$$\langle T\rangle = -\frac{\hbar^2}{2m}\left(\frac{2b}{\pi}\right)^{1/2}\left(\underbrace{-2\sqrt{\frac{\pi}{2}}\, b^{1/2} + 4\cdot\frac{1}{4}\sqrt{\frac{\pi}{2}}\, b^{2}\frac{1}{b^{3/2}}}_{-\sqrt{\frac{\pi}{2}}\, b^{1/2}}\right)$$

$$\boxed{\langle T\rangle = \frac{\hbar^2 b}{2m}}$$

$b\uparrow$, wavefunction smaller

$\langle T\rangle \uparrow$

(vice versa)

$$\langle V\rangle = K\left(\frac{2b}{\pi}\right)^{1/2}\underbrace{\int_{-\infty}^{\infty}|x|^n e^{-2bx^2}\,dx}$$

$$\xi \equiv \sqrt{2b}\, x$$

$$x = \xi(2b)^{-1/2} \qquad dx = d\xi\,(2b)^{-1/2}$$

$$\langle V\rangle = K\left(\frac{2b}{\pi}\right)^{\cancel{1/2}}(2b)^{-n/2}\cancel{(2b)^{-1/2}}\underbrace{\int_{-\infty}^{\infty}|\xi|^n e^{-\xi^2}\,d\xi}_{\text{pure \#},\ \nu(n)}$$

$$= \frac{K}{\sqrt{\pi}}\,\frac{1}{(2b)^{n/2}} \times \nu(n)$$

$$\# = \int_{-\infty}^{\infty}|\xi|^n e^{-\xi^2}\,d\xi = 2\int_{0}^{\infty}\xi^n e^{-\xi^2}\,d\xi$$

$$2\int_0^\infty \xi^n e^{-\xi^2} d\xi = \underbrace{\Gamma\left(\frac{n+1}{2}\right)}$$

known as the Γ function, finite when

$$\frac{n+1}{2} > 0$$

$$n > -1$$

Here, lets keep that... usually $n > 0$

$$\Gamma(n+1) = n\Gamma(n) = n(n-1)\Gamma(n-1) \;---$$

when $n =$ integer, $\Gamma(n+1) = n!$

$$\Gamma(2) = 1! = 1 \qquad \Gamma(1) = 0! \equiv 1$$

$$\Gamma\left(\tfrac{1}{2}\right) = \sqrt{\pi} \quad \text{(work!)}$$

$$\Gamma\left(\tfrac{3}{2}\right) = \frac{1}{2}\Gamma\left(\tfrac{1}{2}\right) = \frac{\sqrt{\pi}}{2} \quad \text{(WIKI!)}$$

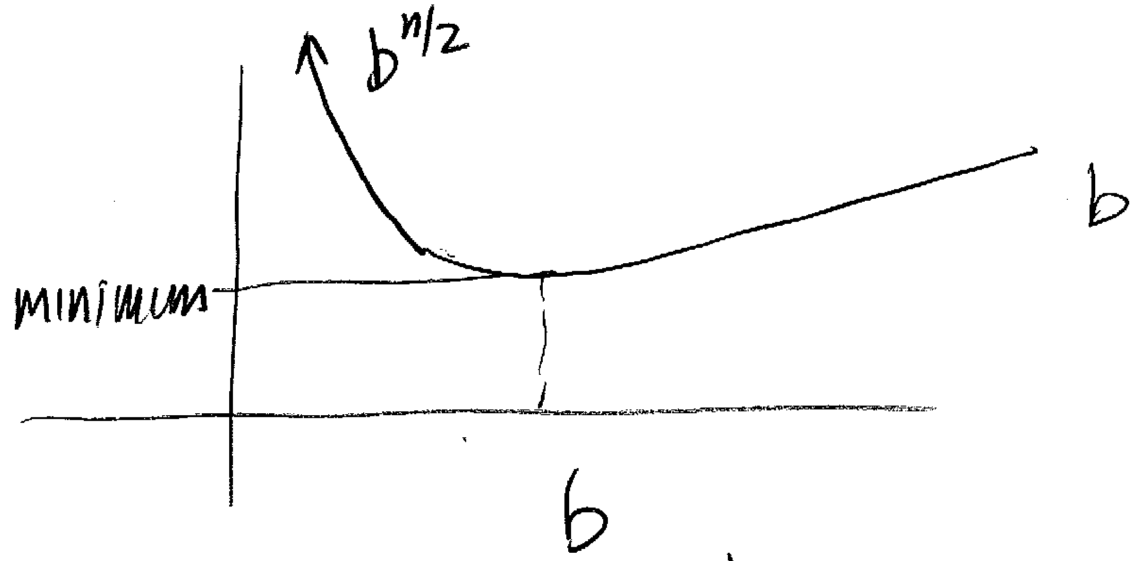
$$\boxed{\langle V \rangle = \frac{K}{\sqrt{\pi}} \frac{1}{(2b)^{n/2}} \Gamma\left(\frac{n+1}{2}\right)}$$

