# Lecture 5

## Variational principle.

Here we will discuss a method to estimate the energy eigenvalues and eigenfunctions of a quantum mechanical system. It works only when combined with physical intuition, and even then is usually applied to estimate low-lying energy levels.

Suppose we are given an arbitrary wave function $\psi(x,t)$ and a Hamiltonian $\hat{H}$.

Consider $\int dx \, \psi^* H \psi(x,t)$ which can be written $\langle \psi | H | \psi \rangle$ in a basis-independent language.

We have the result that:

$$\langle H \rangle \equiv \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \geqslant E_0$$

where $E_0$ is the ground-state energy.

This is obvious: since all allowed energies are $\geqslant E_0$, their average must also be $\geqslant E_0$.

A formal proof is as follows:
any wave fn $|\Psi\rangle$ can be expanded in terms of energy eigenstates $|\varphi_n\rangle$, by completeness:

$$|\Psi\rangle = \sum_n c_n |\varphi_n\rangle$$

Then

$$\langle\Psi|H|\Psi\rangle = \sum_{n_1, n_2} \langle\varphi_{n_1}| c_{n_1}^* \hat{H} c_{n_2} |\varphi_{n_2}\rangle$$

$$= \sum_{n_1, n_2} c_{n_1}^* c_{n_2} E_{n_2} \delta_{n_1 n_2}$$

$$= \sum_n |c_n|^2 E_n \geq E_0 \sum_n |c_n|^2$$

$$= E_0 \langle\Psi|\Psi\rangle$$

$$\therefore \quad \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0 .$$

(In the above, we have assumed that the energy levels are discrete and non-degenerate. The discussion can be extended to the degenerate/ continuous case with some extra work.

**Theorem**

Suppose $|\psi\rangle$ is a trial wave function. then $\langle H\rangle = \dfrac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$ is stationary under arbitrary variations $|\delta\psi\rangle$ if and only if $|\psi\rangle$ is an eigenfunction of $\hat{H}$.

**Proof** We can write:

$$\langle H\rangle\langle\psi|\psi\rangle = \langle\psi|\hat{H}|\psi\rangle$$

Now make an infinitesimal variation $|\psi\rangle \rightarrow |\psi\rangle + |\delta\psi\rangle$. If $\delta\langle H\rangle$ is the change in $\langle H\rangle$ induced by this variation then:

$$\delta\langle H\rangle\langle\psi|\psi\rangle + \langle H\rangle\langle\delta\psi|\psi\rangle + \langle H\rangle\langle\psi|\delta\psi\rangle = \langle\delta\psi|\hat{H}|\psi\rangle + \langle\psi|\hat{H}|\delta\psi\rangle$$

or equivalently:

$$\delta\langle H\rangle\langle\psi|\psi\rangle = \langle\delta\psi|\left(\hat{H}|\psi\rangle - \langle H\rangle|\psi\rangle\right) + \left(\langle\psi|\hat{H} - \langle\psi|\langle H\rangle\right)|\delta\psi\rangle$$

This can be rewritten as:

$$\delta\langle H\rangle . \langle\psi|\psi\rangle = \langle\delta\psi|\, H - \langle H\rangle\, |\psi\rangle$$
$$+ \langle\psi|\, H - \langle H\rangle\, |\delta\psi\rangle$$

Now if $|\psi\rangle$ is an eigenstate $|\varphi_n\rangle$

then ~~[illegible]~~ $\langle H\rangle = E_n$ and

$$\langle\delta\psi|\, H - \langle H\rangle |\psi\rangle = 0$$
$$\langle\psi|\, H - \langle H\rangle |\delta\psi\rangle = 0$$

Therefore $\delta\langle H\rangle = 0$.

For the converse, suppose $\delta\langle H\rangle = 0$ for all variations $|\delta\psi\rangle$ about $|\psi\rangle$.

