$$|\psi_n\rangle = |\psi_n^0\rangle + \sum_{k\neq n} \frac{\langle k|H'|n\rangle |k\rangle}{E_n^{(0)} - E_k^{(0)}}$$

$$\Delta E \propto \frac{1}{L}$$

Variational Principle

$|\psi\rangle$ any state

$$\langle\psi|H|\psi\rangle \geq E_g$$

$$|\psi\rangle = \sum a_n |\psi_n\rangle$$

$$\langle\psi|H|\psi\rangle = \sum_{nm} \langle\psi_m|a_m^* a_n E_n|\psi_n\rangle$$

$$= \sum_{nm} a_m^* a_n E_n \delta_{nm}$$

$$= \sum |a_n|^2 E_n$$

$$E_n \geq E_g$$

$$\langle\psi|H|\psi\rangle = \sum |a_n|^2 E_n$$

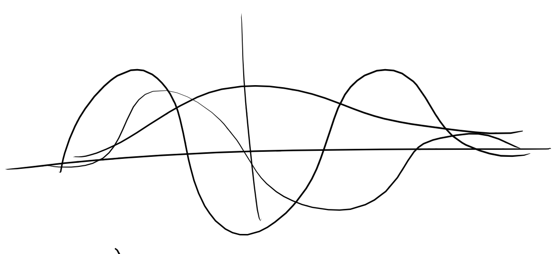
$$\geq \sum |a_n|^2 E_g = \overbrace{\left(\sum_n |a_n|^2\right)}^{1} E_g$$

$$\boxed{\langle\psi|H|\psi\rangle \geq E_g}$$

$$\psi(\vec{r}; a, b, c,)$$

$$\langle\psi|H|\psi\rangle = f(a, b, c, \ldots)$$

$$f_{min} \geq E_g$$



Example 1D H.O.

$$H = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

$$\psi = A e^{-ax^2}$$

$$\int_{-\infty}^{\infty} dx\, |\psi|^2 = |A|^2 \int_{-\infty}^{\infty} dx\ e^{-2ax^2} = |A|^2 \sqrt{\frac{\pi}{2a}} = 1$$

$$\psi = \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}$$

$\langle \psi | H | \psi \rangle$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = -\frac{\hbar^2}{2m}\frac{d}{dx}\left(\frac{2a}{\pi}\right)^{1/4}(-2ax)e^{-ax^2}$$

$$= -\frac{\hbar^2}{2m}(-2a)\left(\frac{2a}{\pi}\right)^{1/4}\left[e^{-ax^2} + x(-2ax)e^{-ax^2}\right]$$

$$= \frac{\hbar^2 a}{m}\left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}\left[1-2ax^2\right]$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2\right)\psi$$

$$= \left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}\left[\left(1-2ax^2\right)\frac{\hbar^2 a}{m} + \frac{1}{2}m\omega^2x^2\right]$$

$$= \frac{\hbar^2 a}{m}\left(\frac{2a}{\pi}\right)^{1/4} e^{-ax^2}\left[1 + x^2\left(\frac{m^2\omega^2}{2a\hbar^2} - 2a\right)\right]$$

$$\langle \psi | H | \psi \rangle = \frac{\hbar^2 a}{m}\left(\frac{2a}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} dx\, e^{-2ax^2}\left[1+x^2\left(\frac{m^2\omega^2}{2a\hbar^2}-2a\right)\right]$$

$$= \frac{\hbar^2 a}{m}\left(\frac{2a}{\pi}\right)^{1/2}\left[1+\left(\frac{m^2\omega^2}{2a\hbar^2}-2a\right)\left(-\frac{1}{2}\frac{\partial}{\partial a}\right)\right]\left(\frac{\pi}{2a}\right)^{1/2}$$

$$\int_{-\infty}^{\infty} dx\, x^2 e^{-2ax^2} = \int_{-\infty}^{\infty} dx \left(-\frac{1}{2}\frac{\partial}{\partial a}\right) e^{-2ax^2}$$

$$= -\frac{1}{2}\frac{\partial}{\partial a}\int_{-\infty}^{\infty} dx\, e^{-2ax^2}$$

$$= -\frac{1}{2}\frac{\partial}{\partial a}\left(\frac{\pi}{2a}\right)^{1/2} = -\frac{1}{2}\left(-\frac{1}{2a}\right)\left(\frac{\pi}{2a}\right)^{1/2}$$

