Variational Method

3.1. Basic idea

If we are trying to find the ground-state energy for a quantum system, we can utilize the following fact: the ground state has the lowest possible energy for the Hamiltonian (by definition).

\[ E_g \leq \langle \psi \mid H \mid \psi \rangle = \langle H \rangle \]  

(3.1)

Therefore, by finding the wavefunction \( |\psi\rangle \) that minimizes \( \langle \psi \mid H \mid \psi \rangle \), we find the ground state and the expectation value \( \langle \psi \mid H \mid \psi \rangle \) is the ground-state energy.

In principle, here we need to compare all possible wavefunctions and to find the smallest possible value for \( \langle \psi \mid H \mid \psi \rangle \). In reality, for a complex Hamiltonian, finding the true minimum is often very challenging (even numerically).

In practice, we do the second best thing. Instead of considering all possible wavefunctions, we first make a "guess" and only consider a small family of wavefunctions. Then among these wavefunctions, we find the one that minimizes \( \langle \psi \mid H \mid \psi \rangle \). This method is known as the "variational method".

3.2. Comments:

1. Exact vs. approximate
   - If one compare all possible wavefunctions and find the one that minimizes \( \langle \psi \mid H \mid \psi \rangle \), then this is an exact solution (i.e. one finds the exact ground state).
   - However, in reality, most of the cases, we cannot find exact solution, so we only compared some of the wavefunctions (not all possible ones). This is an approximation, and thus the results we found would be "approximate" ones, instead of exact ones.

2. Overestimate \( E_g \)
   - The variational method always overestimate the ground-state energy (i.e. the approximation ground state energy that we get in this method is always larger, or equal, to the true ground state energy). In other words, the method produces an upper bound for the ground-state energy. By considering more and more wavefunctions in the minimization procedure, this upper bound is getting closer and closer to the global minimum, which is the real \( E_g \).

3. How accurate is this approximate method?
   - It depends on whether we made a “good guess” or not about the ground-state wavefunction. A “good guess” here means whether the wavefunctions that we considered here is “close” enough to the true ground state or not.
   - How to make a “good guess”? There is no general rule here, and it relies on good physics intuitions (see examples below).

4. Ground state energy vs ground state wavefunctions
Consider a helium atom, which has a nucleon with charge +2e and two electrons. The wavefunction is \( \psi(\mathbf{r}_1, \mathbf{r}_2) \), where \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) are the coordinates of the two electrons respectively. Hamiltonian is

\[
H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{2e^2}{4\pi\varepsilon_0} \frac{1}{r_1} - \frac{2e^2}{4\pi\varepsilon_0} \frac{1}{r_2} + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}
\]

Here, the first term is the kinetic energy of the two electrons. The last three terms are the Coulomb interactions between the nucleon and electron #1, nucleon and electron #2, and between the two electrons respectively.

Experiments told us that the ground state energy of an helium atom is

\[
E_g = -78.975 \text{ eV}
\]

Now, let’s try to find the ground state energy using variational methods:

3.3. Example: Helium atom

Consider a helium atom, which has a nucleon with charge +2e and two electrons. The wavefunction is \( \psi(\mathbf{r}_1, \mathbf{r}_2) \), where \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) are the coordinates of the two electrons respectively. Hamiltonian is

\[
H = -\frac{\hbar^2}{2m} \left( \nabla_1^2 + \nabla_2^2 \right) - \frac{2e^2}{4\pi\varepsilon_0} \frac{1}{r_1} - \frac{2e^2}{4\pi\varepsilon_0} \frac{1}{r_2} + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}
\]

Here, the first term is the kinetic energy of the two electrons. The last three terms are the Coulomb interactions between the nucleon and electron #1, nucleon and electron #2, and between the two electrons respectively.

Experiments told us that the ground state energy of an helium atom is

\[
E_g = -78.975 \text{ eV}
\]
3.3.1. First guess: Maybe the ground-state wavefunction is very similar to a hydrogen atom?

