CH-110 Advanced General Chemistry I

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The Hydrogen Atom

Topic 1D

Last Tuesday: Topic 1D.1 Energy levels
Last Tuesday: Topic 1D.2 Atomic orbitals
Topic 1D.3 Quantum numbers, shells, and subshells
Topic 1D.4 The shapes of orbitals
Topic 1D.5 Electron spin
Topic 1D.6 The electronic structure of hydrogen: a summary

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- The hydrogen atom is the **simplest atom of all** and is used to discuss the **structures of all atoms**.
- It is therefore **central** to many explanations in chemistry.

WHAT DO YOU NEED TO KNOW ALREADY?

- Features of spectrum of atomic hydrogen (Topic 1A)
- Concepts of wavefunction and energy level in quantum mechanics (Topic 1C)

1D The hydrogen atom

Last Tuesday: Setting the stage

In Topic 1A, we have seen this puzzle

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$with\ n_1 = 1,2, \ldots \ , \qquad and\ n_2 = n_1 + 1, n_1 + 2, \ldots$$

Value of Rydberg constant, $R = 3.29 \text{ x } 10^{15} Hz$

- Why such a **pattern** and why does R have that **value**?

1D.1 Energy levels

Last Tuesday: Relationship to Bohr frequency condition

Allowed energy levels in the hydrogen atom (Schrödinger's solution):

$$E_n = -\frac{hR}{n^2}$$

$$R = \frac{m_e e^4}{8h^3\varepsilon_0^2} \text{ with } n = 1, 2, \dots$$

Bohr frequency condition:

$$h\nu = \Delta E$$

Insert into previous equation. In the case of the hydrogen atom, if the electron falls from a level with quantum number n_2 to one with quantum number n_1, then:

$$h\nu = \Delta E = \left(-\frac{hR}{n_2^2}\right) - \left(\frac{hR}{n_1^2}\right) = hR\left\{\frac{1}{n_1^2} - \frac{1}{n_2^2}\right\} \; with \; n_1 = 1,2,\dots, n_2 = n_1 + 1, n_1 + 2, \dots$$

Compare to previous Rydberg equation:

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \; with \; n_1 = 1,2,\dots, n_2 = n_1 + 1, n_1 + 2, \dots$$

1D.1 Energy levels

Last Tuesday: Finally, it makes sense

Rydberg constant

$$R = \frac{m_e e^4}{8h^3\varepsilon_0^2} = \mathbf{3.29 \times 10^{15}\ Hz}$$

- Imagine Schrödinger calculating this constant!

You can now see:

- Balmer series, for example, arises from transitions starting at $n_2 = 3, 4, 5 \ldots$ and all ending at $\boldsymbol{n_1 = 2}$
- Lyman series: $n_2 = 2, 3, 4, 5 \ldots$ to $\boldsymbol{n_1 = 1}$

