Variational Principle

- Estimating ground state energy (time-dependent H again)
  - We have used perturbation theory to estimate energy eigenvalues for Hamiltonians we can't solve exactly. This is another approach that can work even when H is not "close" to solvable
  - Statement: The ground state energy E_{gs} satisfies
$$E_{gs} \leq \langle \psi | H | \psi \rangle$$
    for any normalized state $|\psi\rangle$. (Called a trial state)

    Proof:
    - Write $|\psi\rangle = \sum_n c_n |E_n\rangle$ for energy eigenstates $|E_n\rangle$
    - Since $|E_n\rangle$ are orthonormal,
$$\langle \psi | \psi \rangle = \sum_n |c_n|^2 = 1$$
    - Then
$$\langle \psi | H | \psi \rangle = \sum_{n,m} c_m^* c_n \langle E_m | H | E_n \rangle = \sum_n E_n |c_n|^2$$
    But since E_{gs} is the smallest energy eigvalue,
$$\langle \psi | H | \psi \rangle \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$
  - This is just a limit. But if we find better and better limits by choosing $|\psi\rangle$ differently, we can keep getting closer to the correct ground state energy
    - If you know the ground state $|\psi_{gs}\rangle$, you can make sure the trial state is $\perp$. Then you can estimate the 1st excited state energy, etc
    - Can have a free parameter and minimize over it.
- Examples
  - One-dimensional case: Delta-function potential
$$H = p^2/2m - \alpha \delta(x) \quad \text{for } \alpha > 0$$
    - Have already solved this exactly
$$E_{gs} = -m\alpha^2/2\hbar^2$$
    - Take a Gaussian as a smooth trial wavefunction

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

- The kinetic energy expectation is

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

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

This is useful in general b/c a Gaussian is a simple trial wave function in many 3D cases

- Potential

$$\langle V\rangle = -\alpha\langle\delta(x)\rangle = -\alpha\sqrt{\frac{2b}{\pi}}\int dx\,\delta(x)e^{-2bx^2} = -\alpha\sqrt{2b/\pi}$$

- Then

$$E_{gs} \leq \min\left(\hbar^2 b/2m - \alpha\sqrt{2b/\pi}\right)$$

+ Minimal value is $\Rightarrow$ $\hbar^2/2m - \alpha/2\sqrt{2/\pi b} = 0$

$\Rightarrow$ $b = 2m^2\alpha^2/\pi\hbar^4$

+ so $E_{gs} = -m\alpha^2/2\hbar^2 \leq -m\alpha^2/\pi\hbar^2$.

This is true, and the estimate is close.

— Helium Atom

- From 3301 remember

$$H = \vec{P}_1^2/2m + \vec{P}_2^2/2m - e^2/4\pi\epsilon_0\left(2/r_1 + 2/r_2 - 1/|\vec{x}_1 - \vec{x}_2|\right)$$

for electrons at $\vec{x}_1$ and $\vec{x}_2$ ↑ repulsion

+ In perturbation theory, treat the Coulomb repulsion as perturbation, so: $E_{gs}' \approx \langle\psi|H_1|\psi\rangle$

where $|\psi\rangle = |\psi_{100}\rangle|\psi_{100}\rangle$ in terms of hydrogen-like states.

+ This is not a very valid approximation, but the E_{gs} estimate is not so terrible b/c it's an ok trial state

- We can improve the trial wave function by incorporating screening of the nuclear charge by the other electron.

Take

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

for $Z < 2$.

- After some algebra, (see text) $\langle H\rangle = \left(\frac{27}{4}Z - 2Z^2\right)E_{hyd}$
- Minimized at $Z = 27/16 \approx 1.69$, $E_{gs} \lesssim -77.5\,eV$

Experimental value is $E_{gs} \approx -79\,eV$.