

The Quantum Theory of Atoms and Molecules

*The Schrödinger equation and
how to use wavefunctions*

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An equation for matter waves?

De Broglie postulated that every particles has an associated wave of wavelength:

$$\lambda = h / p$$

Wave nature of matter confirmed by electron diffraction studies *etc* (see earlier).

If matter has wave-like properties then there must be a mathematical function that is the solution to a differential equation that describes electrons, atoms and molecules.

Postulate: For a physical system consisting of a single particle there is an associated wavefunction, Ψ , **which determines everything that can be known about the system.**

The differential equation is called the *Schrödinger equation* and its solution is called the *wavefunction*, Ψ .

The time-dependent Schrödinger equation

The equation for matter waves in *free space* is: $-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} = i\hbar \frac{\partial \Psi}{\partial t}$

$$\text{For } \Psi(x, t) = e^{i(kx - \omega t)} \Rightarrow \frac{k^2 \hbar^2}{2m} \Psi(x, t) = \hbar \omega \Psi(x, t)$$

which has the form

(KE) \times wavefunction = (Total energy) \times wavefunction

For a particle in a potential $V(x, t)$ then $E = \frac{p^2}{2m} + V(x, t)$

and we have $-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x, t) \Psi = i\hbar \frac{\partial \Psi}{\partial t}$

TDSE 😊

(KE + PE) \times wavefunction = (Total energy) \times wavefunction

Points of note:

1. **The TDSE is one of the postulates of quantum mechanics.** Though the SE cannot be derived, it has been shown to be consistent with all experiments.
2. SE is first order with respect to *time* (*cf.* classical wave equation).
3. SE involves the complex number i and so its *solutions are essentially complex*. This is different from classical waves where complex numbers are used simply for convenience – see later.

The Hamiltonian operator

LHS of TDSE can be written as:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x,t) \Psi = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x,t) \right) \Psi = \hat{H} \Psi$$

where \hat{H} is called the **Hamiltonian operator** which is the differential operator that represents the **total energy** of the particle.

Thus

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) = \frac{\hat{p}_x^2}{2m} + \hat{V}(x)$$

where we define the **momentum operator** as

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

Thus shorthand for TDSE is:

$$\hat{H} \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

NOT SO SCARY NOW!!!!

Solving the TDSE – Aaargh!

Suppose the potential is independent of time i.e. $V(x, t) = V(x)$ then TDSE is:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi$$

LHS involves variation of Ψ with t while RHS involves variation of Ψ with x . Hence look for a separated solution:

$$\Psi(x, t) = \psi(x)T(t)$$

then

$$-\frac{\hbar^2}{2m} T \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi T = i\hbar \psi \frac{\partial T}{\partial t}$$

Now divide by ψT :

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{\partial^2 \psi}{\partial x^2} + V(x) = i\hbar \frac{1}{T} \frac{\partial T}{\partial t}$$

LHS depends only upon x , RHS only on t . True for all x and t so both sides must equal a constant, E (E = separation constant).

$$i\hbar \frac{1}{T} \frac{\partial T}{\partial t} = E$$

Thus we have:

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{\partial^2 \psi}{\partial x^2} + V(x) = E$$

Time-independent Schrödinger equation

Solving the time equation: $i\hbar \frac{1}{T} \frac{dT}{dt} = E \Rightarrow \frac{dT}{T} = -\frac{iE}{\hbar} dt \Rightarrow T(t) = Ae^{-iEt/\hbar}$

This is exactly like a wave $e^{-i\omega t}$ with $E = \hbar\omega$. Therefore $T(t)$ depends upon the energy E .

To find out what the energy actually is we must solve the space part of the problem....

The space equation becomes $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi$ or $\hat{H}\psi = E\psi$

This is the **time independent Schrödinger equation (TISE)**.

**** All Prelims problems are concerned with solving TISE rather than the TDSE!**

The TISE can often be very difficult to solve – it depends upon $V(x)$!

