EIGENVALUE EQUATION

Eigenvalue equations

The *Schrödinger Equation* is the form of an *Eigenvalue Equation*: $\hat{H}\psi = E\psi$

where $\hat{H}$ is the Hamiltonian operator, $\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$

ψ is the wavefunction and is an *eigenfunction* of $\hat{H}$;

E is the total energy ($T + V$) and an *eigenvalue* of $\hat{H}$. E is just a constant!

Later in the course we will see that the eigenvalues of an operator give the possible results that can be obtained when the corresponding physical quantity is measured.

Time Independent Schrodinger Equation (TISE) for a free-particle

For a free particle $V(x) = 0$ and TISE is: $$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi$$

and has solutions $$\psi = e^{ikx} \;\; or \;\; e^{-ikx} \quad where \quad E = \frac{k^2\hbar^2}{2m}$$

Thus the full solution to the full TDSE is: $$\Psi(x,t) = \psi(x)\,T(t) = e^{i(\pm kx - Et/\hbar)}$$

Corresponds to waves travelling in either $\pm x$ direction with:

(i) an angular frequency, $\omega = E/\hbar \Rightarrow E = \hbar\,\omega$! ☺

(ii) a wavevector, $k = (2mE)^{1/2}/\hbar = p/\hbar \Rightarrow p = h/\lambda$! ☺

WAVE-PARTICLE DUALITY!

Interpretation

As mentioned previously the TDSE has solutions that are inherently complex $\Rightarrow \Psi\,(x,t)$ *cannot* be a physical wave (e.g. electromagnetic waves). Therefore how can $\Psi\,(x,t)$ relate to real physical measurements on a system?

The Born Interpretation

Probability of finding a particle in a small length dx at position x and time t is equal to

$$\Psi^*(x,t)\Psi(x,t)dx = |\Psi(x,t)|^2\,dx = P(x,t)dx$$

$\Psi^*\Psi$ is real as required for a probability distribution and is the probability *per unit length* (or volume in 3d).

The Born interpretation therefore calls Ψ the ***probability amplitude***, $\Psi^*\Psi$ (= $P(x,t)$) the ***probability density*** and $\Psi^*\Psi\, dx$ the ***probability***.

Expectation values

Thus if we know $\Psi(x, t)$ (a solution of TDSE), then knowledge of $\Psi^*\Psi\, dx$ allows the *average* position to be calculated:

$$\bar{x} = \sum_i x_i P(x_i)\, \delta x$$

In the limit that $\delta x \to 0$ then the summation becomes:

$$\bar{x} = \langle x \rangle = \int_{-\infty}^{\infty} x P(x) dx = \int_{-\infty}^{\infty} x \left|\Psi(x,t)\right|^2 dx$$

The average is also know as the *expectation value* and are very important in quantum mechanics as they provide us with the average values of physical properties because in many cases precise values cannot, even in principle, be determined – **see later**.

Similarly $$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) dx = \int_{-\infty}^{\infty} x^2 \left|\Psi(x,t)\right|^2 dx$$

Normalisation

Total probability of finding a particle anywhere must be 1:

$$\int_{-\infty}^{\infty} P(x)dx = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx = 1$$

This requirement is known as the *Normalisation condition*. (This condition arises because the SE is linear in Ψ and therefore if Ψ is a solution of TDSE then so is $c\Psi$ where c is a constant.)

Hence if original unnormalised wavefunction is $\Psi(x,t)$, then the normalisation integral is:

$$N^2 = \int_{-\infty}^{\infty} |\Psi(x,t)|^2 dx$$

And the (re-scaled) normalised wavefunction $\Psi_{norm} = (1/N)\,\Psi$.

