Exercise 4: The quantum N-body problem

The ground-state energy of the helium atom
In this exercise, we want to calculate the ground-state energies of two quantum many-body systems. First, we take a look at the two-electron problem of the helium atom which we want to treat via the **Hartree-Fock method**.

In Born-Oppenheimer approximation, the electronic degrees of freedom of the helium atom are described by the following Hamiltonian [in atomic units]

$$\Big[-\frac{1}{2}\nabla_1^2 - \frac{2}{|\vec{r}_1|} + \int d^3\vec{r}_2 |\phi(\vec{r}_2)|^2 \frac{1}{|\vec{r}_1 - \vec{r}_2|} \Big] \phi(\vec{r}_1) = E' \phi(\vec{r}_1)\,. \tag{1}$$

To represent the four different possible states of the two electrons we define a basis of four Gaussian basis functions

$$\chi_p(\vec{r}) = e^{-\alpha_p r^2} \quad \text{with} \quad p = 1, 2, 3, 4$$

such that the overall wavefunction is then given by the superposition

$$\phi(\vec{r}) = \sum_{p=1}^{4} c_p \chi_p(\vec{r}) = \sum_{p=1}^{4} c_p e^{-\alpha_p r^2}\,.$$

Show that inserting the wavefuction into the Schrödinger equation one obtains an equation of the form

$$\sum_{p,q} (h_{pq} + \sum_{rs} c_r c_s Q_{prqs}) c_q = E' \sum_{pq} S_{pq} c_q. \tag{2}$$

Note that the self-consistency of Hamiltonian (1) is not gone from this equation, since solving for the the coefficients c_q we still need to find the (self-consistent) parameters c_r and c_s on the left-hand side of (2). Our route to solve this problem is an iterative approach where we first fix c_r and c_s (with some initial guess), then determine the c_q, which in turn redefines the left-hand side of the equation. Iterate this process until convergence.

To do this, you will need to know the exponents α_p, which we fix to the following values

$$\alpha_1 = 0.298073, \quad \alpha_2 = 1.242567, \quad \alpha_3 = 5.782948, \quad \text{and} \quad \alpha_4 = 38.474970.$$

With this information show that the matrix elements are given by

$$\begin{aligned}
h_{pq} &= -\frac{1}{2}\langle\chi_p|\nabla^2|\chi_q\rangle - 2\langle\chi_p|\frac{1}{r}|\chi_q\rangle = \frac{3\alpha_p\alpha_q\pi^{3/2}}{(\alpha_p+\alpha_q)^{5/2}} - \frac{4\pi}{(\alpha_p+\alpha_q)}, \\
S_{pq} &= \langle\chi_p|\chi_q\rangle = \left(\frac{\pi}{\alpha_p+\alpha_q}\right)^{3/2}, \\
Q_{prqs} &= \int d^3\vec{r}_1 \int d^3\vec{r}_2 \chi_p(\vec{r}_1)\chi_r(\vec{r}_2)\frac{1}{|\vec{r}_1-\vec{r}_2|}\chi_q(\vec{r}_1)\chi_s(\vec{r}_2) \\
&= \frac{2\pi^{5/2}}{(\alpha_p+\alpha_q)(\alpha_r+\alpha_s)sqrt\alpha_p+\alpha_q+\alpha_r+\alpha_s}.
\end{aligned}$$

Finally the ground state energy can be calculated by

$$E_0 = 2\sum_{pq} c_p c_q h_{pq} + \sum_{pqrs} Q_{prqs} c_p c_q c_r c_s. \tag{3}$$

Keep in mind that the vector $\vec{c} = (c_1, c_2, c_3, c_4)$ should always be (re)normalized to unity via the overlap matrix *before* inserting it back into equation (2), i.e. $\sum_{p,q=1}^{4} = c_p S_{pq} c_q = 1$.

The ground-state energy of the helium atom should turn out to be

$$E_0 = -2.85516038$$

(in atomic units).

Collective ground-state of bosons in a one-dimensional lattice
In this second part we want to calculate the ground state of multiple bosons in a one-dimensional lattice (a chain) interacting via the Hubbard Hamiltonian. We further constrain the system by limiting the occupation of a single site to a maximum of two bosons, i.e. the local site basis can be given by states $\{|0\rangle, |1\rangle, |2\rangle\}$, and fix the total number of bosons to correspond to the number of sites in our lattice.
The Bose Hubbard Hamiltonian is then given by

$$\hat{H} = -t\sum_i \left(\hat{b}_i^\dagger \hat{b}_{i+1} + h.c.\right) + \frac{U}{2}\sum_i \hat{n}_i(\hat{n}_i - 1), \text{ where } \hat{n}_i = \hat{b}_i^\dagger \hat{b}_i\,, \tag{4}$$

where we want to consider $t = 1$ and $U > 0$.

1. Construct the basis and Hamitonian matrix for this problem, consider open boundary conditions on the chain.
2. Use a diagonalization routine to calculate the lowest (ground-state) energy for 10 lattice sites.

You might want to use the DSYEVX routine – which computes selected eigenvalues and, optionally, eigenvectors of a real symmetric matrix A – from the LAPACK libraries to perform the last step. We are providing a C/C++ to Fortran interface on the course website http://www.thp.uni-koeln.de/trebst/Lectures/2012-CompManyBody.html

Reference for the LAPACK libraries: http://www.netlib.org/lapack/