$b \uparrow$ $\langle V \rangle \downarrow$

$$\langle \varphi_g | H | \varphi_g \rangle = \frac{\hbar^2 b}{2m} + \left(\frac{K\Gamma\left(\frac{n+1}{2}\right)}{\sqrt{\pi}\, 2^{n/2}} \right) \frac{1}{b^{n/2}}$$

dominates at large b

dominates at small b.



still above E_g!

$$\frac{\partial \langle \varphi_g | H | \varphi_g \rangle}{db} = \frac{\hbar^2}{2m} - \frac{n}{2} \left(\quad \right) \frac{1}{b^{(n/2+1)}}$$

$$\frac{\hbar^2}{2m} = \frac{n}{2} \left(\quad \right) \frac{1}{b^{\frac{(n+2)}{2}}}$$

$$\boxed{b = \left[\frac{2m}{\hbar^2} \frac{K\Gamma\left(\frac{n+1}{2}\right)}{\sqrt{\pi}\; 2^{n/2}} \right]^{\frac{2}{n+2}}}$$

Cases: SHO $n=2$

$$K = \frac{1}{2} m\omega^2$$

$$b = \left[\frac{2m}{\hbar^2} \frac{1}{2} m\omega^2 \frac{\Gamma\left(\frac{3}{2}\right)}{\cancel{\sqrt{\pi}}\, 2}\right]^{\frac{2}{2+2}} \qquad \Gamma\left(\tfrac{3}{2}\right) = \cancel{\sqrt{\pi}}/2$$

$$= \left[\frac{1}{4} \frac{m^2\omega^2}{\hbar^2}\right]^{1/2} = \frac{m\omega}{2\hbar}$$

Don't forget to PLUG back into $\langle \psi_g | H | \psi_g \rangle \ldots$

$n=2$

$$\langle \psi_g | H | \psi_g \rangle = \frac{\hbar^2 m\omega}{2m\, 2\hbar} + \left(\frac{\frac{1}{2} \cancel{m} \omega^{\cancel{2}} \frac{\cancel{\sqrt{\pi}}}{2}}{\cancel{\sqrt{\pi}}\ \cancel{2}}\right)\left(\frac{\cancel{2}\hbar}{\cancel{m\omega}}\right)$$

$$= \frac{1}{4}\hbar\omega + \frac{1}{4}\hbar\omega$$

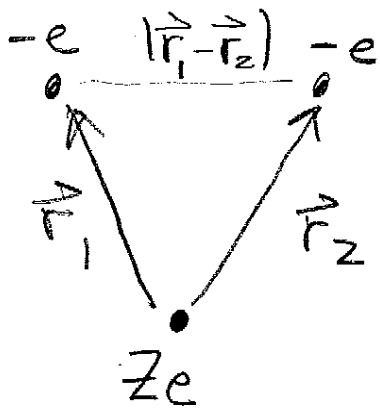
$$= \frac{1}{2}\hbar\omega$$ hits the spot!

2 Classic Cases of Variational Calcs

① Helium → electron-electron repulsion

② H_2^+ → electron glues the protons together.

