Waves and the Schroedinger Equation

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1 The Wave Equation

We have seen from previous discussions that the wave-particle duality of matter requires we describe entities through some wave-form based represenation. The most natural consideration are classical waves, and arriving at a way to describe their **spatial** and **temporal** evolution. In the following discussion, pursuing this description for quantum entities will lead us to the Schroedinger equation, our starting point for treating atomic and molecular systems.

The motion of classical, non-dispersive waves requires some definitions:

$$frequency = \frac{1}{T} = \nu$$
$$wavelength = \lambda$$
$$velocity = v = \lambda\nu$$

A general expression for a wave moving in the +x direction:

$$\psi(x,t) = A\ sin\left[2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right]$$
$$\psi(x,t) = A\ sin\left[\left(\frac{2\pi x}{\lambda} - \frac{2\pi t}{T}\right)\right]$$
$$\psi(x,t) = A\ sin\left(kx - \omega t\right)$$

- wavevector, **k**

$$k = |\mathbf{k}| = \frac{2\pi}{\lambda}$$

  wave vector units of inverse length $(\frac{1}{length})$

  Recall:

$$\lambda = \frac{h}{p} \tag{1}$$

- Angular frequency (radians/second)

$$\omega = 2\pi\nu$$

Note that a phase-shift can be introduced in order to change the origin of the waveform:

$$\psi(x,t) = A \; sin \left(kx - \omega t + \phi\right)$$

Now, let's consider **stationary, or standing, waves**; for such entities, the nodes remain fixed in time and space (though the wave is moving with velocity, v). Standing waves are generated from interference of waves of equal frequency and amplitude traveling in **opposite directions**.

$$
\begin{aligned}
\psi(x,t) &= A \; sin \left(kx - \omega t\right) + A \; sin \left(kx + \omega t\right) \\
\psi(x,t) &= 2A sin(kx) \; cos \left(\omega t\right) \\
\psi(x,t) &= \psi(x) \; cos \left(\omega t\right) \qquad (2) \\
\psi(x,t) = &\underbrace{\psi(x)}_{time-independent} \quad \underbrace{cos \left(\omega t\right)}_{time-dependent}
\end{aligned}
$$

Thus, from the last expression, we see that stationary waves have fixed nodal points; zero amplitude versus time at fixed points). Now, we have gone about things in a reverse manner, but we can consider the following. We have written a representation of a wave-particle entity as a sinusoidal function. This is our attempt to describe the spatial and time dependence of an entity. However, this is one particular **solution** to the more general representation of the represenation of a state of an entitity (particle, wave, etc). We know that a particle's trajectory is determined classically via Newton's equation, $\mathbf{F} = m\mathbf{a}$. Thus, if we were to consider an analogous treatment for a string with certain mass density and tension T, along which we have a wave form moving, we can derive what is known classically as the **wave equation**,

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \psi(x,t)}{\partial t^2}$$

with $v = \lambda\nu$ as the wave velocity. The $\psi x, t$ as stationary waves are solutions of the wave equation.

2 Quantum Mechanical Waves and the Schroedinger Equation

Now, taking the stationary wave form

$$\psi(x,t) = \psi(x) \; cos\,(\omega t)$$

(3)

we will substitute our solution into the wave equation to arrive at:

$$\frac{\partial^2 \psi(x)}{\partial x^2} \; cos(\omega t) + \frac{\omega^2}{v^2}\psi(x) \; cos(\omega t) = 0$$
$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{\omega^2}{v^2}\psi(x) = 0$$

Recalling: $\omega = 2\pi\nu$ and $v = \lambda\nu$,

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

Now let's introduce our quantum mechanical connections to the classical progression we have been following. Consider the **total energy** of a particle moving along the x-direction. We can generally say (from our classical intuition) that:

$$E_{total} = KE + PE$$
$$E_{total} = \frac{p^2}{2m} + V(x)$$

where the general potential energy, V(x), is acknowledged to be some spatially-dependent potential (i.e., graviational potential, harmonic potential,etc.) Now consider,

$$\frac{p^2}{2m} = E_{total} - V(x)$$
$$p = \sqrt{2m \; (E_{total} - V(x))}$$

Recalling the de Broglie relation, $\lambda = \frac{h}{p}$,

$$\lambda^2 = \frac{h^2}{2m \; (E_{total} - V(x))}$$

Thus, recalling (once again),

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{8\pi^2 m}{h^2}\ (E_{total} - V(x))\ \psi(x) = 0$$

$$\hbar = \frac{h}{2\pi}$$

$$\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}\ (E_{total} - V(x))\ \psi(x) = 0$$