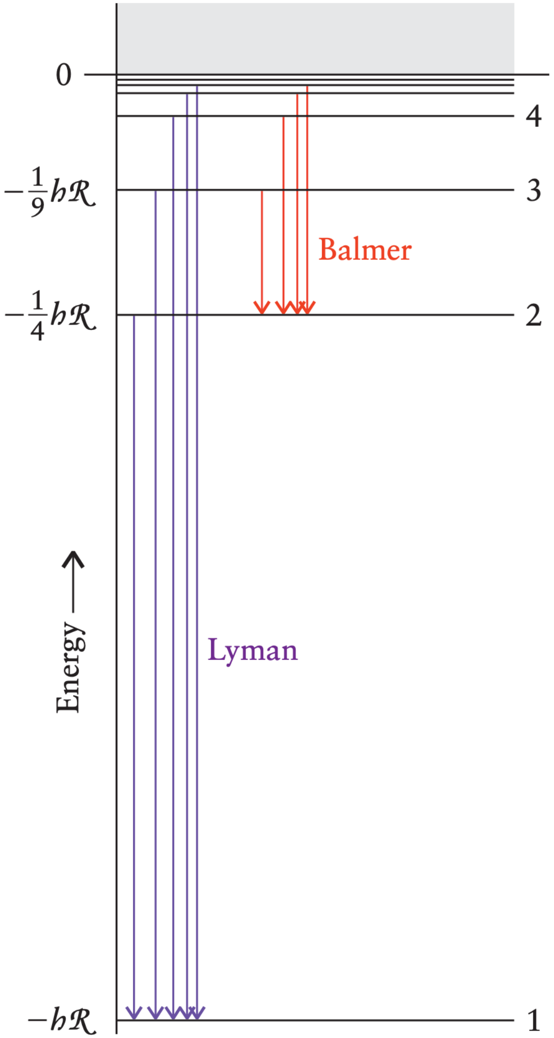


Figure 1D.1

1D.1 Energy levels

Last Tuesday: Finally, it makes sense

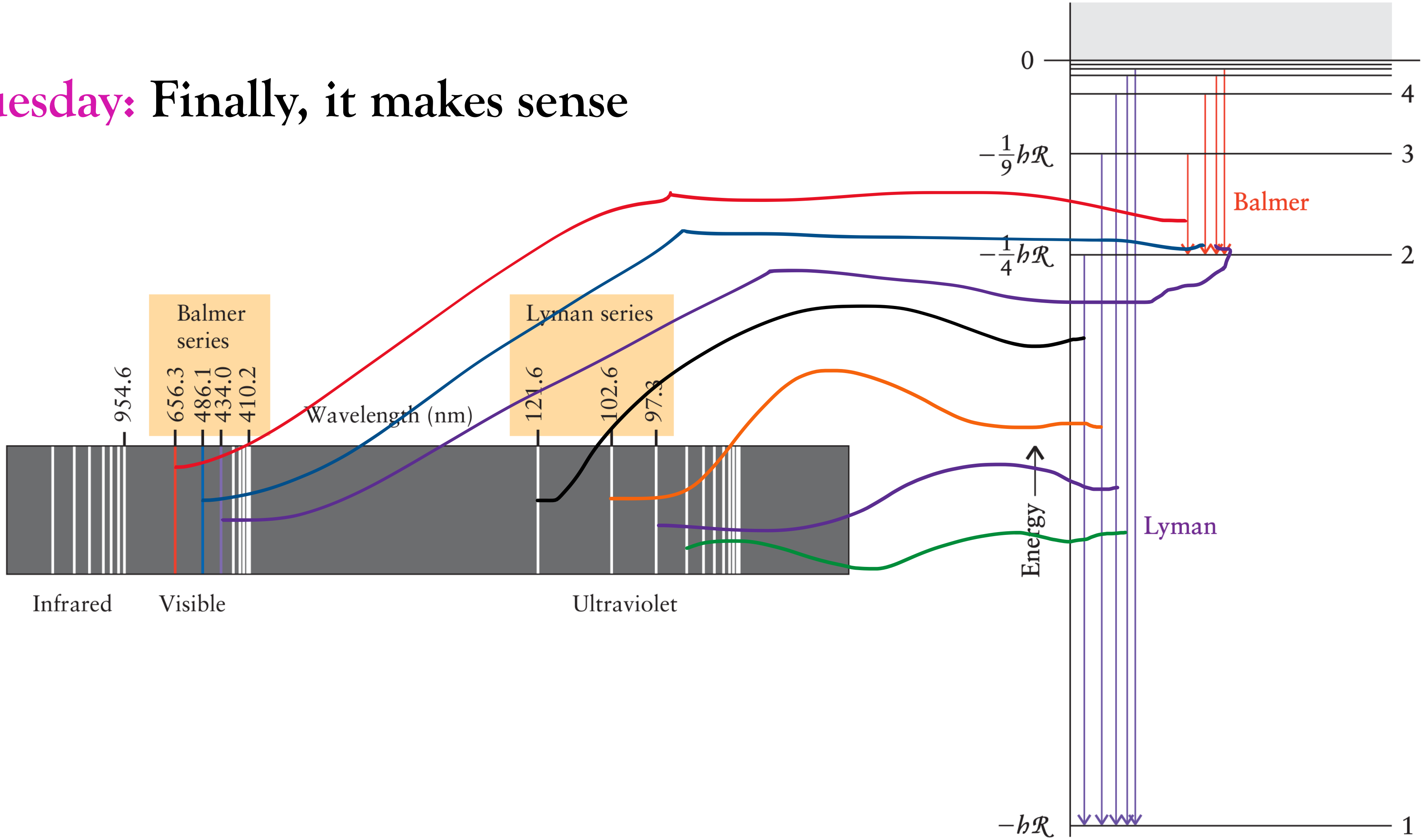


Figure 1A.10

Figure 1D.1

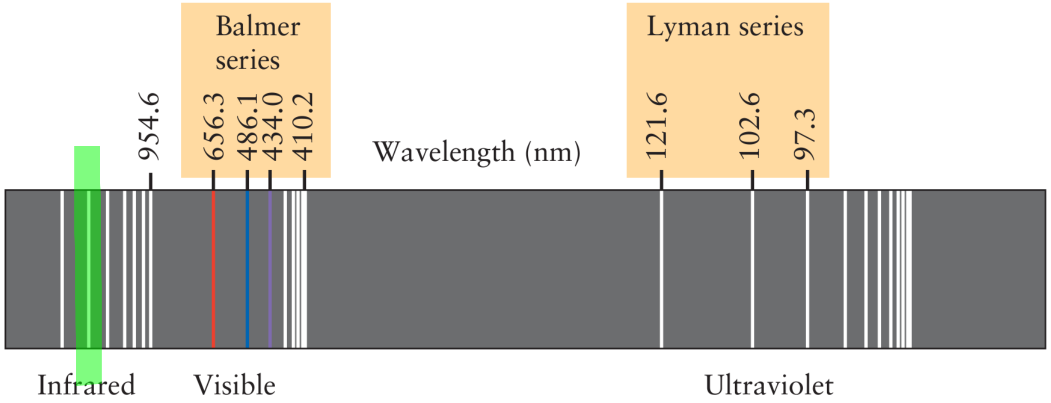
If I wanted to calculate the wavelength of the line highlighted in green, what would be the two values of n_1 and n_2 I would use?

A. $n_1 = 5$ and $n_2 = 3$

B. $n_1 = 3$ and $n_2 = 4$

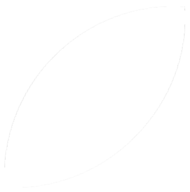
C. $n_1 = 3$ and $n_2 = 5$

D. $n_1 = 5$ and $n_2 = 2$



Quantum Numbers, Shells, and Subshells

Topic 1D.3



1D.3 Quantum numbers, shells, and subshells

Three quantum numbers for the hydrogen atom

When the Schrödinger equation is solved for the hydrogen atom, **three quantum numbers** are needed to specify each wavefunction:

1. Principal quantum number n is related to the **size** and **energy** of the orbital
2. Quantum number l is related to its **shape**
3. Quantum number m_l is related to its **orientation in space**

1D.3 Quantum numbers, shells, and subshells

Principal quantum number n

Principal quantum number n is related to the **size** and **energy** of the orbital, all orbitals with the same principal quantum number have the same energy, belong to the same **shell** of the atom.

1D.3 Quantum numbers, shells, and subshells

Orbital angular quantum number *l*

Quantum number l is related to its **shape**

It can take on the following values:

$$l = 0, 1, 2, \dots, \boldsymbol{n-1}$$

For example, for $n = 3$, l can have three values $0, 1$, and 2.

Orbitals with principal number n are divided into subshells l:

For $n = 1$: there is only one subshell $l = 0$

For $n = 2$: there are two subshells $l = 0, 1$

For $n = 3$: there are three subshells $l = 0, 1, 2$

1D.3 Quantum numbers, shells, and subshells

s-, p-, and d-orbitals

$l = 0$: s-orbital (origin: s-orbital spectroscopic lines described as "sharp")

$l = 1$: p-orbital (origin: p-orbital spectroscopic lines described as "principal")

$l = 2$: d-orbital (origin: d-orbital spectroscopic lines described as "diffuse")

Value of *l*	**0**	**1**	**2**	**3**
Orbital type	s	p	d	f

Higher values of l are possible (g-, h-, … orbitals) are possible, but not often needed in practice.

