ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Computational Quantum Physics
Exercise 8

FS 16
Prof. S. Huber

Problem 8.1 Solving the hydrogen atom in the GTO basis variationally

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* $a_B = \frac{\hbar^2}{me^2} = 0.529\mathring{A}$; *energy unit: hartree energy* $E_h = \frac{e^2}{a_B} = 27.211eV$)

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

The goal of this exercise is to obtain a variational estimate for the energy of the Hydrogen atom. In order to do this we will use a basis of 4 Gaussian Type Orbitals[1] (GTOs) and construct an Ansatz of the form

$$\Psi(\mathbf{r}) = \sum_{j=1}^{4} d_j \chi_j(r),$$

with

$$\chi_j(r) = e^{-\alpha_j r^2} \tag{2}$$

and

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

Using this Ansatz one may obtain a variational estimate of the energy by obtaining the d_j's minimizing the value of $\langle\Psi|H|\Psi\rangle$ subject to the constraint $\langle\Psi|\Psi\rangle = 1$. It is simple to show that one is lead to a generalized eigenvalue problem of the form

$$\sum_j H_{i,j}\, d_j = \epsilon \sum_j S_{i,j} d_j$$

with $H = T + A$ the hamiltonian in the GTO basis and S the overlap matrix. The elements of the overlap matrix S, kinetic energy matrix T and Coulomb matrix A being

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

[1] Chemists call this the STO-4G method.

Problem 8.2 Hartree-Fock solution of the ground state of the helium atom using GTOs 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 $\chi(\sigma_1,\sigma_2)$:

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

As before we use a finite basis set of GTOs to approximate $\phi(r)$:

$$\phi(r) = \sum_{j=1}^{4} d_j f_j(r) \tag{6}$$

$$f_j(r) = e^{-\alpha_j r^2} \tag{7}$$

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

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, so that

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

Problem 8.3 Hartree-Fock solution of the ground state of the hydrogen molecule using GTOs 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:

$$f_j(r) = e^{-\alpha_j (r-R_j)^2} \tag{14}$$

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

Calculate the overlap matrix S_{ij} and the non-interacting matrix t_{ij} by evaluating the integrals involving Gaussian functions[2].

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

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

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

The error function $\mathrm{erf}(x)$ is defined by $\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x dx'\, e^{-x'^2}$ and is available in most high-level programming languages.

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!)

[2] `http://dx.doi.org/10.1017/CBO9781139171397.006` chapter 4.8 (only accessible inside of ETH)