The variational principle

We now introduce another approximation method which is useful in finding an estimate of the ground state energy E_{gs}. Consider a Hamiltonian $\hat{H}$ and let $|\phi\rangle$ be any normalized ket. Then I claim that

$$\boxed{\langle\phi|\hat{H}|\phi\rangle \geq E_{gs}} \tag{1}$$

where E_{gs} is the ground state energy of a system. So $\langle\phi|\hat{H}|\phi\rangle$ is an upper bound for the problem. But if we cleverly choose $|\phi\rangle$ we may get a result which is very close to the actual ground state energy.

Proof of (1): let

$$\hat{H}|n\rangle = E_n|n\rangle \tag{2}$$

and expand $|\phi\rangle$ in the basis $|n\rangle$:

$$|\phi\rangle = \sum_n c_n |n\rangle \tag{3}$$

Then, as we already know from long before

$$\langle\phi|\hat{H}|\phi\rangle = \sum_n |c_n|^2 E_n \tag{4}$$

Assume that the energies are ordered so that

$$E_{gs} = E_0 < E_1 < E_2 < \dots \tag{5}$$

Since $\langle \phi | \phi \rangle = 1$ it follows that

$$\sum_{n=0}^{\infty} |c_n|^2 = 1 \tag{6}$$

Thus

$$\langle \phi | \hat{H} | \phi \rangle - E_0 = \sum_{n=0}^{\infty} |c_n|^2 E_n - \left[\sum_{n=0}^{\infty} |c_n|^2 \right] E_0$$

$$= \sum_{n=1}^{\infty} |c_n|^2 (E_n - E_0)$$

Since $E_0 < E_1 < E_2 < \dots$, the right hand side is positive. Thus

$$\langle \phi | \hat{H} | \phi \rangle - E_0 \geq 0$$

which finally leads to Eq (1). qed.

— " —

We may also use a $|\phi\rangle$ which is not normalized. In this case we get instead

$$F[\phi] = \langle H \rangle = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} \geq E_{gs} \tag{7}$$

The quantity $F[\phi]$ is a functional. A function $f(x)$ has as input a number, x, and then outputs another number $f(x)$. A functional also outputs a number, but the input is an entire function. The key idea of the variational method is to use a trial wave-function ϕ that has many free parameters. Since Eq (7) gives an upper bound, we may then minimize $F[\phi]$ with respect to these parameters and obtain a result which may be very close to E_{gs}

Example : Harmonic Oscillator

Consider the Harmonic oscillator with Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 \qquad (8)$$

Let us apply Eq (7) to estimate the ground state, which in this case we happen to know to be

$$E_{gs} = \frac{\hbar\omega}{2}$$

To do so we must choose a trial wave function. For instance

$$\psi(x) = \frac{A}{x^2+b^2} \qquad (9)$$

here A is a normalization constant and b is a free parameter. There is no good methodology to choose the trial wavefunction, and some cleverness is required. Of course, your choice should reflect certain properties of the problem. For instance, it should represent a bound state!

Now we apply Eq (7) and compute

$$F[\psi] = \frac{\int \psi^*(x)\, H\, \psi(x)\, dx}{\int \psi^*(x)\psi(x)\, dx} \qquad (10)$$

The detailed calculation of all these integrals is done in the appendix. Here I just want to discuss the result, which is

$$F = \frac{\hbar^2}{4mb^2} + \frac{1}{2}m\omega^2 b^2 \qquad (11)$$

According to Eq (7), this F will always be larger than the ground state energy, for any value of b. This is quite remarkable if you think about it. Because of this, we may then minimize F with respect to b, and the result will be the best possible estimate for E_{gs} with this trial function.

