

# Hartree Variational Method for Helium Atom

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## Helium Atom

Helium atom has 2 electrons with coordinates  $\mathbf{r}_1 = (r_1, \theta_1, \phi_1)$  and  $\mathbf{r}_2 = (r_2, \theta_2, \phi_2)$  as well as a single nucleus with coordinate  $\mathbf{R}$  and charge  $Ze$ , with  $Z = +2$ . Within the non-relativistic Born-Oppenheimer (adiabatic) approximation fixing  $\mathbf{R} = 0$  (assuming the nucleus is infinitely heavy and fixed at the origin), the Schrödinger equation for helium atom is:

$$\hat{H}_{he}\psi(\mathbf{r}_1, \mathbf{r}_2) = \left[ \frac{\hbar^2}{2m_e} (-\nabla_1^2 - \nabla_2^2) - \frac{2e^2}{4\pi\epsilon_0} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{r}_1|} \right] \psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2), \quad (1)$$

with the usual constants: electric charge  $e$ , [electric constant](#) - vacuum permittivity  $\epsilon_0$ , etc. Even the simplified Schrödinger equation Eq. (1) (second order differential equation with 6 coordinates of 2 electrons) cannot be solved exactly. For a numerical simulation of Eq. (1) on a small-size cubic grid, see Ref. [1].

## The Independent Electron Approximation

Neglect of electron-electron Coulomb repulsion term  $\frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_2 - \mathbf{r}_1|}$  results in independent electron approximation for helium:

$$\hat{H}_{he} \rightarrow -\left( \frac{\hbar^2}{2m_e} \nabla_1^2 + \frac{2e^2}{4\pi\epsilon_0 r_1} \right) - \left( \frac{\hbar^2}{2m_e} \nabla_2^2 + \frac{2e^2}{4\pi\epsilon_0 r_2} \right). \quad (2)$$

Under the independent electron approximation, if we take the two-electron wave function as a product of the individual electron's wave functions (two hydrogen-like wave functions) we obtain:

$$\begin{aligned} \psi(\mathbf{r}_1, \mathbf{r}_2) &= \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \\ \left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \right) \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) &= (E_1 + E_2)\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2), \end{aligned} \quad (3)$$

where  $E_1$  and  $E_2$  are the eigen values of the Schrödinger equation for hydrogen-like atom:

$$\left( -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0 r_i} \right) \psi_i(\mathbf{r}_i) = E_i \psi_i(\mathbf{r}_i), \text{ with } i = 1, 2.$$

Recall the hydrogen-like wave functions are:

$$\psi_{n\ell m}(\mathbf{r}) = R_{n\ell}\left(\frac{Zr}{a_0}\right)Y_{\ell m}(\theta, \phi), \quad (4)$$

where for helium  $Z = 2$ . Energies  $E_1$  and  $E_2$  are restricted to the following values:

$$E_n = -\frac{Z^2 E_h}{2} \frac{1}{n^2}, \quad n = 1, 2, 3, \dots \quad (5)$$

where the Hartree energy  $E_h = \frac{\hbar^2}{m_e a_0^2} = m_e \left( \frac{e^2}{4\pi\epsilon_0 \hbar} \right)^2 \simeq 27.21 \text{ eV}$ . Thus, electron wave functions and energies

under independent electron approximation (neglecting spin degrees of freedom and need of antisymmetrization for the moment) for helium are:

$$\begin{aligned} \psi_{n_1 \ell_1 m_1, n_2 \ell_2 m_2}(\mathbf{r}_1, \mathbf{r}_2) &= \psi_{n_1 \ell_1 m_1}(\mathbf{r}_1) \psi_{n_2 \ell_2 m_2}(\mathbf{r}_2) = R_{n_1 \ell_1} \left( \frac{Zr_1}{a_0} \right) Y_{\ell_1 m_1}(\theta_1, \phi_1) R_{n_2 \ell_2} \left( \frac{Zr_2}{a_0} \right) Y_{\ell_2 m_2}(\theta_2, \phi_2) \\ E_{n_1 \ell_1 m_1, n_2 \ell_2 m_2} &= -\frac{Z^2 E_h}{2} \left( \frac{1}{n_1^2} + \frac{1}{n_2^2} \right). \end{aligned} \quad (6)$$

Thus, the ground state energy for helium atom within independent electron approximation is:

$$E_0 = E_{100, 100} = -\frac{2^2 E_h}{2} \left( \frac{1}{1^2} + \frac{1}{1^2} \right) = -4E_h \simeq -108.8 \text{ eV}, \quad (7)$$

or 8 times the value of the hydrogen atom's ground state energy, whereas, [the experimentally determined value](#) is  $-79.0052 \text{ eV}$ . Thus, the independent electron approximation entails significant error and gives much lower energy than experimental value (e.g. it neglects considerable positive contribution from electrons' mutual repulsion energy).

