Lecture 2
Variational Principle

For ground-state energy:
(there is also one in stat. mech. for free energy)

<u>want</u>: $H|E_0\rangle = E_0|E_0\rangle$

?

cannot solve exactly
but, note:

normalized arbitrary state

$$E[\psi] \equiv \langle\psi|\hat{H}|\psi\rangle \geq E_0$$

mean value of $\hat{H}$ in state $|\psi\rangle$
(functional of ψ)

<u>Why?</u>

$$E[\psi] = \sum_n E_n |\langle E_n|\psi\rangle|^2$$

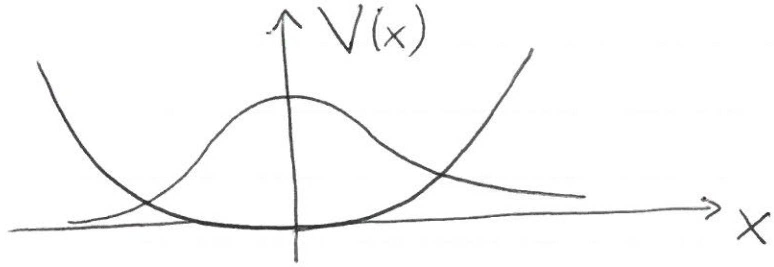
$$\geq E_0 \underbrace{\sum_n \langle\psi|E_n\rangle\langle E_n|\psi\rangle}_{=1} = E_0$$

$\Rightarrow E[\psi] \geq E_0$

<u>Useful:</u> pick <u>any</u> $|\psi\rangle$ (inspired by physical intuition) with some "optimization" parameters. Compute $\langle\psi|\hat{H}|\psi\rangle \Rightarrow$ upper-bound on E_0. Better optimize $|\psi\rangle$ lower upper-bound.

Examples:

1. $H = \frac{p^2}{2m} + \lambda x^4$



Difficult to solve corresp. S.Eqn. analytically but can estimate E_0 variationally.

Take $\Psi_\alpha(x) = e^{-\alpha x^2/2} \left(\frac{\alpha}{\pi}\right)^{1/4}$

$$\Rightarrow E[\alpha] = \int_{-\infty}^{\infty} dx \left(\frac{\alpha}{\pi}\right)^{1/2} e^{-\frac{\alpha x^2}{2}} \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \lambda x^4\right) e^{-\frac{\alpha x^2}{2}}$$

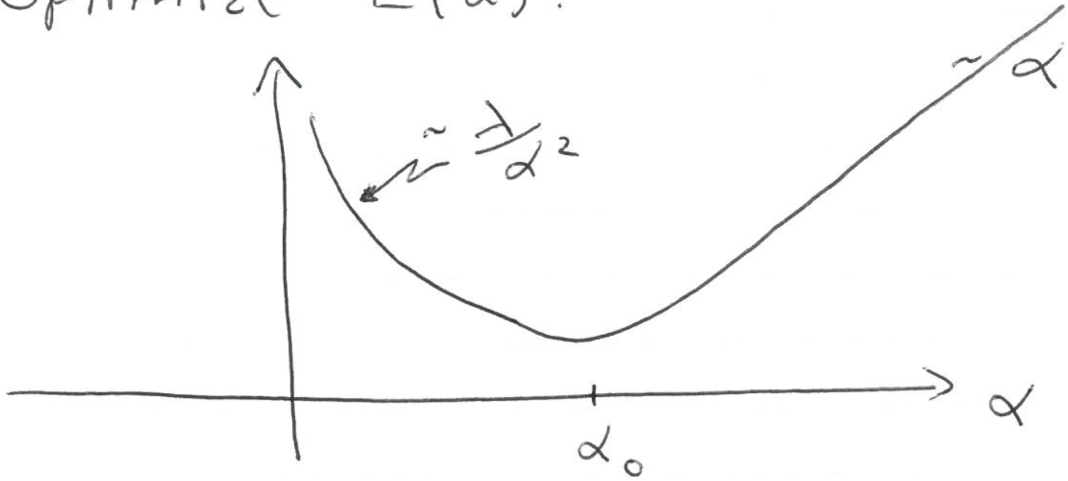
$$= \left(\frac{\alpha}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} dx\, e^{-\alpha x^2} \left(-\frac{\hbar^2 \alpha^2}{2m} x^2 + \frac{\hbar^2}{2m}\alpha + \lambda x^4\right)$$