Then $\mathrm{Re}\left[\, \langle\delta\psi|\, H - \langle H\rangle\, |\psi\rangle \,\right] = 0$

Now, all variations $|\delta\psi\rangle$ include the particular variation

$$|\delta\psi\rangle = (H - \langle H\rangle)\, |\psi\rangle.$$

Hence $\mathrm{Re}\; \| (H - \langle H\rangle)|\psi\rangle \|^2 = 0$

But the object $\| \; \|^2$ is real and positive semi-definite. It vanishes only if $(H - \langle H\rangle)\, |\psi\rangle = 0$

ie $H|\psi\rangle = \langle H\rangle\, |\psi\rangle$

which means $|\psi\rangle$ is an eigenstate.

Note that we do not know in advance which eigenstate we will get! If we are looking for the ground-state wave function, we must check that what we have found is really the ground state. Physical intuition is very important for this.

<u>Example</u> 1d harmonic oscillator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m\omega^2 \hat{x}^2 .$$

Here we can check how well the variational principle works.

Work in position basis:

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

Consider the "trial" wave fn

$$\psi(x,\alpha) = e^{-\alpha x^2} \quad \text{with } \alpha > 0.$$

Then $\langle\psi|\psi\rangle = \int_{-\infty}^{+\infty} |\psi|^2\, dx = \int_{-\infty}^{+\infty} dx\, e^{-2\alpha x^2}$

and $\langle\psi|H|\psi\rangle = \int_{-\infty}^{+\infty} dx\, e^{-\alpha x^2}\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2\right)e^{-\alpha x^2}$

$$= \int_{-\infty}^{+\infty} dx\, e^{-\alpha x^2}\left[\frac{\hbar^2}{m}\alpha - \frac{2\hbar^2}{m}\alpha^2 x^2 + \frac{1}{2}m\omega^2 x^2\right] e^{-\alpha x^2}$$

Now $\int_{-\infty}^{+\infty} x^2 e^{-2\alpha x^2} = \frac{1}{4\alpha} \int_{-\infty}^{+\infty} e^{-2\alpha x^2}$

$$\therefore \langle\psi|H|\psi\rangle = \int dx\, e^{-2\alpha x^2}\left(\frac{\hbar^2}{2m}\alpha + \frac{1}{8}\frac{m\omega^2}{\alpha}\right).$$

$$\therefore \langle H\rangle = \frac{\hbar^2}{2m}\alpha + \frac{1}{8}\frac{m\omega^2}{\alpha}$$

$$\frac{\partial\langle H\rangle}{\partial\alpha} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{1}{8}\frac{m\omega^2}{\alpha^2}$$

$$\Rightarrow \alpha = \frac{m\omega}{2\hbar}$$

(the negative sign is non-normalisable).

Now, $\langle H\rangle = \frac{\hbar^2}{2m}\cdot\frac{m\omega}{2\hbar} + \frac{1}{8}m\omega^2\cdot\frac{2\hbar}{m\omega}$

$$= \frac{1}{4}\hbar\omega + \frac{1}{4}\hbar\omega = \frac{1}{2}\hbar\omega$$

It is because we chose the trial wave fn to lie within the correct (Gaussian) family of wave functions that we got the exact answer. Note that we could have guessed that the ground state had to be an even function of x.

We can also guess that the first excited state is an <u>odd</u> function of $x$. Suppose we try

$$\psi = x e^{-\alpha x^2}$$

In this case one finds:

$$\langle H \rangle = \frac{3\hbar^2}{2m}\alpha + \frac{3}{8}\frac{m\omega^2}{\alpha}$$

which is minimised, again for

$\alpha = \frac{m\omega}{2\hbar}$. The energy is now

$$\langle H \rangle = \frac{3}{4}\hbar\omega + \frac{3}{4}\hbar\omega = \frac{3}{2}\hbar\omega .$$

Thus we have found the exact value of $E_1$ !

