P423

Lecture 9:

Announce practice Midterm available online
- No credit
- Will be solved in Class Tuesday.
- Rec. Try it out before Tuesday.

The Variational principle

Suppose you want to calculate the ground state energy E_G of a system described by $\mathcal{H}$, but you are unable to solve the Schrödinger's eqn. The variational principle gets you an upper bound on E_G, which is often quite close to the exact value.

How it works? Pick any normalized $\psi(\vec{r})$; we claim that

$$E_G \leq \langle\psi|\mathcal{H}|\psi\rangle = \langle \mathcal{H}\rangle .$$

Proof: whatever $|\psi\rangle$ you pick can be expanded in terms of eigenstates of $\mathcal{H}$:

$$|\psi\rangle = \sum_n c_n |E_n\rangle \quad \text{where} \quad \mathcal{H}|E_n\rangle = E_n|E_n\rangle ,$$

with ψ normalized: $\langle\psi|\psi\rangle = \sum_n |c_n|^2 = 1$.

Now,

$$\langle\psi|\mathcal{H}|\psi\rangle = \sum_n c_n^* \langle E_n| \mathcal{H} \sum_{n'} c_{n'} |E_{n'}\rangle = \sum_{n,n'} c_n^* c_{n'} E_{n'} \underbrace{\langle E_n|E_{n'}\rangle}_{=\delta_{n,n'}}$$

$$= \sum_n |c_n|^2 E_n \geq \underbrace{\sum_n |c_n|^2}_{=1} E_G \quad (\text{because } E_n \geq E_G \text{ by def.})$$

$$\boxed{\langle\psi|\mathcal{H}|\psi\rangle \geq E_G}$$

Variational Method: Guess $\psi(\vec{r})$ in terms of a free parameter; minimize $\langle\psi|H|\psi\rangle$ wrt parameter.

Let's see if this works.

Example: 1d Harmonic oscillator

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

Try $\psi(x) = A e^{-bx^2}$

Normalize: $|A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}dx = 1 \Rightarrow |A|^2\sqrt{\frac{\pi}{2b}} = 1 \Rightarrow |A| = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}}.$

$$\langle H\rangle = \langle T\rangle + \langle V\rangle$$

$$\langle T\rangle = -\frac{\hbar^2}{2m}|A|^2\int_{-\infty}^{\infty}dx\; e^{-bx^2}\underbrace{\frac{d^2}{dx^2}\left(e^{-bx^2}\right)} = -\frac{\hbar^2}{2m}\sqrt{\frac{2b}{\pi}}\,(-2b)\int_{-\infty}^{\infty}dx\,(1-bx^2)\,e^{-2bx^2}$$

$$= \frac{d}{dx}\left(-2bx\,e^{-bx^2}\right)$$

$$= \left(-2b\,e^{-bx^2} + 4b^2x^2e^{-bx^2}\right)$$

$$= -2b\,(1-2bx^2)\,e^{-bx^2}$$

$$\langle T\rangle = \frac{\hbar^2 b}{m}\left(\frac{2b}{\pi}\right)^{\frac{1}{2}}\left[\left(\frac{\pi}{2b}\right)^{\frac{1}{2}} \underbrace{-2b\times 2\sqrt{\pi}\times 2\left[\frac{1}{2(2b)^{\frac{1}{2}}}\right]^3}_{=\frac{2b}{2}\frac{\sqrt{\pi}}{\sqrt{2b}}\frac{1}{(2b)} = \left(\frac{\pi}{2b}\right)^{\frac{1}{2}}\frac{1}{2}}\right] = \frac{\hbar^2 b}{m}\left(\frac{2b}{\pi}\right)^{\frac{1}{2}}\left(\frac{\pi}{2b}\right)^{\frac{1}{2}}\frac{1}{2} = \frac{\hbar^2}{2m}b$$

$$\langle V\rangle = \frac{1}{2}m\omega^2|A|^2\int_{-\infty}^{\infty}dx\; e^{-2bx^2}x^2 = \frac{1}{2}m\omega^2\left(\frac{2b}{\cancel{\pi}}\right)^{\frac{1}{2}} 2\cancel{\sqrt{\pi}}\,\frac{2}{8}\,\frac{1}{\cancel{(2b)^{\frac{1}{2}}}}\,\frac{1}{2b} = \frac{1}{8}m\omega^2\frac{1}{b}$$

$$\langle H\rangle = \left(\frac{\hbar^2}{2m}\right)b + \left(\frac{m\omega^2}{8}\right)\frac{1}{b}$$

$$\frac{d\langle H\rangle}{db} = 0 \Rightarrow \left(\frac{\hbar^2}{m}\right) - \frac{m\omega^2}{8}\frac{1}{b^2} = 0 \Rightarrow b^2 = \frac{m\omega^2}{8}\frac{2m}{\hbar^2} = \frac{1}{4}\frac{m^2\omega^2}{\hbar^2}$$

