Computational Quantum Physics Exercise 7

Problem 7.1 Re-solving the hydrogen atom in the GTO basis with the variational method

In Born-Oppenheimer approximation, the electronic degrees of freedom of the hydrogen atom can be described by the following Hamiltonian in atomic units (*length unit: bohr radius* $a_B = \frac{\hbar^2}{me^2} = 0.529\AA$; *energy unit: hartree energy* $E_h = \frac{e^2}{a_B} = 27.211eV$)

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \tag{1}$$

Solve the above equation using a basis of 4 Gaussian type orbital (GTO) basis states (chemists call this STO-4G method) via the variational method. The 4 states relevant to this problem have the following form

$$\chi_p(r) = e^{-\alpha_p r^2} \tag{2}$$

(p=1,2,3,4) with

$$\begin{aligned}\alpha_1 &= 13.00773\\ \alpha_2 &= 1.962079\\ \alpha_3 &= 0.444529\\ \alpha_4 &= 0.1219492\end{aligned} \tag{3}$$

The following may be useful. The elements of the overlap matrix $\mathbf{S}$, kinetic energy matrix $\mathbf{T}$ and Coulomb matrix $\mathbf{A}$ are,

$$\begin{aligned}S_{pq} &= \int d^3r e^{-\alpha_p r^2} e^{-\alpha_q r^2} = \left(\frac{\pi}{\alpha_p + \alpha_q}\right)^{3/2}\\ T_{pq} &= -\frac{1}{2}\int d^3r e^{-\alpha_p r^2}\nabla^2 e^{-\alpha_q r^2} = 3\frac{\alpha_p\alpha_q\pi^{3/2}}{(\alpha_p+\alpha_q)^{5/2}},\\ A_{pq} &= -\int d^3r e^{-\alpha_p r^2}\frac{1}{r}e^{-\alpha_q r^2} = -\frac{2\pi}{\alpha_p+\alpha_q}\end{aligned} \tag{4}$$

Problem 7.2 Hartree-Fock solution of the ground state of the helium atom using Gaussian type orbitals as basis functions

The Schrödinger equation in reduced units for the helium atom is given by

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}\right]\Psi(r_1,\sigma_1;r_2,\sigma_2) = E\Psi(r_1,\sigma_1;r_2,\sigma_2) \tag{5}$$

As ansatz for the ground state wave function we take a product state of two identical single particle wave functions ϕ for each electron and an antisymmetric spin-wave function $\chi(\sigma_1,\sigma_2)$.

$$\Psi(r_1,\sigma_1;r_2,\sigma_2) = \phi(r_1)\phi(r_2)\chi(\sigma_1,\sigma_2)$$

We use a finite basis set (4 elements) of GTOs to approximate $\phi(r)$:

$$\phi(r) = \sum_{i=1}^{4} d_i f_i(r) \tag{6}$$

$$f_i(r) = e^{-\alpha_i r^2} \tag{7}$$

$$\begin{aligned}
\alpha_1 &= 0.297104\\
\alpha_2 &= 1.236745\\
\alpha_3 &= 5.749982\\
\alpha_4 &= 38.216677
\end{aligned} \tag{8}$$

One can show that in this special case the Hartree-(Fock) equations in the finite basis set are

$$\sum_j (t_{ij} + \sum_{kl} d_k d_l V_{ijkl}) d_j = \epsilon \sum_j S_{ij} d_j \tag{9}$$

with overlap matrix S, non-interacting term t, and the Hartree term V

$$t_{ij} = \int d^3r f_i^*(r)(-\frac{1}{2}\nabla^2 - \frac{2}{r})f_j(r) = 3\frac{\alpha_i\alpha_j\pi^{3/2}}{(\alpha_i+\alpha_j)^{5/2}} - \frac{4\pi}{\alpha_i+\alpha_j}, \tag{10}$$

$$V_{ijkl} = \int d^3r \int d^3r' f_i^*(r) f_k^*(r') \frac{1}{|r-r'|} f_l(r') f_j(r) = \frac{2\pi^{5/2}}{(\alpha_i+\alpha_j)(\alpha_k+\alpha_l)\sqrt{\alpha_i+\alpha_j+\alpha_k+\alpha_l}} \tag{11}$$

Equation (9) is not a generalized eigenvalue equation because of the presence of the d_k and d_l between the brackets on the left hand side. But we can fix d_k and d_l (with some initial guess) and then determine d_j. We then replace d_k, d_l by the solution found and iterate the procedure until we obtain a self consistent solution. The ground state energy can then be calculated by

$$E_0 = 2\sum_{i,j} d_i d_j t_{ij} + \sum_{i,j,k,l} V_{ijkl} d_i d_j d_k d_l \tag{12}$$

Make sure that you normalize your vector d after each step

$$\sum_{i,j} d_i S_{ij} d_j = 1 \tag{13}$$

Problem 7.3 Hartree-Fock solution of the ground state of the hydrogen molecule using Gaussian type orbitals as basis functions

We extend the previously discussed helium problem to the hydrogen molecule. As for helium we have only two electrons occupying one orbital, thus we do not need to sum over different orbitals μ like it is described in the lecture notes. We use the same finite basis set as for the single hydrogen atom, but centered at the location of each nucleus R_A and R_B:

$$f_i(r) = e^{-\alpha_i (r-R_i)^2} \tag{14}$$

$$\begin{aligned}
\alpha_1 = \alpha_5 &= 13.00773 \\
\alpha_2 = \alpha_6 &= 1.962079 \\
\alpha_3 = \alpha_7 &= 0.444529 \\
\alpha_4 = \alpha_8 &= 0.121949 \\
R_1, \ldots, R_4 = R_A &= 0 \\
R_5, \ldots, R_8 = R_B &= 1
\end{aligned}$$

Calculate the overlap matrix S_{ij} and the non-interacting matrix t_{ij} by using the integrals in the hand-out.

The Hartree term V is given by

$$V_{ijkl} = 2\sqrt{\frac{(\alpha_i+\alpha_j)(\alpha_k+\alpha_l)}{\pi(\alpha_i+\alpha_j+\alpha_k+\alpha_l)}} S_{ij} S_{lk} F_0(q) \tag{15}$$

with

$$F_0(q) = q^{-1/2}\frac{\sqrt{\pi}}{2}\operatorname{erf}(\sqrt{q}) \tag{16}$$

$$q = \frac{(\alpha_i+\alpha_j)(\alpha_k+\alpha_l)}{\alpha_i+\alpha_j+\alpha_k+\alpha_l}\left|\frac{\alpha_i R_i + \alpha_j R_j}{\alpha_i+\alpha_j} - \frac{\alpha_k R_k + \alpha_l R_l}{\alpha_k+\alpha_l}\right|^2 \tag{17}$$

The error function $\operatorname{erf}(x)$ is given in equation 4.114 in the hand-out.

Proceed in the same way as in the last problem to calculate the ground state energy. You should obtain $E_0 = -1.07855$ (nuclear repulsion +1 included!)