If there is no interactions between the two electrons, the Hamiltonian can be separate into two parts

\[ H_{\text{no-ee-interactions}} = \left( \frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \right) + \left( \frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \right) \]  (3.10)

In other words, the system becomes two (decoupled) hydrogen-atom problems. For electron #1, its Hamiltonian is

\[ H_1 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \]  (3.11)

and for electron #2, it is

\[ H_2 = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \]  (3.12)

Each of these two Hamiltonian is a hydrogen atom Hamiltonian, but the nucleon charge is now doubled. Remember, the typical hydrogen atom Hamiltonian looks like

\[ H_{\text{hydrogen}} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \]  (3.13)

The second term has \( e^2 \) in the numerator, but there it is \( 2e^2 \), because the nucleon of a helium atom has charge \( +2e \).

For a hydrogen atom with nucleon charge \( +e \), the ground state wavefunction is

\[ \psi_{100}(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} \]  (3.14)

where \( a \) is the Bohr radius,

\[ a = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.529 \times 10^{-10} \text{ m} \]  (3.15)

The ground state energy is

\[ E_1 = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 = -13.6 \text{ eV} \]  (3.16)

Now, for a hydrogen like atom with nucleon charge \( Z \times e \) (and one electron), the Hamiltonian is

\[ H_{\text{charge} Z} = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \]  (3.17)

If we compare it with a real hydrogen problem, the only thing we did here is to change \( e^2 \) to \( Ze^2 \). And thus for this charge Ze hydrogen like atom, the solution would be almost the same as an ordinary hydrogen atom, except that we need to change all \( e^2 \) into \( Ze^2 \). As a result, our Bohr radius now becomes

\[ a^* = \frac{4\pi\epsilon_0 \hbar^2}{Ze^2} = \frac{a}{Z} = \frac{0.529 \times 10^{-10} \text{ m}}{Z} \]  (3.18)

And thus the ground state wavefunction is now

\[ \psi_{100}(r) = \frac{1}{\sqrt{\pi a^*^3}} e^{-r/a^*} = \frac{1}{\sqrt{\pi a^3/Z^3}} e^{-r/a} \]  (3.19)

The ground state energy is

\[ E_1^* = -\frac{m}{2\hbar^2} \left( \frac{Ze^2}{4\pi\epsilon_0} \right)^2 = Z^2 \left[ -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \right] = Z^2 E_1 = -13.6 Z^2 \text{ eV} \]  (3.20)

If we ignore the interactions between electrons, the ground state wavefunction would be
\( \psi_0(r_1, r_2) = \psi_{100}(r_1) \psi_{100}(r_2) \)  

where

\[
\psi_{100}(r) = \frac{1}{\sqrt{\pi a^3/2^3}} e^{-2r/a} = \frac{1}{\sqrt{\pi a^3/2^3}} e^{-r/a}
\]

(3.22)

In other words,

\[
\psi_0(r_1, r_2) = \psi_{100}(r_1) \psi_{100}(r_2) = \frac{8}{\pi a^3} \frac{e^{-r_1 - r_2}}{r_1 \cdot r_2}
\]

(3.23)

This wavefunction is NOT the ground state of a helium atom, because we ignored the interaction between electrons. But let's use it as a guess wavefunction for the ground state (which is an approximation) and see what is the energy we get.

\[
(H) = \langle \psi_0(r_1, r_2) | H | \psi_0(r_1, r_2) \rangle
\]

(3.24)

Here, we first rewrite the Hamiltonian as three parts:

\[
H = H_1 + H_2 + H_{ee}
\]

(3.25)

where

\[
H_1 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{4\pi \epsilon_0} \frac{1}{r_1}
\]

(3.26)

and

\[
H_2 = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi \epsilon_0} \frac{1}{r_2}
\]

(3.27)

and

\[
H_{ee} = \frac{e^2}{4\pi \epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}
\]

(3.28)

As a result,

\[
(H) = \langle \psi_0(r_1, r_2) | H | \psi_0(r_1, r_2) \rangle = \langle \psi_0(r_1, r_2) | H_1 + H_2 + H_{ee} | \psi_0(r_1, r_2) \rangle
\]

\[
= \langle \psi_0(r_1, r_2) | H_1 | \psi_0(r_1, r_2) \rangle + \langle \psi_0(r_1, r_2) | H_2 | \psi_0(r_1, r_2) \rangle + \langle \psi_0(r_1, r_2) | H_{ee} | \psi_0(r_1, r_2) \rangle
\]

(3.29)

The first term is very simply

\[
\langle \psi_0(r_1, r_2) | H_1 | \psi_0(r_1, r_2) \rangle = \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^*(r_1) \psi_{100}(r_2) H_1 \psi_{100}(r_1) \psi_{100}(r_2)
\]

