

## Chapter 6: The Hydrogen Atom

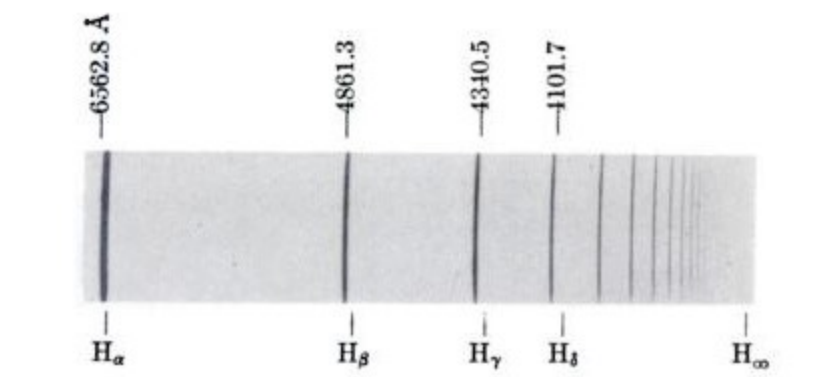
The hydrogen atom problem was one that was very perplexing to the pioneers of quantum theory. While its quantized nature was evident from the known atomic emission spectra, there were no models that could adequately describe the patterns seen in the spectra.

### Older Models of the Hydrogen Atom

Two of the most important (historically) models of the hydrogen atom and its energy levels/spectra were proved by Johannes Balmer, a high school teacher, and Niels Bohr, a Danish physicist. Balmer's model was a completely empirical fit to existing data for the emission spectrum of hydrogen, whereas Bohr provided an actual theoretical underpinning to the form of the model which Balmer derived. In this section, we will discuss the development and ramifications of these two models.

### Balmer's Formula

Balmer (Balmer, 1885) was the first to provide an empirical formula that gave a very good fit to the data, but offered no theoretical reasoning as to why the formula had the simple form it did. Balmer felt, however, that despite the lack of a theoretical foundation, such a simple pattern could not be the result of an "accident".



Balmer suggested the formula

$$\lambda = G \left( \frac{n^2}{n^2 - 4} \right)$$

to calculate the wavelengths ( $\lambda$ ) of the lines in the visible emission spectrum of hydrogen. In this formula,  $G = 3647.053 \text{ Å}$ , which is the series limit (depicted as  $H_{\infty}$  in the figure above.) Balmer

considered this to be a “fundamental constant” for hydrogen and fully expected other elements to have similar fundamental constants.

In modern terms, Balmer’s formula has been extended to describe all of the emission lines in the spectrum of atomic hydrogen.

$$\tilde{\nu} = R_H \left( \frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

where  $n_l$  and  $n_u$  are integers with  $n_l < n_u$ .  $R_H$  is the Rydberg constant for hydrogen and has the value

$$R_H = 109677 \text{ cm}^{-1}$$

The job of subsequent investigators was to provide a theory that explained the form of the Rydberg Equation shown above and to correctly predict the value of the Rydberg Constant.

This model describes all known series of emission lines in the spectrum of atomic hydrogen. Each series is characterized by the lower state quantum number. The following table summarizes the names of these series.

$n_l$	Name	Region
1	Lyman	Vacuum Ultraviolet
2	Balmer	Visible/Ultraviolet
3	Paschen	Near Infrared
4	Brachen	Infrared
5	Pfund	Far Infrared

## The Bohr Model

Niels Bohr (Bohr, 1913) was the first person to offer a successful quantum theory of the hydrogen atom in his 1913 paper. He was later awarded the Nobel Prize in Physics in 1922 for his contributions to the understanding of atomic structures (as well as many other significant contributions.) And while the Bohr model has significant shortcomings in terms of providing the best description of a hydrogen atom, it still provides the basis (a “solar system model”) for how many people view atoms today.

Bohr’s model was mostly an extension of the Rutherford model of an atom, in which electrons exist in a cloud surrounding a dense, positively charged nucleus. The Bohr model suggested a possible structure to this cloud in an attempt to give an explanation of the empirical formula presented by Balmer. The strength of the Bohr model is that it does provide an accurate prediction not only of the form of Balmer’s formula, but also of the magnitude of the Rydberg constant that appears in the formula.