Thus:

$$\frac{\partial F}{\partial b} = \frac{-\hbar^2}{2mb^3} + m\omega^2 b = 0 \quad \Rightarrow \quad b^2 = \frac{1}{\sqrt{2}} \frac{\hbar}{m\omega} \tag{12}$$

So the minimum value of F is

$$F_{min} = \frac{\hbar^2}{2m} \sqrt{2} \frac{m\omega}{\hbar} + \frac{1}{2} m\omega^2 \frac{1}{\sqrt{2}} \frac{\hbar}{m\omega}$$

or

$$\boxed{F_{min} = \sqrt{2} \frac{\hbar\omega}{2}} \tag{13}$$

This is indeed larger than $\hbar\omega/2$, by a factor of $\sqrt{2} \sim 1.4$

The cool thing about the variational method is that it always gives upper bounds. So suppose you didn't know that $E_{gs} = \hbar\omega/2$. With my ψ I obtained $\sqrt{2}\,\hbar\omega/2$. If you try a different ψ and obtain something which is larger, then we know your result is crap! My ψ is better. But if you obtain something which is smaller than $\sqrt{2}\,\hbar\omega/2$, your ψ is better.

In this way we may choose more and more complicated wave functions, with more and more free parameters. Then we will always know if we are improving on our result.

Example: the Helium atom

The Hamiltonian of the Helium atom is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2q^2}{r_1} - \frac{2q^2}{r_2} + \frac{q^2}{r_{12}} \tag{14}$$

The ground state energy is simply the sum of the first two ionization energies:

$$E_{exp} = -78.975 \text{ eV} \tag{15}$$

The last term in Eq (14) is the electron-electron repulsion

$$V_{ee} = \frac{q^2}{r_{12}} \tag{16}$$

If it were possible to neglect this term the problem would be reduced to two independent Hydrogen atoms, so the ground state wavefunction would be

$$\psi(r_1, r_2) = \frac{8}{\pi a_0^3} e^{-2(r_1+r_2)/a_0} \tag{17}$$

and the energy would be

$$E = 4E_J + 4E_J = 8E_J = -109 \text{ eV} \tag{18}$$

Now consider a cool idea. What if, instead, we attempt a trial wave function

$$\psi(r_1, r_2) = \frac{Z^3}{\pi a_0^3} e^{-Z(r_1+r_2)/a_0} \qquad (19)$$

For He we expect $Z = z$, but we may leave Z as a free parameter and use the variational principle.

Eq (19) is the ground state energy of

$$H_0 = \frac{\hat{P}_1^2}{2m} + \frac{\hat{P}_2^2}{2m} - \frac{Zq^2}{r_1} - \frac{Zq^2}{r_2} \qquad (20)$$

so

$$H_0 \psi = (2 Z^2 E_1)\psi$$

Thus we write

$$H = H_0 + (Z-2)\frac{q^2}{r_1} + (Z-2)\frac{q^2}{r_2} + V_{ee} \qquad (21)$$

then our functional F becomes

$$\langle H \rangle = \langle H_0 \rangle + (Z-2)q^2 \left\langle \frac{1}{r_1} \right\rangle + (Z-2)\, q^2 \left\langle \frac{1}{r_2} \right\rangle + \langle V_{ee} \rangle \qquad (22)$$

But

$$\langle H_0 \rangle = 2 Z^2 E_1$$

$$\left\langle \frac{1}{r_1} \right\rangle = \left\langle \frac{1}{r_2} \right\rangle = \frac{Z}{a_0}$$

Thus

$$\langle H \rangle = 2 Z^2 E_1 + 2Z(Z-2)\frac{q^2}{a_0} + \langle V_{ee} \rangle$$

Recall also that

$$E_1 = -\frac{q^2}{2a_0} \Rightarrow \frac{q^2}{a_0} = -2E_1$$

Thus

$$\boxed{\langle H \rangle = 2Z^2 E_1 - 4Z(Z-2)E_1 + \langle V_{ee} \rangle} \qquad (24)$$

For the last term there is no short cut, we must compute the integral:

$$\langle V_{ee} \rangle = q^2 \int \frac{|\psi|^2}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 \, d^3r_2$$

This is not an easy integral. The calculation is done in detail in appendix B. The result is

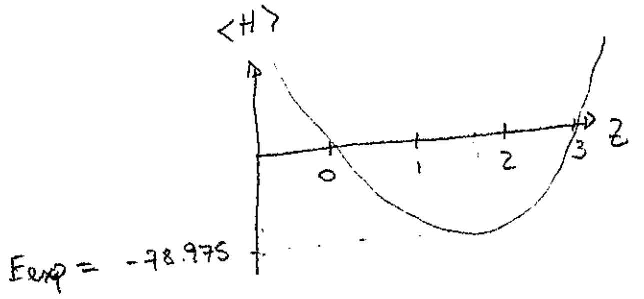
$$\langle V_{ee} \rangle = -\frac{5}{4} Z E_1 \qquad (25)$$