$$\left[\begin{array}{l} \langle x^2 \rangle = \frac{1}{2\alpha}, \quad \langle x^4 \rangle = \left(\frac{1}{2\alpha}\right)^2 \cdot 3 \\ \langle x^{2n} \rangle = \langle x^2 \rangle^n (2n-1)!! \end{array} \right.$$

$$E(\alpha) = -\frac{\hbar^2 \alpha}{4m} + \frac{\hbar^2}{2m}\alpha + \lambda \frac{3}{4\alpha^2}$$

$$\boxed{E(\alpha) = \frac{\hbar^2 \alpha}{4m} + \frac{3}{4}\frac{\lambda}{\alpha^2}}$$

Optimize $E(\alpha)$:



$$\left.\frac{\partial E}{\partial \alpha}\right|_{\alpha_0} = \frac{\hbar^2}{4m} - \frac{3}{2}\frac{\lambda}{\alpha_0^3} = 0$$

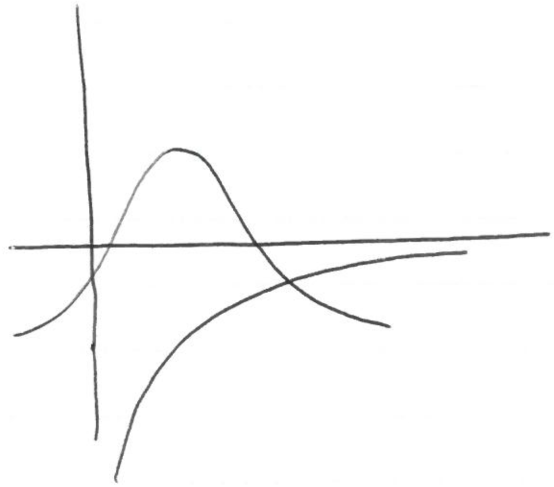
$$\Rightarrow \boxed{\alpha_0 = \left(\frac{6m\lambda}{\hbar^2}\right)^{1/3}}$$

$$\Rightarrow \boxed{E_{min} = E(\alpha_0) = \frac{3}{8}\left(\frac{6\hbar^4\lambda}{m^2}\right)^{1/3}}$$

Note: • $\hbar \to 0$ $E_m \to 0$, $\alpha_0 \to \infty \to$ classical

- Cannot tell how well (close to E_0) doing.
- would be exact for $V(x) = \lambda x^2$.

2. Hydrogen atom E_0 :



$$V(r) = -\frac{e^2}{r}$$

$$H = -\frac{\hbar^2}{2m}\left(\partial_r^2 + \frac{2}{r}\partial_r\right) - \frac{e^2}{r}$$

take $\psi_0(r) = N e^{-\alpha r^2}$

$$E(\alpha) = \int_0^\infty dr\, r^2 e^{-\alpha r^2} (H) e^{-\alpha r^2} \Big/ \int_0^\infty dr\, r^2 e^{-2\alpha r^2}$$

$$= \frac{3\hbar^2}{2m}\alpha - \left(\frac{2}{\pi}\right)^{1/2} 2 e^2 \alpha^{1/2}$$

$$\Rightarrow \alpha_0 = \left(\frac{me^2}{\hbar^2}\right)^2 \frac{8}{9\pi}$$

$$E(\alpha_0) = -\frac{me^4}{2\hbar^2}\frac{8}{3\pi} \simeq -0.85\,\mathrm{Ry}$$

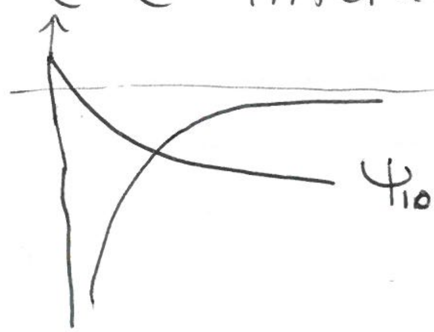
$$> -1\,\mathrm{Ry}.$$

(from e^{-r/r_0}).

