

Chapter 7 - The Hydrogen Atom in Wave Mechanics

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7.1 Schrodinger Equation with Coulomb Potential

Schrodinger created the first fully quantum-mechanical model of the hydrogen atom in 1926. Because the electron can orbit around the proton in any direction, we need to use the three-dimensional time-independent Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U\psi = E\psi,$$

where $\nabla^2\psi$ is the Laplacian operator. The solution to this equation is simplest in spherical coordinates (see Figure 1), so the Laplacian becomes (yikes!):

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}.$$

The potential energy of an electron and a proton at a distance r is

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}.$$

Thus, the partial differential equation that Schrodinger was able to solve (with help from his friend and mathematician Hermann Weyl) is

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi(r,\theta,\phi) - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi).$$

The solution to this equation becomes a bit more manageable when one realizes that standing wave solutions are separable along the three spherical coordinates:

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

where the r , θ and ϕ dependences are confined to the R , Θ and Φ functions respectively.

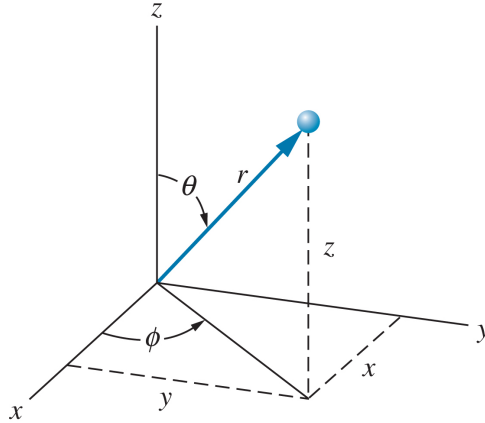


Figure 1: Spherical coordinate system.

7.2 Quantum Numbers

Through the process of solving the Schrodinger equation and setting boundary conditions, three quantum numbers emerge, one for each degree of freedom of the electron. They are:

n	principal quantum number	$1, 2, 3, \dots$
l	angular momentum quantum number	$0, 1, 2, \dots, n - 1$
m_l	magnetic quantum number	$0, \pm 1, \pm 2, \dots, \pm l$

7.2.1 Principal Quantum Number

The principle quantum number determines the energy levels of the atom:

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \frac{1}{n^2}.$$

or

$$E_n = -13.6\text{eV} \frac{1}{n^2}.$$

These energy levels agree with the prediction of the classical-quantum Bohr model discussed in Chapter 6.

7.2.2 Angular Momentum Quantum Number

The angular momentum quantum number l quantizes the magnitude of the angular momentum vector $\vec{\mathbf{L}}$ as follows:

$$|\vec{\mathbf{L}}| = \sqrt{l(l+1)} \quad l = 0, 1, 2, \dots, n - 1.$$

While Bohr's energy levels agreed with the Schrodinger's energy levels, his assumptions about angular momentum (i.e. that $L = n\hbar$) did not hold up. In Bohr's model, each electron "orbit" has a distinct angular momentum: the ground state $n = 1$, first excited state $n = 2$ and second excited state $n = 3$ have angular momentum values $L = \hbar, 2\hbar, 3\hbar$. However, in Schrodinger's model, each energy level n has $n - 1$ angular momentum values:

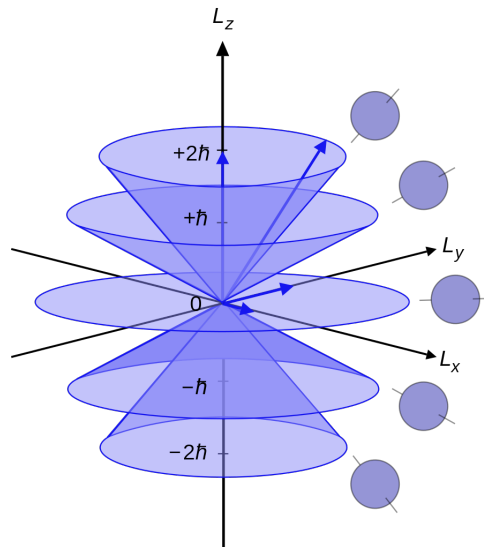


Figure 2: Angular momentum states for $l = 2$ (d orbital).