## Variational Method and Upper Bound of the Ground State Energy

The variational method allows us to arrive at an upper bound for the ground state energy of the system. Recall the relations between Hamiltonian, ground state (normalized), and the ground state energy:

$$\hat{H}|\psi_0\rangle = E_0|\psi_0\rangle, \quad \langle\psi_0|\hat{H}|\psi_0\rangle = \langle\psi_0|E_0|\psi_0\rangle = E_0. \quad (8)$$

If  $|\psi_0\rangle$  is not known, that is always the case in reality except for the hydrogen atom, we can take a trial normalized function  $|\psi_{var}\rangle$  and determine the expectation of the Hamiltonian,  $\hat{H}$ , in this state, and define it to be the variational energy,  $E_{var}$ :

$$E_{var} = \langle\psi_{var}|\hat{H}|\psi_{var}\rangle. \quad (9)$$

The variational theorem states:

$$E_{var} \geq E_0 \quad (10)$$

for any normalized state  $|\psi_{var}\rangle$  and there is a strict inequality in Eq. (10) if the ground state is non-degenerate (a unique state). The proof of Eq. (10) leverages orthonormality and completeness of the energy eigenbasis  $|E_j\rangle$ , with  $j = 0$  corresponding to the ground state ( $|E_0\rangle = |\psi_0\rangle$ ).

Proof:

$$\langle\psi_{var}|\hat{H} - E_0|\psi_{var}\rangle = \sum_j (E_j - E_0) |\langle\psi_{var}|E_j\rangle|^2 \geq 0,$$

as  $E_j - E_0 \geq 0$ , and hence

$$\langle\psi_{var}|\hat{H}|\psi_{var}\rangle = E_{var} \geq E_0$$

as  $\langle\psi_{var}|\psi_{var}\rangle = 1$ .

Note, in case of non-degenerate ground state  $E_j - E_0 > 0$ , for  $j \neq 0$  and strict inequality holds:

$$\langle\psi_{var}|\hat{H}|\psi_{var}\rangle = E_{var} > E_0. \quad (11)$$

The practical variational method requires that variational parameters appear in the formulation explicitly to allow us optimization over them. In the following section we demonstrate it on example of helium atom.

## Hartree Variational Method for Ground State of Helium Atom

We can attempt to use the variational principle to determine the approximate ground-state wave function and energy of the helium atom described by Hamiltonian rewritten in the following way:

$$\hat{H}_{he} = \frac{m_e}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \left( -\frac{a_0^2}{2} \nabla_1^2 - \frac{a_0^2}{2} \nabla_2^2 - \frac{2a_0}{r_1} - \frac{2a_0}{r_2} + \frac{a_0}{|\mathbf{r}_1 - \mathbf{r}_2|} \right). \quad (12)$$

A factor in front of the brackets in the right hand side of Eq. (12) is the [Hartree energy](#):

$E_h = \frac{m_e}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 = \hbar^2/(m_e a_0^2)$ . We can divide both sides of Eq. (12) with  $E_h$  to obtain:

$$\hat{H}_{he}/E_h = -\frac{1}{2} (a_0^2 \nabla_1^2 + a_0^2 \nabla_2^2) - 2 \left( \frac{a_0}{r_1} + \frac{a_0}{r_2} \right) + \frac{a_0}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (13)$$

We can try a wave function that is a product of two hydrogen 1s-like orbitals, but with an effective charge  $z$  as a variational parameter. Such simple product wave function is referred to as the **Hartree product state**,

$$\psi_{var}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}^z(\mathbf{r}_1) \psi_{1s}^z(\mathbf{r}_2). \quad (14)$$

There is a single variational parameter  $z$  that enters the definition of the trial (normalized) wave function:

$$\psi_{1s}^z(\mathbf{r}) = \frac{1}{\sqrt{\pi}} \left( \frac{z}{a_0} \right)^{3/2} e^{-zr/a_0}. \quad (15)$$

Putting  $z = 1$ , Eq. (15) gives us the ground state wave function of the hydrogen atom and putting  $z = 2$  it gives us single particle states  $\Psi_{100}(\mathbf{r})$  participating in the ground state of helium obtained within the independent electron approximation Eq. (6). If we take into consideration presence of the second electron cloud around the helium nucleus, then we can anticipate that effective electric charge that a given electron feels is less than 2, due to screening nuclear charge by another electron. Hartree took this effective charge as a single variational parameter when writing the trial wave function as:

$$\psi_{var}(\mathbf{r}_1, \mathbf{r}_2) = \left( \frac{z^3}{\pi a_0^3} \right) e^{-\frac{z(r_1+r_2)}{a_0}}. \quad (16)$$

