Learning Objectives

- The Schrödinger Equation gives the solutions to the problem and is an eigenvalue problem.

As per the definition, an operator acting on a function gives another function, however a special case occurs when the generated function is proportional to the original

\[
|\hat{A}|\psi \propto |\psi|\label{3.3.1a}
\]

This case can be expressed in terms of a equality by introducing a proportionality constant \(k\)

\[
|\hat{A}|\psi = k|\psi|\label{3.3.1b}
\]

The \(k\) constant that is corresponds to the specific \(|\psi|\) that solves this equation since not all equations will do so. In this special case, \(|\psi|\) is known as an eigenfunction (typically one of many function that satisfy Equation \ref{3.3.1b}) and the constant \(k\) is called an eigenvalue (these terms are hybrids with German, the purely English equivalents being characteristic function' and 'characteristic value'). Solving eigenvalue problems is a key objective from linear algebra courses. To every dynamical variable \(\hat{a}\) in quantum mechanics, there corresponds an eigenvalue equation, usually written

\[
|\hat{A}|\psi = a|\psi|\label{3.3.2a}
\]

The \(a\) eigenvalues represents the possible measured values of the \(|\hat{A}|\) operator. Classically, \(|\hat{a}|\) would be allowed to vary continuously, but in quantum mechanics, \(|\hat{a}|\) typically has only a sub-set of allowed values (hence the quantum aspect). Both time-dependent and time-independent Schrödinger equations are the best known instances of an eigenvalue equations in quantum mechanics, with its eigenvalues corresponding to the allowed energy levels of the quantum system.

\[
\left(-\dfrac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right)|\psi(\vec{r})| = E|\psi(\vec{r})|\label{3.3.3}
\]

The object on the left that acts on \(|\psi(x)|\) is an example of an operator.

\[
\left(-\dfrac{\hbar^2}{2m}\nabla^2+V(\vec{r})\right)|\psi(x)| = E|\psi(x)|\label{3.3.4}
\]

In effect, what is says to do is "take the second derivative of \(|\psi(x)|\), multiply the result by \((-\hbar^2 /2m)) and then add \(|V(x)|\psi(x)|\) to the result of that." Quantum mechanics involves many different types of operators. This one, however, plays a special role because it appears on the left side of the Schrödinger equation. It is called the Hamiltonian operator and is denoted as

\[
|\hat{H}|=-\dfrac{\hbar^2}{2m}\nabla^2+V(\vec{r})\label{3.3.5}
\]

Therefore, the time-dependent Schrödinger equation can be (and it more commonly) written as

\[
|\hat{H}|\psi(x,t) = i\hbar \dfrac{\partial}{\partial t}|\psi(x,t)|\label{3.3.6a}
\]

and the time-independent Schrödinger equation
\[ \hat{H} \psi (x) = E \psi (x) \]  \hspace{1cm} \label{3.3.6b}\]

The Hamiltonian, named after the Irish mathematician Hamilton, comes from the formulation of Classical Mechanics that is based on the total energy, \( H = T + V \), rather than Newton's second law, \( F = ma \). Equation \( \ref{3.3.6b} \) says that the Hamiltonian operator operates on the wavefunction to produce the energy \( E \), which is a scalar (e.g., expressed in Joules) times the wavefunction.

**Correspondence Principle**

Note that \( \hat{H} \) is derived from the classical energy \( p^2 / 2m + V(x) \) simply by replacing \( p \rightarrow -i \hbar \frac{d}{dx} \). This is an example of the *Correspondence Principle* initially proposed by Niels Bohr that states that the behavior of systems described by quantum theory reproduces classical physics in the limit of large quantum numbers.

It is a general principle of Quantum Mechanics that there is an operator for every physical observable. A physical observable is anything that can be measured. If the wavefunction that describes a system is an eigenfunction of an operator, then the value of the associated observable is extracted from the eigenfunction by operating on the eigenfunction with the appropriate operator. The value of the observable for the system is the eigenvalue, and the system is said to be in an eigenstate. Equation \( \ref{3.3.6b} \) states this principle mathematically for the case of energy as the observable.

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### Common Operators

Although we could theoretically come up with an infinite number of operators, in practice there are a few which are much more important than any others.

- **Linear Momentum:**

  The linear momentum operator of a particle moving in one dimension (the \( x \)-direction) is

  \[ \hat{p}_x = -i \hbar \frac{\partial}{\partial x} \]  \hspace{1cm} \label{3.3.7}\]

  and can be generalized in three dimensions:

  \[ \hat{\mathbf{p}} = -i \hbar \nabla \]  \hspace{1cm} \label{3.3.8}\]

- **Kinetic Energy**

  Classically, the kinetic energy of a particle moving in one dimension (the \( x \)-direction), in terms of momentum, is

  \[ KE_{\text{classical}} = \frac{p_x^2}{2m} \]  \hspace{1cm} \label{3.3.9}\]

  Quantum mechanically, the corresponding kinetic energy operator is

  \[ \hat{KE}_{\text{quantum}} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \]  \hspace{1cm} \label{3.3.10}\]

  and can be generalized in three dimensions:

  \[ \hat{KE}_{\text{quantum}} = -\frac{\hbar^2}{2m} \nabla^2 \]  \hspace{1cm} \label{3.3.11}\]
Angular Momentum:

Angular momentum requires a more complex discussion, but is the cross product of the position operator \(\hat{\vec{r}}\) and the momentum operator \(\hat{p}\)

\[
\hat{\vec{L}} = -i\hbar (\vec{r} \times \nabla)
\]

Hamiltonian:

The Hamiltonian operator corresponds to the total energy of the system

\[
\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)
\]

and it represents the total energy of the particle of mass \(m\) in the potential \(V(x)\). The Hamiltonian in three dimensions is

\[
\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})
\]

Total Energy:

The energy operator from the time-dependent Schrödinger equation

\[
i\hbar \frac{\partial}{\partial t} \Psi(x,t) = \hat{H} \Psi(x,t)
\]

The right hand side of Equation \(\ref{3.3.5}\) is the Hamiltonian Operator. In addition determining system energies, the Hamiltonian operator dictates the time evolution of the wavefunction

\[
\hat{H} \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}
\]

This aspect will be discussed in more detail elsewhere.

Eigenstate, Eigenvalues, Wavefunctions, Measurables and Observables

Often in discussions of quantum mechanics, the terms eigenstate and wavefunction are used interchangeably. The term eigenvalue is used to designate the value of measurable quantity associated with the wavefunction. For example, when discussing the eigenstates of the Hamiltonian \(\hat{H}\), the associated eigenvalues represent energies and within the context of the momentum operators, the associated eigenstate refer to the momentum of the particle.

Contributors

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- Adapted from "Quantum States of Atoms and Molecules" by David M. Hanson, Erica Harvey, Robert Sweeney, Theresa Julia Zielinski