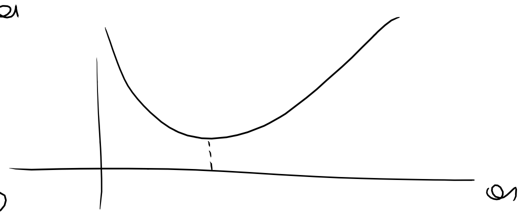
$$= \frac{\hbar^2 a}{m}\cancel{\left(\frac{2a}{\pi}\right)^{1/2}}\left[1+\left(\frac{m^2\omega^2}{2a\hbar^2}-2a\right)\left(-\frac{1}{2}\right)\left(-\frac{1}{2}\right)\frac{1}{a}\right]\cancel{\left(\frac{\pi}{2a}\right)^{1/2}}$$

$$= \frac{\hbar^2 a}{m}\left[1+\left(\frac{m^2\omega^2}{2a\hbar^2}-2a\right)\frac{1}{4a}\right]$$

$$= \frac{\hbar^2 a}{m} + \frac{\hbar^2}{4m}\left(\frac{m^2\omega^2}{2a\hbar^2} - 2a\right)$$

$$= \frac{\hbar^2 a}{m} - \frac{\hbar^2 a}{2m} + \frac{1\, m\omega^2}{8a}$$

$$\langle\psi|H|\psi\rangle = \frac{\hbar^2 a}{2m} + \frac{m\omega^2}{8a}$$



$$\frac{d}{da}\langle H\rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8a^2} = 0$$

$$\frac{\hbar^2}{2m} = \frac{m\omega^2}{8a^2} \Rightarrow a^2 = \frac{m^2\omega^2}{4\hbar^2} \Rightarrow a = \frac{m\omega}{2\hbar}$$

$$\langle H\rangle_{min} = \frac{\hbar^{\cancel{2}}}{2\cancel{m}}\,\frac{\cancel{m}\omega}{2\cancel{\hbar}} + \frac{\cancel{m}\omega^{\cancel{2}}}{8}\,\frac{2\hbar}{\cancel{m}\cancel{\omega}}$$

$$= \frac{\hbar\omega}{4} + \frac{\hbar\omega}{2} = \frac{\hbar\omega}{2} = \langle H\rangle_{min}$$ exact value!

<u>Example</u>

$$\psi(x) = A\begin{cases} e^{-xa} & x>0 \\ e^{xa} & x<0 \end{cases} = Ae^{-a|x|}$$

$$\int_{-\infty}^{\infty} dx\,|\psi|^2 = 2|A|^2\int_0^{\infty} e^{-2ax}\,dx = 2|A|^2\frac{1}{2a} = 1$$

$$\Rightarrow A = \sqrt{a}$$

$$\psi(x) = \sqrt{a}\,e^{-a|x|}$$

$$\frac{d\psi}{dx} = \sqrt{a}\,a\,e^{-a|x|}\begin{cases} -1 & x>0 \\ 1 & x<0 \end{cases}$$

$$= -a^{3/2}e^{-a|x|}\,\mathrm{sign}(x) = -a\psi\,\mathrm{sign}(x)$$

$$\frac{d^2\psi}{dx^2} = -a\left[2\delta(x)\psi(x) + \mathrm{sign}(x)\left(-a\,\mathrm{sign}(x)\psi(x)\right)\right]$$

$$\frac{d}{dx}\mathrm{sign}(x) = 0 \quad \text{if } x \neq 0$$

$$\int_{0^-}^{0^+} dx\frac{d}{dx}\mathrm{sign}(x) = \mathrm{sign}(x)\Big|_{x=0^-}^{0^+} = 1-(-1) = 2$$

$$\frac{d}{dx}\mathrm{sign}(x)$$

$$\frac{d^2\psi}{dx^2} = -a\psi(x)\left[2\delta(x) - a\right]$$

$$\langle H\rangle = \int_{-\infty}^{\infty} dx \left(\sqrt{a}\,e^{-a|x|}\right)^2 \left[\left(\frac{-\hbar^2}{2m}\right)\left(-a\left[2\delta(x)-a\right]\right) + \frac{1}{2}m\omega^2x^2\right]$$

