Coursework #4

Hartree-Fock treatment of He and H_2

1   Introduction

He atom and H_2 molecule both have two electrons and thus exchange and correlation between the electrons come into play. The waveucntion may be written as the product of a spin part and a spatial part. If the spin part of the wave function is antisymmetric (i.e. satisfies the exchange requirement), the spatial part should include only the correlation effects. In the lectures, we converted the spatial part of the SE of a helium atom to the matrix form

$$F\vec{c} = ES\vec{c}.$$

Despite the latter looks like the equation obtained for a hydrogen atom, it is not really a generalized eigenvalue problem, because the Fock matrix F depends on the solution vector $\vec{c}$

$$F_{ij} = h_{ij} + \sum_{kl} c_k c_l Q_{ijkl}.$$

The non-interacting

$$h_{ij} = \frac{3\alpha_i \alpha_j \pi^{3/2}}{(\alpha_i + \alpha_j)^{5/2}} - \frac{4\pi}{\alpha_i + \alpha_j}$$

and Hartree

$$Q_{ijkl} = \frac{2\pi^{5/2}}{(\alpha_i + \alpha_j)(\alpha_k + \alpha_l)\sqrt{\alpha_i + \alpha_j + \alpha_k + \alpha_l}}$$

terms are fixed and need to be calculated only once at the beginning of the program.

To solve this equation, we start from a guess solution $\vec{c}_0$ to evaluate an initial Fock matrix. The solution to $F\vec{c} = ES\vec{c}$ is then used to improve the Fock matrix and so on. The iterations stops when convergence between input and output $\vec{c}$ is achieved.

As before, expand the wavefunction using a set of s-GTOs, $\phi = \sum_k c_k \chi_k$. Your program is supposed to find the coefficients c_k of the series while the pre-optimized exponents α_k are taken from literature and kept fixed. On the webpage of the course, you will find two-center integrals (Eqs. P.1 to P.4). For He, you need one-center integrals (all GTOs are centered at He nucleus), so $\mathbf{R}_p - \mathbf{R}_q = 0$. Notice that Eq. P.5 may be written as $F_0(t) = \frac{\sqrt{\pi}}{2\sqrt{t}}\mathrm{erf}(\sqrt{t})$, where $\mathrm{erf}(x)$ denotes the error function.

2   He atom

Just like hydrogen atom, use $M = 4$ primitive s-type GTOs $\chi_k = \exp(-\alpha_k r^2)$, $k = 1, \ldots, M$. The optimized exponents for He are however different: $\alpha_1 = 0.297104, \alpha_2 = 1.23675, \alpha_3 = 5.74998, \alpha_4 = 38.21679$ in atomic units.

2.1   Programming

Fill in h and Q and S matrices using the given formula above. Start your program with an arbitrary vector $\vec{c}$. For instance you may choose $\vec{c}_0 = (1, 0, 0, 0)^T$. Make a loop to do the following two steps:

1. Update the matrix F using the current $\vec{c}$.

2. Solve $F\vec{c} = ES\vec{c}$ as a generalized eigenvalue problem. Take the eigenvector corresponding to the smallest eigenvalue as the new solution $\vec{c}$. [1]

3. Iterate until convergence is achieved. You may check the convergence on different quantities. For instance, the energy of the ground state

$$E_0 = 2 \sum_{ij} c_i c_j h_{ij} + \sum_{ijkl} c_i c_j c_k c_l Q_{ijkl}$$

or the Euclidean norm of the groundstate eigenvector $\|\vec{c}_{\text{new}} - \vec{c}_{\text{old}}\|$ should go down at each iteration.

2.2 Tasks

Once your solution converges,

1. Compare the calculated energy with the exact value $E_0 = -2.86166$ Ha.

2. Plot the ground state wave function.

3 H$_2$

Like the He atom, the hydrogen molecule has two electrons. However, the two protons are at two different positions. Let us denote the protons separation by d. Our aim is to calculated the bond-length d.

Unlike He atom, one cannot use one single-electron orbital for both electrons because the orbitals are centered on different protons. Use eight s-type GTOs: four centered at one proton and four on the other one. What are the mathematical representation of these basis functions? Now you need two-center integrals to evaluate Fock and overlap matrices. Express the elements of the Fock and overlap matrices in terms of exponents α_k, and coefficients c_k.

3.1 programming

Make a copy of your program for He. Adapt the parts calculating Fock and overlap matrices for a given bond-length d. Write a program to solve the equation iteratively for 8 unknowns coefficients while keeping the exponents fixed: $\alpha_1 = 13.00774, \alpha_2 = 1.96208, \alpha_3 = 0.44453, \alpha_4 = 0.121949$. Verify that the energy goes down in all iterations. Stop the loop as soon as energy differs only by less than 0.00001 Ha.

3.2 Tasks

1. Run your program for 10 different bondlengths d in range [0.5, 2.5] in atomic units. Plot the energy versus d and fit a parabola to the data (only those close enough to the minimum) to determine the minimum point. What is the meaning and value of the minimum?

2. Calculate and plot the electronic charge density $|\psi|^2$ along the molecular axis. (If the molecule is along the x-axis, plot $|\psi(x, y = 0, z = 0)|^2$.)

Good luck,
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[1] Do not forget to normalize the vector with respect to the overlap matrix: $\vec{c}^T S \vec{c} = 1$. If you are using LAPACK subroutines DSYGV or DSYGVD, the vector $\vec{c}$ is already normalized.