$n = 1$	$l = 0$	s orbitals
$n = 2$	$l = 0, 1$	s and p orbitals
$n = 3$	$l = 0, 1, 2$	s, p, d orbitals

Chemists and atomic physicists often label the angular momentum states using spectroscopic notation, where the $l = 0$ state is called the “s orbital,” the $l = 1$ state is called the “p orbital,” the $l = 2$ state is called the “d orbital,” etc. Notice also that the magnitude of the angular momentum vector depends on the angular momentum quantum number in a nonlinear way:

s orbital	p orbital	d orbital	f orbital
$l = 0$	$l = 1$	$l = 2$	$l = 3$
$L = 0$	$L = \sqrt{2}\hbar$	$L = \sqrt{6}\hbar$	$L = 2\sqrt{3}\hbar$

To a good approximation, the energy of the electron does not depend on the the angular momentum quantum number l . This is true for classical orbits as well. Two planets with identical semi major axes will have the same total energy even if their eccentricities (how elliptical their orbits are) are different. In classical physics the angular momentum determines the shape and eccentricity of the orbit.

7.2.3 Magnetic Quantum Number

Knowing the magnitude of the angular momentum $|\vec{L}|$ as specified by the angular momentum quantum number l doesn’t tell you anything about the direction it points in space. Classically, to know \vec{L} you would have to know two more pieces of information: either two components such as

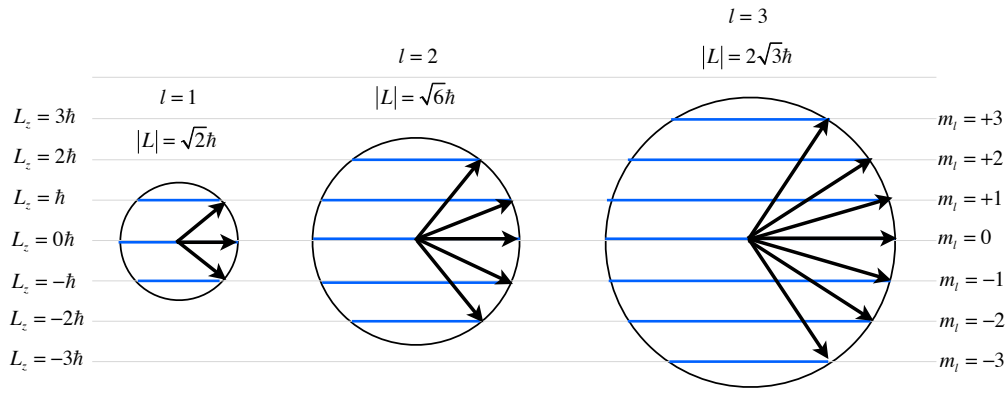


Figure 3: Angular momentum states for p , d and f orbitals.

L_z and L_x or two angles θ and ϕ describing the direction in which it points. However, in quantum mechanics, it turns out that you cannot know all three components of the angular momentum of the electron simultaneously (this is another form of the Heisenberg uncertainty principle). All you can know is the magnitude of the angular momentum vector $|\vec{\mathbf{L}}|$ and **one** of its components. By convention, we call this component the z component, i.e. L_z . The magnetic quantum number tells us that the z component of the angular momentum vector is quantized and lies in the range $[-l, +l]$:

$$L_z = m_l \hbar \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l.$$

Thus, the possible magnetic quantum numbers for different angular momentum states are

s orbital	$l = 0$	$m_l =$	0
p orbital	$l = 1$	$m_l =$	-1, 0, +1
d orbital	$l = 2$	$m_l =$	-2, -1, 0, +1, +2
f orbital	$l = 3$	$m_l =$	-3, -2, -1, 0, +1, +2, +3

