

Introduction to numerical projects

Here follows a brief recipe and recommendation on how to write a report for each project.

- Give a short description of the nature of the problem and the eventual numerical methods you have used.
- Describe the algorithm you have used and/or developed. Here you may find it convenient to use pseudocoding. In many cases you can describe the algorithm in the program itself.
- Include the source code of your program. Comment your program properly.
- If possible, try to find analytic solutions, or known limits in order to test your program when developing the code.
- Include your results either in figure form or in a table. Remember to label your results. All tables and figures should have relevant captions and labels on the axes.
- Try to evaluate the reliability and numerical stability/precision of your results. If possible, include a qualitative and/or quantitative discussion of the numerical stability, eventual loss of precision etc.
- Try to give an interpretation of you results in your answers to the problems.
- Critique: if possible include your comments and reflections about the exercise, whether you felt you learnt something, ideas for improvements and other thoughts you've made when solving the exercise. We wish to keep this course at the interactive level and your comments can help us improve it. We do appreciate your comments.
- Try to establish a practice where you log your work at the computerlab. You may find such a logbook very handy at later stages in your work, especially when you don't properly remember what a previous test version of your program did. Here you could also record the time spent on solving the exercise, various algorithms you may have tested or other topics which you feel worthy of mentioning.

Format for electronic delivery of report and programs

The preferred format for the report is a PDF file. You can also use DOC or postscript formats. As programming language we prefer that you choose between C/C++ and Fortran90/95. You could also use Java or Python as programming languages. Matlab/Maple/Mathematica/IDL are not accepted, but you can use them to check your results where possible. Finally, we do prefer that you work together. Optimal working groups consist of 2-3 students, but more people can collaborate. You can then hand in a common report.

Project 2, Hartree-Fock, improved Monte Carlo and density functional theory, deadline May 31

The aim of this project is twofold: first we will perform Hartree-Fock calculations in order to obtain an optimal basis for the single-particle wave functions Beryllium. These new single-particle wave functions are in turn used in an improved variational Monte Carlo calculation (VMC). We will reuse our VMC from project 1, but this time there is no need to vary the parameter α of the single-particle wave functions. However, we will introduce a slightly more complicated Pade-Jastrow correlation function.

The second step is to parameterize, using the VMC wave function, a density functional for beryllium. This functional will then be compared with the simple local density approximation discussed in for example Thijssen's text, chapter 5.

Exercise 1: Hartree-Fock and Variational Monte Carlo calculations of the beryllium atom

The Hartree-Fock functional is written as

$$E[\Phi] = \sum_{\mu=1}^N \int \psi_{\mu}^*(\mathbf{r}_i) \hat{h}_i \psi_{\mu}(\mathbf{r}_i) d\mathbf{r}_i + \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \left[\int \psi_{\mu}^*(\mathbf{r}_i) \psi_{\nu}^*(\mathbf{r}_j) \frac{1}{r_{ij}} \psi_{\mu}(\mathbf{r}_i) \psi_{\nu}(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j - \int \psi_{\mu}^*(\mathbf{r}_i) \psi_{\nu}^*(\mathbf{r}_j) \frac{1}{r_{ij}} \psi_{\nu}(\mathbf{r}_i) \psi_{\mu}(\mathbf{r}_j) d\mathbf{r}_i d\mathbf{r}_j \right].$$

The more compact version is

$$E[\Phi] = \sum_{\mu=1}^N \langle \mu | h | \mu \rangle + \frac{1}{2} \sum_{\mu=1}^N \sum_{\nu=1}^N \left[\langle \mu \nu | \frac{1}{r_{ij}} | \mu \nu \rangle - \langle \mu \nu | \frac{1}{r_{ij}} | \nu \mu \rangle \right].$$

With the given functional, we can perform at least two types of variational strategies.

- Vary the Slater determinant by changing the spatial part of the single-particle wave functions themselves.
- Expand the single-particle functions in a known basis and vary the coefficients, that is, the new function single-particle wave function $|a\rangle$ is written as a linear expansion in terms of a fixed basis ϕ (harmonic oscillator, Laguerre polynomials etc)

$$\psi_a = \sum_{\lambda} C_{a\lambda} \phi_{\lambda},$$

Both cases lead to a new Slater determinant which is related to the previous via a unitary transformation. The second one is the one we will use in this project.

- 1a) Consider a Slater determinant built up of single-particle orbitals ψ_λ , with $\lambda = 1, 2, \dots, N$.

The unitary transformation

$$\psi_a = \sum_{\lambda} C_{a\lambda} \phi_\lambda,$$

brings us into the new basis. Show that the new basis is orthonormal. Show that the new Slater determinant constructed from the new single-particle wave functions can be written as the determinant based on the previous basis and the determinant of the matrix C . Show that the old and the new Slater determinants are equal up to a complex constant with absolute value unity. (Hint, C is a unitary matrix).

- 1b) Minimizing with respect to $C_{k\alpha}^*$, remembering that $C_{k\alpha}^*$ and $C_{k\alpha}$ are independent and defining

$$h_{\alpha\gamma}^{HF} = \langle \alpha | h | \gamma \rangle + \sum_{a=1}^N \sum_{\beta\delta} C_{a\beta}^* C_{a\delta} \langle \alpha\beta | V | \gamma\delta \rangle_{AS},$$

show that you can write the Hartree-Fock equations as

$$\sum_{\gamma} h_{\alpha\gamma}^{HF} C_{k\gamma} = \epsilon_k C_{k\alpha}.$$

Explain the meaning of the different terms.

