

The Variational Principle

Here is another technique to address a quantum system which you don't know how to solve exactly.

The idea is (almost embarrassingly) simple. Suppose you're trying to solve the time-independent Schrödinger Equation

$$\hat{H}\psi = E\psi \quad , \text{ and you'd like to know the ground state energy } E_{\text{gs}}.$$

Now, if you can't solve the Schrödinger equation, you don't know ψ_{gs} or E_{gs} . But, you can determine an upper bound on E_{gs} as follows.

- ① Make up a normalized wave function ψ . This function will probably not be an energy eigenstate of \hat{H} (unless you made a very lucky guess.)
- ② Calculate $\langle \psi | \hat{H} | \psi \rangle$, the expectation value of H in this state.
- ③ I claim that $\langle \psi | \hat{H} | \psi \rangle \geq E_{\text{gs}}$ for any wave function ψ .

proof: Because ψ is a function, it can be expressed as a combination of the (unknown) true energy eigenstates.

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x)$$

$$\hat{H}\psi(x) = \sum_{n=1}^{\infty} c_n \hat{H}\psi_n(x) = \sum_{n=1}^{\infty} c_n E_n \psi_n(x)$$

$$\begin{aligned} \psi^*(x) \hat{H}\psi(x) &= \left[\sum_{m=1}^{\infty} c_m^* \psi_m^*(x) \right] \left[\sum_{n=1}^{\infty} c_n E_n \psi_n(x) \right] \\ &= \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} c_n c_m^* E_n \psi_m^*(x) \psi_n(x) \end{aligned}$$

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Now calculate $\langle \psi | \hat{H} | \psi \rangle = \int_{-\infty}^{\infty} \psi^*(x) \hat{H} \psi(x) dx$

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n c_m^* E_n \underbrace{\int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx}_{= S_{m,n}}$$

By orthonormality:

$$\langle \psi | \hat{H} | \psi \rangle = \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n c_m^* E_n S_{m,n}$$

In the double sum, only terms where $m=n$ are non-zero.

$$= \sum_{n=1}^{\infty} c_n c_n^* E_n$$

$$= \sum_{n=1}^{\infty} |c_n|^2 E_n \geq \sum_{n=1}^{\infty} |c_n|^2 E_{gs}$$

since $E_n \geq E_{gs}$

$$\langle \psi | \hat{H} | \psi \rangle \geq E_{gs} \sum_{n=1}^{\infty} |c_n|^2$$

\hookrightarrow Probability that system is found in state ψ_n if a measurement is made.

$$\langle \psi | \hat{H} | \psi \rangle \geq E_{gs} \quad \text{since } \sum_n |c_n|^2 = 1$$

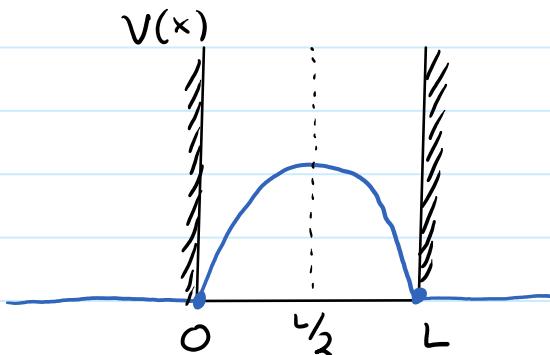
which is what we wanted to show. \blacksquare

Put another way, $\langle \psi | \hat{H} | \psi \rangle = \langle E \rangle$ in the state $\psi(x)$. It's the average of a bunch of energy measurements. This average will be equal to E_{gs} if $\psi = \psi_{gs}$. But if it's any other state, there will be some probability that measuring E will collapse to E_2, E_3, \dots etc ... and therefore $\langle E \rangle > E_{gs}$.

This technique is most useful if your guess $\psi_a(x)$ depends on some parameter (call it "a"). Then, by minimizing $\langle E \rangle$ as a function of a , you have an upper bound on E_{gs} .