Knowing both $|\vec{\mathbf{L}}|$ and L_z means that you can know the angle θ the angular momentum vector points with respect to the z axis, but not the azimuthal angle ϕ around the “equator.” In other words, you can specify a “cone” within which the angular momentum vector must lie, but you cannot know the position with the cone (see Figures 2 and 3). The angle from the “pole” is

$$\theta = \frac{L_z}{|\vec{\mathbf{L}}|} = \frac{m_l}{\sqrt{l(l+1)}}.$$

7.2.4 All Together Now (So Far)

Let’s put all the quantum numbers together in one place. The quantum numbers look like the following for the first three energy levels:

$n = 1$	$l = 0$	(s orbital)	$m_l = 0$
$n = 2$	$l = 0$	(s orbital)	$m_l = 0$
	$l = 1$	(p orbital)	$m_l = 0 \pm 1$
$n = 3$	$l = 0$	(s orbital)	$m_l = 0$
	$l = 1$	(p orbital)	$m_l = 0 \pm 1$
	$l = 3$	(d orbital)	$m_l = 0 \pm 1 \pm 2$

Because the energy of the atom only depends on the principal quantum number, we see that the $n = 2$ and $n = 3$ energy levels are degenerate, with 4-fold and 9-fold degeneracy, respectively. Later in this chapter we'll see that the spin of the electron adds an additional quantum state, so the actual degeneracy is 2, 8, and 18 for the $n = 1, 2,$ and 3 levels.

7.3 Magnetic Dipole Moment

We know from classical physics that a current loop will create a magnetic field (see Figure 4). The **magnetic dipole moment** $\vec{\mu}$ of the field is defined as

$$\mu = IA$$

where I is the current and A is the area of the loop. We can express the magnetic dipole moment in terms of the angular momentum of the orbiting particle as follows. The current of a moving charge may be calculated as

$$\begin{aligned} I &\approx \frac{\Delta q}{\Delta t} \\ &= \frac{q}{2\pi r/v} \\ &= \frac{qv}{2\pi r} \end{aligned}$$

The magnitude of the magnetic moment is then

$$\begin{aligned} \mu &= IA \\ &= \left(\frac{qv}{2\pi r}\right) \pi r^2 \\ &= \frac{q}{2m} mvr \\ &= \frac{q}{2m} L \end{aligned}$$

Written as a vector and substituting $q = -e$, this becomes

$$\vec{\mu} = -\frac{e}{2m_e} \vec{L}.$$

Notice that the negative charge of the electron causes the magnetic moment to point in the opposite direction from the angular momentum vector.

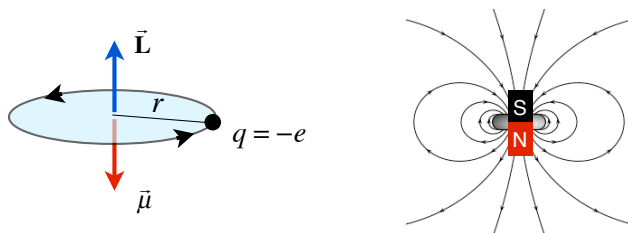


Figure 4: Magnetic moment of a negative charge moving in a circular orbit.

