Physical Chemistry
A Guided Inquiry

Atoms, Molecules, and Spectroscopy

Richard S. Moog
Franklin & Marshall College

James N. Spencer
Franklin & Marshall College

John J. Farrell
Franklin & Marshall College

Houghton Mifflin Company    Boston    New York
Quantum Mechanics
(Time Independent)

The fundamental equation of classical mechanics is \( f = ma \), or more exactly, \( f = \frac{dp}{dt} \). There is no derivation of this equation. There is no proof of this equation. Scientists use this equation because it is useful.

The fundamental equation of quantum mechanics is \( \hat{H} \Psi = \epsilon \Psi \). This is often called the time independent Schrödinger equation. There is no derivation of this equation. There is no proof of this equation. Scientists use this equation because it is useful.

The application of quantum mechanics for time-independent systems (such as the structure of atoms and molecules in their ground states) is based on several postulates.\(^1\) As stated above, there is no derivation or proof of these postulates. They are assumed to be true and are then used to describe physical systems. They have proved to be very useful, so we will use them also!

Postulate I. The state of a system is completely defined by \( \Psi \), a mathematical function of the coordinates of the components of the system. This function must be finite, continuous, and single valued. \( \Psi \) contains all of the information about the system, and is called a wavefunction or an eigenfunction.

Postulate II. Every dynamical variable (or physical observable) is represented by a corresponding linear operator.

Postulate III. When a dynamical variable \( A \) is measured (without experimental error), there are only certain possible values that may be obtained. These values are the eigenvalues \( a \) of the operator \( A \) as given by

\[
\hat{A} \phi = a \phi
\]

Here \( \phi \) is an eigenfunction of the operator \( \hat{A} \) that represents the dynamical variable \( A \).

Postulate IV. The wavefunction \( \Psi \) for the state of a system is provided as a solution of the equation

\[
\hat{H} \Psi = \epsilon \Psi
\]

where \( \hat{H} \) is the operator for the total energy of the system, also known as the Hamiltonian operator.

\(^1\)For time-dependent phenomena, a more complicated form of the Schrödinger equation is required. In these materials, we will not be concerned with this more complicated formulation.
Because you are probably not familiar with many of these terms, or the quantum mechanical way of thinking about things, we will begin with some explanations.

- $\Psi$ is a mathematical description of a single particle or a system of particles. It is a function of the position of the particle (or the positions of the particles). Thus, $\Psi$ for a single particle inside a 3-dimensional box would be $\Psi(x,y,z)$.

- $\Psi^2$ is a probability function. $\Psi$ (and $\Psi^2$) is zero in any region where the probability of finding the particle is zero. $\Psi$ can be positive or negative (or imaginary), but $\Psi^2$ is always positive and real. $\Psi$ can never be infinite.

- $\varepsilon$ is the numerical value of the energy of the particle (system).

- The concept of an operator is important in quantum mechanics. Operators are represented by symbols such as $\hat{A}$. The hat above the $A$ designates a mathematical operation or a series of mathematical operations. For example, the "2" in the quantity $x^2$ is a mathematical operator; in this case, it says to multiply $x$ by $x$. The symbol $\frac{d}{dx}$ is also an operator; it says take the derivative with respect to $x$ of any function to the right of the operator. The square root sign, as in $\sqrt{5}$, is also an operator; it says find a quantity such that the quantity squared is 5. The Hamiltonian operator $\hat{H}$ is a set of mathematical operations such that when applied to the wavefunction that describes the particle (system) the value of the energy multiplied by the wavefunction is produced.

- An operator is a linear operator if it obeys the distribution law with respect to addition of functions. That is, an operator $\hat{A}$ is linear if

$$\hat{A} (\Psi_1 + \Psi_2) = \hat{A} \Psi_1 + \hat{A} \Psi_2.$$ 

For example, the operator $\frac{d}{dx}$ is linear; $\sqrt{}$ is not.

---

2This is only rigorously correct for real functions $\Psi$. We will address this subtlety in CA 3.

1. Write the classical energy for the particle (system).

   Explanation. The classical energy, $U$, is a sum of the kinetic energy, $T$, and the potential energy, $V$.

   $U = T + V$  \hspace{1cm} (1)

2. Convert velocity, $v$, to linear momentum, $p$. (Sometimes it is more convenient to convert velocity to angular momentum, $L$; these cases will be treated later.)

   Explanation. The kinetic energy of a single particle is

   \[ \frac{1}{2} \, mv^2 \]

   Convert to linear momentum as follows:

   \[ \frac{1}{2} \, mv^2 = \frac{1}{2} \, \frac{m \, v^2}{m} = \frac{p^2}{2m} \]

3. Substitute the appropriate operators for all terms in the total energy, $T + V$. This is an application of Postulate II.

   The fundamental operator is the operator for linear momentum in one direction, $\hat{p}_x$.

   $\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$

   where $\hbar = \frac{\hbar}{2\pi}$, $\hbar$ is Planck's constant, and $i = \sqrt{-1}$.

