

FYS-4096 Computational Physics:

Project work 2

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General remarks and instructions:

- You should have access to teacher's repo for help files.
- **Choose only one of the problems 1-14!** (12 points)
- Deadline is at noon on May 10, 2021. You are not allowed to choose the same problem as in project work 1.
- Notice that Project work 2 is not required (this time) for passing the course as long as you have already passed project work 1 and you have enough points altogether for passing the course. However, the maximum of 12 points from Project work 2 is accounted for in the maximum number of points in the course. That is, maximum number of points from exercises is $12 \times 4 = 48$, and from project works it is $2 \times 12 = 24$, which yields 72 points in total. Therefore, not doing project work 2 will definitely affect your grade (roughly a decrease of one).

Returning your Project work

1. Make a folder "ProjectWork2" in your existing Computational Physics repo.
2. Create a file solvedProblems.txt in your "ProjectWork2" folder. Inside it, write for example "problem 2".
3. Make sure all your source files and relevant figures are under version control and push them to GitLab.
4. Push your commits to GitLab before noon on Monday May 10, 2021:
`git push --all && git push --tags`

Problem 1: Hartree and Hartree-Fock of 1D many electron atoms

- Make a code that can be used in calculation of total energies and ionization energies for 1D atoms H, He, Li, Be, and B using both Hartree and Hartree-Fock methods.
- The ionization energy is the minimum amount of energy required to remove an electron, that is, $E_{N-1} - E_N$, where N is the number of electrons in the atom. Moreover, according to Koopman's theorem the ionization energy in Hartree-Fock is approximately equal to the negative of the highest occupied orbital energy.
- For one dimensional atoms the Coulomb potential is described by the smoothed interaction

$$V(x_i, x_j) = \frac{Z_i Z_j}{\sqrt{(x_i - x_j)^2 + a^2}}, \quad (1)$$

where Z_i is the charge of particle i . For this problem use $a = 1$. Notice that for electrons $Z = -1$.

- Compare your Hartree and Hartree-Fock energies and ionization energies to those in Table II of article [“Density functional theory beyond the linear regime: validating adiabatic LDA”](#).
- Consider the ionization energy in the two different ways described above in the second bullet point.
- Make plots of the energies and ionization energies as a function of nuclear charge with proper labeling.
- For each case also compare the electron densities between Hartree and Hartree-Fock, and make plots.

Problem 2: Electron density of rutile TiO₂ from density functional theory

- Use Quantum Espresso and Nexus workflow tool to study the rutile phase of titanium dioxide (TiO₂). Use Puhti at CSC for your calculations, and remember to use the scratch directory for your runs!
- Perform a k-grid convergence test, e.g. with k-grids of (1,1,1), (2,2,2), (3,3,3), and (4,4,4) using energy cut-off of 200 Rydbergs.
- Using the (2,2,2) k-grid perform an energy cut-off test, e.g., with energy cut-offs of 100, 200, 250, and 300 Rydbergs.
- With a suitable combination of energy cut-off and k-grid, compute your “production run” both with LDA and PBE exchange correlation functionals. What do LDA and PBE stand for?
- For your production runs your workflow also needs to include the calculation of electron density. You can obtain the electron density using `pp.x` executable. That is, you need to modify your `machine_configs.py` to include, e.g., job “pp” that uses `pp.x`. In addition, (in your workflow) you need to import `generate_pp` from `nexus`. For the pp-object a proper set of variables could be

```
pp = generate_pp(  
    path = scf_path,  
    outdir = 'pwscf_output',  
    prefix = 'pwscf',  
    job = jobs['pp'],  
    plot_num = 0,  
    iflag = 3,  
    output_format = 5,  
    fileout = 'TiO2_density.xsf',  
    dependencies = (scf, 'other')  
)
```

when your DFT run is in the scf-object.

- Consider how you should modify the variables in the pp-object, in order to obtain spin polarization, and write this information into a file ‘spin_polarization.txt’. Along with that information, describe briefly what is calculated for the spin polarization. In order to answer these questions, look at the INPUT options for PP from [this link](#).
- Use XCrySDen or VESTA (or similar) to visualize the electron density and the difference in the electron density between LDA and PBE results. Make nice figures!
- Plot your convergence test results, that is, energy vs. k-grid and energy vs. energy cut-off.
- You should be good with “cores=4” and “minutes=10”. For the heaviest of these calculations you might need to increase minutes a bit (and maybe cores also, e.g., to 10 or 20).
- The rutile structure is given as an xsf file, and a slightly unfinished script is provided for a simple single DFT run. Modify, for example, machine name etc. to suit your environment, after which you should be able to run a test run. For the project work assignment you need to make somewhat larger modifications to the workflow script.