(3.30)

Because, \( H_1 \) only depends on \( r_1 \) and is independent of \( r_2 \), we know that

\[
\langle \psi_0(r_1, r_2) | H_1 | \psi_0(r_1, r_2) \rangle = \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^*(r_1) \psi_{100}(r_2) H_1 \psi_{100}(r_1) \psi_{100}(r_2)
\]

\[
= \int d\vec{r}_1 \psi_{100}^*(r_1) H_1 \psi_{100}(r_1) \int d\vec{r}_2 \psi_{100}^*(r_2) \psi_{100}(r_2)
\]

(3.31)

The second integral is identity, because it is the normalization condition of a wavefunction

\[
\int d\vec{r}_2 \psi_{100}^*(r_2) \psi_{100}(r_2) = 1
\]

(3.32)

The first integral is also easily to compute, because \( \psi_{100}(r_1) \) is the ground state of \( H_1 \), and thus the integral is the ground state energy for \( H_1 \), which we already know

\[
E_1 = -13.6 \text{ Z}^2 \text{ eV} = -13.6 \times 2^2 \text{ eV} = -54.4 \text{ eV}
\]

(3.33)

So we find that

\[
\langle \psi_0(r_1, r_2) | H_1 | \psi_0(r_1, r_2) \rangle = -54.4 \text{ eV}
\]

(3.34)
Similarly, we can show that
\[
\langle \phi_0(r_1, r_2) | H_2 | \phi_0(r_1, r_2) \rangle = -54.4 \text{ eV}
\] 
Evaluating the last term, we have
\[
\langle \phi_0(r_1, r_2) | H_2 | \phi_0(r_1, r_2) \rangle = -54.4 \text{ eV} - 54.4 \text{ eV} + \langle \phi_0(r_1, r_2) | H_{ae} | \phi_0(r_1, r_2) \rangle
\]
\[
\approx -109 \text{ eV} + \langle \phi_0(r_1, r_2) | H_{ae} | \phi_0(r_1, r_2) \rangle
\]
To compute the last term, we evaluate the following integral
\[
\langle \phi_0(r_1, r_2) | H_{ae} | \phi_0(r_1, r_2) \rangle = \int d\vec{r}_1 \int d\vec{r}_2 \psi_0^*(r_1, r_2) H_{ae} \psi_0(r_1, r_2)
\]
\[
= \int d\vec{r}_1 \int d\vec{r}_2 \left( \frac{8}{\pi a^3} e^2 \frac{1}{4 \pi \epsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \frac{8}{\pi a^3} e^2 \right)
\]
\[
= \frac{64 e^4}{\pi^2 a^6} \int d\vec{r}_1 \int d\vec{r}_2 \frac{e^{-\frac{\pi}{(r_1 r_2)}}}{|\vec{r}_1 - \vec{r}_2|}
\]
We first do the integral for \( r_2 \).
\[
\int d\vec{r}_2 \frac{e^{-\frac{\pi}{(r_1 r_2)}}}{|\vec{r}_1 - \vec{r}_2|}
\]
For this integral, without loss of generality, we can assume \( \vec{r}_1 \) is along the z direction, and thus we can convert the integral into spherical coordinates
\[
\int d\vec{r}_2 \frac{e^{-\frac{\pi}{(r_1 r_2)}}}{|\vec{r}_1 - \vec{r}_2|} = \int_0^{2\pi} \int_0^\infty \int_0^\pi \sin \theta d\theta d\phi \int_0^{\infty} \frac{2 \pi e^{-\frac{\pi}{(r_1 r_2)}}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta}}
\]
Here, \( \int_0^{2\pi} d\phi = 2\pi \), because nothing depends on \( \phi \) in the integral.
\[
\int d\vec{r}_2 \frac{e^{-\frac{\pi}{(r_1 r_2)}}}{|\vec{r}_1 - \vec{r}_2|} = \int_0^{2\pi} \int_0^\infty \int_0^\pi \sin \theta d\theta d\phi \int_0^{\infty} \frac{2 \pi e^{-\frac{\pi}{(r_1 r_2)}}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta}}
\]
For the \( \theta \) integral, we can define \( x = \cos \theta \), as a result,
\[
dx = d\cos \theta = -\sin \theta d\theta
\]
and thus
\[
\int_0^\pi \sin \theta d\theta = -\int_{\cos 0}^{\cos \pi} dx = -\int_{1}^{-1} dx = \int_{-1}^{1} dx
\]
And therefore,
\[
\int d\vec{r}_2 \frac{e^{-\frac{\pi}{(r_1 r_2)}}}{|\vec{r}_1 - \vec{r}_2|} = \int_0^{2\pi} \int_0^\infty \int_{-1}^{1} dx \frac{2 \pi e^{-\frac{\pi}{(r_1 r_2)}}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 x}} = \int_0^{2\pi} \frac{2 \pi e^{-\frac{\pi}{(r_1 r_2)}}}{\sqrt{2 r_1 r_2}} d\phi \int_{-1}^{1} dx \frac{1}{\sqrt{2 r_1 r_2 - x}}
\]
We know that
\[
\int dx \frac{1}{\sqrt{a - x}} = -2 \sqrt{a - x}
\]
\[
\int_{-1}^{+1} dx \frac{1}{\sqrt{\frac{r_1^2 + r_2^2}{2} - x}} = -2 \sqrt{\frac{r_1^2 + r_2^2}{2 r_1 r_2}} - x \mid_{x=-1}^{x=1} = -2 \sqrt{\frac{r_1^2 + r_2^2}{2 r_1 r_2}} - 1 + 2 \sqrt{\frac{r_1^2 + r_2^2}{2 r_1 r_2}} + 1
\]

