PHYS 4410

Quantum Mechanics 2

Spring 2023

Lecture 20

The variational principle

March 8

$\boxed{1}$ Most H cannot be diagonalized exactly. E.g.

$$H = \underbrace{\left[\frac{\vec{p}_1^{\,2}}{2m} - \frac{2e^2}{4\pi\varepsilon_0|\vec{r}_1|}\right] + \left[\frac{\vec{p}_2^{\,2}}{2m} - \frac{2e^2}{4\pi\varepsilon_0|\vec{r}_2|}\right]}_{\text{exactly solved}} + \underbrace{\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|}}_{\text{"small" perturbation.}}$$

In this class:

1) variational principle: "good guess"
   - quantum chemistry
   - numerical methods (HW7 Prob 4)

2) perturbation theory
   - particle physics ...

3) WKB/ semiclassical

2 The variational principle:

For any state $|\psi\rangle$: $\dfrac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0.$

Why? Assume $\langle\psi|\psi\rangle = 1$:

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n |E_n\rangle \qquad \underbrace{E_0}_{\text{g.s}} \leq E_1 \leq E_2 \leq \cdots$$

$$\langle\psi|H|\psi\rangle = \sum_{n=0}^{\infty} |c_n|^2 E_n = \sum_{n=0}^{\infty} |c_n|^2 \left[E_0 + (E_n - E_0)\right]$$

$$= \underbrace{E_0}_{\langle\psi|\psi\rangle = \sum |c_n|^2 = 1} + \underbrace{\sum_{n=0}^{\infty} \underbrace{|c_n|^2}_{\geq 0} \cdot \underbrace{(E_n - E_0)}_{\geq 0}}_{\geq 0}$$

Thus: $\boxed{\langle\psi|H|\psi\rangle \geq E_0}$

$\boxed{3}$ Example: $H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$. $\quad \underbrace{\psi(x;\sigma) = \frac{e^{-x^2/4\sigma^2}}{(2\pi\sigma^2)^{1/4}}}_{|\psi_{trial}(\sigma)\rangle}$

Variational method: guess @ g.s energy.

$$\langle \psi_{trial}(\sigma) | H | \psi_{trial}(\sigma)\rangle = E_0(\sigma) \geq E_{0,true}$$

Pick value of σ minimizes $E_0(\sigma)$.

$$\underline{\langle \psi | H | \psi \rangle} = \frac{1}{2m}\left(\frac{\hbar}{2\sigma}\right)^2 + \frac{1}{2} m\omega^2\sigma^2$$

Treat σ as continuous parameter... minimize $\langle H \rangle = E_0(\sigma)$:

$$\frac{dE_0}{d\sigma} = -\frac{\hbar^2}{4m\sigma^3} + m\omega^2\sigma = 0 \quad \text{or} \quad \underline{\sigma = \sqrt{\frac{\hbar}{2m\omega}}}$$

$$\langle \psi | H | \psi \rangle = \frac{\hbar^2}{8m} \frac{1}{\frac{\hbar}{2m\omega}} + \frac{m\omega^2}{2} \frac{\hbar}{2m\omega} = \frac{1}{2}\hbar\omega$$

exact g.s. energy.

Why? True g.s $\psi_0(x)$ was a Gaussian.

(Generally won't happen).

$\boxed{4}$ Suppose particle in 1d: $\quad H = \frac{p^2}{2m} + V(x)$

$$\langle\psi|H|\psi\rangle = \int_{-\infty}^{\infty} dx\, \psi^*(x)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi(x)$$

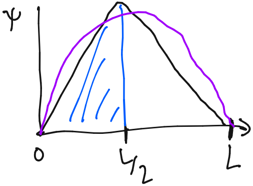
$$= \int_{-\infty}^{\infty} dx\, V(x)|\psi|^2 - \frac{\hbar^2}{2m}\left(\cancelto{0}{\left[\psi^*\frac{d\psi}{dx}\right]_{-\infty}^{\infty}} - \int_{-\infty}^{\infty} dx\, \frac{d\psi^*}{dx}\frac{d\psi}{dx}\right)$$

$$= \int_{-\infty}^{\infty} dx\left[V(x)|\psi|^2 + \frac{\hbar^2}{2m}\left|\frac{d\psi}{dx}\right|^2\right]$$

Generalize to higher dimensions:

$$\langle\psi|H|\psi\rangle = \int dV\left[V(\vec{r})|\psi(\vec{r})|^2 + \frac{\hbar^2}{2m}\overbrace{|\nabla\psi|^2}^{\nabla\psi\cdot\nabla\psi^*}\right]$$

5 Example: particle in inf. sq. well.



$$\psi(x) = \begin{cases} Ax & 0<x<L/2 \\ A(L-x) & L/2<x<L \\ 0 & \text{otherwise} \end{cases}$$

Step 1: Normalize. (Find A).

$$1 = \int_0^L dx\, |\psi|^2 = 2\int_0^{L/2} dx\, |\psi|^2 = 2\int_0^{L/2} dx\, A^2 x^2 = 2A^2 \cdot \underbrace{\left.\frac{x^3}{3}\right|_0^{L/2}}_{L^3/24}$$

$$A = \sqrt{\frac{12}{L^3}}$$

Step 2: $$\langle\psi|H|\psi\rangle = \int_0^L dx\, \frac{\hbar^2}{2m}\left|\frac{d\psi}{dx}\right|^2 = 2\int_0^{L/2} dx\, \frac{\hbar^2}{2m} A^2 = 2\cdot\frac{\hbar^2}{2m}\cdot\frac{12}{L^3}\cdot\frac{L}{2}$$

$$= \frac{6\hbar^2}{mL^2} > \text{ground state energy} = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2.$$

What $\psi(x)$ would minimize $\langle H\rangle$? $\psi(x) = \sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$.