Learning Outcomes

You will be able to:

- write down the variational method/principle
- describe features of a suitable test wavefunction
- apply your understanding to example potentials in one or more dimensions.

Variational methods

Chapter 8

So far we've been studying various formal topics in quantum mechanics, which extend the basic one-particle, nonrelativistic, confined systems.

We're now going back to similar systems that you studied in QM I, but we'll consider systems that cannot be understood or, rather, solved analytically.

We're now going to turn to approximate solutions, starting with the most conceptually straightforward – the <u>variational method</u>.

This allows to place an <u>upper bound</u> on the ground state energy, and the method is straightforward

1. pick any normalised wavefunction
2. calculate the upper bound on the ground state energy

yes, it's basically that straightforward

$$\boxed{E_{GS} \leq \langle \psi | H | \psi \rangle}$$

Best to pick ψ close to true ground state wavefunction.

provided $\langle \psi | \psi \rangle = 1$

This is almost literally everything you need to know from this chapter - honestly. Of course, the trick comes in picking a good "trial wavefunction" so that your bound makes some physical sense. So after we prove that this statement is true, most of the chapter is just applying it.

G+S say "the variational principle is extraordinarily powerful, and embarrassingly easy to use." p. 331

Our proof goes as follows

The unknown eigenfunctions (if we knew them, we wouldn't be doing this) are a complete basis, so we can write

$$\psi = \sum_n c_n \psi_n \qquad \text{where } H\psi_n = E_n \psi_n \quad \text{and } \langle \psi_m | \psi_n \rangle = \delta_{mn}$$

We require

$$\langle \psi | \psi \rangle = 1$$

so

$$1 = \langle \psi | \psi \rangle = \langle \sum_m c_m \psi_m | \sum_n c_n \psi_n \rangle = \sum_{m,n} c_m^* c_n \overbrace{\langle \psi_m | \psi_n \rangle}^{=\delta_{mn}}$$

$$= \sum_{m,n} c_m^* c_n \delta_{mn} = \sum_n |c_n|^2$$

Now

$$\langle H \rangle = \langle \psi | H | \psi \rangle = \langle \sum_m c_m \psi_m | H \sum_n c_n \psi_n \rangle$$

$$= \sum_{m,n} c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2$$

But $E_{GS} \leq E_n \; \forall n$, so $\langle H \rangle \geq \sum_n E_{GS} |c_n|^2 = E_{GS} \underbrace{\sum_n |c_n|^2}_{=1} = E_{GS}$

this is what we're trying to prove!

□

Example 8.1

Let's apply this to some situations with which we are familiar – for example the 1D SHO.

In this case

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

Let's take as our trial wavefunction

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

We need to normalise it, so

$$1 = |A|^2 \int_{-\infty}^{\infty} e^{-2bx^2}\, dx^2 \leftarrow = \int_{-\infty}^{\infty} \varphi^*(x)\varphi(x)\, dx$$

$$= |A|^2 \sqrt{\frac{\pi}{2b}} \quad \Rightarrow \quad A = \sqrt[4]{\frac{2b}{\pi}}$$

Now we need to calculate the matrix element

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

We can do these separately as

$$\langle \varphi | T | \varphi \rangle = \int_{-\infty}^{\infty} \varphi^* \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \varphi \right) dx$$

$$= -\frac{\hbar^2}{2m} \int_{-\infty}^{\infty} A^* e^{-bx^2} \left(A \cdot 2b\, e^{-bx^2}(2bx^2 - 1) \right)$$

$$= -\frac{\hbar^2}{2m} |A|^2 \cdot 2b \int_{-\infty}^{\infty} e^{-2bx^2}(2bx^2 - 1)\, dx$$

$$= -\frac{\hbar^2}{2m} \sqrt{\frac{2b}{\pi}}\, 2b \left(\frac{-1}{2}\sqrt{\frac{\pi}{2b}} \right) = \frac{\hbar^2 b}{2m}$$

and

$$\langle\varphi|V|\varphi\rangle = \int_{-\infty}^{\infty} \varphi^* V \varphi \, dx$$

$$= \int_{-\infty}^{\infty} A^* e^{-bx^2}\left(\frac{1}{2}m\omega^2x^2\right) A e^{-bx^2} dx$$

$$= \frac{|A|^2 m\omega^2}{2} \int_{-\infty}^{\infty} e^{-2bx^2} x^2 \, dx$$

$$= \frac{|A|^2 m\omega^2}{2} \left(\frac{1}{4b}\sqrt{\frac{\pi}{2b}}\right)$$

$$= \sqrt{\frac{2b}{\pi}} \frac{m\omega^2}{8b} \sqrt{\frac{\pi}{2b}} = \frac{m\omega^2}{8b}$$