3. He atom

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

without e-e interaction $\Rightarrow$ exact soln:



$$\psi^{0}_{gs.Z}(r_1, r_2) = \psi_{100}(r_1)\,\psi_{100}(r_2)\,\chi_{singlet}.$$

$$\psi_{100}(r) = \left(\frac{Z^3}{\pi a_0^3}\right)^{1/2} e^{-Zr/a_0} \qquad (Z=2)$$

$$\Rightarrow \psi^{0}_{gs}(r_1 r_2) = \left(\frac{8}{\pi a_0^3}\right) e^{-2(r_1+r_2)/a_0}\, \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

$$E_{nonint} \simeq -8\,Ry \simeq -108.8\,eV$$

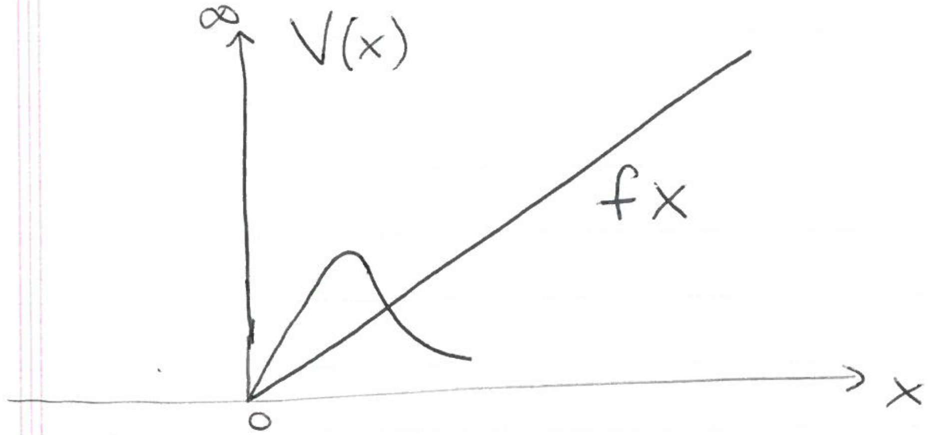
$$\text{experim.} \simeq -78.6\,eV.$$

Include $\frac{e^2}{r_{12}}$ & use $\psi^{0}_{gs\,Z}(r_1, r_2)$

as variational wavefnc. Optimize over Z. $\Rightarrow$ $E(Z) = -2Ry\left(4Z - Z^2 - \frac{5}{8}Z\right)$

$\Rightarrow$ $\underline{E(Z_0) \simeq -77.5\,eV}$!

4. Linear potential



$$V(x) = \begin{cases} fx , & x > 0 \\ \infty , & x \le 0 \end{cases}$$

variational $\psi(x) = x e^{-\alpha (x - x_0)^2/2}$

optimize over α, x_0 :

See hw 1.

<u>Note</u>: accuracy of variational method is due to fact that error in choosing ψ_{variat} (e.g $\frac{1}{10}$) affects the energy only <u>quadratically</u> in ψ error i.e 1%.

because $|\psi\rangle = |E_0\rangle + \frac{1}{10} |E_1\rangle + \dots$

$$E[\psi] = \langle E_0 | H | E_0 \rangle + \frac{1}{100} \langle E_1 | H | E_1 \rangle$$

$$\simeq E_0 + 0.01 E_1$$

- Application to excited states

Choose ψ_{var} to be orthogonal to ψ_m for $m<n$ will give

$E[\psi_{var}] \geq E_n$

Ex. $\rightarrow$ 1d want to approx E_1 for $V(x) = V(-x)$ $\Rightarrow$ pick $\psi_{var}(x)$ to be odd under parity

$\Rightarrow$ $E[\psi_{var}^{odd}] \geq E_1$

$\rightarrow$ To get estimate of E_2 take $|\psi_{var}\rangle$ orthogonal to $|E_0\rangle$, $|E_1\rangle$

$\rightarrow$ In 3d can choose different values of $l \neq 0$, $m \neq 0$.

$\Rightarrow$ $E[\psi] \geq E_{l=1}$