Lecture 7

Third Stage

Time Dependent Schrödinger Equation (T.D.S.E) and Solution of T.D.S.E

By

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Time-dependent Schrödinger equation

At the same time that Schrödinger proposed his time-independent equation to describe the stationary states, he also proposed a time-dependent equation to describe how a system changes from one state to another. By replacing the energy E in Schrödinger's equation with a time-derivative operator, he generalized his wave equation to determine the time variation of the wave function as well as its spatial variation. The time-dependent Schrödinger equation reads

special composition for article "Quantum Mechanics": Schrodinger equation

The quantity i is the square root of −1. The function Ψ varies with time t as well as with position x, y, z. For a system with constant energy, E, Ψ has the form

special composition for article "Quantum Mechanics"

where exp stands for the exponential function, and the time-dependent Schrödinger equation reduces to the time-independent form.

The probability of a transition between one atomic stationary state and some other state can be calculated with the aid of the time-dependent Schrödinger equation. For example, an atom may change spontaneously from one state to another state with less energy, emitting the difference in energy as a photon with a frequency given by the Bohr relation.

If electromagnetic radiation is applied to a set of atoms and if the frequency of the radiation matches the energy difference between two stationary states, transitions can be stimulated. In a stimulated transition, the energy of the atom may increase—i.e., the atom may absorb a photon from the radiation—or the energy of the atom may decrease, with the emission of a photon, which adds to the energy of the radiation. Such stimulated emission processes form the basic mechanism for the operation of lasers. The probability of a transition from one state to another depends on the values of the l, m, ms quantum numbers of the initial and final states. For most values, the transition probability is effectively zero. However, for certain changes in the quantum numbers, summarized as selection rules, there is a finite probability. For example, according to one important selection rule, the l value changes by unity because photons have a spin of 1. The selection rules for radiation relate to the angular momentum properties of the stationary states. The absorbed or emitted photon has its own angular momentum, and the selection rules reflect the conservation of angular momentum between the atoms and the radiation.

Axiomatic approach

Although the two Schrödinger equations form an important part of quantum mechanics, it is possible to present the subject in a more general way. Dirac gave an elegant exposition of an axiomatic approach based on observables and states in a classic textbook entitled The Principles of Quantum Mechanics. (The book, published in 1930, is still in print.)

An observable is anything that can be measured—energy, position, a component of angular momentum, and so forth. Every observable has a set of states, each state being represented by an algebraic function. With each state is associated a number that gives the result of a measurement of the observable. Consider an observable with N states, denoted by $\psi 1$, $\psi 2$, . . ., ψN, and corresponding measurement values a1, a2, . . ., aN. A physical system—e.g., an atom in a particular state—is represented by a wave function Ψ, which can be expressed as a linear combination, or mixture, of the states of the observable. Thus, the Ψ may be written as

special composition for article "Quantum Mechanics"

For a given Ψ, the quantities c1, c2, etc., are a set of numbers that can be calculated. In general, the numbers are complex, but, in the present discussion, they are assumed to be real numbers.

Solving the TDSE

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

We assume that the solution is separable. i.e. $\Psi(x,t)=\psi(x)f(t)$

$$-\frac{\hbar^2}{2m}\frac{f(t)\partial^2\psi(x)}{\delta x^2}+U(x)\psi(x)f(t)=i\hbar\psi(x)\frac{\delta f(t)}{\delta t}$$

Divide by $\Psi(x,t)=\psi(x)f(t)$

This yields $-\frac{\hbar^2}{2m\psi(x)}\frac{\partial^2\psi(x)}{\delta x^2}+U(x)=\frac{i\hbar}{f(t)}\frac{\delta f(t)}{\delta t}$.

Left side only depends on *x*, right only depends on *t*.

Separating the equations

$$-\frac{\hbar^2}{2m\psi(x)}\frac{\partial^2\psi(x)}{\delta x^2}+U(x)=\frac{i\hbar}{f(t)}\frac{\delta f(t)}{\delta t}$$

To be true for all times and positions we require that both sides equal a constant. Call it *E*.

So $\frac{df(t)}{dt}=\frac{E}{i\hbar}f(t)$ (Ordinary differential equation!)

Which has a solution $\boxed{f(t)=e^{-iEt/\hbar}.}$

If we identify $E=\hbar\omega$.

then $f(t)=e^{-i\omega t}$.

