Chapter 8: The variational principle

This is a common occurrence: Suppose you have a Hamiltonian that (i) cannot be solved exactly and (ii) where perturbation theory cannot be applied because there is no simple H_0 and/or because there is no small H'.

Then, what do we do? ☹

One possibility is to use the variational principle: it does not give you the exact answer but gives you an upper bound to the energy, which is often sufficient.

Select any wave function you wish. Call it Ψ. The claim is that **always**:

$$E_{gs} \leq \langle \psi | H | \psi \rangle \equiv \langle H \rangle$$

Although we do not know explicitly the eigenstates of *H*, because we cannot solve the problem exactly, we know they exist.

$$H\psi_n = E_n\psi_n$$

Then, in an "abstract" manner we can expand our proposed variational wave function in the complete basis of eigenstates:

$$\psi = \sum_n c_n \psi_n$$

If Ψ is normalized, then:

$$1 = \langle\psi|\psi\rangle = \left\langle \sum_m c_m \psi_m \middle| \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* c_n \langle\psi_m|\psi_n\rangle = \sum_n |c_n|^2$$

Repeating with the full *H* included, we find:

$$\langle H \rangle = \left\langle \sum_m c_m \psi_m \middle| H \sum_n c_n \psi_n \right\rangle = \sum_m \sum_n c_m^* E_n c_n \langle \psi_m | \psi_n \rangle = \sum_n E_n |c_n|^2$$

But the ground state has the lowest energy by definition:

$E_{gs} \leq E_n$. Then:

$$\langle H \rangle \geq E_{gs} \sum_n |c_n|^2 = E_{gs}$$

The variational principle is powerful, easy to use, and accurate if you have a good intuition on how the wave function should look like. But there is a problem: you do NOT know how close your result is compared to the exact result. **You only know you are above.**

Example 8.1:

Consider the 1D Harmonic Oscillator with Hamiltonian:

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

Here we know the answer exactly, but we pretend we do not.

As a "trial" wave function we will use a Gaussian exponential. Using Gaussians is very common, because the integrals are easy to do.

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

A is the normalization and *b* is called a "variational parameter" that we will optimize by minimizing the energy.

Normalization: $\left|\psi(x)\right|^2$ ★ means do the integral!

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

Next, we need the expectation value of the Hamiltonian:

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

For the kinetic energy:

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

For the potential energy:

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

Mathematical Formulas

Trigonometry:

$$\sin(a \pm b) = \sin a \cos b \pm \cos a \sin b$$

$$\cos(a \pm b) = \cos a \cos b \mp \sin a \sin b$$

Law of cosines:

$$c^2 = a^2 + b^2 - 2ab\cos\theta$$

Integrals:

$$\int x \sin(ax)\,dx = \frac{1}{a^2}\sin(ax) - \frac{x}{a}\cos(ax)$$

$$\int x \cos(ax)\,dx = \frac{1}{a^2}\cos(ax) + \frac{x}{a}\sin(ax)$$

Exponential integrals:

$$\int_0^\infty x^n e^{-x/a}\,dx = n!\,a^{n+1}$$

Gaussian integrals:

$$\int_0^\infty x^{2n} e^{-x^2/a^2}\,dx = \sqrt{\pi}\,\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1}$$

$$\int_0^\infty x^{2n+1} e^{-x^2/a^2}\,dx = \frac{n!}{2}a^{2n+2}$$

Integration by parts:

$$\int_a^b f\frac{dg}{dx}\,dx = -\int_a^b \frac{df}{dx}g\,dx + fg\Big|_a^b$$

Note in back of the book the gaussian integrals are from 0 to ∞

Adding kinetic and potential energy: $\langle H \rangle = \frac{\hbar^2 b}{2m} + \frac{m\omega^2}{8b}$

Let us now "optimize" the "variational parameter"

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

If we introduce the "optimal b" into $\langle H \rangle$, we obtain:

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

which is the exact result, by chance, in this simple example. In the vast majority of cases, you will **not** find the exact result.