So

$$E_{GS} \leq \langle\varphi|H|\varphi\rangle$$

tells us that

$$E_{GS} \leq \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b} \qquad \text{for } \underline{\text{any}} \ b$$

To get the best bound though, we want to minimise this expression with respect to b. So we need to solve

$$\frac{d}{db}\langle\varphi|H|\varphi\rangle = 0 \quad \text{for } b$$

Now

$$\frac{d}{db}\langle\varphi|H|\varphi\rangle = \frac{d}{db}\left(\frac{\hbar^2}{2m}b + \frac{m\omega^2}{8}\frac{1}{b}\right) = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2}$$

Thus

$$\frac{\hbar^2}{2m} - \frac{m\omega^2}{8b^2} = 0 \Rightarrow b = \frac{m\omega}{2\hbar}$$

this minimises $\langle\varphi|H|\varphi\rangle$

The minimum value of $\langle \varphi | H | \varphi \rangle$ is thus

$$\langle \varphi | H | \varphi \rangle_{min} = \langle \varphi | H | \varphi \rangle \Big|_{b = \frac{m\omega}{2\hbar}}$$

$$= \left(\frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b} \right)_{b = \frac{m\omega}{2\hbar}}$$

$$= \left(\frac{\hbar^2}{2m} \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \frac{2\hbar}{m\omega} \right)$$

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

Thus

$$E_{gs} \leq \frac{\hbar\omega}{2}$$

Of course, in this case we know the answer is $E_{gs} = \frac{\hbar\omega}{2}$. And we got an excellent bound because we (or, rather, G+S) "happened" to pick a really good trial wavefunction. In fact, they picked the exact ground state wavefunction. But we'll not normally be this "lucky".

What about other examples?

Example 8.2

See example 8.3 for a discontinuous trial functions

Let's pick $V(x) = -\alpha\,\delta(x) \Rightarrow H = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} - \alpha\,\delta(x)$

If we choose the same trial wavefunction, then we know

$$\psi(x) = \sqrt[4]{\frac{2b}{\pi}}\,e^{-bx^2} \quad \text{and} \quad \langle\psi|T|\psi\rangle = \frac{\hbar^2 b}{2m}, \text{ so all we need}$$

is

$$\langle\psi|V|\psi\rangle = \int_{-\infty}^{\infty} A^* e^{-bx^2}\left(-\alpha\,\delta(x)\right) A e^{-bx^2}\,dx$$

$$= -|A|^2\alpha \int_{-\infty}^{\infty} e^{-2bx^2}\,\delta(x)\,dx$$

$$= -\alpha|A|^2 = -\alpha\sqrt{\frac{2b}{\pi}}$$

So

$$E_{GS} \le \langle\psi|H|\psi\rangle = \frac{\hbar^2 b}{2m} - \alpha\sqrt{\frac{2b}{\pi}} \quad \text{for all } b$$

$$\frac{d}{db}\langle\psi|H|\psi\rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} \Rightarrow \frac{d}{db}\langle\psi|H|\psi\rangle = 0 \text{ has solution } b = \frac{2m^2\alpha^2}{\pi\hbar^4}$$

Thus

$$E_{GS} \le \langle\psi|H|\psi\rangle\Big|_{b=\frac{2m^2\alpha^2}{\pi\hbar^4}} = \left(\frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}}\right)_{b=\frac{2m^2\alpha^2}{\pi\hbar^4}} = -\frac{m\alpha^2}{\pi\hbar^2}$$

the exact result $E_{GS} = \frac{-m\alpha^2}{2\hbar^2} < \frac{-m\alpha^2}{\pi\hbar^2}$ ← our bound

The variational method is wonderful, but how well it works all depends on how well you can approximate the true ground state wavefunction with your trial wavefunction.