And for the time dependent part

$$-\frac{\hbar^2}{2m\psi(x)}\frac{\partial^2\psi(x)}{\delta x^2}+U(x)=\frac{i\hbar}{f(t)}\frac{\delta f(t)}{\delta t}$$

ψ must satisfy the TISE

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=E\psi(x).}$$

General characteristics of TISE solutions

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=E\psi(x)$$

$$\frac{\partial^2\psi}{\partial x^2}=\frac{-2m}{\hbar^2}\left(E-U(x)\right)\psi$$

<u>When E > U(x) (i.e. K > 0)</u>

$$\partial^2\psi/\partial x^2 = -cnst.\times\psi$$

In this case the wave function always curves towards the axis (oscillations).

<u>When E < U(x) (i.e. K < 0)</u>

$$\partial^2\psi/\partial x^2 = cnst.\times\psi$$

In this case the wave function always curves away from the axis.

To avoid diverging it must asymptote to the axis for large absolute value of x.

Solving the Time-independent Schrodinger Equation

1) Write the SE with the appropriate potential in all regions of space.

2) Solve the resulting differential equation in each region of space.

3) Apply boundary conditions (this usually determines the allowed energies).

4) For discontinuous potentials – require continuity of the wave function, and usually its derivative.

5) Evaluate all undetermined constants.

6) Normalize – the probability of finding the particle somewhere should be one.

7) Discard any solutions with infinite probabilities (they are non-physical).

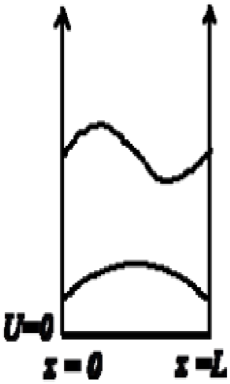
8) Calculate the expectation values of the quantities of interest.

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

Particle in a Box

With $U(x) = 0$ if $0 \le x \le L$

and $U(x) = \infty$ if $x < 0$ or if $x > L$



Inside the box we have

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} = E\psi(x) \quad \text{or} \quad \frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{2m}{\hbar^2}E\psi(x) \equiv -k^2\psi(x)$$

The equation is that of a harmonic oscillator with solutions

$$\psi(x) = A\sin(kx) + B\cos(kx).$$

We match these solutions within the well to the Boundary Condition that the wavefunction must vanish a 0 and at L. These imply that B=0 and that the constant $k = {}^{n\pi}/_{L}$, with n an integer.

Thus $k_n = n\pi / L = \sqrt{2mE_n} / \hbar$ with n = 1, 2, 3, ..

Applying the normalization condition on the solutions yields the eigenstates:

$$\psi_n(x) = \sqrt{2/L}\,\sin\left(\frac{n\pi\, x}{L}\right) \quad \text{where n = 1, 2, 3, ...}$$

And the corresponding energies are $E_n = \dfrac{k^2\hbar^2}{2m} = \dfrac{n^2\pi^2\hbar^2}{2mL^2}$.

Any linear combination of these solutions is also a solution. Including the time dependence we have the general solution:

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}$$

The c_n are the coefficients that determine the admixture of the different states.

$$\psi_n(x) = \sqrt{2/L}\,\sin\left(\frac{n\pi\, x}{L}\right) \quad \text{where n = 1, 2, 3, ...}$$

It can be easily shown that the ψ_n form a complete orthonormal set of functions on the interval between $x = 0$ and L (Fourier's theorem).

i.e. $$\int \psi_m(x)^* \psi_n(x)dx = \delta_{mn} \qquad \text{(Orthonormal)}$$

Any arbitrary function can be written as a linear combination of these eigenfunctions.

$$f(x) = \sum_n c_n \psi_n(x) \qquad \text{(Complete)}$$

One may use Fourier's trick to determine the coefficients.

$$\int \psi_m(x)^* f(x)dx = \sum_{n=1}^{\infty} c_n \int \psi_m(x)^* \psi_n(x)dx$$

$$= \sum_{n=1}^{\infty} c_n \delta_{mn} = c_m$$

Once the coefficients are determined (usually from the initial conditions) the general solution of the TDSE is known.

$$\boxed{\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar}}$$