   The three-dimensional counterpart is

   $\hat{p} = \frac{\hbar}{i} \left( \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right)$

   The operator for a number is simply the number. The operator for a physical constant is simply the constant (the operator for the mass of an electron is $m_e$ or $9.109 \times 10^{-31}$ kg; the operator for the charge on an electron is $-e$; the operator for the nuclear charge is $Ze$). The operator for a coordinate is simply the coordinate (the operator for $\phi$ is $\phi$).

   All other operators are derived from the momentum operator. For example, the operator for kinetic energy in the x direction, $\hat{T}_x$ is derived as follows:

   $T_x = \frac{1}{2} \, mv_x^2 = \frac{p_x^2}{2m}$
\[ \hat{T}_x = \frac{1}{2m} \hat{p}_x^2 = \frac{1}{2m} \hat{\hat{p}}_x \hat{\hat{p}}_x = \frac{1}{2m} \frac{\hbar}{i} \frac{d}{dx} \hbar \frac{d}{dx} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \]

Table 1 gives some quantities and the associated operators.

**Table 1. Operators for Physical Quantities.**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Operator Symbol</th>
<th>Operator Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_A ) (Avogadro's number)</td>
<td>( \hat{N}_A )</td>
<td>( N_A ) (or (6.022 \times 10^{23}))</td>
</tr>
<tr>
<td>( m_e ) (mass of electron)</td>
<td>( \hat{m}_e )</td>
<td>( m_e ) (or (9.109 \times 10^{-31} \text{ kg}))</td>
</tr>
<tr>
<td>( x )</td>
<td>( \hat{x} )</td>
<td>( x )</td>
</tr>
<tr>
<td>( z )</td>
<td>( \hat{z} )</td>
<td>( z )</td>
</tr>
<tr>
<td>( \phi )</td>
<td>( \hat{\phi} )</td>
<td>( \phi )</td>
</tr>
<tr>
<td>( r )</td>
<td>( \hat{r} )</td>
<td>( r )</td>
</tr>
<tr>
<td>( \hat{p}_x )</td>
<td>( \hat{\hat{p}}_x )</td>
<td>( \frac{\hbar}{i} \frac{d}{dx} )</td>
</tr>
<tr>
<td>( \hat{T}_x )</td>
<td>( \hat{T}_x )</td>
<td>( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} )</td>
</tr>
<tr>
<td>( T ) (Cartesian coordinates)</td>
<td>( \hat{T} )</td>
<td>( -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) )</td>
</tr>
<tr>
<td>( T ) (spherical coordinates)</td>
<td>( \hat{T} )</td>
<td>( -\frac{\hbar^2}{2m} \left{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right} )</td>
</tr>
<tr>
<td>( L_x ) (Cartesian coordinates)</td>
<td>( \hat{L}_x )</td>
<td>( \frac{\hbar}{i} \left( \frac{\partial}{\partial y} - \frac{\partial}{\partial z} \right) )</td>
</tr>
<tr>
<td>( L_x ) (spherical coordinates)</td>
<td>( \hat{L}_x )</td>
<td>( \frac{\hbar}{i} \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) )</td>
</tr>
<tr>
<td>( L_y ) (Cartesian coordinates)</td>
<td>( \hat{L}_y )</td>
<td>( \frac{\hbar}{i} \left( \frac{\partial}{\partial z} - \frac{\partial}{\partial x} \right) )</td>
</tr>
<tr>
<td>( L_y ) (spherical coordinates)</td>
<td>( \hat{L}_y )</td>
<td>( \frac{\hbar}{i} \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) )</td>
</tr>
<tr>
<td>( L_z ) (Cartesian coordinates)</td>
<td>( \hat{L}_z )</td>
<td>( \frac{\hbar}{i} \left( \frac{\partial}{\partial x} - \frac{\partial}{\partial y} \right) )</td>
</tr>
<tr>
<td>( L_z ) (spherical coordinates)</td>
<td>( \hat{L}_z )</td>
<td>( \frac{\hbar}{i} \frac{\partial}{\partial \phi} )</td>
</tr>
<tr>
<td>( L^2 ) (spherical coordinates)</td>
<td>( \hat{L}^2 )</td>
<td>( -\hbar^2 \left{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right} )</td>
</tr>
</tbody>
</table>
4. Let \( \hat{U} = \hat{T} + \hat{V} = \hat{H} \) Recall that \( \hat{H} \) is the **Hamiltonian operator**. 

\[ (2) \]

5. Now it is time to apply Postulate IV. Right-hand multiply \( \hat{H} \) by \( \Psi \) and set equal to \( \varepsilon \Psi \). \( \Psi \) is called the **wavefunction**. At this point in the process the form of \( \Psi \) is not known. \( \Psi \) is, however, some mathematical function that contains all of the pertinent information about the physical system under consideration.

\[ \hat{H} \Psi = \varepsilon \Psi \]  

Equation (3) is called the Schrödinger equation. This type of equation is frequently encountered in mathematics and science. The general form is:

\[ \hat{A} \phi = a \phi \quad \text{where } a \text{ is some constant} \]

In general, the function \( \phi \) is called the **eigenfunction** of the operator \( \hat{A} \), and \( a \) is called the **eigenvalue**. Note that Postulate III indicates that the eigenvalues \( a \) are the only possible values which can be obtained by measurement of the variable \( A \).