Problem 3: Variational and Diffusion Monte Carlo

- Make a code that can calculate simple variational and diffusion Monte Carlo simulations.
- Your task now is to look into wave function optimization related to H and He atoms.
- For H atom there is a single electron at 1s orbital. For the Helium atom you will be considering both the ground state ($S = 0$) and the triplet state ($S = 1$). In the $S = 0$ state both electrons are on 1s orbitals and have unlike spins. In the triplet $S = 1$ case one electron is occupying the 1s orbital and the other electron is at the 2s orbital, and the electrons have like spins.
- Use Slater-type orbitals for your trial wave function, i.e.,

$$R_n(r) = N r^{n-1} e^{-ar}, \quad (2)$$

where n is the principal quantum number, a is an optimizable parameter and N is a normalization constant (that is not needed with VMC or DMC).

- As your Jastrow factor use the linear Pade form for particle pairs, i.e.,

$$u(r) = \frac{br}{1.0 + cr}, \quad (3)$$

where $b = 1/2$ for electrons with unlike spins, $b = 1/4$ for electrons like spins, and for the electron-nuclei term $b = -Z$ with Z being the nuclear charge. Hence, c is your optimizable parameter in each term of the Jastrow factor.

a) H atom: exact energy -0.5 Hartree

- Perform VMC runs without Jastrow factor using either 7 or 11 values of $a \in [0.5, 1.5]$, e.g., `linspace(0.5, 1.5, 7)`.
- Plot the total energy as a function of a . Also, plot the variance as a function of a . What is (roughly) your optimal value for a ? What is the variance with the optimal a ?
- With the optimal value of a run a short DMC calculation. What is the variance in the DMC run?

b) He atom ground state reference energy: -2.9037 Hartree ($S = 0$)

- Perform VMC runs without Jastrow factor using 11 values of $a \in [1.1, 2.1]$.
- Plot the total energy as a function of a . Also, plot the variance as a function of a . What is (roughly) your optimal value for a ? What is the variance with the optimal a value?
- Include the Jastrow factor to the problem with appropriate values for b values and test with a few different combinations how the optimizable parameter c will affect the VMC energy and variance. Notice: c can be different for the electron-electron and electron-nuclei terms (e.g., $c \in [0.0001, 1000.0]$).
- Run DMC calculation with the optimal a value, and some jastrow parameters.

c) He atom triplet state reference energy: -2.1752 Hartree ($S = 1$)

- Perform VMC runs without Jastrow factor using 11 values of $a \in [1.1, 2.1]$.
- Plot the total energy as a function of a . Also, plot the variance as a function of a . What is (roughly) your optimal value for a ? What is the variance with the optimal a value?
- Include the Jastrow factor to the problem with appropriate b values and test with a few different combinations how the optimizable parameter c will affect the VMC energy and variance. Notice: c can be different for the electron-electron and electron-nuclei terms (e.g., $c \in [0.0001, 1000.0]$).
- Notice that now in the $S = 1$ case the two electrons are identical. That is, use a determinant for the wave function. Also, if $\Psi_T(R)\Psi_T(R') \leq 0$, then you can assume that the move is unacceptable, since it has crossed a node. This is 100% true if Ψ_T equals the exact wave function of the system. Otherwise, it is an approximation.
- Run DMC calculation with the optimal a value, and some jastrow parameters.

Problem 4: 2D Ising model of a ferromagnet

- Simulate the Ising model of a ferromagnet in regular 2D grid with Monte Carlo.
- Perform simulations in two ways:
 - a) Using only the nearest neighbor interactions with $J_1 = 4$.
 - b) Using both the nearest neighbor and next nearest neighbor interactions, i.e., $J_1 = 4$ and $J_2 = 1$.
- For each case consider energy, heat capacity, magnetization, and magnetic susceptibility as a function of temperature. Use a 10×10 spin lattice.
- Make appropriate figures and consider the differences of a) and b) approaches, e.g., how does the transition temperature change.
- With one of the above approaches (a or b) consider the finite size effects of the system. That is, how does, e.g., the energy per spin (at some temperature) change as a function of N , where the lattice is given as $N \times N$. Use for example, $N = 4, 8, 16$, and 32 . Make a figure of the finite size effects. Notice: $N \times N$ is the total number of the spins.
- What are finite size effects?