(3.45)

and thus

\[
\int d^2 r_2 \frac{e^{-\frac{r_1 r_2}{2(r_1 + r_2)}}}{|\vec{r}_1 - \vec{r}_2|} = \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} r_2^2 d r_2 \int_{-1}^{+1} dx \frac{1}{\sqrt{\frac{r_1^2 + r_2^2}{2} - x}}
\]

\[
= \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} \left( \frac{r_1^2 + r_2^2}{2 r_1 r_2} + 1 - \frac{r_1^2 + r_2^2}{2 r_1 r_2} \right) r_2^2 d r_2
\]

(3.46)

\[
= \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} \left( r_1 + r_2 - |r_1 - r_2| \right) r_2^2 d r_2
\]

If \( r_1 > r_2, r_1 + r_2 - |r_1 - r_2| = r_1 + r_2 - r_1 - r_2 = 2 r_2 \)

If \( r_2 > r_1, r_1 + r_2 - |r_1 - r_2| = r_1 + r_2 - r_1 + r_2 = 2 r_1 \)

\[
\int d^2 r_2 \frac{e^{-\frac{r_1 r_2}{2(r_1 + r_2)}}}{|\vec{r}_1 - \vec{r}_2|} = \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} \left( r_1 + r_2 - |r_1 - r_2| \right) r_2^2 d r_2
\]

\[
= \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} \left( r_1 + r_2 - |r_1 - r_2| \right) r_2^2 d r_2 + \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} \left( r_1 + r_2 - |r_1 - r_2| \right) r_2^2 d r_2
\]

\[
= \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} \left( r_1 + r_2 - |r_1 - r_2| \right) r_2^2 d r_2
\]

\[
= \int_0^{\pi} 2 \pi e^{\frac{r_1 r_2}{2(r_1 + r_2)}} \left( r_1 + r_2 - |r_1 - r_2| \right) r_2^2 d r_2
\]

(3.47)

\[
= 4 \pi e^{\frac{r_1}{r_2}} \int_0^{\pi} d r_2 e^{\frac{r_1 r_2}{r_1 + r_2}} + 4 \pi e^{\frac{r_1}{r_2}} \int_0^{\pi} d r_2 4 \pi e^{\frac{r_1}{r_2}} r_2
\]

\[
= 4 \pi e^{\frac{r_1}{r_2}} \left[ \frac{r_2^3}{32} - \frac{1}{32} a e^{-\frac{r_1}{a}} (a^2 + 4 a r_1 + 8 r_1^2) \right] + 4 \pi e^{\frac{r_1}{r_2}} \left[ \frac{1}{16} a e^{-\frac{r_1}{a}} (a + 4 r_1) \right]
\]

\[
= \frac{\pi a^3 e^{\frac{r_1}{r_2}}}{8 r_1} \left[ 1 - e^{-\frac{r_1}{a}} \left( 1 + \frac{2 r_1}{a} \right) \right]
\]

