Variational Principle (back to time-independent H)

- Estimating groundstate energy:
  - We've been using perturbation theory to estimate energy eigenvalues for Hamiltonians we can't solve exactly.
    Here's another approach that even works when H is not "close to solvable."
  - Statement: for <u>any</u> normalized wave function $|\psi\rangle$, the ground state energy E_{gs} satisfies

$$E_{gs} \leq \langle\psi|H|\psi\rangle$$

Proof:

- Write $|\psi\rangle = \sum_n c_n |E_n\rangle$ where $|E_n\rangle$ are energy eigenstates.
- By normalization $1 = \langle\psi|\psi\rangle = \sum_n |c_n|^2$ ($|E_n\rangle$ are orthonormal)
- Then the expectation value

$$\langle\psi|H|\psi\rangle = \sum_{n,m} c_m^* c_n \langle E_m|H|E_n\rangle = \sum_n |c_n|^2 E_n \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

- Examples:
  - A simple one: A delta-function potential $H = \frac{p^2}{2m} - \alpha\delta(x)$
    - Exact groundstate energy $E_{gs} = \frac{-m\alpha^2}{2\hbar^2}$
    - Trial wave function: use a Gaussian, since it's smooth + easy

$$\langle x|\psi\rangle = \psi(x) = \left(\frac{2b}{\pi}\right)^{1/4} e^{-bx^2}$$

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$$\left\langle \frac{p^2}{2m} \right\rangle = \frac{-\hbar^2}{2m}\sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} dx\, e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right)$$

$$= \frac{-\hbar^2}{2m}\sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} dx\, e^{-2bx^2}\left(4b^2x^2 - 2b\right) = \frac{\hbar^2 b}{2m}$$

- $\langle V \rangle = -\alpha \langle \delta(x) \rangle = -\alpha \sqrt{\frac{2b}{\pi}} \int_{-\infty}^{\infty} dx\, \delta(x) e^{-2bx^2} = -\alpha \sqrt{\frac{2b}{\pi}}$
- So $E_{gs} \leq \min \left(\frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}} \right)$

The minimal value is at $\frac{\hbar^2}{2m} - \frac{\alpha}{2}\sqrt{\frac{2}{\pi b}} = 0$ or $b = \frac{2m^2\alpha^2}{\pi \hbar^4}$

and $E_{gs} = -\frac{m\alpha^2}{2\hbar^2} \leq -\frac{m\alpha^2}{\pi\hbar^2}$. This is true, and the estimate is close.

— Helium Atom.

- Remember $H = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\vec{x}_1 - \vec{x}_2|} \right)$ for e^- at $\vec{x}_1, \vec{x}_2$.

On a HW, we treated this by letting $|\psi_{gs}\rangle \simeq |\psi_{100}\rangle |\psi_{100}\rangle$ and assuming electron screening is a perturbation. But that's not too valid

- But we got a decent result b/c that wavefunction is a decent trial wavefunction. Improve it by letting

$$\psi(\vec{x}_1, \vec{x}_2) = \frac{Z^3}{\pi a^3} e^{-Z(r_1 + r_2)/a}$$

where $Z \leq 2$ represents screening of the nucleus by other electron.

- After some algebra

$$\langle H \rangle = \left(\frac{27}{4} Z - 2Z^2 \right) E_{hyd}$$

Minimized at $Z = \frac{27}{16} \simeq 1.69$, $E_{gs} \lesssim \langle H \rangle = -77.5\,eV$

Experimental value is $E_{gs} \simeq -79\,eV$. Not bad.