Bohr’s approach was to balance the electrostatic attractive force between an electron and a positively charged nucleus, with the centrifugal force the electron feels as it orbits the nucleus

in a circular orbit. He derived these orbits by making the assumption that the angular momentum of an orbiting electron is an integral multiple of  $\hbar$ .

While successful in predicting the form of the Rydberg Equation and the magnitude of  $R_H$ , the Bohr model presented some difficulty. First, it ignored the reality that a charged particle orbiting another (oppositely) charged nucleus would see its orbit decay over time, eventually colliding with the nucleus. This clearly does not happen with hydrogen! Also, the Bohr model was not extendable to larger atoms. Quantum mechanics would have to address these problems, while also providing the kind of explanations for the Rydberg Equation provided by Bohr.

## 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.

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

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

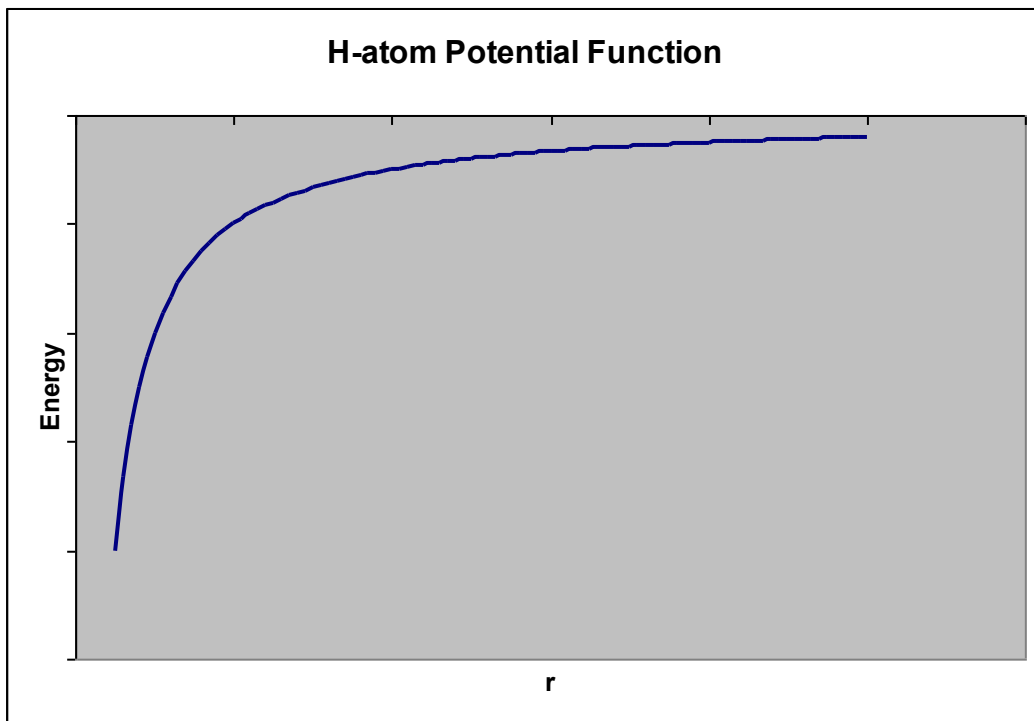
where  $\mu$  is the reduced mass for the electron/nucleus system. The Laplacian operator has the form

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

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  $\epsilon_0$  is the vacuum permittivity.



The  $1/r$  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  $\infty$ , 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  $\infty$ , 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

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

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,  $\mu$  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 equally 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

$$R_{\infty} = \frac{m_e e^4}{(hc)2\hbar^2 (4\pi\epsilon_0)^2}$$

$$= 109737.316 \text{ cm}^{-1}$$

where  $R_{\infty}$  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  $1 \times 10^{-6}$  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,  $R_M$ .