$$\Rightarrow \boxed{b = \frac{1}{2}\frac{m\omega}{\hbar}}.$$

Plug back into $\langle H\rangle_{min} = \frac{\hbar^2}{m}b + \frac{m\omega^2}{8}\frac{1}{b} = \frac{\hbar^{\cancel{2}}}{2\cancel{m}}\frac{1}{2}\frac{\cancel{m}\omega}{\cancel{\hbar}} + \frac{\cancel{m}\omega^{\cancel{2}}}{8}\frac{2\hbar}{\cancel{m}\cancel{\omega}} = \frac{1}{4}\hbar\omega + \frac{1}{4}\hbar\omega$

$= \frac{1}{2}\hbar\omega$ //

$\Rightarrow$ Exact energy because we guessed the exact wave fn!

<u>Example</u>: Delta fn potential

$$H = -\frac{\hbar^2}{m}\frac{d^2}{dx^2} - \alpha\,\delta(x) \qquad \text{we know exact } E_G = -\frac{1}{2}\frac{m\alpha^2}{\hbar^2}.$$

Like before, let's guess $\psi(x) = \left(\frac{2b}{\pi}\right)^{\frac{1}{4}} e^{-bx^2}$:

$$\langle T\rangle = \frac{\hbar^2}{m} b \quad \text{and } \langle V\rangle = -\alpha\int_{-\infty}^{\infty}\left(\frac{2b}{\pi}\right)^{\frac{1}{2}} e^{-2bx^2}\delta(x) = -\alpha\left(\frac{2b}{\pi}\right)^{\frac{1}{2}}$$

$$\langle H\rangle = \frac{\hbar^2}{m}b - \alpha\sqrt{\frac{2}{\pi}}\sqrt{b}$$

$$\frac{d}{db}\langle H\rangle = 0 \Rightarrow \frac{\hbar^2}{2m} - \alpha\sqrt{\frac{2}{\pi}}\frac{1}{2}\frac{1}{\sqrt{b}} = 0 \Rightarrow \sqrt{b} = \frac{\cancel{2}m}{\hbar^2}\alpha\sqrt{\frac{2}{\pi}}\frac{1}{\cancel{2}} = \sqrt{\frac{2}{\pi}}\frac{m\alpha}{\hbar^2}$$

$$\Rightarrow \langle H\rangle_{min} = \frac{\hbar^2}{2m}\frac{2}{\pi}\frac{m^2\alpha^2}{\hbar^4} - \alpha\sqrt{\frac{2}{\pi}}\sqrt{\frac{2}{\pi}}\frac{m\alpha}{\hbar^2} = \frac{2}{\pi}\frac{m\alpha^2}{2\hbar^2} - \frac{2}{\pi}\frac{m\alpha^2}{\hbar^2} = \underbrace{\left(\frac{2}{\pi}\right)}_{\approx 0.64}\underbrace{\left(-\frac{m\alpha^2}{2\hbar^2}\right)}_{=E_G}$$

This is greater than E_G, as expected from our theorem!

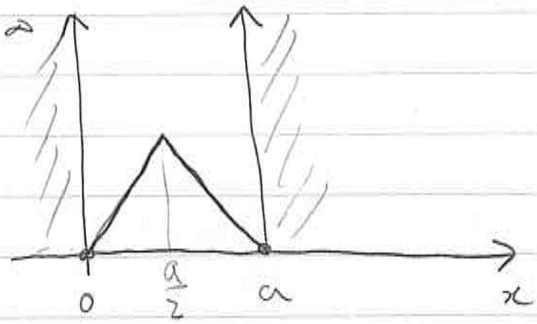
Of course, if we guessed $\psi \propto e^{-a|x|}$ instead we would get the exact answer.

Example: How to deal with discontinuous trial fncs

Triangular trial wave fnc for the infinite square well

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < a \\ \infty & \text{for } x \leq 0 \text{ and } x \geq a . \end{cases}$$

Trial fnc: $$\psi(x) = \begin{cases} Ax & \text{for } x \in [0, \frac{a}{2}) \\ A(a-x) & \text{for } x \in [\frac{a}{2}, a] \\ 0 & \text{otherwise} \end{cases}$$