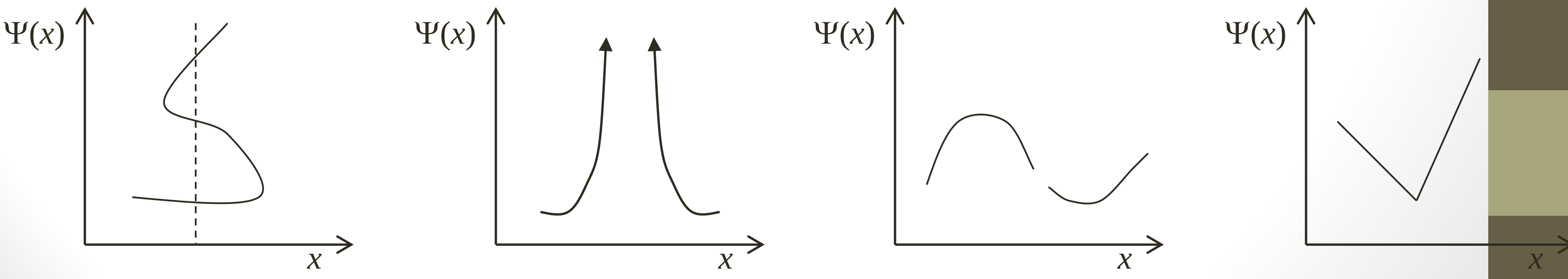
Example 1: What value of N normalises the function $N\,x\,(x - L)$ of $0 \le x \le L$?

Example 2: Find the probability that a system described by the function $2^{1/2}\sin(\pi x)$ where $0 \le x \le 1$ is found anywhere in the interval $0 \le x \le 0.25$.

Boundary conditions for Ψ

In order for ψ to be a solution of the Schrödinger equation to represent a physically observable system, ψ must satisfy certain constraints:

1. Must be a single-valued function of x and t;
2. Must be normalisable; This implies that the $\psi \rightarrow 0$ as $x \rightarrow \infty$;
3. $\psi(x)$ must be a continuous function of x;
4. The *slope* of ψ must be continuous, specifically $\mathrm{d}\psi(x)/\mathrm{d}x$ must be continuous (except at points where potential is infinite).



Stationary states

Earlier in the lecture we saw that even when the potential is independent of time the wavefunction still oscillates in time:

Solution to the full TDSE is: $\Psi(x,t) = \psi(x)\,T(t) = \psi(x)e^{-iEt/\hbar}$

But probability distribution is *static*:

$$P(x,t) = \left|\Psi(x,t)\right|^2 = \psi^*(x)e^{+iEt/\hbar}\,\psi(x)e^{-iEt/\hbar} = \left|\psi(x)\right|^2$$

Thus a solution of the TISE is known as a Stationary State.

What other information can you get from ψ? (and how!)

We have seen how we can use the probability distribution $\psi^*\psi$ to calculate the average position of a particle. What happens if we want to calculate the *average energy* or *momentum* because they are represented by the following differential operators:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}.$$

Do the operators work on $\psi^*\psi$, or on ψ, or on ψ^* alone?

Take TISE and multiply from left by ψ^* and integrate:

$$\hat{H}\psi_n = E_n\psi_n$$

$$\int \psi_n^* \hat{H}\psi_n \mathrm{d}x = \int \psi_n^* E_n \psi_n \mathrm{d}x = E_n \int \psi_n^* \psi_n \mathrm{d}x = E_n$$

NB ψ is normalised.

Suggest that in order to calculate the *average value* of the physical quantity associated with the QM operator we carry out the following integration:

$$\int \psi_n^* \hat{\Omega} \psi_n \mathrm{d}x$$

Momentum and energy expectation values

The expectation value of *momentum* involves the representation of momentum as a quantum mechanical operator:

$$\langle p_x \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x,t)\, dx \qquad \text{where} \qquad \hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}.$$

is the operator for the *x* component of momentum.

Example: Derive an expression for the average energy of a free particle.

$$E = \frac{p^2}{2m} \quad \text{then} \quad \langle E \rangle = \frac{\langle p^2 \rangle}{2m}$$

Since $V = 0$ the expectation value for energy for a particle moving in one dimension is

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^*(x,t) \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \Psi(x,t)\, dx$$