Because the orbital angular momentum is quantized, the orbital magnetic moment will also be quantized. The z component of the magnetic moment is

$$\begin{aligned}\mu_z &= -\frac{e}{2m_e}L_z \\ &= -\frac{e}{2m_e}m_l\hbar \\ &= -m_l\mu_B\end{aligned}$$

where the **Bohr magneton** is defined as

$$\mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \text{ J/T.}$$

7.4 Dynamics of Magnetic Dipoles

The behavior of a magnetic dipole placed in an external magnetic field will depend on the geometry of the field:

1. **Uniform magnetic field** - The potential energy of a magnetic dipole in an external, uniform magnetic field is given by $U = -\vec{\mu} \cdot \vec{B}$. Thus, when the dipole is aligned with the field the potential energy is at a minimum. When the dipole is anti-aligned, the potential energy is maximum. However, the dipole feels not *net* force from the external field.
2. **Non-uniform magnetic field** When the external magnetic field is nonuniform, the dipole feels a net force $F_z \approx \mu_z \frac{\partial B_z}{\partial z}$.

7.5 Spin Angular Momentum

In quantum mechanics, we encounter two kinds of angular momentum:

1. **Orbital Angular Momentum, L** - Picture the orbital motion of the electron around the nucleus. The orbital quantum number always takes on integer values: $l = 0, 1, 2, \dots$
2. **Spin Angular Momentum, S** - Picture a planet spinning on its axis (but electrons don't literally "spin"). Spin is *intrinsic* angular momentum of fundamental particles. The spin quantum number of an electron is $s = 1/2$.

All the ideas we have developed so far for orbital angular momentum $\vec{\mathbf{L}}$ translate over to spin angular momentum $\vec{\mathbf{S}}$.

The spin of the electron introduces a new degree of freedom into our picture of the atom. While the magnitude of the electron's spin is fixed, its component along the z axis can take on two values: $S_z = m_s \hbar = \pm(1/2)\hbar$. We often call the $m_s = +1/2$ state the "spin up" state and the $m_s = -1/2$ state as the "spin down" state.

	Orbital	Spin
Quantum number	$l = 0, 1, 2, 3, \dots$	$s = 1/2$
Magnitude of angular momentum vector	$ \vec{\mathbf{L}} = \sqrt{l(l+1)} \hbar$	$ \vec{\mathbf{S}} = \sqrt{s(s+1)} \hbar$
z component of angular momentum	$L_z = m_l \hbar$	$S_z = m_s \hbar$
magnetic quantum number	$m_l = 0, \pm 1, \pm 2, \dots, \pm l$	$m_s = \pm 1/2$

7.6 Hydrogen Wave Functions

Solving the three-dimensional Schrodinger equation in spherical coordinates for the Coulomb potential requires a bit of work. Even Erwin Schrodinger looked for help from his mathematician friend, Hermann Weyl, when he originally solved the problem. As mentioned in section 7.1, the energy eigenfunctions (or standing waves) are separable in terms of the three spherical coordinates. We can write the solution like this

$$\psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r) Y_l^{m_l}(\theta, \phi)$$

where $R_{n,l}(r)$ is called the radial wave function and $Y_l^{m_l}(\theta, \phi)$ are known as **spherical harmonics**. The spherical harmonics are separable in terms of θ and ϕ :

$$Y_l^{m_l}(\theta, \phi) = \Theta_{l,m_l}(\theta) \Phi_{m_l}(\phi).$$

Examples of hydrogen wave functions for the first three energy levels are given in Figure 5.

7.7 Probability Densities

In one-dimensional wave mechanics, we saw that the probability of finding a particle in an infinitesimal element dx is $P(x) = |\psi(x)|^2 dx$. Thus, the probability of finding it on the interval (a, b) is $P(a, b) = \int_a^b |\psi(x)|^2 dx$. In spherical coordinates, we replace the infinitesimal line element dx with a volume element

$$dV = r^2 \sin \theta dr d\theta d\phi$$

The probability of finding our electron in this volume element is

$$P(r, \theta, \phi) = |\psi_{n,l,m_l}(r, \theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi$$

The condition for normalization (i.e. that there is a 100% chance of finding the electron *somewhere*) is

$$\int_0^\pi \int_0^{2\pi} \int_0^\infty |\psi_{n,l,m_l}(r, \theta, \phi)|^2 r^2 \sin \theta dr d\phi d\theta = 1.$$

