L72-Variational Principle

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* a very powerful & simple way to solve for the ground state (g.s.) energy and wave function:

- Parametrize $\psi_{gs}(x; \alpha, \beta \ldots)$ and minimize $E_{g.s.}(\alpha, \beta, \ldots) = \langle \psi | \mathcal{H} | \psi \rangle$

* principle: $E_{gs} \leq \langle \psi | \mathcal{H} | \psi \rangle \equiv \langle \mathcal{H} \rangle$ for any $|\psi\rangle$
  thus the minimum $\langle \mathcal{H} \rangle$ will be closest to E_{gs}.

proof: let $\mathcal{H}|\phi_n\rangle = E_n|\phi_n\rangle$, a complete set, then

$|\psi\rangle = \sum_n c_n |\phi_n\rangle$, where $\langle \psi | \psi \rangle = \sum_n |c_n|^2 = 1$. Thus,

$$\langle \psi | \mathcal{H} | \psi \rangle = \langle \psi | \mathcal{H} \sum_n c_n |\phi_n\rangle = \sum_n \langle \psi | E_n c_n | \phi_n \rangle = \sum_n c_n^* E_n c_n$$

$$\geq \sum_n E_{gs} |c_n|^2 = E_{gs}$$ since $E_n \geq E_{gs}$ by defn.

* Variational Principle VS. Perturbation theory

— both can start with a ψ_n^0 basis —

— both are better at energies than eigenfunctions —

Variational Principle	Perturbation theory
- any parametrization $\psi(x; \alpha, \beta \ldots)$	- separate $\mathcal{H} = \mathcal{H}^0 + \mathcal{H}'$, calculate $\mathcal{H}^0|\psi_n^0\rangle = E_n^0|\psi_n^0\rangle$
- single-step [multiparameter] minimization	- exact formulas for order by order refinement
- possible, but difficult to get excited states	- systematic calculation of all states.

* Example 1: ground state of 1-d harmonic oscillator:

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

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let $\psi(x) = Ae^{-bx^2}$ (note: NO basis functions!)

$$\int_{-\infty}^{\infty}|\psi|^2dx = \frac{|A|^2}{\sqrt{2b}}\int_{-\infty}^{\infty}e^{-2bx^2}d\sqrt{2bx^2} = |A|^2\sqrt{\frac{\pi}{2b}} = 1 \qquad A = \left(\frac{2b}{\pi}\right)^{1/4}$$

using: $\int_{-\infty}^{\infty}e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$, $-\frac{d}{da}$: $\int +x^2e^{-ax^2}dx = +\frac{1}{2}\sqrt{\frac{\pi}{a^3}}$

$$\langle T\rangle = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\psi^*\frac{d^2}{dx^2}\psi\,dx = \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left|\frac{d\psi}{dx}\right|^2dx = \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left|-2bx\,Ae^{-bx^2}\right|^2dx$$

$$= \frac{\hbar^2}{2m}\cdot 4b^2\cdot\frac{1}{2}\frac{1}{2b} = \frac{\hbar^2 b}{2m}$$

* note similarities with finite element (Galerkin) method:

$$\int u_i\nabla^2V\,d\tau = -\int\nabla u_i\cdot\nabla u_j\;V_j = -L_{ij}V_j$$

$$\langle V\rangle = \frac{1}{2}m\omega^2\int_{-\infty}^{\infty}\psi^*x^2\psi = \frac{1}{2}m\omega^2\int_{-\infty}^{\infty}|x^2Ae^{-bx^2}|^2dx = \frac{1}{2}m\omega^2\cdot\frac{1}{2}\frac{1}{2b} = \frac{m\omega^2}{8b}$$

$$\frac{d}{db}\mathcal{H} = \frac{d}{db}\left(\frac{\hbar^2b}{2m} + \frac{m\omega^2}{8b}\right) = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \qquad b = \frac{m\omega}{2\hbar}$$

$$\psi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}e^{-\frac{m\omega x}{2\hbar}} \qquad E_0 = \frac{1}{2}\hbar\omega \qquad \text{exact!}$$

* Example 2: $\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\,\delta(x)$ note: $E_{gs} = -\frac{m\alpha^2}{2\hbar^2}$

same trial function: $\psi = Ae^{-bx^2}$ $\langle T\rangle = \frac{\hbar^2b}{2m}$ as before:

$$\langle V\rangle = -\alpha|A|^2\int_{-\infty}^{\infty}e^{-2bx^2}\delta(x)\,dx = -\alpha|A|^2\cdot e^0 = -\alpha\sqrt{\frac{2b}{\pi}}$$

$$\frac{d}{db}\langle\mathcal{H}\rangle = \frac{d}{db}\left(\frac{\hbar^2b}{2m} - \alpha\sqrt{\frac{2b}{\pi}}\right) = \frac{\hbar^2}{2m} - \alpha\cdot\frac{1}{2}\sqrt{\frac{2}{\pi b}} = 0 \qquad b = \frac{2m^2\alpha^2}{\pi\hbar^4}$$

$$E_{gs} = \langle\mathcal{H}\rangle_{min} = \frac{\hbar^2}{2m}\frac{2m^2\alpha^2}{\pi\hbar^4} - \alpha\sqrt{\frac{2}{\pi}\frac{2m^2\alpha^2}{\pi\hbar^4}} = \frac{m\alpha^2}{\pi\hbar^2} - \frac{2m\alpha^2}{\pi\hbar^2} = -\frac{m\alpha^2}{\pi\hbar^2} \qquad \frac{1}{\pi}\text{ vs. }\frac{1}{2}$$

– we could recover exact solution with suitable (exact!) parametrization:

let $\psi = Ae^{-b|x|}$ $\quad \langle\psi|\psi\rangle = \int_{-\infty}^{\infty} |A|^2 e^{-b|x|} dx = \frac{2|A|^2}{b}\int_0^{\infty} e^{-bx} d(bx) = \frac{2|A|^2}{b} = 1$

$$\langle T\rangle = \frac{-\hbar^2}{2m}\int_{-\infty}^{\infty}\psi^* \frac{d^2}{dx^2}\psi\, dx = \frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\left|\frac{d\psi}{dx}\right|^2 dx = \frac{\hbar^2}{2m}\cdot\int_{-\infty}^{\infty}(-b\cdot\psi)^2 dx = \frac{\hbar^2 b^2}{2m}$$

$$\langle V\rangle = -\alpha\int_{-\infty}^{\infty}|\psi|^2\delta(x)\,dx = -\alpha|\psi(0)|^2 = -\alpha|A|^2 = -\frac{\alpha b}{2}$$

$$\frac{d}{db}\langle H\rangle = \frac{d}{db}\left(\frac{\hbar^2 b^2}{2m} - \frac{\alpha b}{2}\right) = 0 \qquad b = \frac{\alpha m}{\hbar^2} \qquad E_{gs} = -\frac{m\alpha^2}{2\hbar^2}$$