$$= -2a\,a\left(\frac{-\hbar^2}{2m}\right) + \left(-\frac{\hbar^2}{2m}\right)a^2 + \frac{1}{2}m\omega^2 a\, 2\int_0^\infty dx\; x^2 e^{-2ax}$$

$$= \frac{\hbar^2a^2}{2m} + m\omega^2 a\left(\frac{1}{4}\frac{\partial^2}{\partial a^2}\right)\underbrace{\int_0^\infty dx\, e^{-2ax}}_{\frac{1}{2a}}$$

$$= \frac{\hbar^2 a^2}{2m} + \frac{m\omega^2 a}{4}\,\frac{(-1)(-2)}{2a^3}$$

$$\boxed{\langle H\rangle = \frac{\hbar^2a^2}{2m} + \frac{m\omega^2}{4a^2}}$$

$$\frac{d\langle H\rangle}{da^2} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{4a^4} = 0$$

$$\frac{m\omega^2}{4a^4} = \frac{\hbar^2}{2m} \Rightarrow a^4 = \frac{m^2\omega^2}{2\hbar^2} \Rightarrow a^2 = \frac{m\omega}{\sqrt{2}\hbar}$$

$$\langle H\rangle_{min} = \frac{\hbar^2}{2m}\,\frac{m\omega}{\sqrt{2}\hbar} + \frac{m\omega^2}{4}\,\frac{\sqrt{2}\hbar}{m\omega}$$

$$= \frac{\hbar\omega}{2\sqrt{2}} + \frac{\hbar\omega}{2\sqrt{2}} = \frac{\hbar\omega}{\sqrt{2}} = \sqrt{2}\,\frac{\hbar\omega}{2} \geq E_g = \frac{\hbar\omega}{2}$$

Corollary For any $|\psi\rangle$ st $\langle\psi_g|\psi\rangle = 0$

$\langle\psi|H|\psi\rangle \geq E_f$ = energy of the first excited state.

$|\psi_g^{trial}\rangle \Rightarrow$ minimize $\langle H\rangle \Rightarrow$ estimate for E_g^{est}, $|\psi_{g,est}\rangle$

find $|\psi_f^{trial}\rangle$ st $\langle\psi_{g,est}|\psi_f^{trial}\rangle = 0$

for H.O

$\psi_g = A e^{-ax^2}$

$\psi_f = B x e^{-ax^2}$ ⇐ HW

Ground state of He

$$H = \underbrace{-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)}_{H^0} \underbrace{+ \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{V_{ee}}$$

$$H = H^0 + V_{ee}$$

$$\psi_g = \psi_{100}(\vec{r}_1)\psi_{100}(\vec{r}_2) \Leftarrow$$

$$H^0_{Z=2}\psi_g = (H_1 + H_2)\psi_g$$

$$= H_1\psi_g + H_2\psi_g$$

$$E \sim \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{\frac{\hbar}{Z\alpha mc}} \propto Z^2$$

$$H_i = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{2e^2}{4\pi\varepsilon_0}\frac{1}{r_i}$$

$$H_i\psi_g = -4E_1\psi_g \quad E_1 = 13.6\,eV$$

$$H^0\psi_g = -8E_1\psi_g$$

$-8E_1 = -109\,eV$

$E_g = -78.976\,eV$ (exp)

$$\langle\psi_g|H|\psi_g\rangle = \langle\psi_g|H^0 + V_{ee}|\psi_g\rangle$$

$$= -8E_1 + \underline{\langle V_{ee}\rangle}$$

$$\psi_g = \psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}$$

$$V_{ee} = \left(\frac{e^2}{4\pi\varepsilon_0}\right)\left(\frac{8}{\pi a^3}\right)^2 \int \frac{e^{-4(r_1+r_2)/a}}{|\vec{r}_1-\vec{r}_2|}\, d^3r_1\, d^3r_2$$

$$|\vec{r}_1-\vec{r}_2| = \sqrt{(\vec{r}_1-\vec{r}_2)^2}$$

$$= \sqrt{r_1^2+r_2^2-2r_1r_2\cos\theta}$$

$$I = \int \frac{e^{-4r_2/a}}{|\vec{r}_1-\vec{r}_2|}\, d^3r_2 = \int_0^\infty dr_2\, r_2^2 \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi\; e^{-4r_2/a}\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)^{-1/2}$$

