Computational Quantum Physics
Exercise 6

PHYS-463
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Problem 6.1 DFT for Helium

The goal of this exercise is to treat the Helium atom within density functional theory. To do this we need to solve the Kohn-Scham equation (Eq. 7.12 in the script) self-consistently. First we need a solver for the Schrödinger equation in (1) for given potential $V(r)$. Given its solution $\psi(r)/u(r)$ we can compute the Hartree potential by solving the Poisson equation (2). Additionally we can compute an approximate exchange-correlation energy, using the free electron approximation and the solution of (1). All in all this procedure provides you with a new effective potential as input to (1). Repeat the above procedure to arrive at a self-consistent solution.
Throughout this exercise we use atomic units ($\hbar = m = 4\pi\epsilon_0 = 1$).

a) Schrödinger Solver

For a spherically symmetric potential $V(r)$ *and* solution $\psi(r)$, the three-dimensional Schrödinger equation $\left(-\frac{1}{2}\Delta + V(r)\right)\psi(r) = \varepsilon\psi(r)$ reduces to the radial equation

$$-\frac{1}{2}u''(r) + V(r)u(r) = \varepsilon u(r), \tag{1}$$

where $u(r) = \sqrt{4\pi}\, r\, \psi(r)$.

- Implement an algorithm for finding the ground state energy and wave function of (1) for a given potential $V(r)$.

  Hint: Use the code that you implemented to solve Exercise 2.1

- Test your code with the $l = 0$ sector of the hydrogen atom, where $V(r) = -\frac{1}{r}$, and compare your result with the analytical solution $\varepsilon_{\text{exact}} = -0.5$ a.u. and $u_{\text{exact}}(r) \propto re^{-r}$).

In part c), you will apply this code to the effective potential as given by density functional theory.

b) Poisson Solver

The Hartree potential $V_{\text{h}}(\vec{r})$ satisfies the Poisson equation $\Delta V_{\text{h}}(\vec{r}) = -4\pi\rho(\vec{r})$. For spherically symmetric $\rho(r)$ and $V_{\text{h}}(r)$, this reduces to

$$U''(r) = -\frac{r}{N}4\pi\rho(r),$$

where $U(r) := rV_{\text{h}}(r)/N$.

For a system of $N = 2$ electrons, we use the ansatz $\rho(r) = N|\psi_0(r)|^2$ for the electron density, where ψ_0 is the *normalized* ground state of the single-electron Schrödinger equation

with the effective potential from density functional theory (see part c) below). Equivalently,

$$U''(r) = -\frac{u^2(r)}{r} \tag{2}$$

where $u(r)$ is the ground state of (1) and normalized to norm one, $\int_0^\infty dr\, u^2(r) = 1$. Note that $U(r)$ satisfies the boundary conditions $U(0) = 0$ and $U(\infty) = 1$.

- Implement a solver for (2) with these boundary conditions for a given function $u(r)$.

  Hint: Use the (velocity free) Verlet algorithm to integrate from $U(0) = 0$, $U(\Delta r) = \Delta r$ to some $r_{\max} \gg 0$ (e.g., $r_{\max} = 20$). Then add a suitable multiple of the homogeneous solution $U_{\text{hom}}(r) = r$ to fix the outer boundary condition.

- Test your code with the $u(r)$ as obtained for the hydrogen atom in part a), and compare your result with the analytical solution $U_{\text{exact}}(r) = -(r+1)e^{-2r} + 1$.

c) Helium

Apply density functional theory to the Helium atom. Use the effective potential $V_{\text{eff}} = V_{\text{en}} + V_{\text{h}} + V_{\text{xc}}$, where V_{en} is the appropriate nuclear potential, V_{h} the Hartree potential as obtained via part b), and

$$V_{\text{xc}}(r) = -\left(\frac{3}{2\pi}\right)^{2/3}\left(\frac{4\pi}{3}\rho\right)^{1/3} = -\left(\frac{3}{2\pi^2}\frac{u^2(r)}{r^2}\right)^{1/3}$$

is a parametrization of the exchange-correlation potential, and can be determined via part a) with ε and $u(r)$.

Repeat these steps iteratively until you reach a self-consistent solution. Decrease your step size Δr and/or increase the cut-off radius $r_{\max}$ to check where your results are not heavily depending on these constants any more.

Hint: You should obtain

$$\epsilon \approx -0.52 \text{ a.u.}$$
$$E \approx -2.72 \text{ a.u.}$$

where energy E is related to the eigenvalue ε by the formula

$$E = 2\epsilon - \int dr\, V_{\text{h}}(r)u^2(r) - \frac{1}{2}\int dr\, V_{\text{xc}}(r)u^2(r).$$

d) (Bonus) PySCF

Use PySCF to do a DFT calculation for the Helium atom and compare your results to those obtained in c).