The electron can be described in terms of both particle and wave character.

**Particle Character**

The electron has both charge and mass which are properties of particles. Mullikin determined the charge of the electron in his oil drop experiment. J. J. Thomson measured the charge to mass ratio for the electron. By knowing the charge and charge to mass ratio both the charge and mass of the electron can be determined ($q = 1.6 \times 10^{-19}$ coulombs and mass $= 9.1 \times 10^{-28}$ grams).

**Wave Character**

A beam of electrons passed through a crystal generates a diffraction pattern. Diffraction patterns are described in terms of wave character.

A French scientist by the name of de Broglie related wave and particle character through the following relationship.

$$\lambda = \frac{h}{mv} \quad ; \quad \text{where} \quad h = 6.6 \times 10^{-27} \text{\ erg sec}$$

Note that the value of $h$ is very small. If a particle such as a lima bean has a mass of 1 gram and a velocity of 1 cm/sec, the wavelength of the particle would be $h$ which is very small and near zero.

$$\lambda = \frac{h}{mv} = \frac{h}{1} = h = 6.6 \times 10^{-27} \text{ cm}$$

On the other hand if that same particle had a mass of $9.1 \times 10^{-28}$ grams (say equal to the mass of the electron) its wavelength would be significant, and the particle would have significant wave character. Of course, one
would expect an electron to move much faster than 1 cm/sec. The point is that wave-particle duality is only relevant for submicroscopic particles such as the electron.

\[ \lambda = \frac{h}{mv} = \frac{h}{9.1 \times 10^{-28} \times 1} = 7.25 \text{ cm} \]

The wave character of the electron in the hydrogen atom is described by the Schrodinger Wave Equation. The Schrodinger wave equation is the wave mechanical or quantum mechanical approach to the description of atomic structure.

\[ H \Psi = E \Psi \quad \text{; (Schrodinger Wave Equation)} \]

\[ \left( \frac{-\hbar^2}{8\pi^2 m} S^2 - \frac{e^2}{r} \right) \Psi = E \Psi \quad \text{; (Schrodinger Wave Equation)} \]

H is the Hamiltonian Operator which is made up of kinetic and potential energy terms and is associated with the total energy of the hydrogen atom.

Kinetic energy term \[ = \frac{-\hbar^2}{8\pi^2 m} S^2 \]

where \[ S^2 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{1}{r^2 \sin \Theta} \frac{d}{d\Theta} \left( \sin \Theta \frac{d}{d\Theta} \right) + \frac{1}{r^2 \sin^2 \Theta} \frac{d^2}{d\Phi^2} \]

Potential energy term \[ = -\frac{e^2}{r} \quad \text{(Electrostatic Energy)} \]

E is the value of the total energy.

\( \Psi \) is a wavefunction which depends on the electron position and is related to the probability of finding the electron in space.

A short commentary on the methods of quantum mechanics is necessary at this point. In normal or classical mechanics (the mechanics of the macroscopic world; our world) properties are associated with formulas or equations. If one want to know the kinetic energy or the momentum of a
tennis ball, one thinks of the relationships $1/2 \ m \ v^2$ and $m \ v$. In quantum mechanics each property is associated with a quantum mechanical operator. An operator is a set of instructions which converts a mathematical function into another mathematical function. For example, the quantum mechanical operators for momentum and kinetic energy in the $x$ direction are as follows. Note that these operators involved the derivative process.

$$p_x \ (\text{momentum}) = -i \ \frac{\hbar}{2\pi} \frac{d}{dx}$$

$$KE_x \ (\text{kinetic energy}) = -\frac{\hbar^2}{8 \pi^2 m} \frac{d^2}{dx^2}$$

In quantum mechanics the system is described by a mathematical function often called the wavefunction. The wavefunction depends upon the coordinates or the positions of the particles that make up the system. In the case of atomic structure that means the position or coordinates of the electron(s). Remember that when an operator operates on a function, the result is a new function. Sometimes the operation of a quantum mechanical operator on a wave function generates a new wavefunction that is simply the original wavefunction multiplied times a constant. When this special case exists the problem is said to be an eigenvalue problem, and the constant (the eigenvalue) is the value of the property associated with the operator for the system described by the wavefunction. How neat! The Schrodinger wave equation is such a problem with the operator ($H$, the Hamiltonian operator) associated with the total energy and the wavefunction ($\psi$) describing position of the electron in the hydrogen atom. $E$ is the eigenvalue and the value of the energy of the electron described by $\psi$. Are you still with me?