Example 8.2:

Consider now the attractive delta function. Here we also know the exact result from P411: $E_{gs} = -m\alpha^2/2\hbar^2$

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

Here we will use again the Gaussian trial wave function.
We know already that this is not the exact ground state.

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

The normalization is independent of the Hamiltonian, thus same as Example 8.1:

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

<T> is the same as well:

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

The only difference between Examples 8.1 and 8.2 arises from <*V*>:

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

Adding kinetic and potential: $\langle H \rangle = \frac{\hbar^2 b}{2m} - \alpha \sqrt{\frac{2b}{\pi}}$

Optimizing *b*: $\frac{d}{db}\langle H \rangle = \frac{\hbar^2}{2m} - \frac{\alpha}{\sqrt{2\pi b}} = 0 \Rightarrow b_{opt} = \frac{2m^2\alpha^2}{\pi \hbar^4}$

we arrive to $\langle H \rangle_{\min} = -\frac{m\alpha^2}{\pi \hbar^2}$ while exact is $E_{gs} = -m\alpha^2/2\hbar^2$

Not perfect but close enough i.e. π instead of 2!

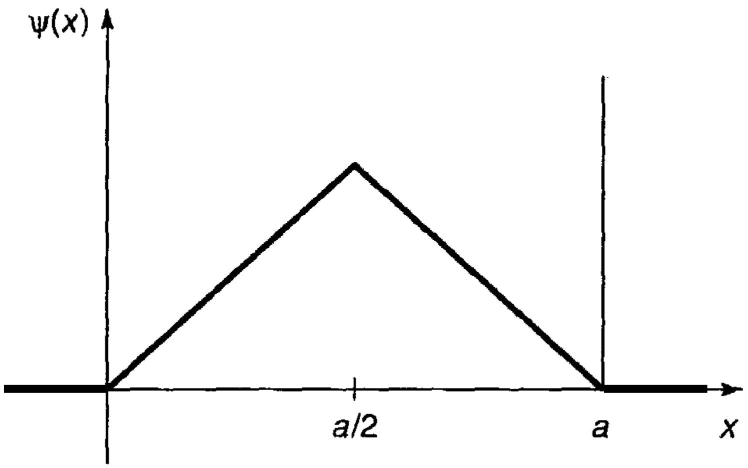
Note: If variational state is known to be orthogonal to ground state (e.g. even vs odd functions), then the upper bound found is for the **first excited state**.

Example 8.3:

As wave function you can use anything, including a function with discontinuous first derivatives:

Consider as potential the infinite square well between 0 and a.

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

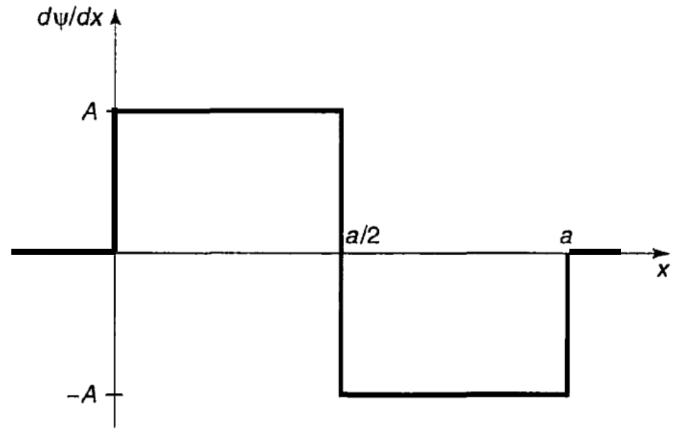


Note that this variational wave function **has no parameters to optimize**. Only *A* to normalize.

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

The challenge is how to handle <*T*> that contains a second derivative!

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



The derivative of a step function is a Dirac delta. Number in front is the jump:

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

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

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

The exact result is:

$$E_{gs} = \pi^2\hbar^2/2ma^2$$

Variational theorem holds because $12 > \pi^2$