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

$$= \left( \frac{m_N}{m_e + m_N} \right) \frac{m_e e^4}{(hc)2\hbar^2 (4\pi\epsilon_0)^2}$$

$$= \left( \frac{m_N}{m_e + m_N} \right) R_{\infty}$$

Clearly as the mass of the nucleus ( $m_N$ ) becomes larger, the value of  $R_M$  will approach that of  $R_{\infty}$  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,  $R_n(r)$  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.

$$p_x = \frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1}) \propto \sin \theta \cos \phi$$

$$p_y = \frac{1}{i\sqrt{2}}(Y_1^1 + Y_1^{-1}) \propto \sin \theta \sin \phi$$

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

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

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

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

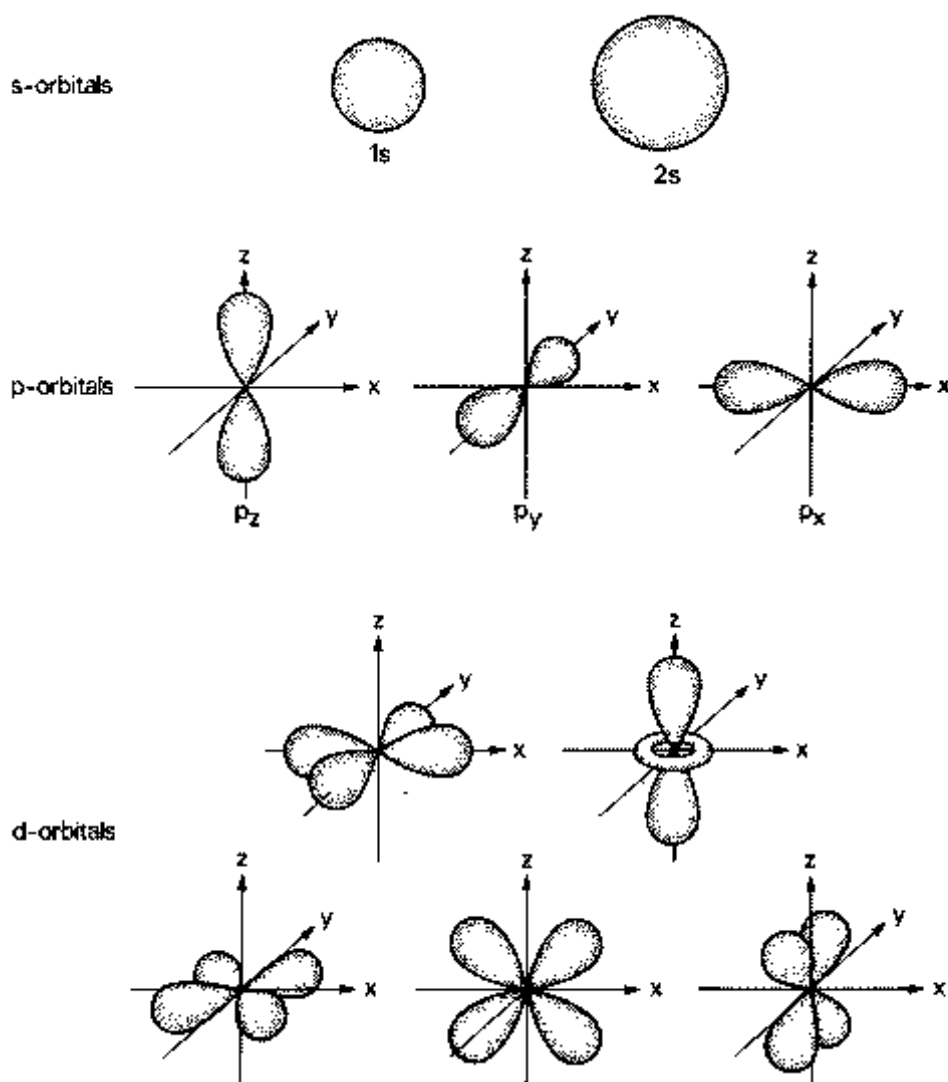
There are multiple choices for how to take linear combinations to generate the f orbital functions (the best choice being determined by the geometry of the complex in which an f-orbital containing atom exists), so these are rarely shown in textbooks! The tables below give the angular parts of s, p and 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.



### *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

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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  $n-\alpha$  and order  $\alpha$ . 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	0
2	0	$L_2^1(x)$	$-2!(2-x)$	1
	1	$L_3^3(x)$	$-3!$	0
3	0	$L_3^1(x)$	$-3!(3-3x-\frac{1}{2}x^2)$	2
	1	$L_4^3(x)$	$-4!(4-x)$	1

	2	$L_5^5(x)$	-5!	0
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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  $r, \rho$ .  $\rho$  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	$\frac{2}{27} \left( \frac{Z}{3a_0} \right)^{3/2} (27-18\rho+2\rho^2) e^{-\rho/3}$
	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  $5.291\,772\,49 \times 10^{-11}$  m.