— x —

Suppose we did not guess a Gaussian but instead:

$$\psi_a(x) = \frac{1}{x^2+a}$$

Now one finds

$$\langle H \rangle = \frac{\hbar^2}{4m}\frac{1}{a} + \frac{1}{2}m\omega^2 a$$

This is minimised by

$$a_0 = \frac{\hbar}{\sqrt{2}\,m\omega}, \quad \text{and } \langle H \rangle = \frac{\hbar\omega}{\sqrt{2}} .$$

Thus we see that the success of a variational calculation of the energy depends on making a good choice for the trial wave function.

How good is the trial wave function

$$\psi_{a_0}(x) = \frac{1}{x^2+a_0} \quad \text{with} \quad a_0 = \frac{\hbar}{\sqrt{2}\, m\omega} \; ?$$

We need to normalise this:

$$\psi_{a_0}(x) = \sqrt{\frac{2}{\pi}}\, \frac{(a_0)^{3/4}}{x^2+a_0}$$

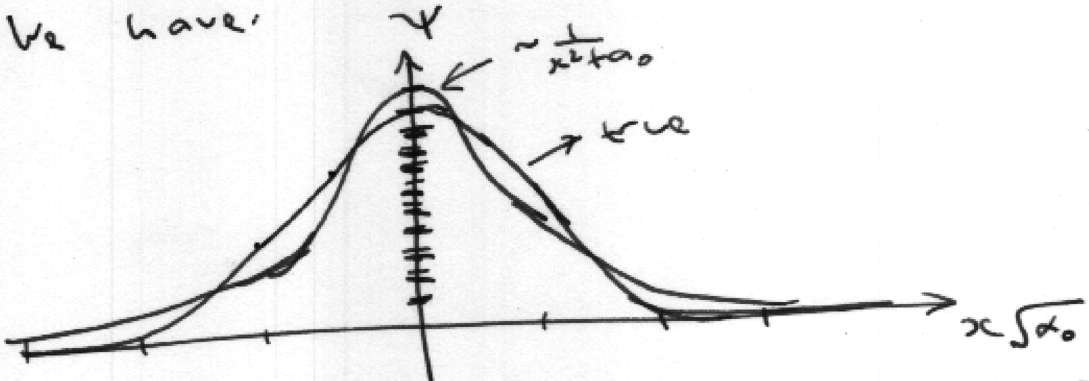
and compare with the true (normalised) wave function:

$$\psi_{\alpha_0}(x) = \left(\frac{2\alpha_0}{\pi}\right)^{\frac{1}{4}} e^{-\alpha_0 x^2}$$

where $\alpha_0 = \frac{1}{2}\frac{m\omega}{\hbar}$

Note that $a_0 = \frac{1}{2\sqrt{2}\,\alpha_0}$.

We have:




At $\sqrt{\alpha_0}\, x = 3$, the true wave fn is 0.0001 while the other one is $\sim 0.04$ : much large!

In fact it is easy to check that

$$\langle \psi_{\alpha_0} | \hat{X}^2 | \psi_{\alpha_0} \rangle = \frac{\hbar}{2m\omega}$$

while $$\langle \psi_{a_0} | \hat{X}^2 | \psi_{a_0} \rangle = \frac{\hbar}{\sqrt{2} m\omega}$$

(here we are using normalised wave fns)

so the approximation is not bad for this calculation. However,

$$\langle \psi_{\alpha_0} | \hat{X}^4 | \psi_{\alpha_0} \rangle \text{ is finite}$$

(in fact $\langle \psi_{\alpha_0} | \hat{X}^{2n} | \psi_{\alpha_0} \rangle$ is finite and nonzero for all $n$)

while $\langle \psi_{a_0} | \hat{X}^4 | \psi_{a_0} \rangle$

$$= \frac{2}{\pi} (a_0)^{3/2} \int_{-\infty}^{+\infty} dx \, \frac{x^4}{(x^2 + a_0)^2}$$

which is logarithmically divergent!

Clearly $\langle \psi_{a_0} | \hat{X}^{2n} | \psi_{a_0} \rangle$ is more and more divergent for higher $n$.

This is because these expectation values probe regions far from $x = 0$ where the trial wave function becomes a worse and worse approximation.