Variational Method

The idea of the variational method comes from its name. It aims to "vary" some trial function and adjust it so that it fits the exact wave function as closely as possible.

Let us consider a system with Hamiltonian H. We will assume that the Hamiltonial is hermitian and is time-independent. We will also assume it is bounded from below. We are interested in finding (or at least estimating) the discrete eigenvalues of H and its normalized eigenstates

$$H\phi_n = E_n\phi_n \qquad n = 1, 2, 3, \dots$$

The energies E_n are real and are ordered such that

$$E_1 \leq E_2 \leq E_3 \leq \dots$$

We will assume the groud state is non-degenerate.

In its basic form the variational method deals with the ground state and takes a particularly simple form. It is based on the Ritz theorem; which reads: For an arbitrary function ψ of the state space the expectation value of H in the state ψ is such that

$$E \equiv \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_1 ,$$

where the equality holds if and only if ψ is an eigenstate of H corresponding to eigenvalue E_1.

Proof: Since the unknown eigenfunctions of H form a complete set, we can formally expand ψ as a linear combination of them:

$$\psi = \sum_n c_n \phi_n$$

Since ψ is normalized

$$1 = \langle\psi|\psi\rangle = \left\langle \sum_m c_m \phi_m \middle| \sum_n c_n \phi_n \right\rangle = \sum_m \sum_n c_m^* c_n \underbrace{\langle \psi_m|\psi_n\rangle}_{\delta_{mn}} =$$

$$= \sum_n |c_n|^2 \quad .$$

Meanwhile

$$\langle H\rangle = \left\langle \sum_m c_m \phi_m \middle| H \middle| \sum_n c_n \phi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \phi_m|\phi_m\rangle =$$

$$= \sum_n E_n |c_n|^2$$

It is easy to see now that

$$E_1 = E_1 \underbrace{\sum_n |c_n|^2}_{1} \leq \sum_n E_n |c_n|^2$$

becase E_1 is the smallest eigenvalue. Therefore

$\langle H\rangle \geq E_1$, which ends our proof.

Let us now consider an example — the ground state of 1D harmonic oscillator:

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

We will pick our "trial" wave function as a Gaussian:

$$\psi(x) = A e^{-bx^2}$$

where A and b are adjustable parameters. As the wave function must be normalized this effectively reduces the number of independent parameters from 2 to 1.

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

Now let us proceed to the calculation of $\langle H\rangle$:

$$\langle H\rangle = \langle T\rangle + \langle V\rangle$$

$$\langle T \rangle = -\frac{\hbar^2}{2m} |A|^2 \int_{-\infty}^{+\infty} e^{-bx^2} \frac{d^2}{dx^2}\left(e^{-bx^2}\right) dx = \frac{\hbar^2 b}{2m}$$

$$\langle V \rangle = \frac{1}{2} m\omega^2 |A|^2 \int_{-\infty}^{+\infty} e^{-2bx} x^2 \, dx = \frac{m\omega^2}{8b}$$

Hence

$$\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$$

For any b value $\langle H \rangle$ exceeds (or equal) to E_1

To get the lowest possible estimate we need to minimize $\langle H \rangle$ with respect to b:

$$\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \implies b = \frac{m\omega}{2\hbar}$$

Plugging this into $\langle H \rangle$ yields

$$\langle H \rangle_{min} = \frac{1}{2}\hbar\omega$$

In this case we obtained <u>exactly</u> the ground state energy. This is because our trial function had the same functional form as the actual ground state. However, Gaussians are very popular even in more sophisticated variational calculations, mainly because it is relatively easy to compute all necessary matrix elements with them.

Now let us consider another example — the delta function potential:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\delta(x)$$

Previously in this course we solved for the ground state of this system analytically. The exact bound state energy (there is only one bound state in this system) is

$$E_{exact} = -\frac{m\alpha^2}{2\hbar^2}$$

Let us again use a Gaussian trial function: $\psi(x) = A e^{-bx^2}$. $\langle T \rangle$ in this case is the same as in the previous example (1D harmonic oscillator): $\langle T \rangle = \frac{\hbar^2 b}{2m}$. The expectation value of the potential energy is

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

Evidently,

$$\langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}}$$

Again, we want to minimize $\langle H \rangle$ and obtain the tightest possible bound:

$$\frac{d}{db} \langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \implies b = \frac{2m^2 \alpha^2}{\pi \hbar^4}$$

and

$$\langle H \rangle_{min} = -\frac{m\alpha^2}{\pi \hbar^2}$$

This value is somewhat higher than the exact energy $E_{exact} = -\frac{m\alpha^2}{2\hbar^2}$

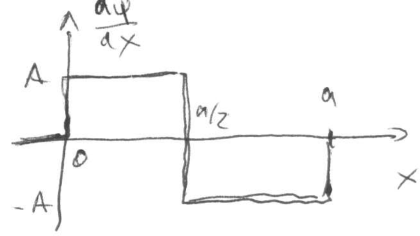
In the third example we will consider one-dimensional infinite square well. Our trial wave function will be

$$\psi(x) = \begin{cases} Ax & 0 \le x \le \frac{a}{2} \\ A(a-x) & \frac{a}{2} \le x \le a \\ 0 & \text{otherwise} \end{cases}$$

Here we only have one parameter, A, which is determined by normalization (so that there is nothing to vary):

$$1 = |A|^2 \left[\int_0^{a/2} x^2 dx + \int_{a/2}^{a} (a-x)^2 dx \right] = |A|^2 \frac{a^3}{12} \implies A = \frac{2}{a}\sqrt{\frac{3}{a}}$$

$$\frac{d\psi}{dx} = \begin{cases} A & 0 < x < \frac{a}{2} \\ -A & \frac{a}{2} < x < a \\ 0 & \text{otherwise} \end{cases}$$



$$\frac{d^2\psi}{dx^2} = A\delta(x) - 2A\delta\left(x-\frac{a}{2}\right) + A\delta(x-a)$$

$$\langle H \rangle = -\frac{\hbar^2 A}{2m}\int\left[\delta(x) - 2\delta\left(x-\frac{a}{2}\right) + \delta(x-a)\right]\psi(x)\,dx$$

$$= -\frac{\hbar^2 A}{2m}\left[\psi(0) - 2\psi\left(\frac{a}{2}\right) + \psi(a)\right] = \frac{\hbar^2 A^2 a}{2m} = \frac{12\hbar^2}{2ma^2}$$

We can compare this result with the exact energy: $E_{exact} = \frac{\pi^2\hbar^2}{2ma^2}$. Despite the somewhat rough approximation to the functional form of the exact wave function, our trial wave function yielded a relatively good estimate.