Variational Method

Theorem

Given a time-independent Hamiltonian H with a set of eigenvalues E_n and eigenvectors $|\psi_n\rangle$ satisfying $H|\psi_n\rangle = E_n|\psi_n\rangle$, then for any arbitrary ket $|\psi\rangle$ in the Hilbert space, the expectation value of H in this ket must satisfy

$$\langle H\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

where, E_0 is the exact ground state energy. Equality holds only if $|\psi\rangle = |\psi_0\rangle$

Proof

If we expand $|\psi\rangle$ in the eigen-states of H, then $|\psi\rangle = \sum_n c_n|\psi_n\rangle$ which therefore implies

$$\langle\psi|\psi\rangle = \sum_n\sum_m c_n^* c_m\langle\psi_n|\psi_m\rangle = \sum_n\sum_m c_n^* c_m\delta_{nm} = \sum_n |c_n|^2$$

and

$$\langle\psi|H|\psi\rangle = \sum_n\sum_m c_n^* c_m\langle\psi_n|H|\psi_m\rangle = \sum_n\sum_m c_n^* c_m E_n\delta_{nm} = \sum_n |c_n|^2 E_n$$

Therefore the expectation value in the arbitrary ket vector is

$$\langle H\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2}$$

Since $|c_n|^2 \geq 0$ and $E_n \geq E_0$, it follows that

$$\frac{\sum_n |c_n|^2 E_n}{\sum_n |c_n|^2} \geq \frac{E_0\sum_n |c_n|^2}{\sum_n |c_n|^2} = E_0$$

Therefore, we have

$$\langle H\rangle \geq E_0$$

It is also clear that the equality holds only if $c_0 = 1$ and $c_n = 0$ for $n > 0$ in which case $|\psi\rangle = |\psi_0\rangle$. The conclusion is that E_0 is, therefore, the lower bound on $\langle H\rangle$, which means that we can approximate E_0 by a minimization of $\langle H\rangle$ *w.r.t* any parameters that $|\Psi\rangle$ might depend on.

Application: 1-D Harmonic oscillator

1. Write down the Hamiltonian: $\mathcal{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2x^2 = \mathcal{T} + \mathcal{V}$
2. Make a judicious choice of the trial wavefunction which somehow resembles the exact ground state e.g. $\Psi_\alpha(x) = Ae^{-\alpha x^2}$; α being the trial parameter
3. Normalize the trial wavefunction: $\Psi_\alpha = \sqrt[4]{\frac{2\alpha}{\pi}}$ with the criterion $\int_{-\infty}^{+\infty}\Psi_\alpha^*(x)\Psi_\alpha(x)dx = 1$

4. Find the expectation value of the $\mathcal{H}$ using $\Psi_\alpha(x)$:
   $\langle \mathcal{T} \rangle = \frac{\hbar^2\alpha}{2m}$ and $\langle \mathcal{V} \rangle = \frac{m\omega^2}{8\alpha}$ so that $\langle \mathcal{H} \rangle = \frac{\hbar^2\alpha}{2m} + \frac{m\omega^2}{8\alpha}$

5. Minimize $\langle H \rangle$ *w.r.t.* parameter α:
   $\frac{d}{d\alpha}\langle H \rangle = 0 \implies \alpha = \frac{m\omega}{2\hbar}$

6. Insert α back into $\langle H \rangle$ and $\Psi_\alpha(x)$:
   $\langle H \rangle_{\texttt{min}} = \frac{1}{2}\hbar\omega$ and $\Psi_{\texttt{opt}} = \sqrt[4]{\frac{m\omega}{\pi\hbar}} e^{-\frac{m\omega}{2\hbar}x^2}$

Assignment

1. Revisit the problem of 1-D harmonic oscialltor with
   (a) The trial wavefunction $\Psi_a(x) = \frac{1}{a^2+x^2}$; a being the trial parameter. Justify your answer.
   (b) The trial wavefunction $\Psi_\beta(x) = Bxe^{-\beta x^2}$; β being the trial parameter. Justify your answer.

2. Find out which of the two trial wavefunctions (a)$\Psi_1 = A(1+\alpha r)e^{-\alpha r}$ (b)$\Psi_2 = Be^{-\frac{\alpha}{2}r^2}$ is better for the ground state of hydrogen atom and why?

3. Consider the Hamiltonian (expressed in spherical polar co-ordinate system) of helium atom (in a.u.) under infinite nuclear mass approximation

$$\mathcal{H} = \mathcal{T}_1 + \mathcal{T}_2 + \mathcal{V}_1 + \mathcal{V}_2 + \mathcal{V}_{12} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

   where, $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l(l+1)}{r^2}$. Consider the trial wavefunction for the ground state (l_1=l_2=0) as $\Psi_\alpha(r_1, r_2) = Ae^{-\alpha(r_1+r_2)}$ to find
   (a) The optimum value of α and therefore the upper-bound of the ground state energy of the helium atom.
   (b) Do the same as of (a) but for $\mathcal{V}_{12} = \frac{1}{r_>}$ where $r_> = \texttt{max}(r_1, r_2)$
   (c) Do the same as of (a) but for $\mathcal{V}_{12} = \frac{1}{r_<}$ where $r_< = \texttt{min}(r_1, r_2)$
   (d) Do the same as of (a) but for $\mathcal{V}_{12} = 0$

Reference

1. Quantum Mechanics, B. H. Bransden and C. Joachin, Dorling Kimberley
2. Quantum Mechanics, A. K. Ghatak and S. Lokanathan, Kluwer Academic Publishers