

6.2: The Quantum Mechanical H-atom

As is so often the case for quantum mechanical systems, the story of the hydrogen atom begins with writing down the Hamiltonian describing the system.

The Potential Energy and the Hamiltonian

The time-independent Schrödinger equation has the following form.

$$\hat{H}\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + U(r) \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$$

where μ is the reduced mass for the electron/nucleus system. The Laplacian operator has the form

$$\begin{aligned} \nabla^2 &= \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \hat{L}^2 \end{aligned}$$

The potential energy is given by the electrostatic attraction of the electron to the nucleus.

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

where Z is the charge on the nucleus in electron charges (also given by the atomic number), e is the charge on an electron and ϵ_0 is the vacuum permittivity.

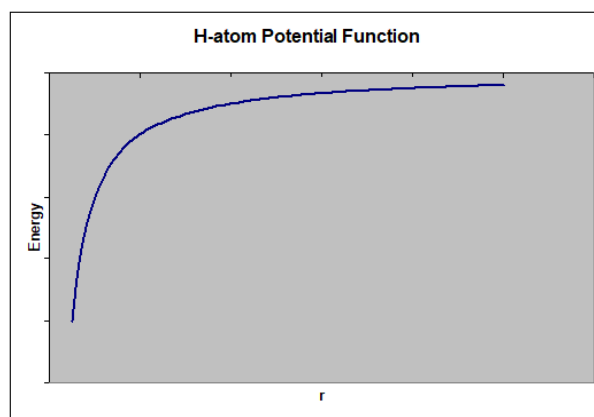


Figure 6.2.1

The $\frac{1}{r}$ dependence means that the electrostatic attraction diminishes as the distance between the electron and the nucleus is increased. The potential energy approaches zero as r goes to ∞ , at which point the atom ionizes.

Putting this all together allows the Hamiltonian to be expressed as

$$\hat{H} = -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Ze^2}{4\pi\epsilon_0 r} + \frac{1}{2\mu r^2} \hat{L}^2$$

The wavefunctions can be expressed as a product of a radial part and an angular part since the Hamiltonian is separable into these two parts.

$$\psi(r, \theta, \phi) = R(r)Y_l^{m_l}(\theta, \phi)$$

The angular part of the function, $Y_l^{m_l}(\theta, \phi)$ are the spherical harmonics and are eigenfunctions of the \hat{L}^2 operator. Substitution into the Schrödinger equation yields

$$Y_l^{m_l}(\theta, \phi) \left(-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) R(r) + \frac{R(r)}{2\mu r^2} \hat{L}^2 Y_l^{m_l}(\theta, \phi) = ER(r) Y_l^{m_l}(\theta, \phi)$$

Since the spherical harmonics are eigenfunctions of the \hat{L}^2 operator, the following substitution can be made.

$$\hat{L}^2 Y_l^{m_l}(\theta, \phi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta, \phi)$$

After making this substitution and dividing both sides by $Y_l^{m_l}(\theta, \phi)$, we get

$$\left(-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{Ze^2}{4\pi\epsilon_0 r} \right) R(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} R(r) = ER(r)$$

However, since l shows up in the equation in which we are solving for the radial wavefunctions $R(r)$, it is not to be unexpected that the solution to the radial part of the equation will place new constraints on the quantum number l . In fact, the radial wavefunctions themselves depend on l and a **principle quantum number** n .

The Energy Levels

Applying the boundary condition that the radial wavefunction $R(r)$ must vanish as $r \rightarrow \infty$, the only wavefunctions that behave properly have the following eigenvalues

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

Notice also that this expression vanishes as n approaches ∞ , which is the ionization limit of the atom. Also, since the energy expression depends only on n (and not on l and m_l) it is expected that there will be a great deal of degeneracy in the wavefunctions.

Taking differences between two energies levels (to derive an expression for the energy differences that can be observed in the spectrum of hydrogen), it is seen that

$$E_{n'} - E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right) = \frac{\mu Z^2 e^4}{2\hbar^2 (4\pi\epsilon_0)^2} \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$

which is exactly the form of the Rydberg Equation. Now dividing both sides by hc in order to convert from energy units to wavenumber units

$$\begin{aligned} \frac{E_{n'} - E_n}{hc} &= \frac{\mu Z^2 e^4}{(hc) 2\hbar^2 (4\pi\epsilon_0)^2} \left(\frac{1}{n^2} - \frac{1}{n'^2} \right) \\ &= 109677.581 \text{ cm}^{-1} \left(\frac{1}{n^2} - \frac{1}{n'^2} \right) \end{aligned}$$

using the reduced mass for the hydrogen atom and a nuclear charge of +1. So this model also predicts the correct value for the **Rydberg constant** R_H .

