The Variational Computation of the Ground State Energy of Helium

I. Introduction to the variational computation

The Hamiltonian for the two-electron system of the helium atom is:

$$H = -\frac{\hbar^2}{2m}(\vec{\nabla}_1^2 + \vec{\nabla}_2^2) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}\,, \tag{1}$$

where

$$r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$$

is the distance between the two electrons. The mass of the electron is denoted by m, and we work in the approximation of an infinitely heavy nucleus that is located at the origin of our coordinate system. The term e^2/r_{12} represented the repulsion energy due to the two electrons.

We shall use the variational principle to compute the ground state energy of the helium atom. The ground state wave function of the helium atom is of the form:

$$\frac{1}{\sqrt{2}}\psi(\vec{r}_1\,,\,\vec{r}_2)\big[|\uparrow\,\downarrow\rangle - |\downarrow\,\uparrow\rangle\big]\,,$$

where the spin-part of the wave function is in an antisymmetric spin-singlet state and the space-part of the wave function is symmetric, $\psi(\vec{r}_1\,,\,\vec{r}_2) = \psi(\vec{r}_2\,,\,\vec{r}_1)$, in order to be consistent with the Pauli principle, which requires that the total wave function should be antisymmetric with respect to the interchange of the two electrons. Since the Hamiltonian is spin-independent (we will not include small corrections due to fine-structure or hyperfine-structure), we can ignore the spin-part of the wave function and focus on the space-part alone.

We choose our variational ground state wave function to be:

$$\psi(\vec{r}_1\,,\,\vec{r}_2\,,\,Z) = \frac{Z^3}{\pi a_0^3}\, e^{-Z(r_1+r_2)/a_0}\,, \tag{2}$$

where a_0 is the usual Bohr radius and Z is the variational parameter. This choice is motivated by the following observation. For $Z = 2$, the wave function of eq. (2) is the product of two ground state hydrogen atom wave functions (but with the total charge of the nucleus set to $2e$). This would be the ground state wave function for the helium atom in the absence of the term e^2/r_{12} in the Hamiltonian given in eq. (1). Including the latter term, each electron sees the nucleus as partially screened due to the presence of the other electron. Hence, we expect that each electron sees and effective value of Z that is somewhat less than two (but certainly greater than one). Consequently, eq. (2) with Z as a variational parameter seems like a suitable candidate for a trial ground state wave function.

According to the variational principle, we must compute

$$E(Z) = \langle\psi(Z)|\, H\, |\psi(Z)\rangle \,, \tag{3}$$

and minimize $E(Z)$ as a function of Z. Suppose the minimum occurs at $Z = Z_{\rm min}$. Then, our estimate for the helium ground state energy is

$$E_g \simeq E_0 \equiv E(Z_{\rm min})\,.$$

The variational principle guarantees that the true ground state energy, E_g, satisfies $E_0 \geq E_g$. If we have chosen our trial wave function wisely, then E_0 will be only slightly larger than E_g and provide a good estimate of the true ground state energy.

II. Details of the computation of $E(Z)$

Inserting the trial wave-function, eq. (2) into eq. (3) and using the coordinate representation for the wave function,

$$E(Z) = \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3r_1\, d^3r_2\, e^{-Z(r_1+r_2)/a_0} \\ \times \left[\frac{\hbar^2}{2m}(\vec{\boldsymbol{\nabla}}_1^2 + \vec{\boldsymbol{\nabla}}_2^2) - 2e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{r_{12}}\right] e^{-Z(r_1+r_2)/a_0}\,. \tag{4}$$

Our task is to evaluate this integral. We can simplify our calculation by noting that:

$$\left[\frac{\hbar^2}{2m}(\vec{\boldsymbol{\nabla}}_1^2 + \vec{\boldsymbol{\nabla}}_2^2) - Ze^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right] e^{-Z(r_1+r_2)/a_0} = (-2Z^2 \text{ Ry})e^{-Z(r_1+r_2)/a_0}\,, \tag{5}$$

where

$$1 \text{ Ry} = \frac{me^4}{2\hbar^2} = \frac{e^2}{2a_0} \simeq 13.6 \text{ eV}\,, \tag{6}$$

is the usual Rydberg of energy. Eq. (5) is simply the statement that if we neglect the repulsive electron–electron energy, e^2/r_{12}, then eq. (2) is the exact ground state energy for two independent hydrogen-like atoms, each with a nucleus charge of Ze. The unnormalized ground state energy-eigenfunction is $e^{-Z(r_1+r_2)/a_0}$ and the corresponding ground state energy eigenvalue is then $-2Z^2$ Ry.