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Example: (Griffiths 8.16). Suppose you didn't know the solution to the infinite square well. Find an upper bound on E_{gs} using



$$a.) \psi(x) = A\left(\frac{x}{L}\right)\left(1 - \frac{x}{L}\right)$$

$$b.) \psi(x) = A \left[\left(\frac{x}{L}\right)\left(1 - \frac{x}{L}\right) \right]^p$$

and find value of p which minimizes the ground state energy.

a.) Normalize : $\int_0^L |\psi(x)|^2 dx = 1$

$$1 = |A|^2 \int_0^L \left(\frac{x}{L}\right)^2 \left(1 - \frac{x}{L}\right)^2 dx$$

$$1 = |A|^2 \int_0^1 u^2 (1-u)^2 L du$$

$$\frac{1}{L} = |A|^2 \int_0^1 u^2 (1-u)^2 du \Rightarrow \frac{1}{L} = |A|^2 \left[\frac{1}{3} - \frac{1}{2} + \frac{1}{5} \right]$$

$$|A| = \sqrt{\frac{30}{L}}$$

Now, calculate $\langle \psi | \hat{H} | \psi \rangle = \int_0^L \psi(x)^* \frac{\hat{p}^2}{2m} \psi(x) dx$

$$\langle \psi | \hat{H} | \psi \rangle = \frac{(-i\hbar)^2}{2m} \int_0^1 \psi(u)^* \frac{\partial^2}{\partial u^2} \psi(u) (L \cdot du)$$

$$\hat{p} = (-i\hbar) \frac{\partial}{\partial x}$$

Change derivative $\frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial u} \cdot \frac{\partial u}{\partial x} = \frac{1}{L} \frac{\partial \psi}{\partial u}$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{L^2} \frac{\partial^2 \psi}{\partial u^2}$$

$$\begin{aligned} \langle \psi | \hat{H} | \psi \rangle &= \frac{(-i\hbar)^2}{2m} \int_0^1 \psi^*(u) \cdot \frac{1}{L^2} \frac{\partial^2}{\partial u^2} \psi(u) \cdot L \cdot du \\ &= \frac{-\hbar^2}{2m} \cdot \frac{1}{L} |A|^2 \int_0^1 u(1-u) \cdot \underbrace{\frac{\partial^2}{\partial u^2} [u(1-u)]}_{(-2)} du \\ &= \frac{\hbar^2}{mL} \cdot \left(\frac{30}{L}\right) \cdot \frac{1}{6} = \underline{\underline{\frac{5\hbar^2}{mL^2}}} \end{aligned}$$

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$$\text{Therefore, } E_{gs} \leq \frac{5\hbar^2}{mL^2}$$

$$\text{Note, the actual value is } E_{gs} = \frac{\pi^2\hbar^2}{2mL^2} = 4.93 \cdot \frac{\hbar^2}{mL^2}$$

It works! $(4.93) \leq 5$ [within $\sim 2\%$ of the true value].

b.) Proceed as above. Normalize:

$$\psi(u) = A[u(1-u)]^p \quad L|A|^2 \int_0^1 [\psi(u)]^2 du = 1$$

$$L|A|^2 \int_0^1 [u(1-u)]^{2p} du = 1 \quad \text{Leave as-is for now.}$$

$$\text{And, } \langle \psi | \hat{H} | \psi \rangle = -\frac{\hbar^2}{2m} \cdot \frac{1}{L} \int_0^1 |A|^2 \int_0^1 [u(1-u)]^p \frac{\partial^2}{\partial u^2} [u(1-u)]^p du$$

$$\text{integrate by parts: } +\frac{\hbar^2 |A|^2}{2mL} \left[\int_0^1 \left\{ \frac{\partial}{\partial u} [u(1-u)]^p \right\}^2 du \right. \\ \left. + \frac{\hbar^2 |A|^2}{2mL} \cdot \int_0^1 \left\{ p [u(1-u)]^{p-1} \cdot [1-2u] \right\}^2 du \right]$$

$$\langle \psi | \hat{H} | \psi \rangle = +\frac{\hbar^2}{2mL^2} \cdot p^2 \frac{\int_0^1 [u(1-u)]^{2p-2} [1-2u]^2 du}{\int_0^1 [u(1-u)]^{2p} du}$$