Thus

$$\langle H \rangle = E_1 \left[2Z^2 - 4Z(Z-2) - \frac{5}{4} Z \right]$$

$$\boxed{\langle H \rangle = E_1 \left[-2Z^2 + \frac{27}{4} Z \right]} \qquad (26)$$

Now here is the key point: according to the variational principle, $\langle H \rangle \geq E_{gs}$. This will be true for <u>any</u> value of Z. If we plot $\langle H \rangle$ as a function of Z we get



If we choose $Z = 2$ we get $\langle H \rangle = -74.8$ eV. This corresponds exactly to the perturbative approach that we studied in another occasion.

We may instead minimize $\langle H \rangle$ w/r to Z:

$$\frac{\partial \langle H \rangle}{\partial Z} = E_1 \left[-4Z + \frac{27}{4} \right] = 0 \qquad (27)$$

thus

$$\boxed{Z = \frac{27}{16} \simeq 1.6875}$$

The best value of Z is smaller than 2. This makes sense since each electron <u>shields</u> the effect of the nucleus on the other.

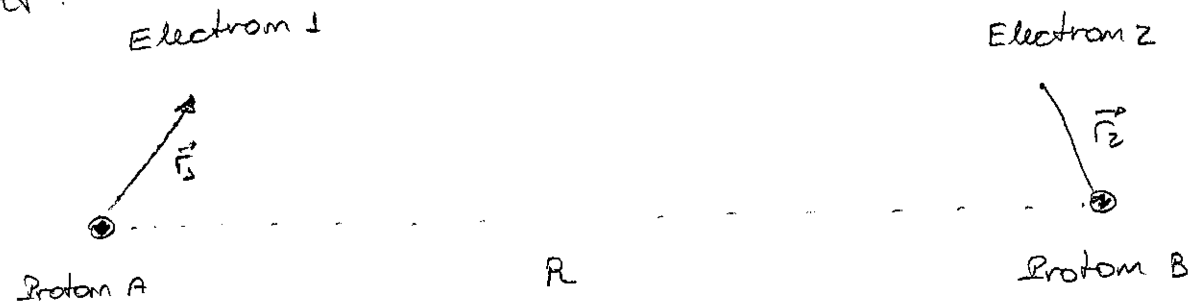
The resulting value of $\langle H \rangle$ is

$$\boxed{\langle H \rangle_{min} = \frac{729}{128} E_1 \simeq -77.45 \text{ eV}} \qquad (28)$$

This is remarkably close to the experimental value. And we did all this with only a single free parameter! Using more complicated wavefunctions with more free parameters we may obtain better and better approximations.

Van der Waals Force

Consider two hydrogen atoms separated a distance R apart:



If $R \to \infty$ the total Hamiltonian would be simply that of two independent Hydrogen atoms:

$$H_0 = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{q^2}{r_1} - \frac{q^2}{r_2} \tag{29}$$

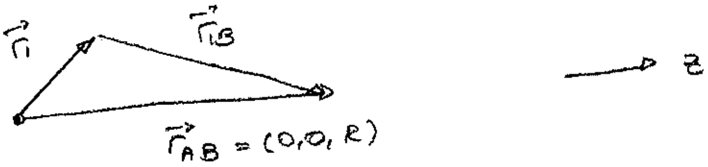
But as we bring them closer together there will be an interaction of the form

$$V = \underbrace{\frac{q^2}{R}}_{\text{p-p}} - \frac{q^2}{r_{1B}} - \frac{q^2}{r_{2A}} + \underbrace{\frac{q^2}{r_{12}}}_{\text{e-e}} \tag{30}$$

e_1 with p_B
e_2 with p_A

e question now is: how will this affect the energy? And will it lead to a repulsive or an attractive force?