The Schrodinger Wave Equation is also a differential equation. Differential equations are a class of equations that have as their solutions functions. The Schrodinger Wave equation has an infinite number of solutions (wave functions). Each wave function describes the position of the electron for a given energy ($E$) and is characterized by a set of three quantum number ($n$, $l$, $m$). A wave function

$$\Psi_{n,l,m}$$
is a solution to the Schrodinger Wave equation and describes the position of the electron when the energy is given by the following relationship.

\[ E_n = \frac{-B}{n^2} \]

Note that the energy expression for the quantum mechanical description of the hydrogen atom is the same as the expression from the Bohr description. Both theories are perfect descriptions of one electron systems. Being a solution simply means that substituting \( \Psi_{n,l,m} \) and \( E \) into the Schrodinger Equation makes each side of the equation equal to one other or that operating the energy operator on the wavefunction yields the wavefunction times the energy of the electron described by that wavefunction. Really neat!

\[ H \ \Psi_{n,l,m} = E_n \ \Psi_{n,l,m} \quad \text{where} \quad E_n = \frac{-B}{n^2} \]

Only certain values are allowed for the quantum numbers. These allowed values come from the mathematics involved with the formal solution of the Schrodinger Equation, and the origin of the allowed values will not be discussed.

\[ n = 1, 2, 3, 4, \ldots \]

\[ l = n-1, n-2, n-3, \ldots 0 \]

\[ m = -l, -l + 1, -l + 2 \ldots 0 \ldots l - 2, l - 1, l \]

Based on these allowed values for the quantum numbers only certain combination of quantum numbers are allowed. Remember that the wavefunction or position probability of the electron is characterized by a set of quantum numbers. If \( n=1 \) then \( l \) and \( m \) can only equal 0; therefore, the only allowable set of quantum numbers with \( n=1 \) is \( n=1, l=0, \) and \( m=0 \). The wavefunction described by this set \( (\Psi_{1,0,0}) \) is a solution to the Schrodinger Wave equation for \( E = -B/1^2 \) which is also the lowest energy for the electron. If \( n=2 \) then \( l = 1 \) and \( l = 0 \). If \( l = 1 \) then \( m = -1, 0, +1 \). If \( l = 0 \) then \( m = 0 \). The only combinations of quantum numbers with \( n=2 \) are the following four, and each set characterizes a wavefunction which is a solution to the Schordinger Wave Equation for \( E = -B/2^2 \)
Another bit of nomenclature is that those functions with \( l=0 \) are called \( S \) functions. Functions with \( l=1 \), \( l=2 \), and \( l=3 \) are called \( p \), \( d \), and \( f \) functions, respectively. The actual wavefunctions for the quantum number sets \( 1,0,0; 2,0,0; \) and \( 2,1,0 \) are as follows.

\[
\Psi_{1,0,0} = \Psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{3/2} e^{-r/a_o}
\]

\[
\Psi_{2,0,0} = \Psi_{2s} = \frac{1}{4\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{3/2} \left( 2 - \frac{r}{a_o} \right) e^{-r/2a_o}
\]

\[
\Psi_{2,1,0} = \Psi_{2p} = \frac{1}{4\sqrt{\pi}} \left( \frac{1}{a_o} \right)^{3/2} \left( \frac{r}{a_o} \right) e^{-r/2a_o} \cos \theta
\]

It is interesting to note that the \( 1s \) and \( 2s \) functions depend only on the variable \( r \). This means that these functions are symmetrical around the nucleus or have a spherical distribution. The \( 2p \) function has an angular dependence, \( \cos \theta \), and is not spherical.

There is an interesting mathematical issue that needs to be addressed at this point. The wavefunctions for \( n = 2 \), \( l = 1 \), and \( m = \pm 1 \) contain "i" and are imaginary. In fact, all \( \Psi \)'s with \( m \) not equal to zero are imaginary.

\[
\Psi_{2,1,\pm1} = \Psi_{2p} = \frac{1}{2} \sqrt{\frac{1}{16\pi}} \left( \frac{1}{a_o} \right)^{3/2} \left( \frac{r}{a_o} \right) e^{-r/2a_o} (\sin \theta) \left( e^{\pm i \phi} \right)
\]

Well, as you can imagine, imaginary functions are not easy to work with. It turns out, however, that a relative simple solution exist for this problem.
In addition to describing the positions of electrons, the wavefunctions are also solutions to a differential equation - the Schrodinger Differential Equation. If $\Psi_1$ and $\Psi_2$ are both solutions to the Schrodinger Differential Equation then the sums and differences (often called **linear combinations**) of $\Psi_1$ and $\Psi_2$ are also solutions.