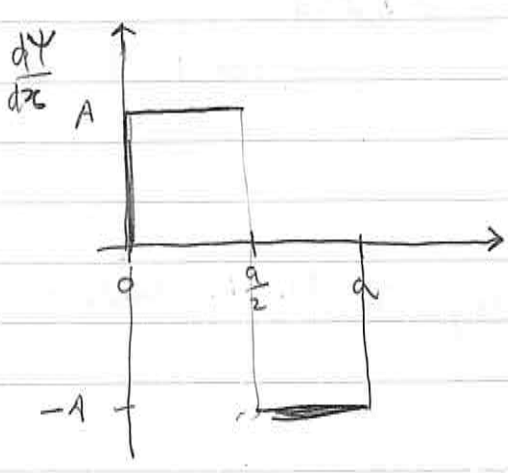


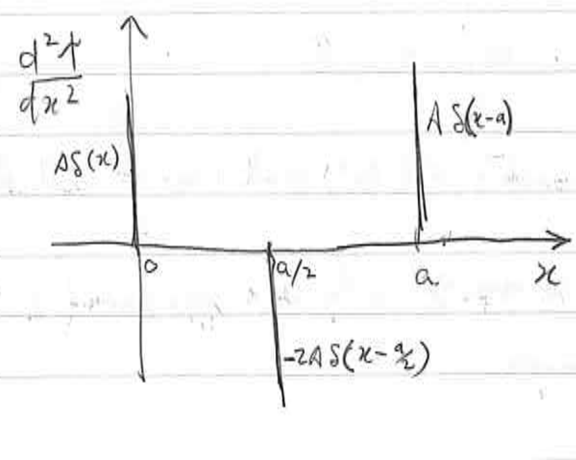
Note that $\psi(x)$ is continuous and satisfies the boundary conditions.

Determine A using normalization:

$$\int_0^a dx\, |\psi|^2 = A^2 \left[\int_0^{\frac{a}{2}} dx\, x^2 + \int_{\frac{a}{2}}^{a} dx\, (a-x)^2 \right] = A^2 \left[\frac{x^3}{3} \Big|_0^{a/2} - \frac{1}{3}(a-x)^3 \Big|_{a/2}^{a} \right]$$

$$= A^2 \left[\frac{1}{3}\left(\frac{a}{2}\right)^3 + \frac{1}{3}\left(\frac{a}{2}\right)^3 \right] = A^2 \frac{2}{3}\left(\frac{a}{2}\right)^3 = 1 \Rightarrow \boxed{A = \sqrt{\frac{3}{2}}\left(\frac{2}{a}\right)^{3/2}} = \boxed{\frac{2}{a}\sqrt{\frac{3}{a}}}$$





$$\frac{\left(\frac{d\psi}{dx}\right)(x+\delta) - \frac{d\psi}{dx}(x)}{\delta} =$$

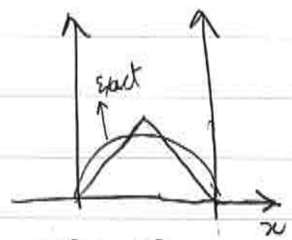
$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}$$

$$\Rightarrow \langle \hat{H} \rangle = -\frac{\hbar^2}{2m}\int_0^a dx\, \psi\frac{d^2\psi}{dx^2} = -\frac{\hbar^2}{2m}\int_0^a dx\, \psi\left[A\delta(x) - 2A\delta\left(x-\frac{a}{2}\right) + A\delta(x-a)\right]$$

$$= -\frac{\hbar^2}{2m}\left[A\cancelto{0}{\psi(0)} - 2A\psi\left(\frac{a}{2}\right) + A\cancelto{0}{\psi(a)}\right]$$

$$= \frac{\hbar^2}{m}A\left(\frac{Aa}{2}\right) = \frac{\hbar^2}{2m}a\,\frac{12}{a^3} = \frac{6\hbar^2}{m}\frac{1}{a^2}$$

Compare to exact:



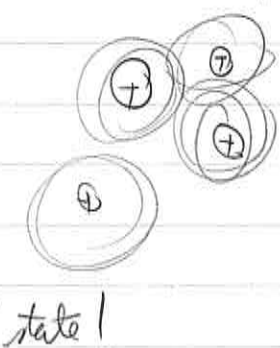
$\underline{n=1}$:

$$E_0^{\text{Exact}} = \frac{\hbar^2}{2m}\left(\frac{\pi}{a}\right)^2(1)^2 = \underbrace{\left(\frac{\pi^2}{2}\right)}_{\approx 4.9}\frac{\hbar^2}{ma^2}$$

Not too far from 6!

Variational principle is very useful for molecules.
In quantum chemistry, people often represent wave fns as a sum of Gaussians

$$\psi_0(\vec{r}) = \sum_i A_i\, e^{-\frac{(\vec{r}-\vec{R}_i)^2}{2\sigma_i^2}}$$



with many "fitting parameters" A_i, σ_i.

$\Rightarrow$ Minimization of all parameters gets you quite close to exact state!

Of course, you always get only an upper bound for the energy. That's the weakness of the variational principle.