The first step is to simplify V since we are only interested in large R. Start with r_{1B}



$$\vec{r}_{1B} = \vec{r}_{AB} - \vec{r}_1 = -(x_1, y_1, z_1 - R)$$

Thus

$$\frac{1}{r_{1B}} = \frac{1}{\sqrt{x_1^2 + y_1^2 + (z_1 - R)^2}} = \frac{1}{\sqrt{x_1^2 + y_1^2 + z_1^2 + R^2 - 2 z_1 R}}$$

$$= \frac{1}{\sqrt{R^2 + r_1^2 - 2 z_1 R}} = \frac{1}{R} \frac{1}{\sqrt{1 + (r_1/R)^2 - 2 z_1/R}}$$

Since R is large, 1/R will be small so we may now expand this term in a Taylor series. We use

$$\frac{1}{\sqrt{1+x}} = 1 - \frac{x}{2} + \frac{3x^2}{8} - \frac{5x^3}{16} + \frac{35x^4}{128} - \frac{63x^5}{256} + \cdots \qquad (3)$$

Then

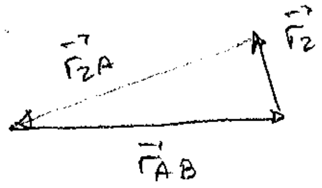
$$\frac{1}{r_{1B}} = \frac{1}{R}\left\{ 1 - \frac{1}{2}\left[\frac{r_1^2}{R^2} - \frac{2z_1}{R}\right] + \frac{3}{8}\left[\frac{r_1^2}{R^2} - \frac{2z_1}{R}\right]^2 + \cdots \right\}$$

$$= \frac{1}{R} + \frac{z_1}{R^2} + \frac{1}{2R^3}\left(3z_1^2 - r_1^2\right) + \cdots$$

Thus

$$\boxed{\frac{1}{r_{1B}} = \frac{1}{\sqrt{R^2 + r_1^2 - 2z_1 R}} \simeq \frac{1}{R} + \frac{z_1}{R^2} + \frac{1}{2R^3}\left(2z_1^2 - x_1^2 - y_1^2\right)} \qquad (3$$

Next we do the same for $\vec{r}_{2A}$:

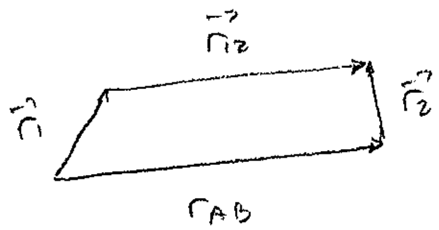


$$\vec{r}_{2A} = -\vec{r}_{AB} - \vec{r}_2 = -(x_2, y_2, z_2 + R)$$

thus, the expansion will be the same as that of (32), with $z \to -z$:

$$\frac{1}{r_{2A}} \simeq \frac{1}{R} - \frac{z_2}{R^2} + \frac{1}{2R^2}\left[2z_2^2 - x_2^2 - y_2^2\right] \qquad (33)$$

Finally



$$\vec{r}_1 + \vec{r}_{12} - \vec{r}_2 = \vec{r}_{AB}$$

$$\vec{r}_{12} = \vec{r}_2 - \vec{r}_1 + \vec{r}_{AB} = (x_2 - x_1, y_2 - y_1, z_2 - z_1 + R)$$

using again Eq (32) we get

$$\frac{1}{r_{12}} \simeq \frac{1}{R} - \frac{(z_2 - z_1)}{R^2} + \frac{1}{2R^3}\left[2(z_2 - z_1)^2 - (x_2 - x_1)^2 - (y_2 - y_1)^2\right] \qquad (34)$$

Now we go back to (30) and add everything together. Note how the terms of order $1/R$ and $1/R^2$ vanish. As a result we get

$$V = \frac{q^2}{2R^3}\left\{x_1^2 + y_1^2 - 2z_1^2 + x_2^2 + y_2^2 - 2z_2^2 + 2(z_2 - z_1)^2 - (x_2 - x_1)^2 - (y_2 - y_1)^2\right\}$$

$$= \frac{q^2}{2R^3}\left\{2x_1x_2 + 2y_1y_2 - 4z_1z_2\right\}$$

Hence, we finally obtain

$$\boxed{V \simeq \frac{q^2}{R^3}\left(x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right)} \qquad (35)$$