The Rydberg Constant for Heavier Nuclei

The expression for the Rydberg constant is

$$R_H = \frac{\mu e^4}{(hc) 2\hbar^2 (4\pi\epsilon_0)^2}$$

which has a value of $R_H = 109677.581 \text{ cm}^{-1}$. In this expression, μ is the reduced mass of the electron-proton system in the hydrogen atom. But what happens when the mass of the nucleus is extremely large? First, consider the reduced mass.

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

Where m_e is the mass of an electron and m_N is the mass of the nucleus. In the case that the nuclear mass is extremely large compared to the mass of an electron, the total mass is approximately equal to the mass of the nucleus.

$$(m_e + m_N) \approx m_N$$

In this case, the reduced mass becomes

$$\begin{aligned}\mu &= \frac{m_e m_N}{m_e + m_N} \\ &\approx \frac{m_e m_N}{m_N} = m_e\end{aligned}$$

And the Rydberg constant expression comes to

$$\begin{aligned}R_\infty &= \frac{m_e e^4}{(hc)2\hbar^2(4\pi\epsilon_0)^2} \\ &= 109737.316 \text{ cm}^{-1}\end{aligned}$$

where R_∞ indicates the Rydberg constant for an infinite mass nucleus atom. It is this value that is usually found in tables of physical constants.

But for lighter atoms, such as hydrogen, the value of the Rydberg constant deviates from this value. In fact, hydrogen shows the largest deviation for any atom, given that it has the lightest nucleus. Compared to experimental precision, this deviation is important (even for atoms where the mass of an electron is only 1×10^{-6} times that of the nucleus!) if one hopes to fit data to experimental precision.

To address this problem, we look back to the expression for the Rydberg constant for an arbitrary mass nucleus, R_M .

$$\begin{aligned}R_M &= \frac{\mu e^4}{(hc)2\hbar^2(4\pi\epsilon_0)^2} \\ &= \left(\frac{m_N}{m_e + m_N}\right) \frac{m_e e^4}{(hc)2\hbar^2(4\pi\epsilon_0)^2} = \left(\frac{m_N}{m_e + m_N}\right) R_\infty\end{aligned}$$

Clearly as the mass of the nucleus (m_N) becomes larger, the value of R_M will approach that of R_∞ asymptotically.

The Wavefunctions

The hydrogen atom wavefunctions $\psi(r, \theta, \phi)$ can be expressed as a product of radial and angular functions.

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

The angular part is simply the spherical harmonics that were described in [Chapter 5](#), depend on the quantum numbers l and m_l . More details of how the spherical harmonics are generally presented as H-atom angular functions is discussed in section 3.i. The radial part of the wave functions, $R_n^l(\theta, \phi)$ will be described in a later section.

The Angular Part of the Wavefunctions

Each orbital wave function can be designated with a letter that indicates the value of l as assigned in the following table.

l	Designation
0	s
1	p
2	d
3	f

The angular parts of the wavefunctions are given by the spherical harmonics. After taking linear combinations to eliminate the imaginary part of the wave functions, the familiar shapes of s, p, d and f orbitals are generated. For example, the p_x and p_y orbitals are generated as linear combinations of the p_{-1} and p_1 orbitals.

$$\begin{aligned}p_x &= \frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1}) \propto \sin \theta \cos \phi \\ p_y &= \frac{1}{i\sqrt{2}}(Y_1^1 + Y_1^{-1}) \propto \sin \theta \sin \phi\end{aligned}$$

Similar linear combinations are used to generate the $d_{x^2-y^2}$, d_{xy} , d_{yz} and d_{xz} functions.

$$d_{z^2} = Y_2^0$$

$$d_{xz} = -\frac{1}{\sqrt{2}}(Y_2^1 - Y_2^{-1}) \quad d_{yz} = -\frac{1}{i\sqrt{2}}(Y_2^1 + Y_2^{-1})$$

$$d_{xy} = -\frac{1}{\sqrt{2}}(Y_2^2 - Y_2^{-2}) \quad d_{x^2-y^2} = -\frac{1}{i\sqrt{2}}(Y_2^2 + Y_2^{-2})$$