6. Solve equation (3), a differential equation, for \( \Psi \). The idea is to find the function (or functions) which, when substituted into equation (3) for \( \Psi \), make the equation true. (That is, the left side equals the right side!)

**Explanation.** Normally, solution of equation (3) is not trivial. The solutions are typically a set of polynomials. Often, the solutions are named after the person who first solved the differential equation or who discovered the polynomials: the Laguerre polynomials; the Hermite polynomials. The solutions always depend on the boundary conditions. That is, the particle might be constrained to a particular region of space (a line, a circle, sphere, a disk, and so on). It is not necessary to know the value of \( \varepsilon \) to solve the differential equation; it is necessary to know or assume that \( \varepsilon \) is constant.

7. If there are any parameters in \( \Psi \), solve for these parameters by normalization or by application of boundary conditions.

**Explanation.** Solution of a differential equation usually results in one or more parameters that depend on the unique character of the problem. For example, often \( \Psi \) is the mathematical description of an electron, and \( \Psi^2 \) is interpreted as being the probability for the electron.

Thus, the probability of finding the electron between \( x_1 \) and \( x_2 \), \( y_1 \) and \( y_2 \), \( z_1 \) and \( z_2 \) is equal to

\[ \int_{x_1}^{x_2} \int_{y_1}^{y_2} \int_{z_1}^{z_2} \Psi^2 \, dz \, dy \, dx \]

Of course, the probability of finding the electron in the range \( x = -\infty \) to \( x = \infty \), \( y = -\infty \) to \( y = \infty \), \( z = -\infty \) to \( z = \infty \), must be one:
\[
\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^2 \, dz \, dy \, dx = 1
\] (4)

If \( \Psi \) contains a parameter, it can now be determined such that equation (4) is valid.

8. Solve for \( \varepsilon \).

Explanation. Now that \( \Psi \) is known, the energy can be obtained from equation (3).

**Critical Thinking Questions**

1. Boltzmann's constant, \( k \), is called the universal gas constant per molecule because it is equal to the universal gas constant, \( R \), divided by Avogadro's constant, \( N_A \). What is the operator for Boltzmann's constant?

2. What is the expression for the translational energy of a particle moving in a straight line in the \( y \) direction?

According to Table 1, what is the operator for translational energy in the \( y \) direction, \( \hat{T}_y \)?

3. At some point in space \( \Psi^2 \) has one of the following values. Which one is correct? Why?

\[
\Psi^2 = 1.57 \times 10^{-5} \text{ pm}^{-3} \\
\Psi^2 = \infty \text{ pm}^{-3} \\
\Psi^2 = -2.64 \times 10^{-4} \text{ pm}^{-3}
\]

4. Of what significance is the unit \( \text{ pm}^{-3} \)?
Exercises

1. The gravitational potential energy of a proton and an electron separated by a distance $r$ is given by:

$$ V = G \frac{(m_p)(m_e)}{r} $$

where $m_p$ is the proton mass, $m_e$ is the electron mass, and $G$ is the Newtonian constant of gravitation.

What is the operator for this potential energy?

2. Recall that the $z$-component of angular momentum is given by:

$$ L_z = x p_y - y p_x $$

Show that the operator for $L_z$ in Table 1 is correct.

3. According to Table 1, what is the operator for:

$$ \frac{1}{2} m v_z^2 + \frac{1}{2} k z^2 $$

given that $z$ is a coordinate, $m$ is the mass of a particle, and $k$ is some constant?

4. The potential energy of a proton and an electron separated by a distance $r$ is given by Coulomb's law:

$$ \frac{(e)(-e)/4 \pi \varepsilon_0}{r} = \frac{-e^2/4 \pi \varepsilon_0}{r} $$

where $e$ is the magnitude of the charge on an electron and $\varepsilon_0$ is the vacuum permittivity (a fundamental constant).

What is the operator for this potential energy?

5. The classical expression for the kinetic energy of a particle under certain conditions is:

$$ T = \frac{L^2}{2I} $$

where $L^2$ is the square of the magnitude of the angular momentum and $I$ is the moment of inertia, $mr^2$.

What is the operator for this kinetic energy?
Problems

1. Evaluate \( g = \hat{Q} f \), where \( \hat{Q} \) and \( f \) are given below:

<table>
<thead>
<tr>
<th>( \hat{Q} )</th>
<th>( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) ( \sqrt{\frac{d^2}{dx^2}} )</td>
<td>( x^6 )</td>
</tr>
<tr>
<td>(b) ( \frac{d^2}{dx^2} )</td>
<td>( e^{-ax} )</td>
</tr>
<tr>
<td>(c) ( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} )</td>
<td>( x^2y^3z^5 )</td>
</tr>
</tbody>
</table>

2. Show that \( e^{\alpha x} \) is an eigenfunction of the operator \( d^2/dx^2 \). What is the eigenvalue?

3. Show that \( \sin \beta x \) is an eigenfunction of the operator \( d^2/dx^2 \). What is the eigenvalue?