Advanced Computational Physics - Exercise 2

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Hydrogen Atom with a Gaussian Basis

A method that has become very popular in quantum chemistry consists of expanding atomic and/or molecular orbitals on a basis of Gaussian orbitals. Since electrons are Fermions it is necessary to build antisymmetric wavefunctions (e.g. by using Slater determinants), which make the problem quite hard. However, the basic concepts can be well illustrated by the case of the Hydrogen atom, for which we also have an exact solution to compare with. We will consider an Hamiltonian:

$$\hat{H} = -\frac{\hbar}{2m}\nabla^2 + \frac{e^2}{r},$$

where r is the distance of the elctron from the proton. The idea is to find the variational solution to the problem using an expansion of the wavefunction over two different kind of (Cartesian, **not** spherical) basis sets:

- An "s-wave" set:
$$\phi_i(\vec{r}) = \exp(-\alpha_i r^2);$$
- A "p-wave" set:

$$\phi_i^x(\vec{r}) = x\exp(-\alpha_i^x r^2) \quad \phi_i^y(\vec{r}) = y\exp(-\alpha_i^y r^2) \quad \phi_i^z(\vec{r}) = z\exp(-\alpha_i^z r^2).$$

These are obviously non orthogonal basis sets.You will need to implement a code solving the generalized eigenvalue problem based on the gsl subroutines illustrated in class.

1. Given the well known expressions for the Gaussian integrals:

$$\int_0^\infty e^{\alpha x^2} x^{2n} dx = \frac{(2n-1)!!\pi^{1/2}}{2^{n+1}\alpha^{n+1/2}}$$

$$\int_0^\infty e^{\alpha x^2} x^{2n+1} dx = \frac{n!}{2\alpha^{n+1}}$$

   Compute the analytic expressions of the matrix elements of the Hamiltonian, $H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle$ and of the overlap matrix $S_{ij} = \langle\phi_i|\phi_j\rangle$.[5 points]

2. In order to solve the generalized eigenvalue problem you need to perform matrix multiplications like:

$$\mathbf{\Phi_1 \Lambda \Phi_2}$$

   where Φ_1 and Φ_2 are generic matrices, and Λ is a diagonal matrix. Write a test code to learn how to use the blas - Level 3 subroutine `gsl_blas_dgemm` gsl subroutine. You can find the definitions and a worked out example at

   `https://www.gnu.org/software/gsl/doc/html/blas.html`.

   Write a code for solving a generalized eigenvalue problem for some generic 3x3 symmetric matrices using the procedure illustrated in class, and compare your results to those obtained using the subroutine `gsl_eigen_gensymmv`. [30 points]

3. Solve the generalized eigenvalue problem using the "s-wave" basis using 1, 2, and 3 Gaussians. In each case try to determine your optimal values of the parameters α_i, and describe the procedure used to find the minimum. Use atomic units ($\hbar = m_e = e = 1$). Energies will be expressed in Hartrees (H) and lengths in Bohr radii a_0. [20 points]

4. Try to compare your results to those obtained using a basis in which $\alpha_1 = 0.109818$,$\alpha_2 = 0.405771$,$\alpha_3 = 2.22776$ (the so called STO-3G basis of standard quantum chemistry calculations). [15 points]

5. Repeat the analysis with the "p-wave" set (think of the symmetry!). Point out the differences between the ground state found for the "s-wave" set. Can you mix together the two sets in order to improve the ground state solution? Explain your answer.[30 points]