What we just did is called a <u>multipole expansion</u>. This term, which is the first non-vanishing one, is the <u>dipole-dipole interaction</u>. Essentially we are treating the two atoms as electrical dipoles, which is a good approximation when they are far apart. The next terms in the expansion would represent quadrupole-dipole interactions, then quadrupole-quadrupole and so on. The next terms in the expansion are

$$\begin{aligned} V = & \frac{q^2}{R^3}\left(x_1 x_2 + y_1 y_2 - 2 z_1 z_2\right) \\ & + \frac{q^2}{R^4}\frac{3}{2}\left[r_1^2 z_2 - r_2^2 z_1 + (z_1 - z_1)\left(2x_1x_2 + 2y_1y_2 - 3z_1z_2\right)\right] \\ & + \frac{q^2}{R^5}\frac{3}{4}\left[r_1^2 r_2^2 - 5 r_2^2 z_1^2 - 5 r_1^2 z_2^2 - 15 z_1^2 z_2^2 \right. \\ & \qquad \left. + 2\left(x_1x_2 + y_1y_2 + 4 z_1 z_2\right)^2 \right] \\ & + \cdots \end{aligned}$$

Let us try to apply perturbation theory to the ground state, which corresponds to both atoms in the 100 state

$$\psi_0(r_1, r_2) = \psi_{100}(r_1)\,\psi_{100}(r_2)$$

$$= \frac{1}{\pi^2 a_0^3}\, e^{-(r_1+r_2)/2} \qquad (36)$$

The first order correction involves

$$\langle V \rangle = \int |\psi_0|^2\, V\, d^3r_1\, d^3r_2$$

$$= \frac{q^2}{R^3}\left\{ \langle x_1\rangle\langle x_2\rangle + \langle y_1\rangle\langle y_2\rangle - 2\langle z_1\rangle\langle z_2\rangle \right\}$$

here the averages are computed in the ground state of hydrogen. ut in this state all these averages are zero! Thus

$$\langle V \rangle = 0 \qquad (37)$$

e must then move to 2^{nd} order perturbation theory. This is uch more complicated since the basis now involves both lectrons and it should include spin. But it doesn't matter: e will see what we want without having to perform the alculation. According to our known formula

$$E^{(2)} = \sum_{n\neq 0} \frac{|\langle n|V|0\rangle|^2}{E_0^0 - E_n^0}$$

here $|n\rangle$ generically denotes a basis.

Thus we see two things. First, this correction will be of the order of q^4/R^6. And secondly since E_0^0 is the ground state, $E_0^0 - E_n^0 < 0$ $\forall n$. Thus we conclude that

$$\boxed{E^{(2)} \sim -\frac{q^4}{R^6}} \tag{38}$$

The interaction is always negative and therefore corresponds to an attractive force. Moreover, it goes proportionally to $1/R^6$. This is the Van der Waals force.

Appendix: detailed solution of the Harmonic oscillator problem

Here I show how to go from Eq (10) to Eq (11). Start with

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = |A|^2 \int_{-\infty}^{\infty} \frac{1}{(x^2+b^2)^2} dx \quad := I_1$$

Define $x = b\tan(u)$, then

$$x^2 + b^2 = b^2\left[\tan^2 u + 1\right]$$

$$= \frac{b^2}{\cos^2 u}$$

Moreover

$$dx = b\sec^2 u \, du = \frac{b}{\cos^2 u} du$$

and

$$x = \pm\infty \rightarrow u = \pm \pi/2$$

Then

$$I_1 = \frac{|A|^2 b}{b^4} \int_{-\pi/2}^{\pi/2} \cos^4 u \, \frac{du}{\cos^2 u}$$

$$= \frac{|A|^2}{b^3} \int_{-\pi/2}^{\pi/2} \left[\frac{1+\cos(2u)}{2}\right] du$$

$$= \frac{|A|^2}{b^3}\left[\frac{u}{2}\Big|_{-\pi/2}^{\pi/2} + \underbrace{\frac{\sin(2u)}{4}\Big|_{-\pi/2}^{\pi/2}}_{0} \right]$$

$$= |A|^2 \frac{\pi}{2b^3}$$

Next we look at

$$I_2 = \frac{1}{2} m\omega^2 \int_{-\infty}^{\infty} \psi^*(x)\, x^2\, \psi(x)\, dx$$

$$= \frac{1}{2} m\omega^2 |A|^2 \int_{-\infty}^{\infty} \frac{x^2}{(x^2+b^2)^2}\, dx$$