Thus, if we replace $-2e^2$ with $-Ze^2 + (Z-2)e^2$ in eq. (4), and use the fact that the trial wave function, eq. (2) is normalized to unity,

$$\left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3r_1\, d^3r_2\, e^{-2Z(r_1+r_2)/a_0} = 1\,,$$

then eqs. (4) and (5) yield:

$$E(Z) = -2Z^2 \text{ Ry} + \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3r_1\, d^3r_2\, \left[(Z-2)e^2\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \frac{e^2}{r_{12}}\right] e^{-2Z(r_1+r_2)/a_0}$$

$$= -2Z^2 \text{ Ry} + \frac{2e^2(Z-2)Z}{a_0} + \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3r_1\, d^3r_2\, \frac{e^2}{r_{12}}\, e^{-2Z(r_1+r_2)/a_0}\,,$$

where I have used the fact that:[1]

$$\left\langle \frac{1}{r} \right\rangle_{100} \equiv \int d^3r\, \frac{1}{r} |\psi_{100}(\vec{\boldsymbol{r}})|^2 = \frac{Z^3}{\pi a_0^3} \int d^3r\, \frac{1}{r} e^{-2Zr/a_0} = \frac{Z}{a_0}\,.$$

Using eq. (6), it follows that:

$$E(Z) = -2\ \mathrm{Ry}(4Z - Z^2) + \left(\frac{Z^3}{\pi a_0^3}\right)^2 \int d^3r_1\, d^3r_2\, \frac{e^2}{r_{12}}\, e^{-2Z(r_1+r_2)/a_0}\,. \tag{7}$$

The remaining integral is challenging. However, it can be done with the help of a couple of identities. The first identity involves the expansion of $1/r_{12}$ in terms of Legendre polynomials:

$$\frac{1}{r_{12}} \equiv \frac{1}{|\vec{\boldsymbol{r}}_1 - \vec{\boldsymbol{r}}_2|} = \frac{1}{r_>} \sum_{\ell=0}^{\infty} \left(\frac{r_<}{r_>}\right)^{\ell} P_\ell(\cos\beta)\,, \tag{8}$$

where β is the angle between $\vec{\boldsymbol{r}}_1$ and $\vec{\boldsymbol{r}}_2$, and the quantities $r_<$ and $r_>$ are defined by:[2]

$$r_> = \max\{r_1\,,\, r_2\}\,, \qquad\qquad r_< = \min\{r_1\,,\, r_2\}\,. \tag{9}$$

Eq. (8) can be easily derived using the generating formula,

$$(1 - 2\mu s + s^2)^{-1/2} = \sum_{\ell=0}^{\infty} P_\ell(\mu) s^\ell\,, \qquad |s| < 1\,,$$

which is the first property of the Legendre polynomials given in Table 9.2 of Liboff on p. 374. Note that:

$$|\vec{\boldsymbol{r}}_1 - \vec{\boldsymbol{r}}_2| = \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\beta} = r_> \sqrt{1 - \frac{2r_<}{r_>}\cos\beta + \left(\frac{r_<}{r_>}\right)^2}\,,$$

where $0 \leq \frac{r_<}{r_>} < 1$ due to the definition of eq. (9). In particular, we identify $\mu \equiv \cos\beta$ and $s \equiv \frac{r_<}{r_>}$, in which case eq. (8) then follows.

The second identity is the addition formula for spherical harmonics,

$$P_\ell(\cos\beta) = \frac{4\pi}{2\ell + 1} \sum_{m=-\ell}^{\ell} Y_\ell^m(\theta_1, \phi_1)^*\, Y_\ell^m(\theta_2, \phi_2)\,, \tag{10}$$

which is given as identity (b) in the caption to Figure 9.16 in Liboff on p. 390. Here, θ_1 and ϕ_1 are the polar and azimuthal angles of the vector $\vec{\boldsymbol{r}}_1$, and θ_2 and ϕ_2 are the polar and azimuthal angles of the vector $\vec{\boldsymbol{r}}_2$, respectively.

[1]The derivation of this result can be found in Supplement 8A to S. Gasiorowicz, *Quantum Physics*, 3rd Edition (John Wiley & Sons, Inc., Hoboken, NJ, 2003), which you can download from Section IV of the class website.