Now, we go back to \( \langle \phi_0(r_1, r_2) | H_{ac} | \phi_0(r_1, r_2) \rangle \)

\[
\langle \phi_0(r_1, r_2) | H_{ac} | \phi_0(r_1, r_2) \rangle = \frac{64}{\pi^2 a^6 4 \pi \varepsilon_0} \int d^2 r_1 \int d^2 r_2 \frac{e^{-\frac{r_1 r_2}{2(r_1 + r_2)}}}{|\vec{r}_1 - \vec{r}_2|}
\]

\[
= \frac{64 e^2}{\pi^2 a^6 4 \pi \varepsilon_0} \int d^2 r_1 \frac{\pi a^3 e^{\frac{r_1}{r_2}}}{8 r_1} \left[ 1 - e^{-\frac{r_1}{a}} \left( 1 + \frac{2 r_1}{a} \right) \right]
\]

\[
= \frac{64}{\pi^2 a^6 4 \pi \varepsilon_0} \int d^2 r_1 \int d \Omega \frac{e^{\frac{r_1}{r_2}}}{r_1} \left[ 1 - e^{-\frac{r_1}{a}} \left( 1 + \frac{2 r_1}{a} \right) \right]
\]

(3.48)
In the previous section, we assumed that the wavefunction to be

$$\langle \psi | H_{109} | \psi \rangle = 3.34 eV$$

3.3.2. Second guess: a better guess

$$E = \frac{8 \times 4 \pi}{\pi a^3} \int dr_1 r_1 e^{-2r_1/a} \left[ 1 - e^{-\frac{2r_1}{a}} \left( 1 + \frac{2r_1}{a} \right) \right]$$

$$= \frac{8 \times 4 \pi}{\pi a^3} \int dr_1 r_1 e^{-2r_1/a} - e^{-\frac{2r_1}{a}} \left( 1 + \frac{2r_1}{a} \right)$$

$$= \frac{8 \times 4 \pi}{\pi a^3} \frac{5 a^2}{128} = \frac{5 e^2}{128}$$

Notice that $E_1 = -\frac{1}{2a} \frac{\hbar^2 e^2}{4 \pi e_0} = -13.6 eV$

$$\langle \psi \r_1, r_2 | H_{109} | \psi \r_1, r_2 \rangle = \frac{5}{4 a} \frac{e^2}{4 \pi e_0} \left( \frac{1}{2} \frac{e^2}{a} \right) \left( \frac{1}{2} \frac{e^2}{2a} \right) \left( \frac{1}{2} \frac{e^2}{4a} \right) \left( \frac{1}{2} \frac{e^2}{8a} \right) = \frac{5}{2} = 13.6 eV = 34 eV$$

(3.49)

As a result, we find that

$$\langle H \rangle = -109 eV + \langle \psi \r_1, r_2 | H_{109} | \psi \r_1, r_2 \rangle = -109 eV + 34 eV = -75 eV$$

(3.50)

Compare it with the experimental result: $E_g = -78.975 eV$, we found that our result is not so bad, with error bar about 5%.

NOTE: as we said early one, variational methods always overestimate the ground state energy. Here, indeed, we find that the result is slightly larger than the real value.

3.3.2. Second guess: a better guess

In the previous section, we assumed that the wavefunction to be

$$\psi \r_1, r_2 = \psi_{100} \r_1, r_2 \psi_{100} \r_2$$

(3.51)

where

$$\psi_{100} \r_1, r_2 = \frac{Z^2}{\pi a^3} e^{-\frac{Z \r_1}{a}}$$

(3.52)

We specifically assumed that the wavefunction $\psi_{100} \r$ are ground state of a hydrogen like atom with $Z = 2$. Now, let’s consider $Z$ as a adjustable parameter. And try to find which value of $Z$ give us the lowest energy. Now our wavefunction is

$$\psi \r_1, r_2 = \frac{Z^2}{\pi a^3} e^{-\frac{Z \r_1}{a}}$$

(3.53)

This structure of wavefunctions include the wavefunctions that we used above, and in addition, we adds other possible wavefunctions into our consideration, and thus the results must be better than what we did above.