If $\Psi_1$ is a solution and if $\Psi_2$ is also a solution, then $\Psi_3 = \Psi_1 + \Psi_2$ and $\Psi_4 = \Psi_1 - \Psi_2$ are also solutions and can describe the position of electrons.

This notion of linear combinations of solutions also being solutions and electron descriptions is also used to generate hybrid orbitals.

$$\Psi_{\text{sp (hybride)}} = \Psi_s + \Psi_p \quad \text{and} \quad \Psi_{\text{sp (hybride)}} = \Psi_s - \Psi_p$$

So, how does this apply to the imaginary wavefunction problem? Well, $\Psi_{2,1,1}$ and $\Psi_{2,1,-1}$ are imaginary, but linear combinations of these functions are

1) solutions to the Schrodinger Differential Equation,
2) descriptions of electrons, and
3) real functions.

$$\Psi_{2\text{px (real)}} = \frac{1}{\sqrt{2}} \left( \Psi_{2,1,1} \text{ (imaginary)} + \Psi_{2,1,-1} \text{ (imaginary)} \right)$$

$$\Psi_{2\text{py (real)}} = \frac{1}{i\sqrt{2}} \left( \Psi_{2,1,1} \text{ (imaginary)} - \Psi_{2,1,-1} \text{ (imaginary)} \right)$$

$$\Psi_{2\text{pz (real)}} = \Psi_{2,1,0} \text{ (real)}$$

A similar issue exists for the d orbitals.

$$\Psi_{3, 2, 0 \text{ (real)}} = \Psi_{3d_2} \text{ (real)} \quad \text{note that } m = 0$$
When m is not equal to zero, the wavefunctions are imaginary and linear combinations of the imaginary functions are required to generate real functions.

\[ \Psi_{3dxz} \text{ (real)} = \frac{1}{\sqrt{2}} (\Psi_{3,2,1} \text{ (imaginary)} + \Psi_{3,2,-1} \text{ (imaginary)}) \]

\[ \Psi_{3dyz} \text{ (real)} = \frac{1}{i\sqrt{2}} (\Psi_{3,2,1} \text{ (imaginary)} - \Psi_{3,2,-1} \text{ (imaginary)}) \]

\[ \Psi_{3d(x^2 - y^2)} \text{ (real)} = \frac{1}{\sqrt{2}} (\Psi_{3,2,2} \text{ (imaginary)} + \Psi_{3,2,-2} \text{ (imaginary)}) \]

\[ \Psi_{3dxy} \text{ (real)} = \frac{1}{i\sqrt{2}} (\Psi_{3,2,2} \text{ (imaginary)} - \Psi_{3,2,-2} \text{ (imaginary)}) \]

Well, perhaps that is enough on the issue of imaginary functions. Let's next consider the plots of the real functions or just what do the functions look like.

The following figures represent the angular distribution of the different types wavefunctions in space.

The way in which the wavefunction yields information on the position of the particles that make up a system is in terms of probability. The wavefunction squared gives the probability of finding an electron described by that wavefunction at a point in space. If one plots the wavefunction squared for a series of coordinates, one gets a profile that describes the variation of the probability for the different sets of coordinates. The s type functions depend only on the r variable which means that the probability
depends on the distance from the nucleus and not on the direction one move away from the nucleus. Said another way; the probability is spherical or the same in every direction. The p function has angular dependence which means the probability depends on both the distance and the direction that one moves away from the nucleus. For example the probability distribution of the $p_z$ function is different along the $x$ axis and $z$ axis. Considerations of the s type functions are clearly easier because of their spherical character. Let's consider the $1s$ and $2s$ functions. A plot of $4\pi r^2 \psi^2$ versus $r$ yields the radial probability or the probability of finding the electron on the surface of a sphere of radius $r$. The following are figures of such plots for the $1s$ and $2s$ function.
The 1s radial probability plot reaches a maximum at 0.528 angstroms, and the 2s probability maximizes at 2.8 angstroms. Since the s type functions are spherical, the radial probability is the same in every direction outward from the nucleus, up, down, right, left, and etc. A sphere with a radius of 0.528 angstroms is the surface with the greatest probability of finding the 1s electron, and a sphere with a radius of 2.8 angstroms is the surface where it is most probable to find a 2s electron. Note that the 2s electron has a maximum probability surface larger (farther out from the nucleus) than that of the 1s electron, and it has an energy that is higher than that of the 1s electron \( E(2s) = -\frac{B}{2^2} > E(1s) = -\frac{B}{1^2} \).

Well, this explanation of the wave mechanical approach turned out to be much longer than I expected. I think that most everything above is correct, possibly some over simplification, a few typos, and a few small lies to make it work for introductory chemistry.

JLK