Mathematica

$$\text{FullSimplify} \left[\frac{\text{Integrate}[(u(1-u))^{2p-2} (1-2u)^2, \{u, 0, 1\}]}{\text{Integrate}[u^{2p} (1-u)^{2p}, \{u, 0, 1\}]} \right]$$

$$-\frac{2+8p}{p-2p^2} \text{ if } \text{Re}[p] > \frac{1}{2}$$

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$$\langle \psi | \hat{H} | \psi \rangle = \frac{\hbar^2}{mL^2} \left[\frac{p}{2} \frac{(2+8p)}{(2p-1)} \right]$$

minimize this!

$$\frac{d}{dp} \left[\frac{p(1+4p)}{2p-1} \right] = 0$$

$$\frac{1+8p}{(2p-1)} - \frac{p(1+4p)}{(2p-1)^2} \cdot 2 = 0$$

$$(1+8p)(2p-1) - 2p - 8p^2 = 0$$

$$16p^2 - 6p - 1 - 2p - 8p^2 = 0$$

$$8p^2 - 8p - 1 = 0$$

$$p = \frac{8 \pm \sqrt{64 + 32}}{16} = \frac{8 \pm 4\sqrt{6}}{16} = \frac{1 \pm \sqrt{6}}{4}$$

$$\approx -0.11 \text{ or } 1.11$$

only the + sign is a minimum, see graph above.

$$\text{So, } \langle \psi | \hat{H} | \psi \rangle = \frac{\hbar^2}{mL^2} \left[\frac{p(1+4p)}{2p-1} \right] = \frac{\hbar^2}{mL^2} \left[\frac{\left(\frac{1}{2} + \frac{\sqrt{6}}{4}\right)(1+2+\sqrt{6})}{1 + \frac{\sqrt{6}}{2} - 1} \right]$$

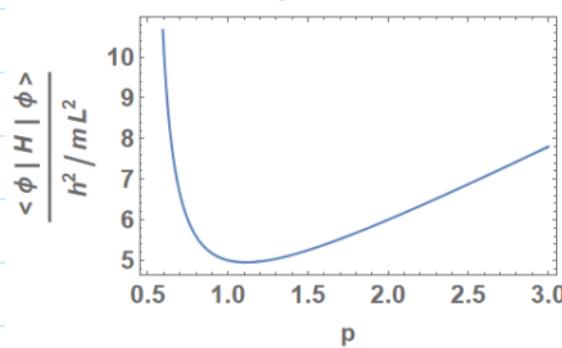
$$= \frac{\hbar^2}{mL^2} \left[\frac{\left(\frac{1}{2} + \frac{\sqrt{6}}{4}\right)(3+\sqrt{6})}{\sqrt{6}/2} \right] = \frac{\hbar^2}{mL^2} \left[\frac{\left(1 + \frac{\sqrt{6}}{2}\right)(3+\sqrt{6})}{\sqrt{6}} \right]$$

$$= \frac{\hbar^2}{mL^2} \left[\frac{6 + \frac{5\sqrt{6}}{2}}{\sqrt{6}} \right] = \frac{\hbar^2}{mL^2} \left[\sqrt{6} + \frac{5}{2} \right]$$

$$\therefore E_{gs} \leq \frac{\hbar^2}{mL^2} \cdot (4.949)$$

$$\left[\text{Actual value} = \frac{\hbar^2}{mL^2} (4.935) \right]$$

We are within about 0.3% of the true value!