Now, we rewrite the Hamiltonian into three terms:

$$H = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z e^2}{4 \pi e_0} \left( \frac{1}{r_1} \right) + \left( -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z e^2}{4 \pi e_0} \left( \frac{1}{r_2} \right) \right) + \frac{e^2}{4 \pi e_0} \left( \frac{1}{r_1} - \frac{1}{r_2} \right)$$

(3.54)

The first two terms are both the Hamiltonian of a hydrogen-like atom whose nucleon has change $Z \times e$. Because our wavefunction is the ground state of such a Hamiltonian,

$$\langle \psi \left| -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z e^2}{4 \pi e_0} \frac{1}{r_1} \right| \psi \rangle \langle \psi \left| -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z e^2}{4 \pi e_0} \frac{1}{r_2} \right| \psi \rangle = E_1^* = -13.6 Z^2 eV$$

(3.55)

As a result,

$$\langle \psi \left| H \right| \psi \rangle \langle \psi \left| -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Z e^2}{4 \pi e_0} \frac{1}{r_1} \right| \psi \rangle + \langle \psi \left| -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Z e^2}{4 \pi e_0} \frac{1}{r_2} \right| \psi \rangle + \langle \psi \left| (Z - 2) \frac{e^2}{4 \pi e_0} \frac{1}{r_1} \right| \psi \rangle + \langle \psi \left| (Z - 2) \frac{e^2}{4 \pi e_0} \frac{1}{r_2} \right| \psi \rangle$$

$$= -13.6 Z^2 eV$$
\[ -27.2 Z^2 \text{ eV} + \left( \frac{(Z - 2) e^2}{4 \pi \varepsilon_0} \frac{1}{r_1} + \frac{(Z - 2) e^2}{4 \pi \varepsilon_0} \frac{1}{r_2} + \frac{e^2}{4 \pi \varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \psi \]

\[ = -27.2 Z^2 \text{ eV} + \frac{(Z - 2) e^2}{4 \pi \varepsilon_0} \frac{1}{r_1} \psi(1 - \psi) + \frac{(Z - 2) e^2}{4 \pi \varepsilon_0} \frac{1}{r_2} \psi(1 - \psi) + \frac{e^2}{4 \pi \varepsilon_0} \left( \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \psi \]

Here,

\[ \int d\vec{r}_1 \int d\vec{r}_2 \psi_0^* \psi_0 = \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^* \psi_{100} = \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^* \psi_{100} = \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^* \psi_{100} \]

The second integral is 1, because it is the normalization condition of a wavefunction.

\[ \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^* \psi_{100} = \frac{1}{\pi a^3} \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^* \psi_{100} = \frac{4 Z^3}{a^3} \int d\vec{r}_1 \int d\vec{r}_2 \psi_{100}^* \psi_{100} = 4 \frac{Z^3}{a^3} \frac{a^2}{Z} = \frac{Z}{a} \]

Similarly, we can show that \( \frac{1}{r_1} |\psi| = \frac{Z}{a} \).

So we have,

\[ \langle \psi | H | \psi \rangle = -27.2 Z^2 \text{ eV} + 2 \frac{Z (Z - 2) e^2}{4 \pi \varepsilon_0 a} + \frac{e^2}{4 \pi \varepsilon_0} \left( \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \psi \]

We know from the study on hydrogen atom,

\[ E_1 = -\frac{1}{2} \frac{e^2}{4 \pi \varepsilon_0 a} = -13.6 \text{ eV} \]

So,

\[ \langle \psi | H | \psi \rangle = -27.2 Z^2 \text{ eV} + 4 Z (Z - 2) \left[ \frac{1}{2} \frac{e^2}{4 \pi \varepsilon_0 a} + \frac{e^2}{4 \pi \varepsilon_0} \left( \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \psi \right] \]

\[ = -27.2 Z^2 \text{ eV} + 4 Z (Z - 2) [13.6 \text{ eV}] + \frac{e^2}{4 \pi \varepsilon_0} \left( \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \psi \]

\[ = [4 Z (Z - 2) - 2 Z^2] \times 13.6 \text{ eV} + \frac{e^2}{4 \pi \varepsilon_0} \left( \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \psi \]

Now, we come to the last term, \( \langle \psi | \frac{1}{|\vec{r}_1 - \vec{r}_2|} | \psi \rangle \), the calculation here is pretty much the same as what we did in the previous section, so we skip the details.

\[ \frac{e^2}{4 \pi \varepsilon_0} \left( \frac{1}{|\vec{r}_1 - \vec{r}_2|} \right) \psi = -\frac{5 Z}{4} \]

