


12.3.1: Schrödinger Theory of Hydrogen

The Schrödinger theory of quantum mechanics extends the de Broglie concept of matter waves by providing a formal method of treating the dynamics of physical particles in terms of associated waves. One expects the behavior of this wavefunction, generally called , to be governed by a wave equation, which can be written

$$\left(\frac{p^2}{2m} + V(\mathbf{x}, t) \right) \Psi(\mathbf{x}, t) = H\Psi(\mathbf{x}, t) \quad (12.3.1.1)$$

where the first term of the left represents the particle's kinetic energy, the second the particle's potential energy, and H is called the Hamiltonian of the system. Making the assertion that p and H are associated with differential operators,

$$p = -i\hbar\nabla \quad (12.3.1.2)$$

$$H = i\hbar\frac{\partial}{\partial t}, \quad (12.3.1.3)$$

this becomes

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}, t) \right) \Psi(\mathbf{x}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x}, t) \quad (12.3.1.4)$$

which is known as the *time-dependent Schrödinger equation*. For the specific case of a hydrogenic atom, the electron moves in a simple Coulomb potential, and hence the Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \right) \Psi(\mathbf{x}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x}, t). \quad (12.3.1.5)$$

The solution proceeds by the method of separation of variables. First one writes the wavefunction as a product of a space component and a time component, for which the solution for the time part is easy and yields

$$\Psi(\mathbf{x}, t) = \psi(\mathbf{x})e^{-iEt/\hbar} \quad (12.3.1.6)$$

Here E is the constant of the separation and is equal to the energy of the electron. The remaining equation for the spatial component is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r} \right) \psi(\mathbf{x}) = E\psi(\mathbf{x}) \quad (12.3.1.7)$$

and is called the *time-independent Schrödinger equation*. Due to the spherical symmetry of the potential, this equation is best solved in spherical polar coordinates, and hence one separates the spatial wavefunction as

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi). \quad (12.3.1.8)$$

The equations are more difficult but possible to solve and yield

$$\Theta(\theta)\Phi(\phi) = Y_l^{m_l}(\theta, \phi) \quad (12.3.1.9)$$

$$R(r) = e^{-Zr/na_0} \left(\frac{Zr}{a_0} \right)^l L_{n-l-1}^{2l+1} \left(\frac{2Zr}{na_0} \right), \quad (12.3.1.10)$$

where L is an associated Laguerre polynomial, and for convenience the product of the angular solutions are written together in terms of a single function, the spherical harmonic Y . With foresight the separation constants $-m_l^2$ and $l(l+1)$ were used. The meaning of the numbers n , l , and m_l will now be discussed.

The physics of the Schrödinger theory relies on the interpretation of the wave function in terms of probabilities. Specifically, the absolute square of the wavefunction, $|\Psi(\mathbf{x}, t)|^2$, is interpreted as the probability density for finding the associated particle in the vicinity of \mathbf{x} at time t . For this to make physical sense, the wavefunction needs to be a well-behaved function of \mathbf{x} and t ; that is, Ψ should be a finite, single-valued, and continuous function. In order to satisfy these conditions, the separation constants that appear while solving the Schrödinger equation can only take on certain discrete values. The upshot is, with the solution written as it is here, that the numbers n , l , and m_l , called quantum numbers of the electron, can only take on particular integer values, and each of

these corresponds to the quantization of some physical quantity. The allowed values of the energy turn out to be exactly as predicted by the Bohr theory,

$$E = -\frac{mc^2}{2}(Z\alpha)^2 \frac{1}{n^2} \quad (12.3.1.11)$$

The quantum number n is therefore called the principle quantum number. To understand the significance of l and m_l , one needs to consider the orbital angular momentum of the electron. This is defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, or as an operator, $\mathbf{L} = -i\hbar \mathbf{r} \times \nabla$. With proper coordinate transformations, one can write the operators L^2 and the z -component of angular momentum L_z in spherical coordinates as