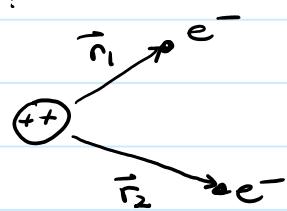


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Application: The Ground State energy of Helium

We analyzed the Helium atom earlier in the course:

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{2ke^2}{r_1} - \frac{2ke^2}{r_2} + \underbrace{\frac{ke^2}{|r_1 - r_2|}}_{\text{electron repulsion}}$$



Previously, we ignored the e-e repulsion term to get

$$\psi_{11}(\vec{r}_1, \vec{r}_2) = \frac{8}{\pi a^3} e^{-\frac{2}{a}(r_1+r_2)} \quad \text{and } E_{11} = 4 \cdot (-13 \text{eV}) \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) = -109 \text{eV}$$

This doesn't compare very well with the experimental value of $E_{\text{gs}} \approx -79 \text{eV}$. So how can we do better?

We know $\psi_{11}(\vec{r}_1, \vec{r}_2)$ is not the actual ground state energy; we calculated it by ignoring the e-e repulsion. But, we can use this in the variational principle.

$\langle \psi_{11} | \hat{H} | \psi_{11} \rangle \geq E_{\text{gs}}$ to get an upper bound on E_{gs} .

Let's write $\hat{H} = \underbrace{\frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} - \frac{2ke^2}{r_1} - \frac{2ke^2}{r_2}}_{\hat{H}^0} + \underbrace{\frac{ke^2}{|r_1 - r_2|}}_{\hat{H}_{\text{int}} \text{ (interaction)}}$

Now, we know that $\hat{H}^0 |\psi_{11}\rangle = E_{11} |\psi_{11}\rangle$. This was the solution to the Schrödinger equation with $\hat{H}_{\text{int}} = 0$

$$\begin{aligned} \langle \psi_{11} | \hat{H} | \psi_{11} \rangle &= \langle \psi_{11} | \hat{H}^0 | \psi_{11} \rangle + \langle \psi_{11} | \hat{H}_{\text{int}} | \psi_{11} \rangle \geq E_{\text{gs}} \\ &= E_{11} \langle \psi_{11} | \psi_{11} \rangle + \langle \psi_{11} | \hat{H}_{\text{int}} | \psi_{11} \rangle \geq E_{\text{gs}} \end{aligned}$$

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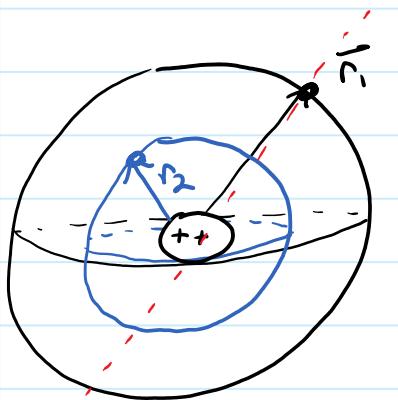
So, let's calculate $\langle \psi_{11} | \hat{H}_{\text{int}} | \psi_{11} \rangle$

Remember $\psi_{11}(\vec{r}_1, \vec{r}_2)$ depends on both \vec{r}_1 and \vec{r}_2 so we need

$$\int_0^\infty dr_1 \int_0^\infty dr_2 \underbrace{\int d\Omega_1 \int d\Omega_2}_{\text{from } r^2 \sin\theta_1 d\theta_1 d\phi_1} \psi_{11}^*(r_1, r_2) \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \psi_{11}(r_1, r_2) \cdot r_1^2 r_2^2$$

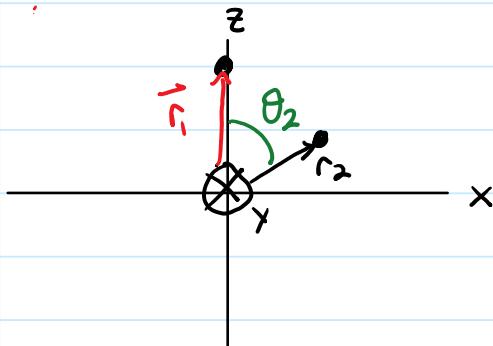
Remember $\int d\Omega_1 = \int_0^{2\pi} \int_0^\pi \sin\theta_1 d\theta_1 d\phi_1$

from $\underline{r^2 \sin\theta_1 d\theta_1 d\phi_1}$
volume element.