1D.3 Quantum numbers, shells, and subshells

Orbital angular quantum number *l*

l is used to calculate orbital angular momentum of the electron, a measure of the rate (in classical terms) at which the electron circulates around the nucleus.

$$Orbital\ angular\ momentum = \sqrt{l(l+1)}\hbar$$

- An electron in an **s-orbital** for which $l = 0$ has zero orbital angular momentum (not circulating around nucleus, and evenly distributed around it).
- An electron in a **p-orbital** for which $l = 1$ has a non-zero orbital angular momentum of magnitude $\sqrt{2}\hbar$ (can be thought of as circulating around nucleus).
- An electron in a **d-orbital** ($l = 2$) has a higher angular momentum ($\sqrt{6}\hbar$) and an electron in an f-orbital ($l = 3$) an even higher one ($\sqrt{12}\hbar$) and so on.

1D.3 Quantum numbers, shells, and subshells

Magnetic quantum number m_l

Distinguishes the **individual orbitals** within a subshell

Can take positive and negative integer values:

$$m_l = l, l-1, \dots, -l$$

E.g.

- p-orbital: $l = 1$ and $m_l = +1, 0, -1$: there are three p-orbitals in a subshell with $l = 1$.
- d-orbital: $l = 2$ and $m_l = +2, +1, 0, -1, -2$

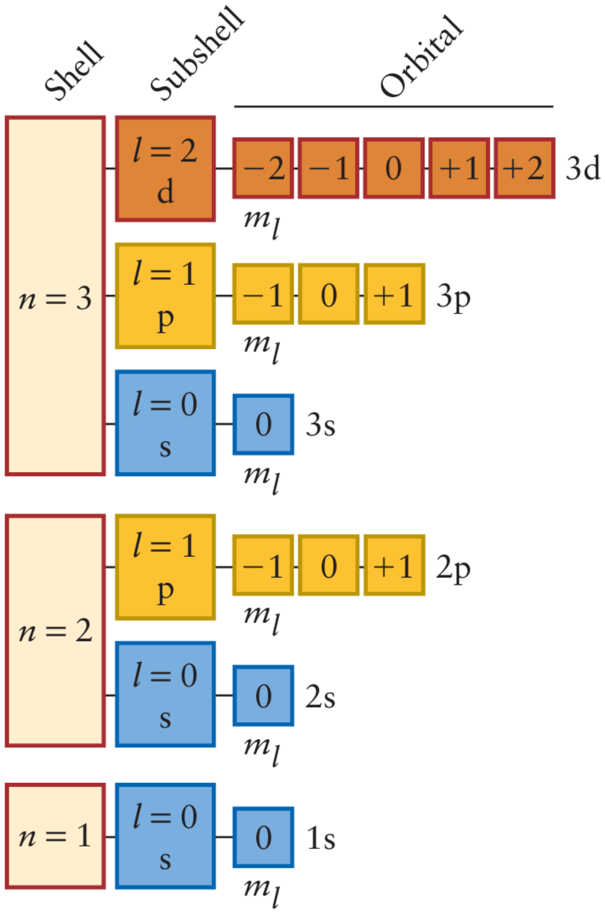


Figure 1D.3

How many subshells are there for quantum number *n*?

A. n-1 subshells
B. n subshells
C. n^2 subshells

1D.3 Quantum numbers, shells, and subshells

Magnetic quantum number m_l

- Specifies the orientation of the **orbital motion of the electron**
- Orbital angular momentum around an arbitrary axis is equal to $m_l\hbar$
- For example if $m_l = +1$, then the orbital angular momentum around an arbitrary axis is $+\hbar$, whereas if $m_l = -1$, the orbital angular momentum around the same arbitrary axis is $-\hbar$.
- **Direction of motion is opposite**: the electron in one state circulates clockwise around the chosen axis, in the other counterclockwise.
- $m_l = 0$, the electron is **not circulating** around the selected axis but, at a given radius, evenly distributes around it.

