Brief introduction of variational methods

Strength: can calculate ground-state energy for system without known solutions

Weakness: need a good guess for the ground-state wave-function $|\tilde{0}\rangle$

Then we can calculate

$$\bar{H} = \frac{1}{\langle\tilde{0}|\tilde{0}\rangle} \langle\tilde{0}|\hat{H}|\tilde{0}\rangle$$

and $\hat{H} \geq E_0$ (theorem)

Proof: if $\{|k\rangle\}$ is the set of true eigenfunctions then

$$|\tilde{0}\rangle = \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle$$

$$\hat{H}|\tilde{0}\rangle = \sum_{k=0}^{\infty} E_k |k\rangle\langle k|\tilde{0}\rangle \geq E_0 \sum_{k=0}^{\infty} |k\rangle\langle k|\tilde{0}\rangle = E_0 |\tilde{0}\rangle$$

thus $\langle\tilde{0}|\hat{H}|\tilde{0}\rangle \geq E_0 \langle\tilde{0}|\tilde{0}\rangle$ upper bound on ground-state eigen energy

Also, $|\tilde{0}\rangle$ is a good approximation if for $|\tilde{0}\rangle \to |\tilde{0}\rangle + \delta|\tilde{0}\rangle$ $\delta\bar{H} = 0$ stable

In practice $\langle x|\tilde{0}\rangle = f(x; \lambda_1, \lambda_2 \dots)$

Then we need to minimize $\bar{H}$ with respect to the parameters λ_i

$$\frac{\partial \bar{H}}{\partial \lambda_1} = 0 \qquad \frac{\partial \bar{H}}{\partial \lambda_2} = 0$$

Fundamental limitation: even a rather poor trial function can yeild a close upper bound on the experimentally determined ground state energy

$$\langle 0|0\rangle = \langle k|k\rangle = 1$$

$$|\tilde{0}\rangle = |0\rangle + \delta|k\rangle \qquad \text{such that } \langle 0|k\rangle = 0$$

$$\langle\tilde{0}|\hat{H}|\tilde{0}\rangle = \left(\langle 0| + \delta^*\langle k|\right)\hat{H}\left(|0\rangle + \delta|k\rangle\right) =$$

$$= \langle 0|\hat{H}|0\rangle + \delta^*\underbrace{\langle k|\hat{H}|0\rangle}_{E_k \cancel{\langle k|0\rangle} = 0} + \delta\underbrace{\langle 0|\hat{H}|k\rangle}_{E_0 \cancel{\langle 0|k\rangle} = 0} + \delta^2\langle k|\hat{H}|k\rangle$$

$$\langle\tilde{0}|\hat{H}|\tilde{0}\rangle = \bar{H} = E_0 + \underbrace{\delta^2\langle k|\hat{H}|k\rangle}_{\text{error in the energy estimate}}$$

The first-order error in the trial wave function leads to the second-order error in the estimated ground-state energy.

Example 1: estimate the ground state energy of the 1D rigid box

$$V = \begin{cases} 0 & |x| < a \\ \infty & |x| > a \end{cases}$$

We know exact solution $E_0 = \frac{\hbar^2 \pi^2}{8ma^2}$

Need to guess the wavefunction

$$\langle x | \tilde{0} \rangle = a^2 - x^2$$

$$\langle \tilde{0} | \hat{H} | \tilde{0} \rangle = \langle \tilde{0} | \frac{\hat{p}^2}{2m} | \tilde{0} \rangle = \left(-\frac{\hbar^2}{2m}\right) \int_{-a}^{a} (a^2 - x^2) \frac{d^2}{dx^2} (a^2 - x^2) \, dx$$

$$\langle \tilde{0} | \tilde{0} \rangle = \int_{-a}^{a} (a^2 - x^2)^2 \, dx$$

$$E_0 \leq \bar{H} = \frac{\langle \tilde{0} | \hat{H} | \tilde{0} \rangle}{\langle \tilde{0} | \tilde{0} \rangle} = \frac{10}{\pi^2} \left(\frac{\pi^2 \hbar^2}{8ma^2} \right) \simeq 1.0132 \, E_0$$

1.3% error

Better trial function

$$\langle x | \tilde{0} \rangle = |a|^\lambda - |x|^\lambda$$

$$\bar{H} = \underbrace{\frac{(\lambda+1)(2\lambda+1)}{2\lambda - 1}}_{\text{minimize}} \left(\frac{\hbar^2}{4ma} \right)$$

$$\lambda_{min} = \frac{1+\sqrt{6}}{2}$$

$$E_0 \leq \bar{H}_{min} = \left(\frac{5 + 2\sqrt{6}}{\pi^2} \right) E_0 \simeq 1.003 \, E_0$$

0.3% error

How good is our guessed wave-function?

$$\bar{H}_{min} = \langle \tilde{0} | \hat{H}_{min} | \tilde{0} \rangle = \sum_{k=0}^{\infty} |\langle k | \tilde{0} \rangle|^2 E_k = |\langle 0 | \tilde{0} \rangle|^2 E_0 +$$

$$+ \sum_{k=1}^{\infty} |\langle k | \tilde{0} \rangle|^2 E_k \geq |\langle 0 | \tilde{0} \rangle|^2 E_0 + E_2 \left(1 - |\langle 0 | \tilde{0} \rangle|^2\right)$$