[2]This notation allows us to write one formula instead of two formulae for the two separate cases of $r_1 < r_2$ and $r_1 > r_2$. Technically, the series does not converge in the case of $r_1 = r_2$.

Combining eqs. (8) and (10), one obtains a very useful identity:

$$\boxed{\frac{1}{r_{12}} \equiv \frac{1}{|\vec{\boldsymbol{r}}_1 - \vec{\boldsymbol{r}}_2|} = \frac{1}{r_>} \sum_{\ell=0}^{\infty} \left(\frac{r_<}{r_>}\right)^{\ell} \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} Y_\ell^m(\theta_1,\phi_1)^* \, Y_\ell^m(\theta_2,\phi_2)} \tag{11}$$

We can use this identity to perform the integration:

$$\begin{aligned}\int d^3r_1\, d^3r_2\, \frac{1}{r_{12}} \quad e^{-2Z(r_1+r_2)/a_0} &= \int_0^\infty r_1^2\, dr_1 \int_0^\infty r_2^2\, dr_2\, e^{-2Z(r_1+r_2)/a_0} \\ &\quad \times \sum_{\ell=0}^{\infty} \frac{r_<^\ell}{r_>^{\ell+1}} \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{\ell} \int d\Omega_1\, Y_\ell^m(\theta_1,\phi_1)^* \int d\Omega_2\, Y_\ell^m(\theta_2,\phi_2)\,. \end{aligned} \tag{12}$$

The integrals over the solid angles Ω_1 and Ω_2 are trivial. If one recalls the orthonormality condition:

$$\int d\Omega\, Y_\ell^m(\theta,\phi)^*\, Y_{\ell'}^{m'}(\theta,\phi) = \delta_{\ell\ell'}\, \delta_{mm'}\,,$$

and remembers that

$$Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}}\,,$$

then it follows that

$$\int d\Omega\, Y_\ell^m(\theta,\phi) = \sqrt{4\pi} \int d\Omega\, Y_\ell^m(\theta,\phi) Y_0^0(\theta,\phi) = \sqrt{4\pi}\, \delta_{\ell,0}\, \delta_{m,0}\,.$$

Inserting this result into eq. (12), we see that the only term that survives in the sum over ℓ and m is the $\ell = m = 0$ term. Thus, after writing $d^3r_1 = r_1^2 dr_1 d\Omega_1$ and $d^3r_2 = r_2^2 dr_2 d\Omega_2$, we can easily perform the integration over the solid angles Ω_1 and Ω_2. We are then left with:

$$\int d^3r_1\, d^3r_2\, \frac{1}{r_{12}}\, e^{-2Z(r_1+r_2)/a_0} = (4\pi)^2 \int_0^\infty r_1^2\, e^{-2Zr_1/a_0}\, dr_1 \int_0^\infty r_2^2\, e^{-2Zr_2/a_0} \frac{1}{r_>}\, dr_2\,.$$

Since $r_> \equiv \max\{r_1\,,\, r_2\}$, it is convenient to break up the integration over r_2 into two parts: $0 \leq r_2 < r_1$ and $r_1 < r_2 < \infty$. Note that in the region where $0 \leq r_2 < r_1$ we have $r_> = r_1$, whereas in the region where $r_1 < r_2 < \infty$ we have $r_> = r_2$. Thus,

$$\begin{aligned}\int d^3r_1\, d^3r_2\, \frac{1}{r_{12}}\, e^{-2Z(r_1+r_2)/a_0} &= (4\pi)^2 \int_0^\infty r_1\, e^{-2Zr_1/a_0}\, dr_1 \int_0^{r_1} r_2^2\, e^{-2Zr_2/a_0}\, dr_2 \\ &\quad + (4\pi)^2 \int_0^\infty r_1^2\, e^{-2Zr_1/a_0}\, dr_1 \int_{r_1}^\infty r_2\, e^{-2Zr_2/a_0}\, dr_2\,. \end{aligned} \tag{13}$$

The remaining integrals are all elementary. I list the relevant integrals below:

$$\int e^{Ar}\,dr = \frac{1}{A}\,e^{Ar}\,,$$

$$\int re^{Ar}\,dr = \frac{1}{A}\left(r - \frac{1}{A}\right)\,e^{Ar}\,,$$

$$\int r^2 e^{Ar}\,dr = \frac{1}{A}\left(r^2 - \frac{2r}{A} + \frac{2}{A^2}\right)\,e^{Ar}\,.$$