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (12.3.1.12)$$

$$L_z = -i\hbar \frac{\partial}{\partial \phi}. \quad (12.3.1.13)$$

It can be shown that when these operators act on the solution Ψ , the result is

$$L^2 \Psi = l(l+1)\hbar^2 \Psi \quad (12.3.1.14)$$

$$L_z \Psi = m_l \hbar \Psi \quad (12.3.1.15)$$

It can also be shown that this means that an electron in a particular state has orbital angular momentum of constant magnitude $\sqrt{l(l+1)}\hbar$ and constant projection onto the z -axis of $m_l \hbar$. Since the electron obeys the timeindependent Schrödinger equation $H\Psi = E\Psi$, and hence has constant energy, one says that the wavefunction Ψ is a simultaneous eigenstate of the operators H , L^2 , and L_z . Table 1 summarizes this information and gives the allowed values for each quantum number. It is worth repeating that these numbers can have only these specific values because of the demand that Ψ be a well-behaved function.

It is common to identify a state by its principle quantum number n and a letter which corresponds to its orbital angular momentum quantum number l , as shown in table 2. This is called spectroscopic notation. The first four designated letters are of historical origin. They stand for sharp, primary, diffuse, and fundamental, and refer to the nature of the spectroscopic lines when these states were first studied.

Table 12.3.1.1: Some quantum numbers for the electron in the hydrogen atom.

Quantum number	Integer values	Quantized quantity
n	$n \geq 1$	Energy
l	$(0 \leq l < n)$	Magnitude of orbital angular momentum
m_l	$(-l \leq m_l \leq l)$	z -component of orbital angular momentum

Table 12.3.1.2: Spectroscopic notation

Quantum Number l	0 1 2 3 4...
Letter	s p d f g...

Figure 12.3.1.1 shows radial probability distributions for some different states, labelled by spectroscopic notation.

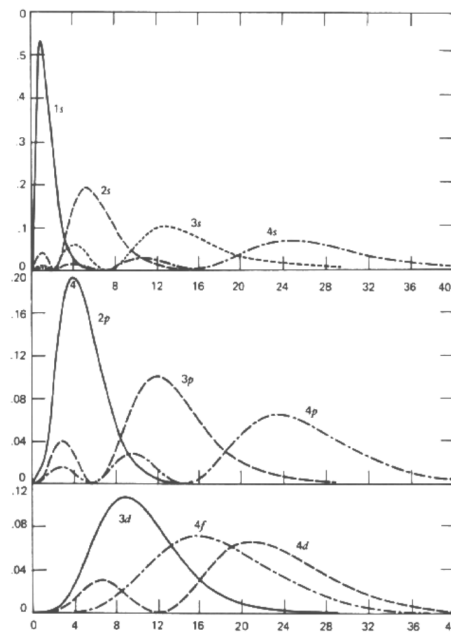


Figure 12.3.1.1: Radial probability distribution for an electron in some low-energy levels of hydrogen. The abscissa is the radius in units of a_0 .

The radial probability density P_{nl} is defined such that

$$P_{nl}(r)dr = |R_{nl}(r)|^2 4\pi r^2 dr \quad (12.3.1.16)$$

is the probability of finding the electron with radial coordinate between r and $r + dr$. The functions are normalized so that the total probability of finding the electron at some location is unity. It is interesting to note that each state has $n - l - 1$ nodes, or points where the probability goes to zero. This is sometimes called the radial node quantum number and appears in other aspects of quantum theory. It is also interesting that for each n , the state with $l = n - 1$ has maximum probability of being found at $r = n^2 a_0$, the radius of the orbit predicted by Bohr theory. This indicates that the Bohr model, though known to be incorrect, is at least similar to physical reality in some respects, and it is often helpful to use the Bohr model when trying to visualize certain effects, for example the spin-orbit effect, to be discussed in the next section. The angular probability distributions will not be explored here ¹, except to say that they have the property that if the solutions with all possible values of l and m_l for a particular n are summed together, the result is a distribution with spherical symmetry, a feature which helps to greatly simplify applications to multielectron atoms

Footnote

¹ See Eisberg and Resnick, chapter 7, for a more thorough discussion.

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