↑ due to parity

$$|\langle 0 | \tilde{0} \rangle|^2 \geq \frac{9E_0 - \bar{H}_{min}}{8E_0} = 0.99963$$

$$\langle 0 | \tilde{0} \rangle = \cos\theta \qquad \theta \lesssim 1.1^\circ$$

Example 2: Potential $V(x) = \frac{\lambda x^4}{4} + \frac{\lambda a x^3}{4} - \frac{\lambda a^2 x^2}{8}$

a) Find the global minimum x_0
b) Estimate the ground-state energy using the variational method and the trail function $\psi(x) = \sqrt[4]{\beta/\pi}\, e^{-\beta(x-x_0)^2/2}$

Here we will take $\lambda = \hbar^2/ma^6$

Solution: $V'(x) = 0 \qquad \lambda\left(x^3 + \frac{3ax^2}{4} - \frac{1}{2}a^2 x\right) = 0$

$x = 0 \longrightarrow \max$

$x = a/4 \qquad V(x) = -\frac{3}{1024}\lambda a^4$ local min

$x = -a \qquad V(x) = -\frac{1}{8}\lambda a^4$ global min

Trial wavefunction: $\psi(x) = \sqrt[4]{\beta/\pi}\, e^{-\beta(x+a)^2/2}$ (normalized)

$$\bar{H} = \langle\psi|\hat{H}|\psi\rangle = \langle\psi|\frac{\hat{p}^2}{2m} + V|\psi\rangle =$$

$$= \frac{\hbar^2}{4ma^2}\left[\beta a^2 + \left(\frac{\lambda m a^6}{\hbar^2}\right)\left(\frac{3}{4a^4\beta^2} + \frac{5}{4a^2\beta} - \frac{1}{2}\right)\right]$$

for $\lambda = \frac{\hbar^2}{ma^6}$ and $\beta a^2 = \xi$

$$\bar{H}(\xi) = \frac{\hbar^2}{4ma^2}\left[\xi + \frac{3}{4\xi^2} + \frac{5}{4\xi} - \frac{1}{2}\right]$$

$$\frac{\partial \bar{H}}{\partial \xi} = \frac{\hbar^2}{4ma^2}\left[1 - \frac{3}{2\xi^3} - \frac{5}{4\xi^2}\right] = 0 \implies \xi^3 - \frac{3}{2} - \frac{5}{4}\xi = 0$$

$$\xi = 3/2$$

$$\bar{H} = \frac{\hbar^2}{2ma^2}\cdot\frac{13}{12} \approx 1.083\cdot\left(\frac{\hbar^2}{2ma^2}\right)$$

Another estimate $\rightarrow$ harmonic expansion around $x_0 = -a$

$$V(x) \approx -\frac{\lambda a^4}{8} + \frac{5\lambda a^2}{8}(x-a)^2 + \bar{O}(x-a)^2$$

$$\omega = \sqrt{\frac{5}{4}\left(\frac{\lambda a^2}{m}\right)} = \sqrt{\frac{5}{4}}\,\frac{\hbar}{ma^2} \quad \text{for } \lambda = \frac{\hbar^2}{ma^6}$$

$$E_0 = \frac{1}{2}\hbar\omega = \sqrt{\frac{5}{4}}\left(\frac{\hbar^2}{2ma^2}\right) = 1.118\left(\frac{\hbar^2}{2ma^2}\right)$$

He atom - example of a two-electron system

$$\hat{H} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|}$$

Experimentally measured ground state energy
$E_{exp} = -78.8\ eV$

Non-spherically symmetric potential, no analytical solution

Ground state: $(1s)^2$, both electrons $n=1, l=0$
spin singlet state

Very rough guess $\psi(\bar{r}_1, \bar{r}_2) = \psi_0(\bar{r}_1)\psi_0(\bar{r}_2)$

where $\psi_0(\bar{r})$ is a single-particle wavefunction

$$\psi_{ground} = \frac{Z^3}{4a_0^3} e^{-Z(r_1+r_2)/a_0} \cdot \underbrace{\frac{1}{\sqrt{2}}\left(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle\right)}_{\chi_-}$$

neglect electron - electron interactions

$$E_0 = 2 \times 4\left(-\frac{e^2}{2a_0}\right) = -108.8\ eV$$ too large

More accurate — use e-e interaction as a perturbation

$$\Delta_{(1s)^2} = \left\langle \frac{e^2}{r_{12}} \right\rangle = \iint \frac{Z^6}{\pi^2 a_0^6} e^{-2Z(r_1+r_2)/a_0} \times$$

$$\times \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 d\vec{r}_2$$

can evaluate using decomposition

$$\frac{1}{r_{12}} = \frac{1}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \cos\theta}} = \sum_{l=0}^{\infty} \frac{r_{<0}^l}{r_{>0}^{l+1}} P_l(\cos\theta)$$

$$\Delta(s_1)^2 = \frac{5}{2}\left(\frac{e^2}{2a_0}\right) \Rightarrow E_{ground} = -\frac{8e^2}{2a_0} + \frac{5}{2}\frac{e^2}{2a_0}$$

$$E_{ground} = -\frac{11}{2}\left(\frac{e^2}{2a_0}\right) \simeq 74.8\,eV$$

compare to $E_{exp} = -78.8\,eV$

Overestimate the correction, since in reality electrons are farther from each other

Let's try to approximate this effect by introducing an effective charge

$$\psi(r_1, r_2) = \frac{Z_{eff}^3}{\pi a_0^3} e^{-Z_{eff}(r_1 - r_2)/a_0}$$

Use variational method

$$\overline{H} = \left(2\frac{Z_{eff}^2}{2} - 2Z Z_{eff} + \frac{5}{8} Z_{eff}\right)\left(\frac{e^2}{a_0}\right)$$

minimize $\overline{H}$ using Z_{eff} $\rightarrow$ $Z_{eff} = 2 - \frac{5}{16} = 1.687$

$E_{cal} = -77.5\,eV$ much closer to $-78.8\,eV$