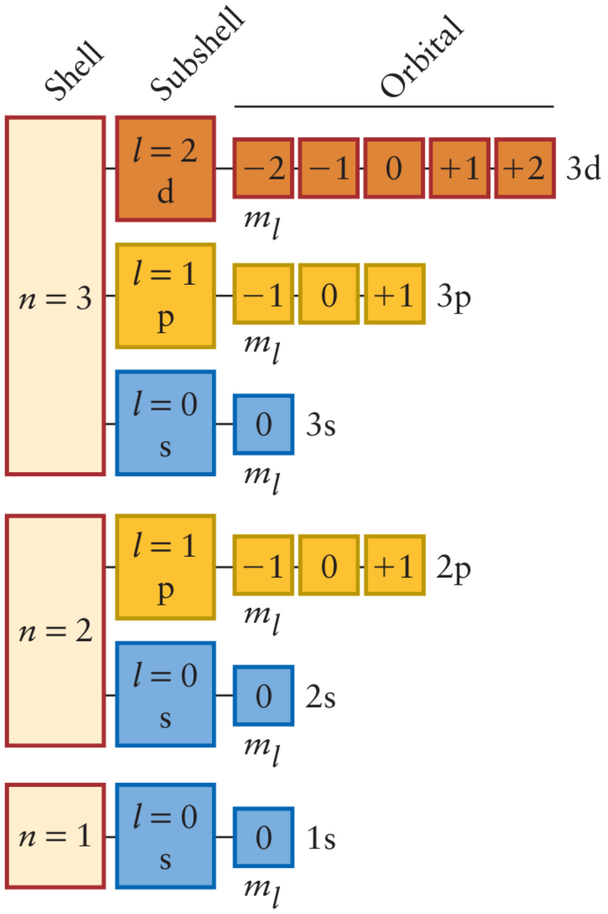


Figure 1D.3

1D.3 Quantum numbers, shells, and subshells

Summary

Atomic orbitals are designated by the quantum numbers n, l, and m_l and fall into shells and subshells.

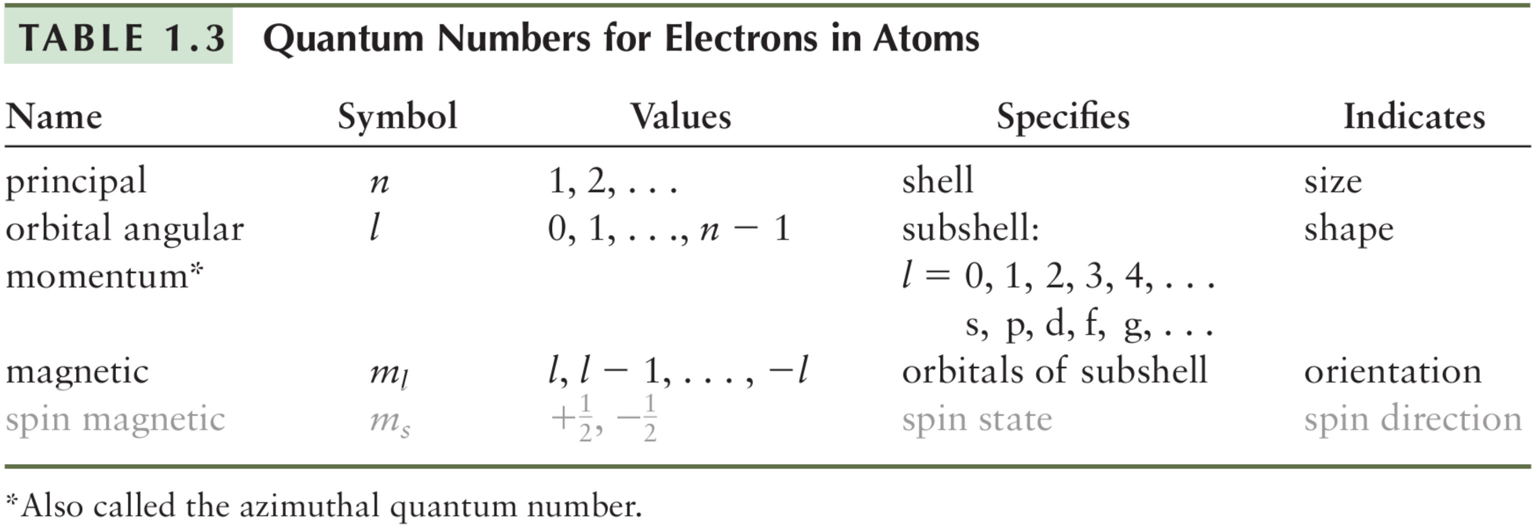


TABLE 1.3 Quantum Numbers for Electrons in Atoms

Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	0, 1, . . ., $n - 1$	subshell: l = 0, 1, 2, 3, 4, . . . s, p, d, f, g, . . .	shape
magnetic	m_l	$l, l - 1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the azimuthal quantum number.