There are multiple choices for how to take linear combinations to generate the f orbital functions (the best choice being determined by the geometry of the complex in which an f-orbital containing atom exists), so these are rarely shown in textbooks! The tables below give the angular parts of s, p and d hydrogen atom orbitals. The linear combinations shown above have been used to eliminate the imaginary parts of the wave functions. The result is what is usually plotted for the shapes of these orbitals.

l	Orbital	$Y_l^{m_l}(\theta, \phi)$
0	s	$\sqrt{\frac{1}{4\pi}}$
1	p_x	$\sqrt{\frac{3}{4\pi}} \sin(\theta) \cos(\phi)$
	p_y	$\sqrt{\frac{3}{4\pi}} \sin(\theta) \sin(\phi)$
	p_z	$\sqrt{\frac{3}{4\pi}} \cos(\theta)$

l	Orbital	$Y_l^{m_l}(\theta, \phi)$
2	d_{z^2}	$\sqrt{\frac{5}{16\pi}} (3 \cos^2(\theta) - 1)$
	d_{xz}	$\sqrt{\frac{15}{16\pi}} \sin(\theta) \cos(\theta) \sin(\phi)$
	d_{yz}	$\sqrt{\frac{15}{16\pi}} \sin(\theta) \cos(\theta) \cos(\phi)$
	d_{xy}	$\sqrt{\frac{15}{64\pi}} \sin^2(\theta) \sin(2\phi)$
	$d_{x^2-y^2}$	$\sqrt{\frac{15}{64\pi}} \sin^2(\theta) \cos(2\phi)$

These functions generate the familiar angular parts of the hydrogen atom wavefunctions. Some depictions are shown in the figure below.

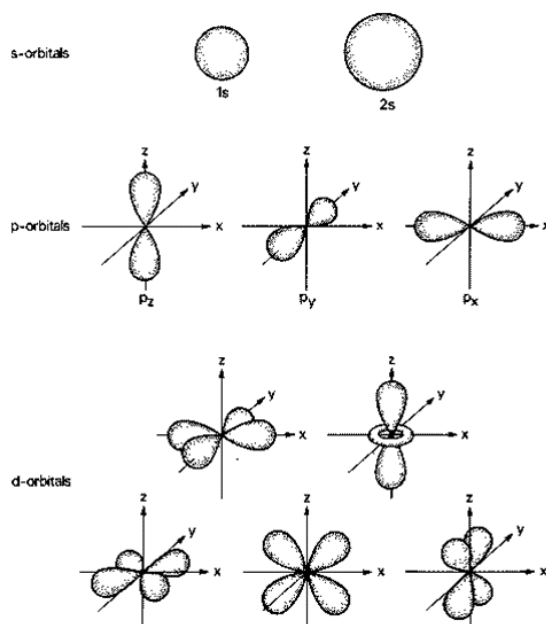


Figure 6.2.2

The Radial Part of the Wavefunctions

The radial part of the wavefunction has three parts. 1) a normalization constant, 2) an associated Laguerre Polynomial and 3) an exponential part that ensures the wavefunction vanishes as $r \rightarrow \infty$. The associated Laguerre polynomials are derived from the Laguerre polynomials (much like the associated Legendre Polynomials were from the Legendre polynomials.) The Laguerre polynomials can be derived from the expression

$$L_n(x) = \frac{e^x}{n!} \frac{d^n}{dx^n} x^n e^{-x}$$

The first few Laguerre polynomials are given by

n	$L_n(x)$
0	1
1	$-x + 1$
2	$\frac{1}{2}(x^2 - 4x + 2)$
3	$\frac{1}{6}(-x^3 + 9x^2 - 18x + 6)$

A recursion formula for these functions is given by

$$L_{n+1}(x) = (2n + 1 - x) L_n(x) - n^2 L_{n-1}(x)$$

The associated Laguerre polynomials can be generated using the expression

$$L_n^\alpha(x) = \frac{d^\alpha}{dx^\alpha} L_n(x)$$

This expression is used to generate an associated Laguerre polynomial of degree $n - \omega$ and order ω . The functions of interest to the hydrogen atom radial problem are the associated Laguerre polynomials of degree $n - l - 1$ and order $2l + 1$. It can be shown that these functions can be generated from the relationship

$$L_{n+l}^{2l+1}(x) = \sum_{k=0}^{n-l-1} (-1)^{k+1} \frac{[(n+l)!]^2}{(n-1-l-k)! (2l+1+k)! k!} x^k$$