**Example:** 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:** 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
4p	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 5f<sub>1</sub> 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:

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

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

Subshell	n	l	$m_l$	$m_s$	degeneracy	
					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	$+\frac{1}{2}, -\frac{1}{2}$		
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

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

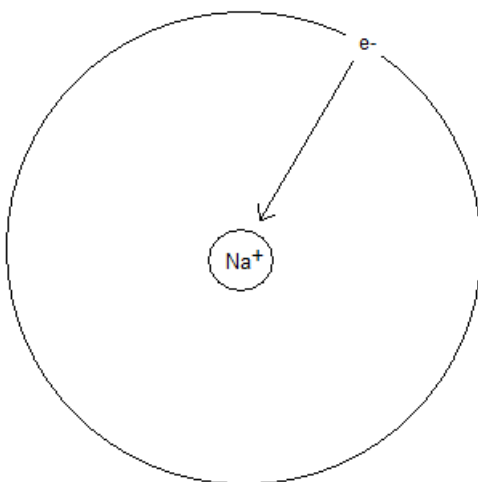
The first few hydrogen atom orbital wavefunctions are given in the table below.

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



## Rydberg Spectra of Polyelectronic Atoms

To a very good approximation, the electronic spectra of highly excited atoms look a lot like the spectrum of hydrogen. These highly excited states of atoms are called “Rydberg States” and to a good approximation, the excited electron in a Rydberg state “feels” the nucleus of the atom as a point charge. As this occurs, the atom comes to be in a state that looks much like a state in a hydrogen-like atom, with a heavy nucleus that has a +1 charge (the residual ion if the excited electron is removed).



In cases such as this, the energy levels of the excited electron can almost be treated using the Rydberg formula proposed by Balmer, and with the correct Rydberg constant ( $R_M$ ) and nuclear charge. The formula does not work perfectly, but can be forced to fit the data by introducing a “fudge factor.”

### Approximating a Hydrogen-like Atom

Scientists like to force the descriptions of real systems in terms of the limiting ideal cases with slight perturbations. In the case of real atoms, there are two common ways that this is typically done. One is to fudge the nuclear charge and the other is to fudge on the principle quantum number.

### Shielding and Effective Nuclear Charge

One “fudges” the nuclear charge by noting that the excited electron will not “see” the inner core ion as a point charge with a +1 charge. Instead, it will feel the full charge of the nucleus, but shielded by the electrons that remain in the ion. Thus, the **effective nuclear charge** ( $Z^*$ ) can be used.

$$\tilde{\nu} = (Z^*)^2 R_M \left( \frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

where  $Z^*$ , the effective nuclear charge, is defined by

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$$Z^* = Z - \sigma$$

where  $\sigma$  is the **shielding constant** and is determined by adding the effects of each of the inner electrons. The trouble with this approach is that the degree of shielding is dependent on the excitation level of the excited electron. The shielding constant  $\sigma$  should reach a limiting value for highly excited Rydberg states of the atom.

### *Quantum Defect and the Effective Principle Quantum Number*

Another approach is to “fudge” on the principle quantum number of the excited electron. The utility of using this method is that there is only one electron to treat, rather than a slew of electrons in the core ion, the shielding of each will be variable. In this method, the **effective principle quantum number**  $n^*$  is defined as

$$n^* = n - \delta$$

where  $\delta$  is the **quantum defect**. The quantum defect has the useful property that it reaches a constant value for electrons in atoms at high levels of excitation.

### *The ionization potential*

The ionization potential of an atom I defined by the enthalpy change at 0 K for the following reaction



If one pictures ionization as a series of excitations of the electron to be removed through a set of Rydberg states, one can deduce the ionization potential of an atom. (This is how atomic spectroscopy is used to determine highly accurate ionization potentials.)