<u>Heliumic</u> (charge Z at origin, $Z=2$ actually



$$H = \frac{-\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}\right)$$

dd

$$\boxed{+\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1-\vec{r}_2|}}$$

- new + different
- repulsive

- <u>neglecting</u> repulsive term, one would <u>guess</u>

$$E_{gs} = \underset{\substack{\uparrow \\ \#\text{ electrons}}}{2} \times \left(\underbrace{\boxed{-\frac{1}{2}}\,2^2\,\boxed{\alpha^2 m_e c^2}}\right)$$

Rydberg, $= -13.6\,eV$

$$E_{gs} \simeq 2\times(2)^2\times(-13.6)\,eV$$
$$\simeq -109\,eV$$

Measurement:

$E_{gs} = -78.975\,eV$

higher due to repulsion of electrons

$$\langle V_{ee} \rangle = \, ? \quad \underbrace{\psi_0(\vec{r}_1, \vec{r}_2)}_{\text{hydrogenic}} = \sqrt{\frac{1}{\pi\left(\frac{a}{Z}\right)^3}}\, e^{-\frac{r_1}{(a/Z)}} \times \sqrt{\frac{1}{\pi\left(\frac{a}{Z}\right)^3}}\, e^{-\frac{r_2}{(a/Z)}}$$

hydrogenic about Ze $\qquad a \to$ Bohr Radius

Ground state

$$\psi_0(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a}$$

$$\langle V_{ee} \rangle = \underbrace{\left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{Z^3}{\pi a^3}\right)^2 \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{e^{-\frac{Z(r_1+r_2)}{a}}}{|\vec{r}_1 - \vec{r}_2|}}$$

scaling with Z/a heart of matter

$$\vec{\xi}_1 = \frac{\vec{r}_1}{(a/Z)} \qquad \frac{\vec{r}_2}{(a/Z)}$$

$$\langle V_{ee} \rangle = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\frac{1}{\pi^2}\left(\frac{Z}{a}\right) \underbrace{\int d^3\vec{\xi}_1 d^3\vec{\xi}_2 \frac{e^{-(\xi_1+\xi_2)}}{|\vec{\xi}_1 - \vec{\xi}_2|}}_{\text{pure number!}}$$

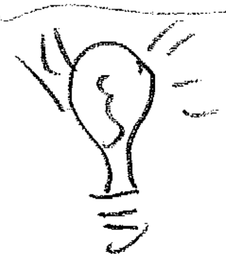
(Book)

$$= +Z \cdot \left(\frac{5}{8} \cdot \frac{1}{2}\alpha^2 m c^2\right)$$

$Z=2$

$\langle V_{ee} \rangle = 34\ eV$

$$\boxed{\langle H \rangle = -109\ eV + 34\ eV = -75\ eV}$$



leave Z as a parameter in the wave function

WARNING

NOT Z!

$$H = \frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2}\right)$$

$$+ \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$$

Think of it the following way

$$= \boxed{\frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1} + \frac{Z}{r_2}\right)} \rightarrow -\frac{1}{2} Z^2 \alpha^2 mc^2$$

$$+ \frac{e^2}{4\pi\varepsilon_0}\left(\underbrace{(Z-2)\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}_{\text{gotta do!}} + \underbrace{\frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{\text{done}}\right)$$

$$\frac{e^2(Z-2)}{4\pi\varepsilon_0}\left(\frac{Z^3}{\pi a^3}\right)^2 \int d^3\vec{r}_1\, d^3\vec{r}_2\, e^{-\frac{Z(r_1+r_2)}{a}}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$$

$$\xi_1 = \frac{Z}{a}\vec{r}_1 \quad \xi_2 = \frac{Z}{a}\vec{r}_2$$

$$\frac{e^2(Z-2)}{4\pi\varepsilon_0}\,\frac{Z}{a}\,\underbrace{\int d^3\vec{\xi}_1\, d^3\vec{\xi}_2\, e^{-(\xi_1+\xi_2)}\left(\frac{1}{\xi_1}+\frac{1}{\xi_2}\right)}_{\#\ =\ 2}$$

Putting terms together

$$\langle H\rangle = \left[2Z^2 - 4Z(Z-2) - \frac{5}{4}Z\right]\left[-\frac{1}{2}\alpha^2 mc^2\right]$$

$$= \left[-2Z^2 + \frac{27}{4}Z\right]\left[-\frac{1}{2}\alpha^2 mc^2\right]$$