The atom is spherically symmetric, so we have the freedom to choose our coordinates.

Let's choose \hat{z} to point in the direction of \vec{r}_1 . We can also rotate our axes so that \vec{r}_2 lies in the $x-z$ plane. Then, we have



$$\begin{aligned} \text{Now, } |\vec{r}_1 - \vec{r}_2| &= \sqrt{(\vec{r}_1 - \vec{r}_2) \cdot (\vec{r}_1 - \vec{r}_2)} \\ &= \sqrt{r_1^2 + r_2^2 - 2\vec{r}_1 \cdot \vec{r}_2} \\ &= \sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2} \end{aligned}$$

Plug into the integrals!

$$\langle \psi_{11} | \hat{H}_{\text{int}} | \psi_{11} \rangle =$$

$$ke^2 \left(\frac{64}{\pi a^6} \right) \int_0^\infty \int_0^\infty \underbrace{\int d\Omega_1 \int d\Omega_2}_{\text{Nothing depends on } \theta_2 \text{ or } \phi_1, \text{ so } \int_0^{2\pi} d\phi_1 \int_0^\pi \sin\theta_1 d\theta_1 = 4\pi} \int d\Omega_2 e^{-\frac{2}{a}(r_1+r_2)} e^{\frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta_2}}} \cdot r_1^2 r_2^2$$

Nothing depends

$$\text{on } \theta_1 \text{ or } \phi_1, \text{ so } \int d\Omega_1 = \int_0^{2\pi} d\phi_1 \int_0^\pi \sin\theta_1 d\theta_1 = 4\pi$$

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Cleaning it up a bit :

$$\langle \psi_1 | \hat{H}_{\text{int}} | \psi_1 \rangle =$$

$$\frac{k e^2 \alpha}{\pi^2 a^6} \cdot 8\pi^2 \cdot \int_0^\infty dr_1 \int_0^\infty dr_2 \int_0^\pi \frac{e^{-\frac{4}{a}(r_1+r_2)}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta}} \frac{r_1^2 r_2^2}{\sin \theta} d\theta$$

Now, do the θ integral :

$$= \frac{S_{12} \cdot k e^2}{a^6} \int_0^\infty dr_1 \int_0^\infty dr_2 \cdot \frac{e^{-\frac{4}{a}(r_1+r_2)} \cdot r_1^2 r_2^2}{\sqrt{r_1^2 + r_2^2}} \int_0^\pi \frac{\sin \theta}{\sqrt{1 - \frac{2r_1 r_2 \cos \theta}{(r_1^2 + r_2^2)}}} d\theta$$

$$\int_0^\pi \frac{\sin \theta}{\sqrt{1 - b \cos \theta}} d\theta$$

$$\text{Let } u = 1 - b \cos \theta \\ du = b \cdot \sin \theta d\theta$$

$$\int_{-b}^{1+b} \frac{\frac{1}{b} \cdot du}{\sqrt{u}} = \frac{2}{b} \sqrt{u} \Big|_{-b}^{1+b} = \frac{2}{b} \left(\sqrt{1+b} - \sqrt{1-b} \right)$$

$$\text{Now, } b \equiv \frac{2r_1 r_2}{r_1^2 + r_2^2}$$

$$1+b = \frac{r_1^2 + r_2^2 + 2r_1 r_2}{r_1^2 + r_2^2} = \frac{(r_1 + r_2)^2}{(r_1^2 + r_2^2)}$$

$$1-b = \frac{r_1^2 + r_2^2 - 2r_1 r_2}{r_1^2 + r_2^2} = \frac{(r_1 - r_2)^2}{r_1^2 + r_2^2}$$

$$2 \left(\frac{\sqrt{1+b} - \sqrt{1-b}}{b} \right) = \left[\frac{(r_1 + r_2)}{\sqrt{r_1^2 + r_2^2}} - \frac{|r_1 - r_2|}{\sqrt{r_1^2 + r_2^2}} \right] \frac{(r_1^2 + r_2^2)}{r_1 r_2}$$