Making the same change of variables,

$$\int_{-\infty}^{\infty} \frac{x^2}{(x^2+b^2)^2}\, dx = \frac{1}{b} \int_{-\pi/2}^{\pi/2} \frac{\cos^4 u \tan^2 u\, du}{\cos^2 u}$$

$$= \frac{1}{b} \int_{-\pi/2}^{\pi/2} \sin^2 u\, du$$

$$= \frac{1}{b} \int_{-\pi/2}^{\pi/2} \left[\frac{1 - \cos(2u)}{2}\right] du$$

$$= \frac{\pi}{2b}$$

Thus

$$I_2 = \frac{\pi m\omega^2 |A|^2}{4b}$$

So

$$\frac{I_2}{I_1} = \frac{\pi m\omega^2 |A|^2}{4b} \cdot \frac{2b^3}{\pi |A|^2} = \frac{1}{2} m\omega^2 b^2$$

Finally I need to compute

$$I_3 = -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \psi^*(x) \frac{d^2\psi}{dx^2} dx$$

$$\frac{d\psi}{dx} = A\left[\frac{-2x}{(x^2+b^2)^2} \right]$$

$$\frac{d^2\psi}{dx^2} = A\left[\frac{-2x(x^2+b^2)^2 + 2x(2x)2(x^2+b^2)}{(x^2+b^2)^4} \right]$$

$$= A\left[\frac{-2x(x^2+b^2) + 8x^2}{(x^2+b^2)^3} \right]$$

$$= A\left[\frac{6x^2 - 2b^2}{(x^2+b^2)^3} \right]$$

thus

$$I_3 = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{\infty} \frac{6x^2 - 2b^2}{(x^2+b^2)^4} dx$$

Doing the same change of variables we get

$$I_3 = -\frac{\hbar^2 |A|^2}{2m} \int_{-\pi/2}^{\pi/2} \frac{\cos^8 u}{b^8} \left[6b^2 \tan^2 u - 2b^2 \right] \frac{b\, du}{\cos^2 u}$$

$$= -\frac{\hbar^2 |A|^2}{2mb^5} \int_{-\pi/2}^{\pi/2} \cos^6 u \left[6\tan^2 u - 2 \right] du$$

$$= -\frac{\hbar^2 |A|^2}{2mb^5} \int_{-\pi/2}^{\pi/2} \cos^6 u \left[\frac{6\sin^2 u - 2\cos^2 u}{\cos^2 u} \right] du$$

$$= -\frac{\hbar^2 |A|^2}{2mb^5} \int_{-\pi/2}^{\pi/2} \cos^4 u \left[6 - 8\cos^2 u \right] du$$

Now

$$\int_{-\pi/2}^{\pi/2} \cos^4 u \, du = \frac{3\pi}{8}$$

$$\int_{-\pi/2}^{\pi/2} \cos^6 u \, du = \frac{5\pi}{16}$$

Thus

$$I_3 = -\frac{\hbar^2 |A|^2}{2 m b^5} \Big[\underbrace{6 \times \frac{3\pi}{8} - 8 \times \frac{5\pi}{16}}_{-\pi/4} \Big] = \frac{\hbar^2 |A|^2 \pi}{8 m b^5}$$

Finally

$$\frac{I_3}{I_1} = \frac{\hbar^2 |A|^2 \pi}{8 m b^5} \frac{2 b^3}{\pi |A|^2} = \frac{\hbar^2}{4 m b^2}$$

Combining the two results we arrive at Eq (11):

$$F = \frac{I_2}{I_1} + \frac{I_3}{I_1} = \frac{\hbar^2}{4 m b^2} + \frac{1}{2} m \omega^2 b^2$$