Chapter 1D.5:

The Shapes of Orbitals

Topic 1D.4

1D.4 The shapes of orbitals

s-orbitals

A combination of **three quantum numbers** specifies an individual orbital, acts as an “address” of the electron that ”occupies” it (meaning the electron has a probability distribution given by its wavefunction)

- E.g. an electron in the **ground state** of a hydrogen atom has $n = 1, l = 0, m_l = 0$.
- Because $l = 0$, the ground-state wavefunction is an example of an s-orbital (1s)
- Each shell has one s-orbital
- The s-orbital with quantum number *n* is called the *n*s orbital (1s, 2s, 3s orbital and so on).

1D.4 The shapes of orbitals

s-orbitals are spherically symmetrical

All s-orbitals are independent of the angles θ and ϕ: **spherically symmetrical**

The **probability density** of an electron at the point $(\mathrm{r}, \theta, \phi)$ when it is in an **1s–orbital** is given by the square of the corresponding wavefunction (given earlier):

$$\Psi^2(\mathrm{r}, \theta, \phi) = \frac{1}{\pi a_0^3} e^{-\frac{2r}{a_0}}$$

In principle, the cloud representing the probability density **never goes to zero**, no matter the value of *r*. However, there is virtually no chance of finding an electron farther from the nucleus than about **250 pm**, so for practical purposes, the atom is very small.

1D.4 The shapes of orbitals

s-orbitals are spherically symmetrical

High density of the cloud at nucleus: electron in an s-orbital has a **nonzero probability of being found right at the nucleus**.

Why? Because there is no orbital angular momentum to fling the electron away.

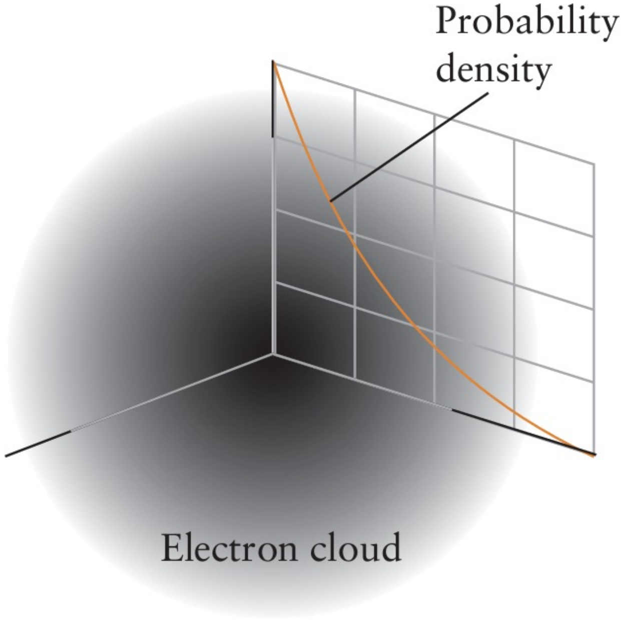
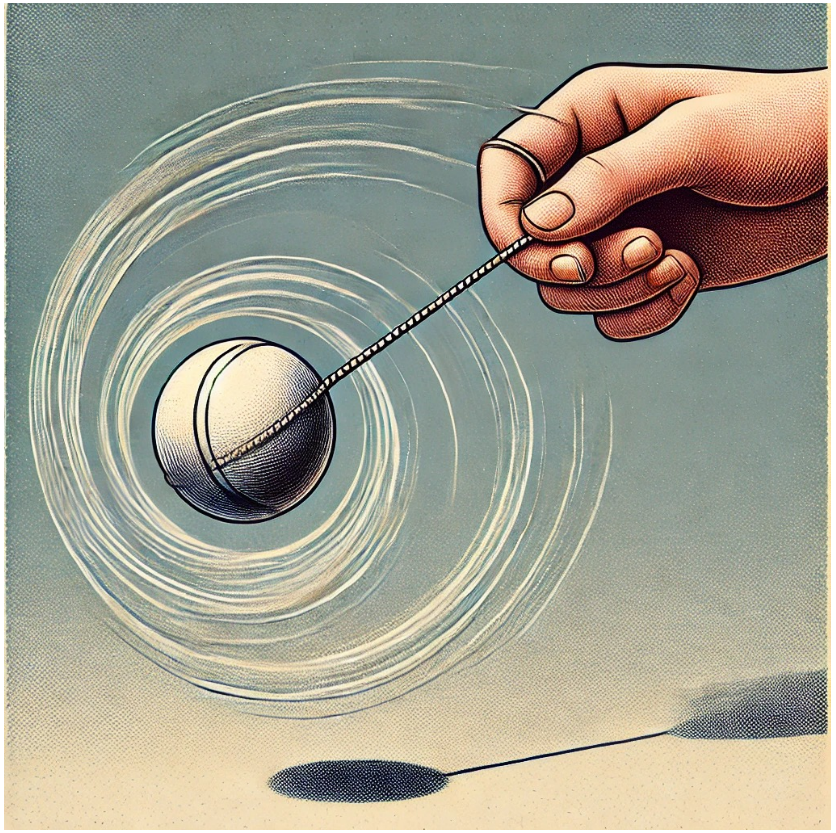