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$$2 \left(\frac{\sqrt{1+b} - \sqrt{1-b}}{b} \right) = \left[\frac{(r_1 + r_2)}{\sqrt{r_1^2 + r_2^2}} - \frac{|r_1 - r_2|}{\sqrt{r_1^2 + r_2^2}} \right] \frac{(r_1^2 + r_2^2)}{r_1 r_2}$$

$$= \frac{\sqrt{r_1^2 + r_2^2}}{r_1 r_2} \left[(r_1 + r_2) - |r_1 - r_2| \right]$$

Now, put it together:

$$\begin{aligned} & \frac{S_{12} \cdot k e^2}{a^6} \int_0^\infty dr_1 \int_0^\infty dr_2 \cdot \frac{e^{-\frac{4}{a}(r_1+r_2)}}{\sqrt{r_1^2 + r_2^2}} \left[\frac{\sqrt{r_1^2 + r_2^2}}{r_1 r_2} (r_1 + r_2 - |r_1 - r_2|) \right] \\ &= \frac{S_{12} k e^2}{a^6} \int_0^\infty dr_1 \int_0^\infty dr_2 e^{-\frac{4}{a}(r_1+r_2)} r_1 r_2 \underbrace{\left(r_1 + r_2 - |r_1 - r_2| \right)}_{\text{green bracket}} \end{aligned}$$

$$\text{since } |x| = \begin{cases} x & \text{if } x > 0 \\ -x & \text{if } x < 0 \end{cases} \Rightarrow = \begin{cases} 2r_2 & \text{if } r_1 > r_2 \\ 2r_1 & \text{if } r_2 > r_1 \end{cases}$$

So now, let's break the r_2 integral into two intervals:

$$\begin{aligned} &= \frac{1024 k e^2}{a^6} \int_0^\infty e^{-\frac{4}{a}r_1} dr_1 \left[\int_0^{r_1} e^{-\frac{4}{a}r_2} r_1 r_2^2 dr_2 + \int_{r_1}^\infty e^{-\frac{4}{a}r_2} r_1^2 r_2 dr_2 \right] \\ &\quad \text{--- } r_2 < r_1 \qquad \text{--- } r_2 > r_1 \\ &= \frac{1024 k e^2}{a^6} \int_0^\infty e^{-\frac{4}{a}r_1^2} \left[\frac{1}{r_1} \int_0^{r_1} e^{-\frac{4}{a}r_2^2} dr_2 + \int_{r_1}^\infty e^{-\frac{4}{a}r_2^2} r_2 dr_2 \right] dr_1 \end{aligned}$$

$$\text{Let } u = \frac{4r_2}{a} \quad du = \frac{4}{a} dr_2$$

$$= \frac{1024 k e^2}{a^6} \int_0^\infty e^{-\frac{4}{a}r_1^2} r_1^2 \left[\frac{1}{r_1} \int_0^{\frac{4r_1}{a}} e^{-u} \left(\frac{u}{4}\right)^2 \left(\frac{a}{4}\right) du + \int_{\frac{4r_1}{a}}^\infty e^{-u} \left(\frac{u}{4}\right) \left(\frac{a}{4}\right) du \right] dr_1$$

