Department of Physics, Chalmers, Göteborg
Göran Wahnström, Anders Lindman 2017-11-27

E5 The Hartree method

In this exercise you are asked to determine the ground state energy for the helium atom using the Hartree method, a mean field description. Atomic units (a.u.) are used throughout this exercise. In order to solve this problem it is useful to make use of available linear algebra routines, such as GSL or LAPACK for `C` (`Fortran`), NumPy/SciPy for `Python` or `Matlab`.

The Hartree method for helium

The Hartree energy for the ground state is obtained by solving the one-electron Schrödinger equation

$$\left[-\frac{1}{2}\nabla^2 - \frac{2}{r} + V_{\rm H}(\boldsymbol{r})\right]\phi(\boldsymbol{r}) = \epsilon\phi(\boldsymbol{r}) \tag{1}$$

with the Hartree potential $V_{\rm H}(\boldsymbol{r})$ given by

$$V_{\rm H}(\boldsymbol{r}) = \int d\boldsymbol{r}' \frac{n_s(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \tag{2}$$

and where $n_s(\boldsymbol{r}) = |\phi(\boldsymbol{r})|^2$ is the ground-state density for a *single* electron. The ground-state energy is then given by

$$E = 2\epsilon - \int d\boldsymbol{r} V_{\rm H}(\boldsymbol{r}) n_s(\boldsymbol{r}) \tag{3}$$

The Hartree potential

Consider first the Hartree potential, the electrostatic potential generated by the charge distribution following from the wave-function. Eq. (2) can also be written on the differential form,

$$\nabla^2 V_{\rm H}(\boldsymbol{r}) = -4\pi n_s(\boldsymbol{r}) \tag{4}$$

which is referred to as the Poisson equation. The density $n_s(\boldsymbol{r})$, and thereby also $V_{\rm H}(\boldsymbol{r})$, is spherical symmetric. Standard electrostatics then implies that the Hartree potential at a distance r from the nucleus is given by

$$V_{\rm H}(r) = \frac{q_{\rm tot}(r)}{r} \tag{5}$$

where

$$q_{\rm tot}(r) = \int_0^r d\boldsymbol{r} n_{\rm s}(\boldsymbol{r}) \tag{6}$$

is the total charge inside the sphere with radius r and with $q_{\rm tot}(r\to\infty) = 1$. If we introduce

$$U(r) = rV_{\rm H}(r) \tag{7}$$

then Poisson's equation [Eq. 4] is transformed to the ordinary differential equation

$$\frac{d^2}{dr^2}U(r) = -4\pi r n_s(r) \tag{8}$$

with the boundary conditions

$$U(r=0) = 0 \quad \text{and} \quad U(r\to\infty) = 1 \tag{9}$$

The radial Schrödinger equation

For the Schrödinger equation [Eq. 1] we make the standard ansatz

$$\phi(\boldsymbol{r}) = \frac{1}{\sqrt{4\pi}}R(r) = \frac{1}{\sqrt{4\pi}}\frac{f(r)}{r} \tag{10}$$

where the wave-function has to fulfil the boundary condition, the cusp condition,

$$\frac{1}{R(r)}\frac{dR(r)}{dr} = -Z \quad \text{when } r\to 0 \tag{11}$$

where Z is the charge of the nucleus. Using the ansatz in Eq. (10) the one-dimensional radial Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{2}{r} + V_{\mathrm{H}}(r)\right] f(r) = \epsilon f(r) \tag{12}$$

is obtained. The normalisation $\int d\boldsymbol{r}\,|\phi(\boldsymbol{r})|^2 = 1$ implies that

$$\int_0^\infty dr\, f^2(r) = 1 \tag{13}$$

and we have the boundary conditions

$$f(r=0) = f(r\to\infty) = 0 \tag{14}$$

The self-consistency loop

The Hartree potential $V_{\mathrm{H}}(r)$ depends on the wave-function $f(r)$ and as a consequence the radial Schrödinger equation [Eq. (12)] is non-linear and has to be solved in an iterative manner. An initial guess for the wave-function is made and the corresponding density is evaluated. The density is used in the Poisson equation [Eq. (8)] to obtain the Hartree potential. This is then used in the radial Schrödinger equation to obtain a new wave-function and the ground-state energy, and the procedure is repeated until the ground-state energy is converged.

Numerical procedure

The boundary value problem in Eq. (8) and the eigenvalue problem in Eq. (12) can be solved with various numerical methods. In the finite difference method space is discretized as

$$x_i = a + ih \ , \quad i = 0, \ldots, n \ , \quad h = (b-a)/n \tag{15}$$

and one seeks an approximate solution at the grid

$$y_i = y(x_i) \tag{16}$$

The derivatives are replaced by finite differences

$$y'(x_i) = \frac{y_{i+1} - y_{i-1}}{2h} \tag{17}$$

$$y''(x_i) = \frac{y_{i+1} - 2y_i + y_{i-1}}{h^2} \tag{18}$$

and the resulting matrix equations can be solved using standard routines. It is also possible to use non-uniform grids to speed up the computations.

Task

1. Consider first the Poisson equation [Eq. (8)]. Discretize the equation and approximate the derivates using a uniform grid. Solve the resulting system of linear equations, which can be written on the form $\mathbf{Ax} = \mathbf{b}$, using proper boundary conditions.

   Test your program by using the ground state electron density for the hydrogen atom as input. You should then obtain the Hartree potential (1p)

   $$V_{\mathrm{H}}(r) = \frac{1}{r} - (1 + \frac{1}{r})e^{-2r}$$

2. Consider now the radial Schrödinger equation [Eq. (12)]. Write a program that solves the eigenvalue problem using the finite difference method.

   Test your program for the hydrogen atom. The nuclear potential is then equal to $1/r$ and $V_{\mathrm{H}}(r) \equiv 0$. Compare your results with the analytical result for the ground state energy and wave function. (1p)

3. You are now ready to construct a program that determines the ground-state energy for the helium atom using the finite difference method. Make an initial guess for the wave-function and determine the ground-state energy through self-consistent iteration. You have to introduce a reasonable criterion for when to stop the iteration.

It is instructive to consider the probability $\rho(r)$ to find the electron at a distance r from the nuclear position. It is given by

$$\rho(r) = 4\pi r^2 n_s(r)$$

Compare your results with the central-field approximation

$$\rho(r) = 4r^2 Z^3 e^{-2Zr}$$

using both $Z = 2$, an unscreened He nucleus, and $Z = 27/16$, a variationally optimized screened He nucleus. The corresponding ground-state energies for these two models are $E = -2.750$ a.u. and $E = -2.848$ a.u., respectively. Compare with your Hartree result. (2p)