Hydrogen Wave Functions

n	l	m_l	$R(r)$	$\Theta(\theta)$	$\Phi(\phi)$
1	0	0	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	0	0	$\frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
2	1	0	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\sqrt{\frac{3}{2}} \cos \theta$	$\frac{1}{\sqrt{2\pi}}$
2	1	± 1	$\frac{1}{\sqrt{3}(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\mp \frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	0	0	$\frac{2}{(3a_0)^{3/2}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
3	1	0	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\sqrt{\frac{3}{2}} \cos \theta$	$\frac{1}{\sqrt{2\pi}}$
3	1	± 1	$\frac{8}{9\sqrt{2}(3a_0)^{3/2}} \left(\frac{r}{a_0} - \frac{r^2}{6a_0^2}\right) e^{-r/3a_0}$	$\mp \frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	0	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\sqrt{\frac{5}{8}} (3 \cos^2 \theta - 1)$	$\frac{1}{\sqrt{2\pi}}$
3	2	± 1	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\mp \sqrt{\frac{15}{4}} \sin \theta \cos \theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$
3	2	± 2	$\frac{4}{27\sqrt{10}(3a_0)^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$

Figure 5: Radial and angular wave functions for the hydrogen atom for the first three energy levels.

After substituting the radial and angular wave functions, we may write the probability of finding the electron in a finite volume of space bounded by $r_1 \leq r \leq r_2$, $\theta_1 \leq \theta \leq \theta_2$ and $\phi_1 \leq \phi \leq \phi_2$ as

$$P(r_1, r_2; \theta_1, \theta_2; \phi_1, \phi_2) = \int_{r_1}^{r_2} |R_{n,l}(r)|^2 r^2 dr \int_{\theta_1}^{\theta_2} |\Theta_{l,m_l}(\theta)|^2 \sin \theta d\theta \int_{\phi_1}^{\phi_2} |\Phi_{m_l}(\phi)|^2 d\phi.$$

All three integrals are independent. All three wave functions are also independently normalized, so the following are true:

$$\begin{aligned} \int_0^\infty |R_{n,l}(r)|^2 r^2 dr &= 1 \\ \int_0^\pi |\Theta_{l,m_l}(\theta)|^2 \sin \theta d\theta &= 1 \\ \int_0^{2\pi} |\Phi_{m_l}(\phi)|^2 d\phi &= 1. \end{aligned}$$

7.7.1 Radial Probability Density

If we only care about calculating the probability of finding the electron as a function of its distance away from the nucleus, then we can integrate out the angular part of the wave function. This gives us the radial probability density:

$$P(r)dr = |R_{n,l}(r)|^2 r^2 dr \int_0^\pi |\Theta_{l,m_l}(\theta)|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi_{m_l}(\phi)|^2 d\phi.$$

or

$$P(r)dr = |R_{n,l}(r)|^2 r^2 dr.$$

The probability of finding the electron between two radii is

$$P(r = a, r = b) = \int_a^b |R_{n,l}(r)|^2 r^2 dr.$$

7.7.2 Radial Expectation Value

Suppose you could measure the distance from the electron to the atomic nucleus. You repeat the experiment over and over. The average of these measurements is the expectation value. We can calculate the expectation value as follows:

$$\begin{aligned} \langle r \rangle &= \int_0^\infty r P(r) dr \\ &= \int_0^\infty r |R(r)|^2 r^2 dr \\ &= \int_0^\infty r^3 |R(r)|^2 dr \end{aligned}$$

7.8 Useful Integrals

You may find the following integrals helpful when doing calculations with the radial probability density:

$$\int x^n e^{-ax} dx = -\frac{e^{-ax}}{a} \left[x^n + \frac{n x^{n-1}}{a} + \frac{n(n-1) x^{n-2}}{a^2} + \dots + \frac{n!}{a^n} \right]$$

and

$$\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}.$$