Appendix B: calculation of $\langle V_{ee} \rangle$ for the Helium atom

Our goal is to compute

$$\langle V_{ee} \rangle = q^2 \int \frac{|\psi|^2}{r_{12}} d^3 r_1 \, d^3 r_2$$

First we change variables to $\vec{r}_{12}' = \frac{Z}{a_0} \vec{r}_{12}$, which gives

$$\langle V_{ee} \rangle = \frac{q^2 Z}{\pi^2 a_0} \int \frac{e^{-2(r_1' + r_2')}}{r_{12}'} d^3 r_1' \, d^3 r_2'$$

Since we are integrating over $\vec{r}_1$ and $\vec{r}_2$ we may drop the primes. We write

$$\langle V_{ee} \rangle = \frac{q^2 Z}{a_0} A = -2 E_1 Z A \qquad (B.1)$$

where

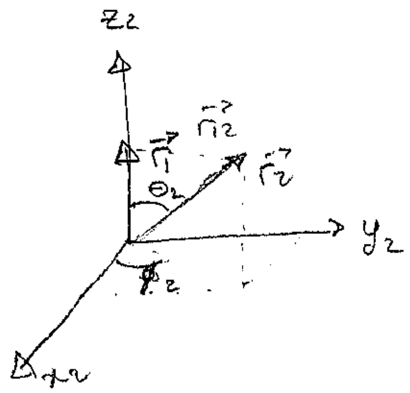
$$A = \frac{1}{\pi^2} \int \frac{e^{-2(r_1 + r_2)}}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 \, d^3 r_2 \qquad (B.2)$$

is a dimensionless integral.

We begin by integrating over $\vec{r}_2$

$$A = \frac{1}{\pi^2} \int d^3 r_1 \, e^{-2 r_1} \underbrace{\int d^3 r_2 \, \frac{e^{-2 r_2}}{|\vec{r}_1 - \vec{r}_2|}}_{I} \qquad (B.3)$$

Since we have a term r_{12}, I will depend on $\vec{r}_1$. The trick to compute I is to note that, since we are integrating over $\vec{r}_2$, we may choose the orientation of the coordinate axis at will. It is therefore convenient to choose



We have

$$\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$$

and

$$r_{12}^2 = \vec{r}_{12} \cdot \vec{r}_{12} = r_2^2 + r_1^2 - 2\,\vec{r}_1 \cdot \vec{r}_2$$

But due to our convenient choice

$$\vec{r}_1 \cdot \vec{r}_2 = r_1 r_2 \cos\theta_2$$

Thus

$$r_{12} = \sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}$$

which leads to

$$I = \int \frac{e^{-2r_2}\, r_2^2 \sin\theta_2}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_2}}\, dr_2\, d\theta_2\, d\phi_2$$

The ϕ_2 integral is trivial:

$$\int_0^{2\pi} d\phi_2 = 2\pi$$

we next perform the θ_2 integral

$$\int_0^{\pi} \frac{\sin\theta_2 \, d\theta_2}{\sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}} = \int_{-1}^{1} \frac{dz}{\sqrt{r_1^2+r_2^2-2r_1r_2 z}}$$

$$z=\cos\theta$$

Next I make

$$y = r_1^2+r_2^2-2r_1r_2 z$$

$$dy = -2r_1r_2\,dz$$

then

$$\int d\theta\,(\ldots) = -\frac{1}{2r_1r_2}\int \frac{dy}{\sqrt{y}} = -\frac{1}{2r_1r_2}\,2\sqrt{y}$$

$$= \frac{-1}{r_1r_2}\sqrt{r_1^2+r_2^2-2r_1r_2 z}\,\Big|_{-1}^{1}$$

$$= -\frac{1}{r_1r_2}\left\{\underbrace{\sqrt{r_1^2+r_2^2-2r_1r_2}}_{|r_1-r_2|} - \underbrace{\sqrt{r_1^2+r_2^2+2r_1r_2}}_{r_1+r_2}\right\}$$

$$= \frac{1}{r_1r_2}\left[r_1+r_2-|r_1-r_2|\right]$$

$$= \begin{cases} \frac{1}{r_1 r_2}\left[r_1 + r_2 - (r_1 - r_2)\right] & r_2 < r_1 \\ \frac{1}{r_1 r_2}\left[r_1 + r_2 - (r_2 - r_1)\right] & r_2 > r_1 \end{cases}$$