Note that when $n - l - 1$ is less than zero, the functions vanish. This leads to the restriction on the quantum number l that comes from the solutions to the radial part of the problem.

$$l \leq n - 1$$

The first few associated Laguerre polynomials that appear in the hydrogen atom wavefunctions are shown below.

n	l	$L_{n+l}^{2l+1}(x)$	# nodes
1	0	$L_1^1(x)$	-1
2	0	$L_2^1(x)$	$-2!(2-x)$
	1	$L_3^3(x)$	$-3!$
3	0	$L_3^1(x)$	$-3!(3-3x-\frac{1}{2}x^2)$
	1	$L_4^3(x)$	$-4!(4-x)$
	2	$L_5^5(x)$	$-5!$

Notice that if $(2l+1)$ exceeds $(n+l)$, the derivative causes the function to go to zero, as was the case for the associated Legendre Polynomials when m_l exceeds l . This provides the constraint on l that was expected to be found in the solution to the radial part given that l shows up in the equation to be solved.

$$l \leq n - 1$$

Typically, x is replaced by a new function in r , ρ . ρ is defined as follows:

$$\rho = \left(\frac{2Zr}{na_0} \right)$$

where a_0 is the Bohr radius. The overall expression for the radial wavefunction is given as follows:

$$R_{nl}(r) = - \left[\frac{(n-l-1)!}{2n[(n+l)!]^3} \right]^{1/2} \left(\frac{Z}{na_0} \right)^{l+3/2} r^l L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right) e^{-r/na_0}$$

The first several radial wavefunctions are given below.

n	l		$R_n^l(\rho)$
1	0	1s	$2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-\frac{Zr}{a_0}}$
2	0	2s	$\left(\frac{Z}{2a_0} \right)^{3/2} (2-\rho) e^{-\rho/2}$
	1	2p	$\frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{3/2} \rho e^{-\rho/2}$
3	0	3s	$\frac{2}{27} \left(\frac{Z}{3a_0} \right)^{3/2} (27-18\rho+2\rho^2) e^{-\rho}$
	1	3p	$\frac{1}{27} \left(\frac{2Z}{3a_0} \right)^{3/2} (6\rho-\rho^2) e^{-\rho/3}$
	2	3d	$\frac{4}{27\sqrt{10}} \left(\frac{Z}{3a_0} \right)^{3/2} \rho^2 e^{-\rho/3}$

where $\rho = Zr/a_0$. a_0 is the Bohr radius, which has a value of $5.29177249 \times 10^{-11}$ m.

✓ Example 6.2.1

What is the expectation value of r for the electron if it is in the 1s subshell of an H atom?

Solution

The expectation value can be found from

$$\langle r \rangle = \int_0^\infty \psi_{1s}^* \cdot r \cdot \psi_{1s} r^2 dr$$

Where $r^2 dr$ comes from the r portion of the volume element $dx dy dz$ after it has been transformed into spherical polar coordinates.

Substituting the wavefunction from above yields

$$\langle r \rangle = \int_0^\infty \left[2 \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \right] r \left[2 \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \right] r^2 dr$$

This expression simplifies to

$$\langle r \rangle = 4 \left(\frac{1}{a_0} \right)^3 \int_0^\infty r^3 \left[e^{-\frac{2r}{a_0}} \right] dr$$

A table of integrals shows

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

Substituting the above integral into the general form results in

$$\begin{aligned} \langle r \rangle &= 4 \left(\frac{1}{a_0} \right)^3 \left(\frac{6}{\left(\frac{2}{a_0} \right)^4} \right) \\ &= \frac{24}{16} \left(\frac{1}{a_0^3} \right) (a_0^4) \\ &= \frac{3}{2} a_0 \end{aligned}$$

✓ Example 6.2.2

What is the most probable value of r for the electron in a hydrogen atom in a 1s orbital?