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.

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} where $E = \frac{k^2 \hbar^2}{2m}$

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, $k = (2mE)^{1/2} / \hbar = p / \hbar \Rightarrow p = \hbar k!$ 😊

WAVE-PARTICLE DUALITY!

Interpretation of $\Psi(x,t)$



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 $\delta x \rightarrow 0$ then the summation becomes:

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

The average is also known 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

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

Normalisation

The **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** and 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 $\Psi_{norm} = (1/N) \Psi$.

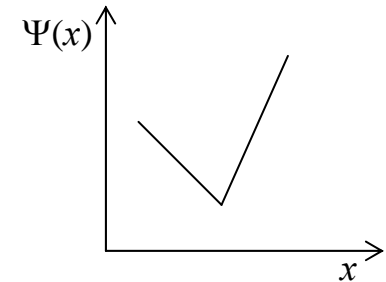
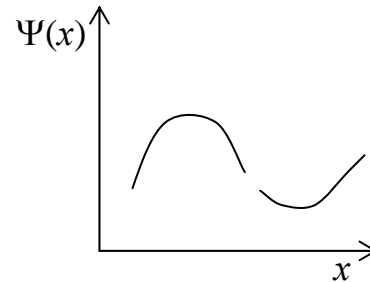
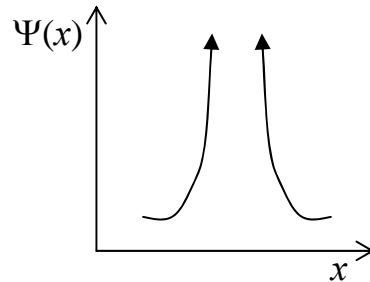
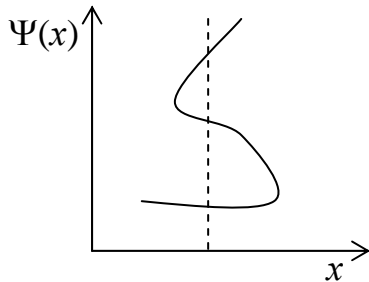
Example 1: What value of N normalises the function $Nx(x-L)$ of $0 \leq x \leq L$?

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

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 $d\psi(x)/dx$ must be continuous (except at points where potential is infinite).



Example: Which of the following are acceptable wavefunctions over the indicated intervals?

(i) e^{-x} $(0, \infty)$

(iii) $\sin^{-1} x$ $(-1, 1)$

(ii) e^{-x} $(-\infty, \infty)$

(iv) $e^{-|x|}$ $(-\infty, \infty)$

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*:

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

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 to 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:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \qquad \hat{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}.$$

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

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

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

NB ψ is normalised.

$$\int \psi_n^* \hat{H}\psi_n dx = \int \psi_n^* E_n\psi_n dx = E_n \int \psi_n^* \psi_n dx = E_n$$

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

$$\int \psi_n^* \hat{\Omega} \psi_n dx$$

Momentum and energy expectation values

Thus the expectation value of the *momentum operator* (in 1d) is:

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

and similarly for $\langle E \rangle$.

Example: Derive an expression for the average energy of a free particle whose normalised wavefunction is $\Psi(x) = Ae^{ikx}$.

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

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

Our definition of the expectation value is another postulate of QM – see later lectures.

Summary

TDSE:
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x,t)\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

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

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

TISE:
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi = E\psi \quad \text{or} \quad \hat{H}\psi = E\psi$$

$$\Psi(x,t) = \psi(x) T(t) = \psi(x) e^{-iEt/\hbar}$$

Boundary conditions on ψ : single-valued, continuous, normalisable, continuous first derivative.

Expectation value of operator $\hat{\Omega}$:
$$\int_{-\infty}^{\infty} \Psi^*(x,t) \hat{\Omega} \Psi(x,t) dx \quad (\text{for a normalised } \Psi)$$

It's never as bad as it seems....