So, we get

\[ \langle \psi | H | \psi \rangle = [4 Z (Z - 2) - 2 Z^2] \times 13.6 \text{ eV} + \frac{5 Z}{4} \times 13.6 \text{ eV} = \left( 2 Z^2 - \frac{27}{4} Z \right) \times 13.6 \text{ eV} \]

To get the ground state, we want to minimize the energy \( \langle \psi | H | \psi \rangle \). Here, it means that we want find the value for \( Z \) that minimizes the
To find the extreme of a function, we request the first order derivative to be zero:

\[
\frac{d}{dZ} \left( 2Z^2 - \frac{27}{4} Z \right) = 4Z - \frac{27}{4} = 0
\]  

(3.65)

And the solution is:

\[
Z = \frac{27}{16} \approx 1.69
\]  

(3.66)

This means that for the wavefunctions that we considered,

\[
\psi_0(r_1, r_2) = \frac{Z^3}{\pi a^3} e^{-\frac{Z}{a}}
\]  

(3.67)

when \(Z = \frac{27}{16} \approx 1.69\), the energy reaches its minimum value, and the minimum value is:

\[
\langle \psi | H | \psi \rangle = \left( 2Z^2 - \frac{27}{4} Z \right) \times 13.6 \text{ eV} = \left[ 2 \times \left( \frac{27}{16} \right)^2 - \frac{27}{4} \times \frac{27}{16} \right] \times 13.6 \text{ eV} = \frac{729}{128} \times 13.6 \text{ eV} = -77.5 \text{ eV}
\]  

(3.68)

The experimental value for ground state energy is \(E_g = -78.975 \text{ eV}\). Here, our estimation is very close to the real value. The error bar is about 1% or 2%.

Comment 1: considering that we are assuming a very simple wavefunction, this accuracy is amazingly good.

Comment 2: If one tries more complicated wavefunctions, the accuracy can be further improved.

Comment 3: as we proved early on, the variation methods always overestimate the ground state energy. Here, indeed, we get a larger energy than the real value.

### 3.4. Example: Hydrogen molecule ion

Consider a hydrogen molecule ion, \(H_2^+\). Here, we have two hydrogen nucleons (separated by distance \(R\)), and one electron moving around both of the nucleons. The Hamiltonian is:

\[
H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 R}
\]  

(3.69)

Here, the first term is the kinetic energy of the electron. The second and the third terms are potential energy between nucleons and the electron. The last term is the potential energy between two nucleons. The textbook missed the last term in the Hamiltonian, but added it back at the end of the day.

For a guess wavefunction, we can use the following one:

\[
\psi(r_1, r_2) = A[\psi_{100}(r_1) + \psi_{100}(r_2)]
\]  

(3.70)

where \(\psi_{100}(r_1)\) is the ground-state wavefunction for a hydrogen atom around the first nucleon. \(\psi_{100}(r_2)\) is the ground-state wavefunction for a hydrogen atom around the second nucleon (remember that the two nucleon is separated by the distance \(R\)). \(A\) is a normalization factor, to make sure that \(\langle \psi | \psi \rangle = 1\).

Here, the separation between to nucleons, \(R\), is a unknown number. This is our tuning parameter when we try to minimize \(\langle \psi | H | \psi \rangle\), i.e. by minimizing \(\langle \psi | H | \psi \rangle\), we will find the value of \(R\) that has the lowest energy. And this value of \(R\) is our theoretical prediction for the spatial separation between the two nucleons in a hydrogen molecule ion.

I will skip the detailed calculation, which can be found in the textbook.

\[
\langle \psi | H | \psi \rangle = E_1 \times \left\{ 1 + 2 \frac{\frac{4\pi\epsilon_0\hbar^2}{m e^2}}{1 + \left( \frac{e}{a} \right)} \frac{e^{-\frac{R}{a}}}{1 + e^{-\frac{R}{a}}} + \left( 1 + \frac{e}{a} \right) \frac{e^{-\frac{a R}{a}}}{1 + e^{-\frac{a R}{a}}} - \frac{2}{R} \right\}
\]  

(3.71)

where \(E_1 = -13.6 \text{ eV}\) and \(a\) is the Bohr radius \(a = \frac{4\pi\epsilon_0\hbar^2}{m e^2} = 0.529 \times 10^{-10} \text{ m}\).