Problem 5: Molecular dynamics of H-He mixture

- Use molecular dynamics to simulate H-He system using Lennard-Jones potentials.
- Use periodic cubic simulation cell with $L = 10a_0$.
- Remember to use the minimum image convention.
- Notice: Do NOT calculate periodic images for the potential energy. Consider Morse potential to be of short range and not extending over the minimum image distance. This means that Ewald summation is not needed!
- Let your system consist of 4 H atoms and 4 He atoms.
- Simulate the system at roughly the room temperature.
- Visualize the time dynamics of energetics and trajectories.
- Report the time averaged energies (after equilibration).
- What is the average H-He distance?
- For He-He use parameters $\epsilon = 3.2 \times 10^{-5}$ Hartree and $\sigma = 4.73a_0$, and for H-H $\epsilon = 0.1745$ Hartree and $\sigma = 1.25a_0$.
- For He-H interaction use the Lorentz-Berthelot mixing rules:

$$\epsilon_{ab} = \sqrt{\epsilon_{aa}\epsilon_{bb}} \quad (4)$$

$$\sigma_{ab} = (\sigma_{aa} + \sigma_{bb})/2. \quad (5)$$

Problem 6: Classical Monte Carlo of H-He mixture

- Use classical Monte Carlo to simulate the H-He system as described in problem 5. Notice that the boundary conditions are periodic.
- Consider the energetics and particle positions as a function of the Monte Carlo steps. Also, report the expectation values for the energies.
- What is the average H-He distance?

Problem 7: Simulation of Hydrogen gas with classical Monte Carlo

- Perform atomistic simulations of many hydrogen atoms confined in a 3D periodic simulation cell.
- Use Morse potential as your H-H interaction.
- Remember to use the minimum image convention.
- Notice: Do NOT calculate periodic images for the potential energy. Consider Morse potential to be of short range and not extending over the minimum image distance. This means that Ewald summation is not needed!
- Use cubic simulations cell with $L = 50a_0$.
- For this project work include 8 H atoms in to the simulation cell.
- Use at least $T = 300, 600, 1200$, and 4000 Kelvin for looking into temperature effects as well.
- Plot the energetics as a function of the Monte Carlo time. Also, plot the expectation value of the energies (with errorbars) as a function of temperature. Make figures of these plots.

Problem 8: Simulation of Hydrogen gas in 3D with path integral Monte Carlo

- Perform atomistic simulations of many hydrogen atoms confined in a 3D periodic simulation cell.
- Use Morse potential as your H-H interaction.
- Remember to use the minimum image convention.
- Notice: Do NOT calculate periodic images for the potential energy. Consider Morse potential to be of short range and not extending over the minimum image distance. This means that Ewald summation is not needed!
- Use cubic simulations cell with $L = 50a_0$.
- For this project work include 8 H atoms in to the simulation cell.
- Use $M = 1$ (classical) and $M = 16$ (“quantum”) for considering quantum effects.
- Use $T = 300, 1200$, and 4000 Kelvin for looking into temperature effects as well.
- Plot the energetics as a function of the Monte Carlo time. Also, plot the expectation value of the energies (with errorbars) as a function of temperature.

Problem 9: 2D many electron quantum dot with Hartree approximation

- Make a 2-dimensional Hartree code for solving many electrons in a harmonic quantum dot.
- Use this to first calculate the ground state energy for 2 electrons with $\omega = m = 1$. This should give you close to 3 in Hartree units.
- Next, calculate the energetics and electron density for $S = 3$ state with $N = 6$.
- Plot the electron density as a surface plot, and report the energetics.

Problem 10: Stationary state Schrödinger equation in 2D

- Using finite difference approach make a code that solves a single particle Schrödinger equation in 2D.

$$H\Psi(x, y) = E\Psi(x, y), \quad (6)$$

where $H = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y)$.

- Use harmonic potential as your test case, i.e., $V(x, y) = \frac{1}{2}m\omega^2(x^2 + y^2)$. Choose for example $\hbar = m = \omega = 1$. Consider the accuracy of at least the two lowest eigenvalues and the ground state density ($|\Psi_{0,0}|^2$) in your testing. Notice that the energies are given as $E_{n_x, n_y} = \hbar\omega(n_x + n_y + 1)$, where $n_x = 0, 1, \dots$ and $n_y = 0, 1, \dots$, and the wave function as $\Psi_{n_x, n_y}(x, y) \propto \phi_{n_x}(x)\phi_{n_y}(y)$, where $\phi_n(\cdot)$ is the solution for the quantum harmonic oscillator in 1D:

$$\phi_n(x) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} H_n \left(\sqrt{\frac{m\omega}{\hbar}} x \right), \quad (7)$$

where H_n are Hermite polynomials.