$$= 2\pi \int_0^\infty dr_2\, r_2^{2}\, e^{-4r_2/a}\, \frac{\left(r_1^2+r_2^2-2r_1r_2\cos\theta\right)^{1/2}}{(-r_1 \cancel{r_2})}\Bigg|_{\cos\theta=-1}^{\cos\theta=+1}$$

$$= -\frac{2\pi}{r_1}\int_0^\infty dr_2\, r_2 e^{-4r_2/a}\left[|r_1-r_2| - (r_1+r_2)\right]$$

$$= -\frac{2\pi}{r_1}\int_0^{r_1} dr_2 + \int_{r_1}^{\infty} dr_2\,(\ldots)$$

$$\langle V_{ee}\rangle = +\frac{5}{2}E_1 = 34\,\mathrm{eV}$$

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

$$\psi_g = \psi_{100}^{z=2}(\vec{r}_1)\,\psi_{100}^{z=2}(\vec{r}_2)$$

$$\left.\begin{aligned}H = -\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2\right) - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\end{aligned}\right\} H^\circ$$

$$+ \frac{(Z-2)e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right) + \underbrace{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|r_1-r_2|}}_{V_{ee}}$$

$$\psi_g = \frac{Z^3}{\pi a^3} e^{-Z(r_1+r_2)/a} \qquad a \to \frac{a}{Z}$$

$$H^\circ = -2Z^2E_1$$

$$\langle V_{ee}\rangle = \frac{5}{4} Z E_1$$

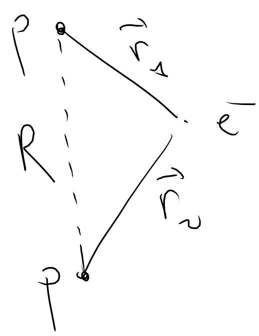
$$\langle H\rangle = -2Z^2E_1 + \frac{5}{4}ZE_1 + (Z-2)\frac{e^2}{4\pi\varepsilon_0} 2\left\langle\frac{1}{r}\right\rangle$$

$$\left\langle\frac{1}{r}\right\rangle = \frac{Z}{a}$$

$$\Rightarrow \frac{d\langle H\rangle}{dZ} = 0 \Rightarrow Z = \frac{27}{16} = 1.69$$

$$\langle H\rangle_{min} = -77.5\ \mathrm{eV}$$

<u>Hydrogen Ion</u> H_2^+



$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1}+\frac{1}{r_2}\right)$$

$$\psi = A\left(\psi_g(\vec{r}_1) + e^{i\phi}\psi_g(\vec{r}_2)\right)$$

LCAO: linear combination of atomic orbitals

$\langle \psi | H | \psi \rangle$

$$H = H_1 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_2} = H_2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_1} \Leftarrow$$

$$H_i = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_i} \quad ; \quad \psi_i = \psi_g(\vec{r}_i)$$

$$\langle \psi | H | \psi \rangle = A^2 \left(\langle \psi_1 + \psi_2 | H | \psi_1 + \psi_2 \rangle \right)$$

$$= A^2 \Big(\langle \psi_1 | H_1 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_2} | \psi_1 \rangle$$

$$+ \langle \psi_1 | H_1 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_2} | \psi_2 \rangle$$

$$+ \ldots \Big)$$

$$= A^2 \Big(-E_1 - \frac{e^2}{4\pi\varepsilon_0} \langle \psi_1 | \frac{1}{r_2} | \psi_1 \rangle$$

$$- E_1 \langle \psi_1 | \psi_2 \rangle - \frac{e^2}{4\pi\varepsilon_0} \langle \psi_1 | \frac{1}{r_2} | \psi_2 \rangle$$

$$- E_1 - \frac{e^2}{4\pi\varepsilon_0} \langle \psi_2 | \frac{1}{r_1} | \psi_1 \rangle$$

$$- E_1 \langle \psi_2 | \psi_1 \rangle - \frac{e^2}{4\pi\varepsilon_0} \langle \psi_2 | \frac{1}{r_1} | \psi_1 \rangle \Big)$$

includes proton proton potential

$$\langle H \rangle = E_1 F\left(\frac{R}{a}\right) \qquad x = \frac{R}{a}$$