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$$\begin{aligned}
 &= \frac{1024ke^2}{a^6} \int_0^\infty e^{-\frac{4r_1}{a}} r_1^2 \left[\frac{1}{r_1} \int_0^{\frac{4r_1}{a}} e^{-u} \left(\frac{ua}{4} \right)^2 \left(\frac{a}{4} \right) du + \int_{\frac{4r_1}{a}}^\infty e^{-u} \left(\frac{ua}{4} \right) \left(\frac{a}{4} \right) du \right] dr_1 \\
 &= \frac{1024ke^2}{a^6} \left(\frac{a}{4} \right)^2 \int_0^\infty e^{-\frac{4r_1}{a}} r_1^2 \left[\left(\frac{a}{4r_1} \right) \int_0^{\frac{4r_1}{a}} e^{-u} u^2 du + \int_{\frac{4r_1}{a}}^\infty e^{-u} u du \right] dr_1
 \end{aligned}$$

$$\text{Now, let } z = \frac{4r_1}{a} \quad dz = \frac{4}{a} dr_1$$

$$\begin{aligned}
 &= \frac{64ke^2}{a^4} \int_0^\infty e^{-z} \left(\frac{az}{4} \right)^2 \left[\frac{1}{z} \int_0^z e^{-u} u^2 du + \int_z^\infty ue^{-u} du \right] \left(\frac{a}{4} \right) dz \\
 &= \frac{64ke^2}{a^4} \left(\frac{a}{4} \right)^3 \int_0^\infty e^{-z} z^2 \left[\frac{1}{z} \int_0^z e^{-u} u^2 du + \int_z^\infty ue^{-u} du \right] dz
 \end{aligned}$$

$$\begin{aligned}
 &= \frac{ke^2}{a} \int_0^\infty e^{-z} z^2 \left[\underbrace{\frac{1}{z} \int_0^z e^{-u} u^2 du}_{\frac{1}{z} [2 - e^{-z}(2+2z+z^2)]} + \underbrace{\int_z^\infty ue^{-u} du}_{e^{-z}(1+z)} \right] dz
 \end{aligned}$$

$$= \frac{ke^2}{a} \int_0^\infty e^{-z} z^2 \left[\frac{2}{z} + e^{-z} \left(1+z - \frac{2}{z} - 2 - z \right) \right] dz$$

$$= \frac{ke^2}{a} \int_0^\infty e^{-z} \left[2z + z^2 e^{-z} \left(-\frac{2}{z} - 1 \right) \right] dz$$

$$\begin{aligned}
 &= \frac{ke^2}{a} \left\{ \underbrace{\int_0^\infty 2ze^{-z} dz}_{2 \cdot 1! = 2} - \underbrace{\int_0^\infty e^{-2z} (2z+z^2) dz}_{-\int_0^\infty e^{-x} \left(x + \frac{x^2}{4} \right) \frac{1}{2} dx} \right\} \\
 &\quad - \frac{1}{2} \left[1! + \frac{2!}{4} \right] = -\frac{3}{4}
 \end{aligned}$$

$$\begin{aligned}
 \text{Let } x &= 2z \\
 dz &= 2dx
 \end{aligned}$$

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$$\langle \psi_{11} | \hat{H}_{\text{int}} | \psi_{11} \rangle = \frac{ke^2}{a} \left(2 - \frac{3}{4} \right) = \frac{5ke^2}{4a}$$

Recall $E_1 = 13.6 \text{ eV} = \frac{ke^2}{2a}$

$$\langle \psi_{11} | \hat{H}_{\text{int}} | \psi_{11} \rangle = \frac{5}{2} E_1 = 34 \text{ eV}$$

And so, $E_{\text{gs}} \leq E_{11} + \langle \psi_{11} | \hat{H}_{\text{int}} | \psi_{11} \rangle$

$$E_{\text{gs}} \leq -109 \text{ eV} + 34 \text{ eV}$$

$$E_{\text{gs}} \leq -75 \text{ eV}$$

Much closer to the experimental value of -79 eV , about 5% too high.

It is possible to get even better bounds by trying more complicated wave functions. Griffiths has an improved estimate with

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

$$\text{In this case, } \langle \psi | \hat{H} | \psi \rangle = \left[-2Z^2 + \left(\frac{27}{4} \right) Z \right] E_1$$

which is minimized for $Z \approx 1.69$ and

$$E_{\text{gs}} \leq -77.5 \text{ eV} \quad \text{which is about 2\% away from the experimental value.}$$