- Also use square domain with same spacing for both x and y directions.
- Remember that the kinetic term (T) in 2D can be represented as the kronecker sum: $T_x \oplus T_y = T_x \otimes I + I \otimes T_y$, where I is the identity matrix. In addition, the potential is diagonal.
- Once you are satisfied with the testing, include a gaussian perturbation into your harmonic potential. Choose such a perturbation that you can see the effect in both the ground state energy and the density.
- Make proper figures of the ground state electron density and of the comparison to the unperturbed case.
- Plot also some densities of the excited states.
- Notice: You might want to normalize the numerical and analytical wave functions before comparison, i.e., both wave functions should obey $\int |\Psi(x, y)|^2 dx dy = 1$, which you can enforce, e.g, via numerical integration. Also, notice that for the excited state the wave function $\tilde{\Psi} = a\Psi_{1,0} - b\Psi_{0,1}$ will also have same eigenvalue as $\Psi_{0,1}$ and $\Psi_{1,0}$, however, $\tilde{\Psi}$ would look as rotated version of the analytical wave functions.

Problem 11: Time-dependent Schrödinger equation in 1D

- Use the **Crank-Nicholson method** for solving the time propagation of a quantum particle in 1D.

$$i\hbar \frac{\partial \phi(x, t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi(x, t) + V(x, t) \phi(x, t). \quad (8)$$

- Use propagation of a Gaussian wave packet as your test case. That is, use for example the initial condition

$$\phi(x, t = 0) = \frac{1}{\sqrt{\sigma_0} \sqrt{\pi}} e^{ik_0 x} e^{-(x-x_0)^2/(2\sigma_0^2)}, \quad (9)$$

where k_0 is the average wave number (or $\hbar k_0$ the average momentum), σ_0 the width of the packet and x_0 the position about which the packet is localized. When $V(x) = 0$ the probability density $P(x, t) = |\phi(x, t)|^2$ evolves as

$$P(x, t) = \frac{\sigma_0}{|\alpha|^2 \sqrt{\pi}} \exp \left[-\frac{\sigma_0^4}{|\alpha|^4} \frac{(x - x_0 - \hbar k_0 t/m)^2}{\sigma_0^2} \right], \quad (10)$$

where $\alpha^2 = \sigma_0^2 + i\hbar t/m$.

- Once your test case is working, consider a case where your wave packet is reflecting from a wall.
- Make proper figures of the electron density before and after reflection. Make also a figure of the electron density in the (x, t) -plane.

Problem 12: LU decomposition and thermal density matrix

- At [this wikipedia link](#) you will find a C code example of LU decomposition, how it can be used in solving linear matrix equations, inverting matrices, and calculating the determinant of a matrix.
- Transform these codes into working Python module with proper commenting.
- Make test functions that compare the results from your implementations against Python's own solvers.
- As your test matrix and equation use the 1D FEM Poisson case (Problem 2) of Exercise 6.
- Once your routines are working your task is to consider a system of three non-interacting identical Fermions. The thermal density matrix for such a system is given as the determinant below

$$\rho(R, R'; \beta) = \begin{vmatrix} \rho^K(\mathbf{r}_1, \mathbf{r}'_1; \beta) & \rho^K(\mathbf{r}_1, \mathbf{r}'_2; \beta) & \rho^K(\mathbf{r}_1, \mathbf{r}'_3; \beta) \\ \rho^K(\mathbf{r}_2, \mathbf{r}'_1; \beta) & \rho^K(\mathbf{r}_2, \mathbf{r}'_2; \beta) & \rho^K(\mathbf{r}_2, \mathbf{r}'_3; \beta) \\ \rho^K(\mathbf{r}_3, \mathbf{r}'_1; \beta) & \rho^K(\mathbf{r}_3, \mathbf{r}'_2; \beta) & \rho^K(\mathbf{r}_3, \mathbf{r}'_3; \beta) \end{vmatrix} \quad (11)$$

with

$$\rho^K(\mathbf{r}, \mathbf{r}'; \beta) = (4\pi\lambda\beta)^{-d/2} e^{-\frac{(\mathbf{r}-\mathbf{r}')^2}{4\lambda\beta}}, \quad (12)$$

where $\beta = 1/(k_B T)$, $\lambda = \hbar^2/(2m)$ and d is the dimensionality.