Integrating over r_2 in eq. (13) yields:

$$\begin{aligned}\int d^3r_1\,d^3r_2\,\frac{1}{r_{12}}\,e^{-2Z(r_1+r_2)/a_0} &= (4\pi)^2\,\frac{a_0^3}{4Z^3}\int_0^\infty r_1\,e^{-2Zr_1/a_0}\,dr_1 \\ &\quad - (4\pi)^2\,\frac{a_0^3}{4Z^3}\int_0^\infty r_1\left(1+\frac{Zr_1}{a_0}\right)\,e^{-4Zr_1/a_0}\,dr_1\,.\end{aligned}$$

Integrating over r_1 then produces the final result,

$$\int d^3r_1\,d^3r_2\,\frac{1}{r_{12}}\,e^{-2Z(r_1+r_2)/a_0} = \frac{5\pi^2 a_0^5}{8Z^5}\,.$$

It follows that:

$$\left(\frac{Z^3}{\pi a_0^3}\right)^2\int d^3r_1\,d^3r_2\,\frac{e^2}{r_{12}}\,e^{-2Z(r_1+r_2)/a_0} = \frac{5Ze^2}{8a_0} = \frac{5Z}{4}\ \text{Ry}\,.$$

Inserting this result back into eq. (7) then yields:

$$E(Z) = -2\ \text{Ry}\left[4Z - Z^2 - \tfrac{5}{8}Z\right] = -2\ \text{Ry}\left[\frac{27}{8}Z - Z^2\right]\,. \tag{14}$$

We minimize $E(Z)$ by taking the derivative and setting it equal to zero:

$$\frac{dE}{dZ} = -2\ \text{Ry}\left[\frac{27}{8} - 2Z\right] = 0\,,$$

or

$$Z_{\text{min}} = \frac{27}{16}\,.$$

Indeed $1 < Z < 2$ as expected from our argument in Section 1 on the screening of the nucleus. We now insert $Z = Z_{\text{min}}$ into eq. (14) to obtain our estimate of the ground state energy of the helium atom:

$$E_0 = E(Z_{\text{min}}) = -2\ \text{Ry}\left[\frac{27}{8}\left(\frac{27}{16}\right) - \left(\frac{27}{16}\right)^2\right] = -2\ \text{Ry}\left(\frac{27}{16}\right)^2 \simeq -5.695\ \text{Ry}\,.$$

Using 1 Ry = 13.6 eV, we end up with:

$$E_0 \simeq -77.4 \text{ eV},$$

which should be compared with the measured value of $E_g = -78.98$ eV. As expected from the variational principle, the ground state energy obtained by the variational computation is slightly larger than the true answer.

REMARK: The ground state energy of helium could also be estimated using first order perturbation theory, in which the repulsive interaction e^2/r_{12} is taken as the perturbation. This computation is performed in problem 12.28 of Liboff on p. 622. He finds a ground state energy of -74.8 eV. Clearly, the variational estimate of the ground state energy is better. The reason is easy to understand. One obtains the first-order perturbative result by inserting $Z = 2$ into eq. (7), as this corresponds to computing the energy shift $E^{(1)} = \langle\psi|\, e^2/r_{12}\, |\psi\rangle$ using the unperturbed ground state wave function for ψ (which corresponds to $Z = 2$). We would then get

$$E(Z = 2) = -\frac{11}{2} \text{ Ry} = -5.5 \text{ Ry} = -74.8 \text{ eV}.$$

However, since the minimum of $E(Z)$ occurs at $Z = 27/16$ (and *not* at $Z = 2$), it follows that the variational estimate of the ground state energy of helium must be better than the estimate based on first order perturbation theory.

III. The Ionization Energy

The ionization energy, I, is defined as the energy needed to remove one electron from the helium atom. That is,

$$I = E_i - E_g,$$

where E_g is the ground state energy of the helium atom and E_i is the energy of the ionized helium atom with one electron removed and the second electron in its ground state. The latter is equal to the ground state energy of a hydrogen-like atom with $Z = 2$. Thus,

$$E_i = -Z^2 \text{ Ry} = -4 \text{ Ry}.$$

Our variational computation of the ground state energy of the helium in Section 2 yielded -5.695 Ry. Hence, we predict:

$$I = (-4 + 5.695) \text{ Ry} = 1.695 \text{ Ry} \simeq 23 \text{ eV}.$$

This should be compared with the experimentally measured helium ionization energy of

$$I = 1.807 \text{ Ry} = 24.481 \text{ eV}.$$

The latter value is given in Table 12.2 of Liboff on p. 605.