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

The last equation is the **1-Dimensional, time-independent Schroedinger Equation** for a particle in a potential, V(x),

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

We can rearrange the equation a little to see that it turns out to be an Eigenvalue equation as follows:

$$\left[\frac{-\hbar^2}{2m}\ \frac{\partial^2}{\partial x^2} + V(x)\right]\ \psi(x) = E_{total}\ \psi(x)$$

If we lump the terms in the square bracket as an **operator**, which is called the **Hamiltonian Operator**, we see that

$$\underbrace{\left[\frac{-\hbar^2}{2m}\ \frac{\partial^2}{\partial x^2} + V(x)\right]}_{\hat{H}}\ \psi(x) = E_{total}\ \psi(x)$$

$$\hat{H}\psi(x) = E_{total}\psi(x)$$

This is an eigenvalue equation since (in words), an operator $(\hat{H})$ acting on a function $(\psi(x))$ yields a scalar (E_{total}) times the original function $(\psi(x))$. This is the operational definition of the eigenvalue problem.

NOTE: the function $\psi(x)$ is an **eigenfunction** or **eigenstate** of the **operator** $\hat{H}$. The scalar E_{total} is the **eigenvalue**.

For completeness, we briefly address the time-dependent Schroedinger Equation, simply introduced here as:

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

The time dependence allows the treatment of non-stationary waves as well as systems where the energy is time-dependent. For stationary states, we know:

$$\psi(x,t) = \psi(x) \ f(t)$$

$$i\hbar\psi(x) \ \frac{\partial f(t)}{\partial t} = E\psi(x) \ f(t)$$
$$\frac{\partial f(t)}{\partial t} = \frac{-iE}{\hbar} \ dt$$
$$d \ ln(f(t)) = \frac{-iE}{\hbar} \ dt$$
$$f(t) = e^{\frac{-iE}{\hbar} \ t}$$

Thus,

$$\psi(x,t) = \psi(x) \ e^{\frac{-iE}{\hbar} \ t}$$

we recover the product of spatial and time-dependent functions.

3   Operators, Observables, Eigenfunctions, and Eigenvalues

- Operators are the actions performed on a wavefunction (or state). Above, we defined the Hamiltonian operator for the total energy of a system.

- Every measureable property (**observable**) such as energy, momentum, position has a quantum mechanical **operator**.

- Operators have associated with them a set of **eigenfuntions**, that in turn have **eigenvalues** associated with them.

- For an operator $\hat{O}$, with wavefunctions, ψ_n related as:

$$\hat{O} \ \psi_n \ = a_n \ \psi_n$$

- The functions are known as **eigenfunctions** and the a_n are **eigenvalues**.

- The eigenvalues for quantum mechanical operators are real-valued since they correspond to experimental observables.

- There are, in general, an *infinite* number of eigenfunctions for a given operator for a specific system under consideration. These eigenfunctions can be considered to form a complete basis.

- Recalling the time-independent Schrodinger Equation for one dimension, we see that the differential equation maps to an eigenvalue problem. Solving the time-independent Schroedinger equation:

$$\underbrace{\left[\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]}_{\hat{H}} \psi_n(x) = E_{total}\ \psi_n(x)$$

corresponds to finding the set of eigenfunctions and eigenvalues that are the solutions to the eigenvalue problem:

$$\hat{H}\psi_n(x) = E_{total}\psi_n(x)$$

4   Relation between eigenfunctions

We have seen that in general, a quantum mechanical operator has an infinite number of eigenfunctions (arising from boundary conditions as we will see later). What is the relation between them and what can we say about each one individually.

- Eigenfunctions of an operator are **orthogonal** to one another. Thus,

$$\int_{-\infty}^{\infty} \psi_i^*(x)\ \psi_j(x)\ dx\ = 0 \qquad i \neq j$$

- Eigenfunctions of an operator are **normalized** . Thus,

$$\int_{-\infty}^{\infty} \psi_i^*(x)\ \psi_j(x)\ dx\ = 1 \qquad i = j$$

- In general, eigenfunctions are **orthonormal**

Keep in mind that physically meaningful wavefunctions are three dimensional. Thus,

$$\int_{-\infty}^{\infty} \psi_i^*(x,y,z)\ \psi_i(x,y,z)\ dx\ dy\ dz\ = 1 \qquad i = j$$

For a spherical coordinate representation of a wavefunction $\psi(r,\theta,\phi)$,

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \psi_i^*(r,\theta,\phi)\ \psi_i(r,\theta,\phi)\ r^2\ sin(\theta)\ dr\ d\theta\ d\phi\ = 1 \qquad i = j$$