Using the effective principle quantum number  $n^*$ , the energy levels can be expressed as

$$\frac{E}{hc} = \frac{IP}{hc} - \frac{R_M}{(n^*)^2}$$

Consider the Rydberg series in  $^{23}\text{Na}$ , the first few levels of which is given below. For Na, the Rydberg constant can be calculated

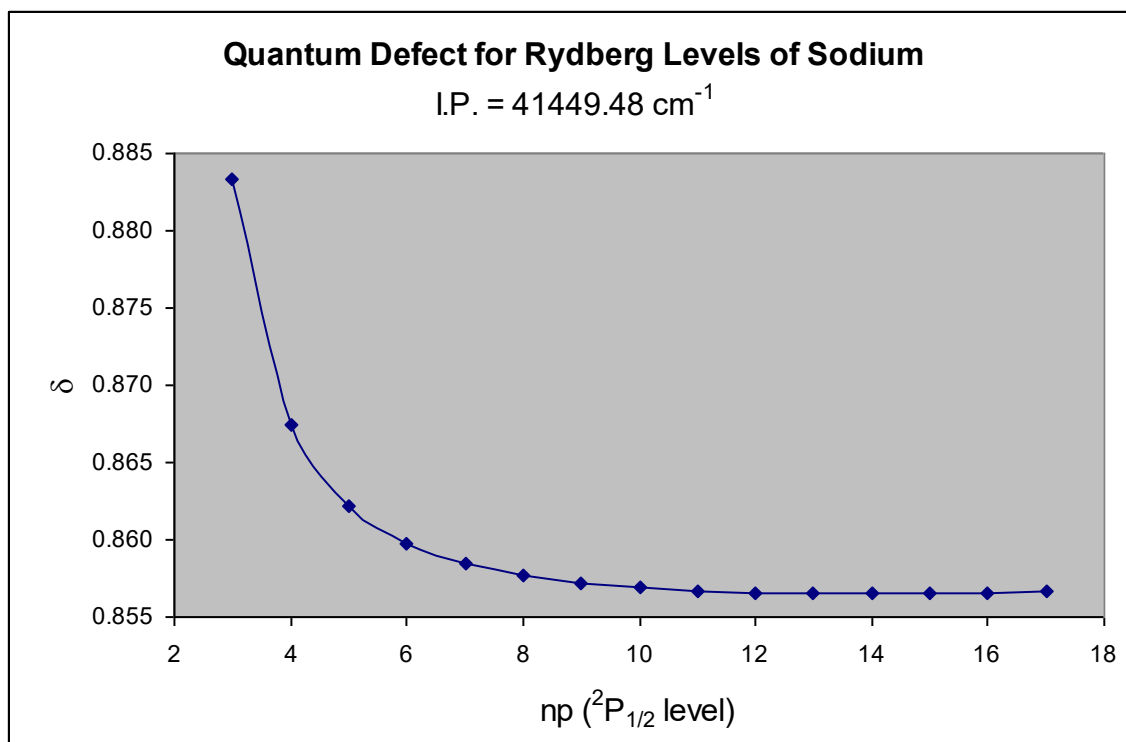
$$\begin{aligned}
 R_{Na} &= \left( \frac{m_{Na}}{m_e + m_{Na}} \right) R_{\infty} \\
 &= \left( \frac{3.81763 \times 10^{-26} \text{ kg}}{9.109 \times 10^{-31} \text{ kg} + 3.81763 \times 10^{-26} \text{ kg}} \right) (109737.316 \text{ cm}^{-1}) \\
 &= 109734.698 \text{ cm}^{-1}
 \end{aligned}$$

Based on a guess of the ionization potential, an effective principle quantum number can be calculated for each level from

$$n^* = \sqrt{\frac{R_{Na}}{IP - E}}$$

From  $n^*$ , one can calculate the quantum defect ( $\delta$ ) and adjust the guess of the ionization potential until  $\delta$  becomes constant for large  $n$ .

