefficients matrix $\mathbf{C}_t$ and the orbital energies $\boldsymbol{\varepsilon}$,. The orbital coefficients can be obtained by undoing the transformation:

$$\mathbf{F}_t = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} \quad \Rightarrow \quad \mathbf{C}_t, \boldsymbol{\varepsilon} \quad \Rightarrow \quad \mathbf{C} = \mathbf{X} \mathbf{C}_t \tag{10}$$

From the obtained **C** matrix, the density matrix **P** is updated with:

$$\mathbf{P}_{\lambda\sigma} = 2 \sum_{j}^{n/2} \mathbf{C}_{\lambda j} \mathbf{C}_{\sigma j}^* \tag{11}$$

Now, the SCF cycle is completed, and it is looped until convergence, which is decided with the difference between density matrices of consecutive iterations, when its lower than a certain threshold (δ):

$$\sqrt{\frac{1}{m^2} \sum_{\mu}^{m} \sum_{\nu}^{m} \left(\mathbf{P}_{\nu\mu}^k - \mathbf{P}_{\nu\mu}^{k+1}\right)^2} \leq \delta$$

Finally, the ground state electronic energy, E_{elec}, and the nucleus-nucleus potential V_{nn} are computed with:

$$E_{elec} = \frac{1}{2} \sum_{\mu}^{m} \sum_{\nu}^{m} \mathbf{P}_{\mu\nu}\left(\mathbf{H}_{\mu\nu} + \mathbf{F}_{\mu\nu}\right) \qquad V_{nn} = \frac{Z_A Z_B}{R} \tag{12}$$

With the above equations and procedure, a complete RHF code has been developed to compute single point energies (at fixed distance) and PES curves for two-electron diatomic molecules. The program reads a molecule with the given inter-nuclear distance and charges and outputs a file with the given information of the calculation performed. Below are examples of the results for H_2 and HeH^+ calculations.

Problem 1.

To test the developed program, the PES for the H_2 and HeH^+ molecules was calculated. In Figure 1 are the results. Both plots follow the expected shape of the fundamental state of a diatomic molecule, where there is a potential well where the equilibrium geometry is found and at larger distances the molecule dissociates. In this case, at the dissociation limit, the molecule breaks down and we have the atoms separated. In the case of H_2, it seems to dissociate into 2 H atoms, with 1 e^- each. The energies don't correspond well to the two isolated H atoms (which would be -1 hartree) since we are using a minimal basis set and the RHF calculations don't give accurate results for open shell systems, UHF or ROHF should be used. In the case of HeH^+, the molecule dissociates in He and H^+, since the density matrix and MO coefficients seem to grant almost all electron density to the He atom, which makes sense since the electrons are more stabilized with the more positive nucleus.

The minimum energy values and corresponding distance for each case is found in Table 1, and the MO coefficient and density matrices at the last distance calculated in the PES (dissociation limit) in Figure 2.
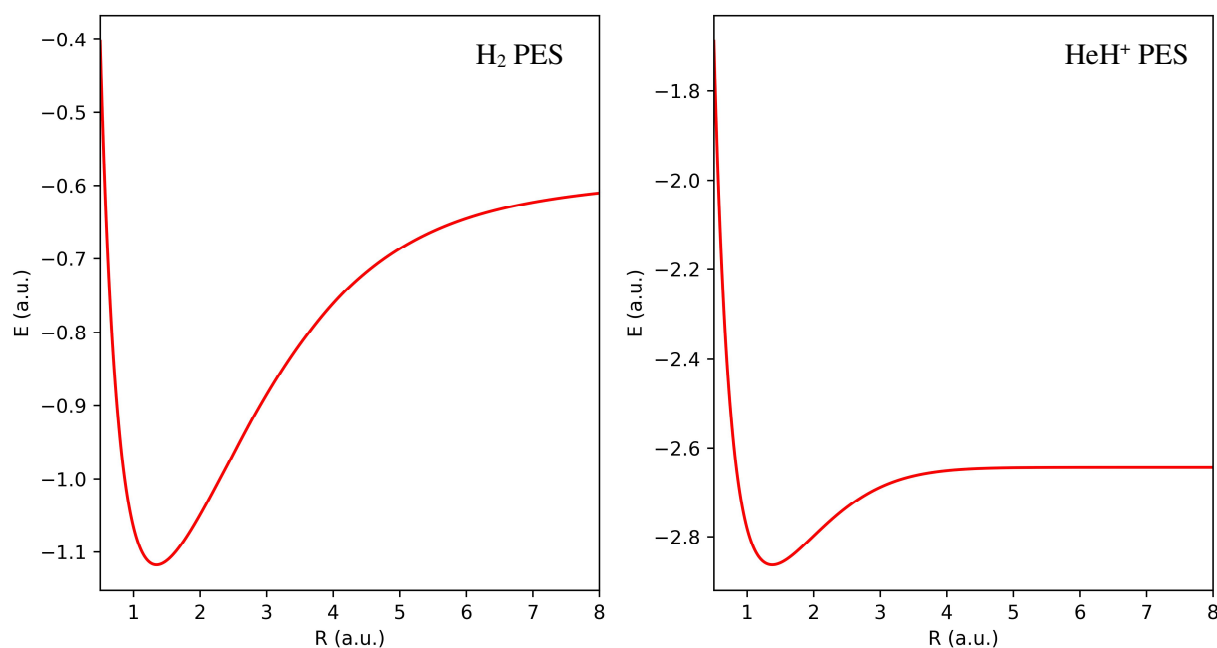

Figure 1. PES for fundamental state of H_2 (left) and HeH^+ (right) molecules. Units in a.u.

	H_2	HeH^+
E (a.u.)	-1.117504	-2.862825
R_e (a.u.)	1.3484	1.3784

Table 1. Minimum energy values E, in a.u., and their corresponding equilibrium geometry, Re, in a.u, for the H_2 and HeH^+ studied cases.

$$\mathbf{C} = \begin{pmatrix} 0.70677 & 0.70745 \\ 0.70677 & -0.70745 \end{pmatrix} \quad \mathbf{C} = \begin{pmatrix} -0.99999 & -5.3 \cdot 10^{-4} \\ -4.7 \cdot 10^{-4} & 0.99999 \end{pmatrix}$$

$$\mathbf{P} = \begin{pmatrix} 0.99904 & 0.99904 \\ 0.99904 & 0.99904 \end{pmatrix} \quad \mathbf{P} = \begin{pmatrix} 1.999997 & 9.38 \cdot 10^{-4} \\ 9.38 \cdot 10^{-4} & -4.4 \cdot 10^{-7} \end{pmatrix}$$

Figure 2. Coefficients, $\mathbf{C}$, and density, $\mathbf{P}$, matrices for H_2 (left) and HeH+ (right) at the last PES distance (dissociation limit).

Moreover, single point calculations performed on the molecules revealed very similar results to the ones obtained with parametrized molecular integrals (practice session number 3), which indicated the code worked correctly.

· Python Scripts available at: `GitHub` or attached to the task as `PES.py` for an example PES calculations or `SP.py` for an example of single point calculation.

`GitHub` repository for the Practical Session 4 (and general RHF): github.com/diegonti/EE/tree/master/Practical%20Session%204