Solution

The most probable value of r will be found at the maximum of the function

$$P(r) = r^2 [R(r)]^2$$

This can be found by taking the derivative and setting it equal to zero. First, let's find the probability function

$$P(r) = r^2 \left[2 \left(\frac{1}{a_0} \right)^{\frac{3}{2}} e^{-\frac{r}{a_0}} \right]^2 = \frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}}$$

At the maximum, the derivative is zero.

$$\frac{d}{dr} P(r) = 0$$

So

$$\frac{d}{dr} \left[\frac{4}{a_0^3} r^2 e^{-\frac{2r}{a_0}} \right] = \frac{4}{a_0^3} \left(2r e^{-\frac{2r}{a_0}} - \frac{2}{a_0} r^2 e^{-\frac{2r}{a_0}} \right) = 0$$

After dividing both sides by $\frac{4}{a_0^3}$, and placing the right-hand term on the other side of the equals sign, this simplifies to

$$2r e^{-\frac{2r}{a_0}} = \frac{2}{a_0} r^2 e^{-\frac{2r}{a_0}}$$

This is further simplified by dividing both sides by $e^{-\frac{2r}{a_0}}$:

$$2r = \frac{2}{a_0} r^2$$

The rest of the algebra is straight forward (actually, all of the algebra was straight-forward, but who is counting?)

$$r = a_0$$

Nodes

A hydrogen atom wavefunction can have nodes in either the orbital (angular) part of the wavefunction or the radial part. The total number of nodes is always given by $n-1$. The number of **angular nodes** is always given by l . The number of radial nodes, therefore, is determined by both n and l . Consider the following examples.

Nodes

	radial	angular	total
1s	0	0	0
4d	2	1	3
5f	1	3	4
2d		-	-
2p	0	1	1

Notice that it is impossible to form a 2d wavefunction as it violates the relationship that

$$l \leq n-1$$

causing the radial wavefunction to vanish. This is easy to see as the combination of $n = 2$ and $l = 3$ implies that there are -1 radial nodes, which is clearly impossible.

Shells, Subshells and Orbitals

It is convenient to name the different subdivisions of the electronic structure of a hydrogen atom. The subdivisions are based on the quantum numbers n , l and m_l . A **shell** is characterized by the quantum number n . (Examples: the $n=2$ shell or the $n=4$ shell.) A **subshell** is characterized by both the quantum number n and l . (Examples: the 2s subshell or the 3d subshell.) An **orbital** is characterized by the quantum number n , l , and m_l . (Examples: the $2p_0$ orbital or the 5f1 orbital.) It should be noted that an orbital can also be constructed from a linear combination of other orbitals! (Example: the $2p_x$ orbital or the $3d_{xy}$ orbital.)

Degeneracy

The hydrogen atom wavefunctions have high degeneracies since the energy of a given level depends only on the principle quantum number n . As such, all wavefunctions with the same value of n will have the same eigenvalue to the Hamiltonian, and are degenerate. Recall the following relationships:

$$l \leq n-1 \text{ and } m_l \leq l$$

These relationships can be used to fill in the following table that indicates the degeneracies of the hydrogen atom energy levels.

Subshell	n	l	m_l	m_s	orbital	total
1s	1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	1	2
2s	2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	4	8
2p		1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$		
3s	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	9	18
3p		1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$		

Subshell	n	l	m_l	m_s		
3d		2	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$		
4s	4	0	0	$+\frac{1}{2}, -\frac{1}{2}$	16	32
4p		1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$		
4d		2	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$		
4f		3	+3, +2, +1, 0, -1, -2, -3	$+\frac{1}{2}, -\frac{1}{2}$		

It is clear that the total degeneracy of a shell is given by $2n^2$.

The Overall Wavefunctions

The total wavefunction, including both angular and radial parts, for hydrogen-like atoms is given by

$$\Psi_{nlm_l} = R_{nl}(r) Y_l^{m_l}(\theta, \phi)$$

The first few hydrogen atom orbital wavefunctions are given in the table below.

Shell	Subshell	m_l	Wavefunction	
1	1s	0	ψ_{100}	$\frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-\rho}$
2	2s	0	ψ_{200}	$\frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0} \right)^{3/2} (2 - \rho) e^{-\rho/2}$
	2p	0	ψ_{210}	$\frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \rho e^{-\rho/2} \cos(\theta)$
		± 1	$\psi_{21\pm 1}$	$\frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_0} \right)^{3/2} \rho e^{-\rho/2} \sin(\theta)$

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