IP =	41449.48 cm <sup>-1</sup>		R <sub>Na</sub> =	109734.7 cm <sup>-1</sup>
level	n	δ	n*	Energy (cm <sup>-1</sup> )
3p	3	0.883	2.117	16956.17
4p	4	0.867	3.133	30266.99
5p	5	0.862	4.138	35040.38
6p	6	0.860	5.140	37296.32
7p	7	0.858	6.142	38540.18
8p	8	0.858	7.142	39298.35
9p	9	0.857	8.143	39794.48
10p	10	0.857	9.143	40136.80
11p	11	0.857	10.143	40382.92
12p	12	0.857	11.143	40565.78
13p	13	0.857	12.143	40705.34
14p	14	0.856	13.144	40814.27
15p	15	0.856	14.144	40900.91
16p	16	0.857	15.143	40970.97
17p	17	0.857	16.143	41028.41



This method is extremely sensitive and can be used to determine very precise values of ionization potentials for atoms. The above result is 5.145 eV, whereas the literature value for the ionization potential of sodium is 5.139 eV (Webelements). The slightly large value determined from this data is a consequence of only using a limited number of excited levels, and not the highest energy levels, which behave most Rydberg-like. A close examination of the data actually reveals that there is some curvature to the  $\delta$  vs  $n$  curve at high values of  $n$ . Since the curve is actually increasing at the larger values of  $n$ , it is an indication that the guess for the ionization potential is slightly high – a fact that is consistent with the literature value!

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## Vocabulary and Concepts

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angular nodes .....	161	quantum defect.....	165
effective nuclear charge .....	164	Rydberg constant .....	155
effective principle quantum number .....	165	shell .....	162
orbital .....	162	shielding constant.....	164
principle quantum number .....	155	subshell .....	162

## Problems

1. Calculate the finite-mass Rydberg constant ( $R_M$ ) for

- a. H
- b. D
- c.  ${}^7\text{N}$
- d.  ${}^{11}\text{Na}$

2. The 1s orbital wavefunction for hydrogen is given by

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left( \frac{1}{a_0} \right)^{3/2} e^{-\frac{r}{a_0}}$$

- a. Show that this wavefunction is normalized.
  - b. Find the expectation value of  $r$  in units of  $a_0$  (the Bohr Radius.)
3. Show that the 2s wavefunction for hydrogen is
    - a. Normalized
    - b. An eigenfunction of the Hamiltonian. (What is the eigenvalue?)
  4. The Laguerre Polynomial  $L_1(x)$  is given by

$$L_1(x) = -x + 1$$

The Associated Laguerre polynomials are generated from the relationship

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

- a. Show that the Associated Laguerre polynomials  $L_1^0(x) = -x + 1$ ,  $L_1^1(x) = -1$ , and  $L_1^2(x) = 0$ . (In fact,  $L_1^\alpha(x) = 0$  for any choice of  $\alpha > 1$ .)
- b. Given that the Associated Laguerre polynomials used in the radial wavefunctions of the Hydrogen atom problem are  $L_{n+l}^{2l+1}(x)$ , derive a relationship between  $n$  and  $l$  that ensure that  $L_{n+l}^{2l+1}(x) \neq 0$ .

5. Using the Laguerre polynomials  $L_2(x) = \frac{1}{2}(x^2 - 4x + 2)$  and  $L_1(x) = -x + 1$ , show that

$$\frac{d}{dx}L_n(x) = \frac{d}{dx}L_{n-1}(x) - L_{n-1}(x)$$

6. Sketch the radial wavefunctions for the 1s, 2s, 2p, 3s, 3p, and 3d orbital wavefunctions of Hydrogen.
7. Determine the number of nodes in each of the following hydrogen atom orbital wavefunctions:

wavefunction	Total nodes	Angular nodes	Radial nodes
2s			
3p			
5d			
6f			

8. Determine the ionization potential for  ${}^3\text{He}^+$ .
- Find  $R_{\text{He}}$  for the He-3 isotope.
  - Use the relationship

$$IP = Z^2 R_M \left( \frac{1}{(1)^2} - \frac{1}{(\infty)^2} \right)$$

9. Based on the following data, find the ionization energy of Rb, using the fact that at high excitation, the quantum defect ( $\delta$ ) becomes constant.

n (for the $np \leftarrow 5s$ transition)	Wavenumber ( $\text{cm}^{-1}$ )
5	12578.950
6	23715.081
7	27835.02
8	29834.94
9	30958.91
10	31653.85
11	32113.55
12	32433.50
13	32665.03
14	32838.02
15	32970.66
16	33074.59
17	33157.54
18	33224.83
19	33280.13
20	33326.13