

CH107 Home Assignment

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Abstract

This is my recap of the past week in the course CH107, which covered Schroedinger's equation and free particle.

1 Schroedinger's Equation

Schroedinger felt the need to develop a non-newtonian theory that could accurately describe behaviour of electrons, atoms and molecules. The classical theory failed at atomic/subatomic level and there were ideas that particles and waves could behave like one-another, so a wavelike *probabilistic* theory was the need of the hour.

The equation

Schroedinger suggested his **time dependent Schroedinger equation (TDSE)**

$$\hat{H}\psi = \hat{E}\psi$$

where \hat{E} is the Energy operator and \hat{H} is the Hamiltonian operator. In 3 dimensions,

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = \hat{H}\psi = \left[\frac{-\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \psi(\vec{r}, t)$$

This is an equation with both spatial and temporal coordinates. Such equations are solved by **separation of variables**. $\psi(x, t)$ can be written as $\phi(x) \cdot \chi(t)$. This simplifies the SE to

$$\frac{i\hbar}{\chi(t)} \frac{\partial \chi(t)}{\partial t} = \frac{\hat{H}\phi(x)}{\phi(x)} = E \text{ (say)}$$

Since both sides of the equation are in different variables, they must be equal to a constant, say E . Solving the time equation yields the time dependent part of $\psi(x, t)$.

$$\chi(t) = \chi(0) \exp\left(-\frac{iEt}{\hbar}\right)$$

*I learnt L^AT_EX for this assignment! I suppose we had to learn something in the process, and poetry isn't exactly my cup of tea.

Time Independent Schroedinger's Equation

$\hat{H}\psi = E\psi$ is the TISE. We can clearly see this is an **eigenvalue equation**. Thus, the solutions $\phi_n(x)$ to the TISE are eigenfunctions of the Hamiltonian with eigenvalues E_n . Equivalently, we can state that each solution is an energy eigenstate with a fixed energy.

Operators All physical observables in quantum mechanics are associated with an operator. When the operator acts on its eigenfunction, the eigenvalue returned is the value of the observable associated with \hat{O} .

Laws of QM

- Only real eigenvalues can be observed which correspond to a physical observable.
- The eigenfunctions of a hermitian operator are **orthogonal**, which means that

$$\langle \psi_m | \psi_n \rangle = \int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) dx = 0 \text{ if } m \neq n.$$

Measurement The act of measurement of an observable associated with an operator forces the wavefunction into an eigenfunction of the operator. This is called **collapse of the wavefunction**.

The value of an observable in quantum mechanics depends on the observer.

The (mysterious) wavefunction

Erwin with his psi can do
Calculations quite a few.
But one thing has not been seen
Just what does psi really mean?

-Walter Huckel (1926)

Born Interpretation

Max Born suggested that the probability density of a particle described by the wavefunction ψ is $\psi^*\psi$. The probability of finding the particle (in one-dimension) in the region $(x - dx/2)$ to $(x + dx/2)$ is $|\psi|^2 dx$.

Normalisation Since the total probability of finding the particle over all space is 1, we must have $\langle \psi | \psi \rangle = 1$. Wavefunctions that are not square integrable are not permitted.

Restrictions on wavefunctions

- The wavefunction must be a continuous function of (x, y, z) .
- ψ must be single valued

Difficulty in understanding For a free particle confined in a 1D box, the wavefunction is not differentiable at $x = 0$ and $x = L$. Then how is the Hamiltonian defined at those points? (since $\frac{\partial^2 \psi(x)}{\partial x^2}$ is apparently ∞ at those points). Is the differentiability requirement for wavefunctions not strictly implemented?

2 Free Particle

A particle under influence of no forces is called a free particle. Solution of TISE for $V(x) = 0$ is of the form $A \sin kx + B \cos kx$, where $k = \pm \frac{\sqrt{2mE}}{\hbar}$. Till now, there are no restrictions on k , and subsequently, on E . Quantisation still isn't apparent.

Particle in 1D Box

Let the particle be trapped in an infinite potential well of length L . So the wavefunction vanishes outside this box since the particle cannot be present there. Thus, $\psi(x) = A \sin kx + B \cos kx$ if $x \in [0, L]$ and 0 elsewhere. Imposing the **boundary conditions of continuity** and normalisability, we obtain

$$\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \text{ where } n = 1, 2, 3, 4, \dots$$

We can see that *quantisation* has been introduced, since n (and thus energy) can only take certain discrete values.

Boundary conditions are the origin of quantisation.

$$E_n = \frac{n^2 h^2}{8mL^2} \text{ where } n = 1, 2, 3, \dots$$

We can see that zero-point energy (lowest energy of the particle) is non zero.

Particle in 2D (square) box

We can again use separation of variables to deal with 2 dimensions.

$$\psi(x, y) = \psi(x)\psi(y) \text{ and } \hat{H} = \hat{H}_x + \hat{H}_y$$

The particle is free in both dimensions, so $\psi(x, y) = \frac{2}{L} \sin \frac{n\pi x}{L} \sin \frac{n\pi y}{L}$.

Degenerate states

Two states that have equal values of energy are called degenerate states. A rectangular box has less degeneracy than a square box since **symmetry and degeneracy go hand in hand**. For a square box, (n, m) and (m, n) states are degenerate since

$$E = E_x + E_y = \frac{h^2}{8mL^2} (n_x^2 + m_x^2)$$