Symbolic derivation below shows all steps leading to the variational energy, energy that we will vary until we arrive at the minimal possible value within the given variational ansatz Eq. (16):

$$E_{var}(z) = \left( z^2 - \frac{27}{8} z \right) E_h. \quad (17)$$

By taking the derivative of variational energy w.r.t.  $z$ , we find the minimal value of variational energy and best value of effective charge (that corresponds to minimal energy):

$$\frac{dE_{var}(z)}{dz} \Big|_{z=z_{\min}} = 0 \implies z_{\min} = \frac{27}{16} \quad (18)$$

$$E_{var}(z_{\min}) = -2.8477 E_h = -77.4887 \text{ eV}. \quad (19)$$

Below we provide a symbolic derivation of Eqs. (17)-(19). We will study the "dimensionless Hamiltonian"  $\hat{H}_{he}/E_h$  given in the right hand side of Eq. (13). At the end of the calculations we will multiply the obtained "dimensionless energy" by  $E_h$  to obtain true energy value:

$$E_{var}(z) = E_h \int \int \psi_{var}^*(\mathbf{r}_1, \mathbf{r}_2) \left[ -\frac{1}{2} (a_0^2 \nabla_1^2 + a_0^2 \nabla_2^2) - 2 \left( \frac{a_0}{r_1} + \frac{a_0}{r_2} \right) + \frac{a_0}{|\mathbf{r}_1 - \mathbf{r}_2|} \right] \psi_{var}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2. \quad (20)$$

## Symbolic Computation

```
syms z r1 r2 a0 theta1 phi1 theta2 phi2 real
assumeAlso(a0,'positive')
assumeAlso(z,'positive')
assumeAlso(r1>=0)
assumeAlso(r2>=0)
% take same wave function (orbital) for both electrons
psi1 = 1/sqrt(sym(pi))*(z/a0)^(3/2)*exp(-z*r1/a0) % Eq.(15) for r=r1
```

psi1 =

$$\frac{e^{-\frac{r_1 z}{a_0}} \left( \frac{z}{a_0} \right)^{3/2}}{\sqrt{\pi}}$$

```
psi2 = 1/sqrt(sym(pi))*(z/a0)^(3/2)*exp(-z*r2/a0) % Eq.(15) for r=r2
```

```
psi2 =
```

$$\frac{e^{-\frac{r_2 z}{a_0}} \left(\frac{z}{a_0}\right)^{3/2}}{\sqrt{\pi}}$$

```
% confirm the normalization condition of wave function
```

```
int(int(int(psi1^2*r1^2*sin(theta1),r1,0,inf),theta1,0,pi),phi1,0,2*pi)
```

```
ans = 1
```

```
% two-electron wave function depends only on radial components of r1 and r2  
% and not on angles
```

```
psi_var = psi1*psi2 % Eq. (14)
```

```
psi_var =
```

$$\frac{e^{-\frac{r_1 z}{a_0}} e^{-\frac{r_2 z}{a_0}} \left(\frac{z}{a_0}\right)^3}{\pi}$$

In Laplacians (represented in spherical coordinates) only the radial derivatives will contribute when acting on two-electron wave function given in Eq. (16):

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right) \rightarrow \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right).$$

```
% kinetic energy density
```

```
K = conj(psi_var) * (-1/2*a0^2/r1^2* diff((r1^2*diff(psi_var,r1)),r1)) ...  
+ conj(psi_var) * (-1/2*a0^2/r2^2* diff((r2^2*diff(psi_var,r2)),r2));
```

```
% integral over electron 1 coordinates: r1, theta1, phi1
```

```
Ek = int(int(int(K*r1^2*sin(theta1),r1,0,inf),theta1,0,pi),phi1,0,2*pi);
```

```
% integral over electron 2 coordinates, giving total kinetic energy
```

```
Ek = int(int(int(Ek*r2^2*sin(theta2),r2,0,inf),theta2,0,pi),phi2,0,2*pi)
```

```
Ek = z^2
```

```
% electron-nucleon attraction energy density
```

```
en = conj(psi_var) * (-2*a0/r1 - 2*a0/r2) * psi_var;
```

```
% integral over electron 1 coordinates
```

```
Een = int(int(int(en*r1^2*sin(theta1),r1,0,inf),theta1,0,pi),phi1,0,2*pi);
```

```
% integral over electron 2 coordinates, giving total electron-nucleon
```

```
% interaction energy
```

```
Een = int(int(int(Een*r2^2*sin(theta2),r2,0,inf),theta2,0,pi),phi2,0,2*pi)
```

```
Een = -4 z
```