Set up the analytic Hartree-Fock equations for the ground state beryllium with the electrons occupying the respective 'hydrogen-like' orbitals $1s$ and $2s$. There is no spin-orbit part in the two-body Hamiltonian.

- 1c) As basis functions for our calculations we will use hydrogen-like single-particle functions. In the computations you will need to program the Coulomb interaction with matrix elements involving single-particle wave functions with $l = 0$ only, so-called s -waves. We need only the radial part since the spherical harmonics for the s -waves are rather simple. Our radial wave functions are

$$R_{n0}(r) = \left(\frac{2Z}{n}\right)^{3/2} \sqrt{\frac{(n-1)!}{2n \times n!}} L_{n-1}^1\left(\frac{2Zr}{n}\right) \exp\left(-\frac{Zr}{n}\right),$$

with energies $-Z^2/2n^2$. A function for computing the generalized Laguerre polynomials $L_{n-1}^1\left(\frac{2Zr}{n}\right)$ is provided at the webpage of the course under the link of project 2. We will use these functions to solve the Hartree-Fock problem for beryllium.

Show that you can simplify the direct term developed during the lectures

$$\int r_1^2 dr_1 \int r_2^2 dr_2 R_{n\alpha 0}^*(r_1) R_{n\beta 0}^*(r_2) \frac{1}{(r_{>})} R_{n\gamma 0}(r_1) R_{n\delta 0}(r_2)$$

as

$$\int_0^\infty r_1^2 dr_1 R_{n\alpha 0}^*(r_1) R_{n\gamma 0}(r_1) \left[\frac{1}{(r_1)} \int_0^{r_1} r_2^2 dr_2 R_{n\beta 0}^*(r_2) R_{n\delta 0}(r_2) + \int_{r_1}^\infty r_2^2 dr_2 R_{n\beta 0}^*(r_2) R_{n\delta 0}(r_2) \right].$$

Find the corresponding expression for the exchange term.

- 1d) With the above ingredients we are now ready to solve the Hartree-Fock equations for the beryllium atom. Write a program which solves the Hartree-Fock equations for beryllium. You will need methods to find eigenvalues (see chapter 12 of lecture notes) and gaussian quadrature (chapter 7) to compute the integrals of the Coulomb interaction. Use as input for the first iteration the hydrogen-like single-particle wave function. Compare the results (make a plot of the 1s and the 2s functions) when self-consistency has been achieved with those obtained using the hydrogen-like wave functions only (first iteration).

Parameterize thereafter your results in terms of the following Slater-type orbitals (STO)

$$R_{10}^{\text{STO}}(r) = N_{10} \exp(-\alpha_{10}r)$$

and

$$R_{20}^{\text{STO}}(r) = N_{20}r \exp(-\alpha_{20}r/2)$$

Find the coefficients α_{10} and α_{20} which reproduce best the Hartree-Fock solutions. These functions are then used in your new VMC calculations.

- (1e) We will now use the obtained STO single-particle wave functions to define an optimized Slater determinant for the variational Monte Carlo calculation. This means that you will not vary the parameter α , as done in project 1. You will use the single-particle functions obtained from the Hartree-Fock calculations.

Perform VMC calculations with blocking, importance sampling and the conjugate gradient method for beryllium using the following three approximations to the correlation function

$$J_1 = \prod_{i<j}^4 \exp\left(\frac{ar_{ij}}{(1 + \beta r_{ij})}\right),$$

with β as the only variational parameter (a is 1/4 in case of equal spins and 1/2 in case of opposite spins),

$$J_2 = \prod_{i<j}^4 \exp\left(a(1 + \beta_1 r_{ij} + \beta_2 r_{ij}^2)\right),$$

with two variational parameters and finally

$$J_3 = \prod_{i<j}^4 \exp\left(\frac{a(1 + \beta_1 r_{ij} + \beta_2 r_{ij}^2)}{(1 + \beta_3 r_{ij})}\right),$$

with three variational parameters. Which Jastrow factors gives the lowest variance and best approximation to the energy? Discuss your results.

Exercise 2: Density functional theory based on the Variational Monte Carlo calculations

- (2a) The first step is to perform a Hartree-Fock calculation using the code developed in the previous exercise but omitting the exchange (Fock) term. Solve the Hartree equation for beryllium and find the total density determined in terms of the single-particle wave functions ψ_i as

$$\rho^H(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2,$$

where the single-particle functions ψ_i are the solutions of the Hartree equations and the index H refers to the density obtained by solving the Hartree equations. Check that the density is normalised to

$$\int d^3r \rho^H(\mathbf{r}) = N.$$

Compare this density with the corresponding density $\rho^{\text{HF}}(\mathbf{r})$ you get by solving the full Hartree-Fock equations. Compare both the Hartree and Hartree-Fock densities with those resulting from your best VMC calculations. Discuss your results.

- (2b) A popular approximation to the exchange potential in the density functional is to approximate the contribution to this term by the corresponding result from the infinite electron gas model. The exchange term reads then

$$V_x(\mathbf{r}) = - \left(\frac{3}{\pi} \right)^{1/3} \rho^{\text{H}}(\mathbf{r}).$$

Use the Hartree results to compute the total ground state energy of beryllium with the above approximation to the exchange potential. Compare the resulting energy with the resulting Hartree-Fock energy from your Monte Carlo calculation without the Jastrow factor.

- (2c) *Optional:* The final step is to construct the exchange energy by using the density from the best VMC result. Compare the exchange energy with the one obtained by the local density approximation from the previous point. Comment your results.