$$= \begin{cases} 2/r_1 & r_2 < r_1 \\ 2/r_2 & r_2 > r_1 \end{cases}$$

Thus, when we substitute this into I we may split the integral of r_2 in 2 parts:

$$I = 2\pi \int_0^{r_1} e^{-2r_2} r_2^2 \frac{2}{r_1}\, dr_2 + 2\pi \int_{r_1}^{\infty} e^{-2r_2} r_2^2 \frac{2}{r_2}\, dr_2$$

$$= 4\pi \left\{ \frac{1}{r_1} \int_0^{r_1} e^{-2r_2} r_2^2\, dr_2 + \int_{r_1}^{\infty} e^{-2r_2} r_2\, dr_2 \right\} \qquad (B.4)$$

Hence, our next task is to compute these integrals. They may be done using integration by parts:

$$\int r e^{-2r} dr = -\frac{e^{-2r} r}{2} + \frac{1}{2}\int e^{-2r} dr = -\frac{e^{-2r} r}{2} - \frac{e^{-2r}}{4}$$

$u = r \quad du = dr$

$dv = e^{-2r} dr \quad v = -\frac{e^{-2r}}{2}$

Thus

$$\int r e^{-2r} dr = -\frac{e^{-2r}}{4}(2r+1) \qquad (B.5)$$

Similarly

$$u = r^2 \qquad du = 2r\,dr$$
$$dv = e^{-2r}dr \qquad v = -\frac{e^{-2r}}{2}$$

$$\int r^2 e^{-2r} dr = -\frac{e^{-2r} r^2}{2} + \int r e^{-2r} dr$$

$$= -\frac{e^{-2r} r^2}{2} - \frac{e^{-2r}}{4}(2r+1)$$

Thus

$$\int r^2 e^{-2r} dr = -\frac{e^{-2r}}{4}(2r^2 + 2r + 1) \qquad (B.6)$$

Eq (B.4) then becomes

$$I = 4\pi \left\{ \frac{-1}{r_1} \frac{e^{-2r_2}}{4}(2r_2^2 + 2r_2 + 1)\Big|_0^{r_1} - \frac{e^{-2r_2}}{4}(2r_2+1)\Big|_{r_1}^{\infty} \right\}$$

$$= 4\pi \left\{ -\frac{1}{4r_1}\left[e^{-2r_1}(2r_1^2 + 2r_1 + 1) - 1 \right] + \frac{e^{-2r_1}}{4}(2r_1 + 1) \right\}$$

$$= \pi \left\{ \frac{1}{r_1} + e^{-2r_1}\left[2r_1 + 1 - 2r_1 - 2 - \frac{1}{r_1} \right] \right\}$$

$$= \pi \left\{ \frac{1}{r_1} + e^{-2r_1}\left[-1 - \frac{1}{r_1} \right] \right\}$$

or, finally

$$I = \frac{\pi}{r_1}\left\{ 1 - e^{-2r_1}(r_1 + 1) \right\} \qquad (B.7)$$

Next we insert this in Eq (B.3):

$$A = \frac{1}{\pi}\int \bar{e}^{2r_1} \frac{1}{r_1}\left[1 + \bar{e}^{2r_1}(r_1+1)\right] r_1^2 \sin\theta_1 \, dr_1 \, d\theta_1 \, d\phi_1$$

$$= \frac{4\pi}{\pi}\int_0^\infty r_1 \bar{e}^{2r_1}\left[1 + \bar{e}^{2r_1}(r_1+1)\right] dr_1$$

$$= 4\int_0^\infty \left[r_1 \bar{e}^{2r_1} + r_1^2 \bar{e}^{4r_1} + r_1 \bar{e}^{4r_1}\right] dr_1$$

$$= 4\left[\frac{1}{4} - \frac{1}{16} - \frac{1}{32}\right] = 4 \times \frac{5}{32} = \frac{5}{8}$$

Thus

$$\langle V_{ee} \rangle = -2E_1 Z A = -2E_1 Z \times \frac{5}{8}$$

or

$$\boxed{\langle V_{ee} \rangle = -\frac{5}{4} E_1 Z} \qquad (B.8)$$