- Consider your three identical Fermions in 2D, that is, $d = 2$. Fix the initial configuration to $\mathbf{r}_1 = (1, 0)$, $\mathbf{r}_2 = (-1, 1)$, and $\mathbf{r}_3 = (0, 0)$. For the primed coordinates keep \mathbf{r}_1 and \mathbf{r}_2 fixed at the same positions, but let $\mathbf{r}_3 = (x, y)$ have any values in the xy -plane, e.g., $x, y \in [-5, 5]$. This way you are able to map out the so-called “nodal surface” for the third particle. This tells you, for example, if the density matrix would change its sign when particle 3 is moving from \mathbf{r}_3 to \mathbf{r}'_3 .
- Use $\lambda = 1$ and at least $\beta = 10, 1$, and 0.1 , and make proper plots of the xy -plane nodal surface, e.g, by using `contourf` and `colormaps`.
- Also, in the same plots make a circle around the initial position of \mathbf{r}_3 that has a radius of the thermal de Broglie wave length, i.e., $\sqrt{2\lambda\beta}$.

Problem 13: Classical scattering

- Consider scattering process of a particle with mass m in a central potential $V(r)$.
- Assume that the particle is coming from the left with an impact parameter b . This is given as the magnitude of $\mathbf{r} - \mathbf{r} \cdot \mathbf{v} / \|\mathbf{v}\|^2 \mathbf{v}$, where \mathbf{r} is the initial position of the particle with respect to the scattering center, and \mathbf{v} is the initial velocity vector.
- Differential cross section of the such a scattering is given by

$$\sigma(\theta) = \frac{b}{\sin(\theta)} \left| \frac{db}{d\theta} \right|, \quad (13)$$

where $\theta \in [0, \pi/2]$ is the deflection angle.

- Due to the spherically symmetric potential the angular momentum and total energy of the system are conserved during the scattering process. Considering these it is possible to derive the following formulas for the minimum value of the distance (r_m) and the deflection angle (θ):

$$1 - \frac{b^2}{r_m^2} - \frac{V(r_m)}{E} = 0, \quad (14)$$

$$\theta = 2b \left[\int_b^\infty \frac{dr}{r^2 \sqrt{1 - b^2/r^2}} - \int_{r_m}^\infty \frac{dr}{r^2 \sqrt{1 - b^2/r^2 - V(r)/E}} \right], \quad (15)$$

where E is the energy of the incident particle, i.e., $E = mv_0^2/2$.

- Code a program that calculates the differential cross section for arbitrary central potential.
- As your test case consider the Yukawa potential

$$V(r) = \frac{\kappa}{r} e^{-r/a}. \quad (16)$$

- In the limit as $a \rightarrow \infty$, the Yukawa potential approaches the Coulomb potential for which there is an analytical result (Rutherford formula):

$$\sigma(\theta) = \left(\frac{\kappa}{4E} \right)^2 \frac{1}{\sin^4(\theta/2)}. \quad (17)$$

- Plot $\ln(\sigma(\theta))$ as a function of θ for a few different values of parameter a , e.g., $a = 0.1, 1, 10, 100$, and compare your result to the Coulomb case with large a .
- Use, for example, $E = m = \kappa = 1$ in your calculations.

Problem 14: Induced magnetic field by current loops

- According to the law of Biot and Savart the magnetic field by a current element is given as

$$d\mathbf{B} = \frac{\mu_0}{4\pi} \frac{I d\mathbf{l} \times \hat{\mathbf{r}}}{r^2}, \quad (18)$$

where $d\mathbf{l}$ is a vector of length dl in the direction of the current, and r is the distance of the segment dl from a position in space.

- For a single circular current loop in the yz -plane with radius a an analytical solution along the x -axis in the middle of the loop is

$$B_x = \frac{\mu_0 I a^2}{2(x^2 + a^2)^{3/2}}. \quad (19)$$

- Write a code for calculating the magnetic field of a circular current loop in the yz -plane, and make a test function that compares your result with the above analytical result.
- Once the above code is working, consider the case where you have two parallel and identical circular current loops. These are placed a distance $4a$ apart from each other in a way that they share the axis going through their mid-points (symmetry axis). The current is flowing in the same direction in both circuit.
- For the two loop system calculate the magnetic field in 3D and make a figure of the 3D vector field. Spend some time in tuning the figure (coloring, shape, labels, etc.).