To simplify calculation of electron-electron repulsion energy, we will orient the coordinate system so that the z axis is directed along the  $\mathbf{r}_1$  vector. Then angle between  $\mathbf{r}_1$  and  $\mathbf{r}_2$  vectors will be  $\theta_2$ . We will calculate the distance between the two electrons in this system, remembering that distance does not depend on orientation of the coordinate system. Out of all 6 integration variables, spherical coordinates of 2 electrons, in electron-electron interaction energy we will integrate over  $\theta_2$  first.

```
dist = sqrt(r1^2+r2^2-2*r1*r2*cos(theta2));
simplify(int((a0/dist)*sin(theta2),theta2,0,pi))
```

ans =

$$\frac{a_0 (r_1 + r_2 - |r_1 - r_2|)}{r_1 r_2}$$

$$a_0 \int_0^\pi \frac{\sin \theta_2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\theta_2 = a_0 \frac{r_1 + r_2 - |r_1 - r_2|}{r_1 r_2} = \begin{cases} 2a_0/r_1, & \text{if } r_1 \geq r_2 \\ 2a_0/r_2, & \text{if } r_1 < r_2 \end{cases}$$

We will use MATLAB's piecewise function below to continue symbolic calculations.

```
% electron-electron interaction energy destiny
ee = conj(psi_var) * piecewise(r1<r2,2*a0/r2,r1>=r2,2*a0/r1) * psi_var;
% multiply by r1^2*r2^2 from unit volume and integrate over radial variables
Eee = int(int(ee*r1^2*r2^2,r2,0,inf),r1,0,inf);
% multiply by sin(theta1) from unit volume and integrate over the remaining
% angles: theta1, phi1, and phi2 (over theta2 we have already integrated)
Eee = int(int(int( Eee*sin(theta1), theta1,0,pi), phi1,0,2*pi), phi2,0,2*pi)
```

Eee =

$$\frac{5z}{8}$$

```
% total energy Etot
```

```
E_var = Ek + Een + Eee % Eq. (20)
```

E\_var =

$$z^2 - \frac{27z}{8}$$

```
z_min = solve(diff(E_var,z) == 0, z) % Eq. (18)
```

z\_min =

$$\frac{27}{16}$$

```
fprintf("E_var(z_min) = %.4f Ha = %.4f eV ", double(subs(E_var,z,z_min)),
double(subs(E_var,z,z_min))* 27.2114 );
```

```
E_var(z_min) = -2.8477 Ha = -77.4887 eV
```

Even though we used the simplest trial wave functions, the variational approach gives us a reasonable upper bound that is within 2% of the experimental value of helium's ground state energy. Effective charge that

single electron feels is reduced from its bare nuclear value of 2 (that electrons feel in independent electron approximation) to  $27/16 \simeq 1.7$ , and the explanation is due to the screening Coulomb attraction (hence reducing it) by the averaged (smeared) charge of another electron. Indeed if we replace 2 by 27/16 in the numerator of independent electron approximation result Eq. (7), we will obtain value that is very close to the Hartree result.

Including more parameters in the trial wave function (increasing variational basis) can decrease the energy, hence increasing the accuracy of the result. We will see this explicitly when we discuss closed-shell formulation of the Hartree-Fock method applied to helium. However, the Hartree variational approach has an inherent limitation: Hartree product wave function for the case of 3 and more electrons [\*] can not describe an antisymmetric state, a state that changes sign when exchanging coordinates and spins of any two electrons. This limitation is overcome in another variational approach, described in live script *Hartree-Fock method*.

## Exercises

**Exercise 1:** Calculate and plot radial dependence of the ground state electron density  $\rho_0(r)$  and radial density  $4\pi r^2 \rho_0(r)$  for helium atom obtained in Hartree approach. Compare them with similar plots obtained within the independent-electron approximation for helium.

**Exercise 2:** Within the symbolic calculation use (normalized) single-electron Gaussian wave function as a variational state  $\psi_G^z(\mathbf{r}) \sim e^{-zr^2/a_0^2}$  and find the value of  $z$  that gives the lowest energy in Hartree approach in the space of Gaussian functions. How does minimal "Gaussian energy" compare to Eq. (19)?

**Exercise 3:** Take antisymmetric coordinate wave function:  $\phi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)]$ , where  $\phi_{1s}$  is the  $1s$  ground state wave function of hydrogen and  $\phi_{2s}$  is  $2s$  hydrogen state, and calculate expectation value of the helium Hamiltonian in this state.

[\*] For the case of 2-electron system such as helium, antisymmetry of the two-electron wave function can be remedied by forming spin-singlet combination, such as in the case of wave function describing the parahelium ground state:

$$\psi_0^{\text{ph}}(\mathbf{r}_1, \mathbf{r}_2) = \phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2) \left[ |\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2 \right] / \sqrt{2}.$$

## References

[1] T. Vekua, [Low-Lying-Spectrum of Hydrogen and Helium Electrons](#)