Figure 1D.4

1D.4 The shapes of orbitals

Analogy: angular momentum to swinging ball on string.

Imagine a ball attached to a string, representing an electron in a p-orbital. When you swing this ball around in a circle, it has a certain angular momentum. The faster you swing it, the farther it moves away from the center. If you try to bring the ball closer to the center, it becomes difficult; the tension in the string and the motion cause the ball to naturally stay at a distance from the center, similar to how a p-orbital behaves with a non-zero angular momentum.



1D.4 The shapes of orbitals

Example 1D.1: Calculating the probability of finding an electron at a certain location

Suppose an electron is in a 1s-orbital of a hydrogen atom.

What is the **probability** of finding the electron ina small region a **distance $\boldsymbol{a_0}$** from the nucleus **relative** to the probability of finding it in the small region located right **at the nucleus**?

Anticipate: lower probability (exponential decay)

Plan: compare the probability densitites at the two locations: ratio of the squares of the wavefunctions at the two locations.

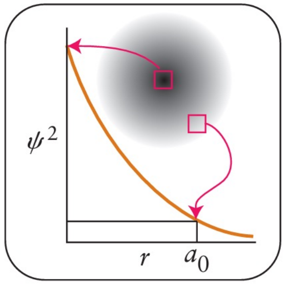
For 1s: $\psi(r, \theta, \phi)$ becomes $\psi(r)$

1D.4 The shapes of orbitals

Example 1D.1: Calculating the probability of finding an electron at a certain location

SOLVE

The ratio of the probability that the electron is found at the nucleus or at $r = a_0$ is:



$$\frac{\text{Probability density at } r = a_0}{\text{Probability density at } r = 0} = \frac{\psi^2(a_0)}{\psi^2(0)}$$

From $\psi^2(r, \theta, \phi) = (1/\pi a_0^3)e^{-2r/a_0}$,

$$\frac{\psi^2(a_0)}{\psi^2(0)} = \frac{(1/\pi a_0^3)\overbrace{e^{-2a_0/a_0}}^{e^{-2}}}{(1/\pi a_0^3)\underbrace{e^0}_{1}} = e^{-2} = 0.14$$

Evaluate As expected, the probability of finding the electron in a small region at a distance a_0 from the nucleus is lower than at the nucleus itself: the probability is only 14% of that of finding the electron in a region of the same volume located at the nucleus.

At $r = 2a_0$:

$$\Psi^2(\mathrm{r}) = \frac{1}{\pi a_0^3} e^{-\frac{2\times 2a_0}{a_0}}$$

Ratio becomes:
$e^{-4} = 0.018$

At $r = 3a_0$:

$$\Psi^2(\mathrm{r}) = \frac{1}{\pi a_0^3} e^{-\frac{2\times 3a_0}{a_0}}$$

Ratio becomes:
$e^{-6} = 0.0025$

1D.4 The shapes of orbitals

The radial distribution function

- Value of ψ^2 lets you predict the probability of finding an electron at a given **region** at distance r from the nucleus
- Maybe you want to know: the total probability of finding an electron at a distance r in all possible directions: you need the **radial distribution function.**
- **Analogy:** for the population on earth, the radial distribution function is zero up to about 6400 km from the center of the earth, rises sharply, and then falls back to almost zero (except people climbing mountains or flying in airplanes.
- The probability that an electron will be found in a thin spherical shell around the nucleus with radius r and thickness δr is given by $P(r)\delta r$ with

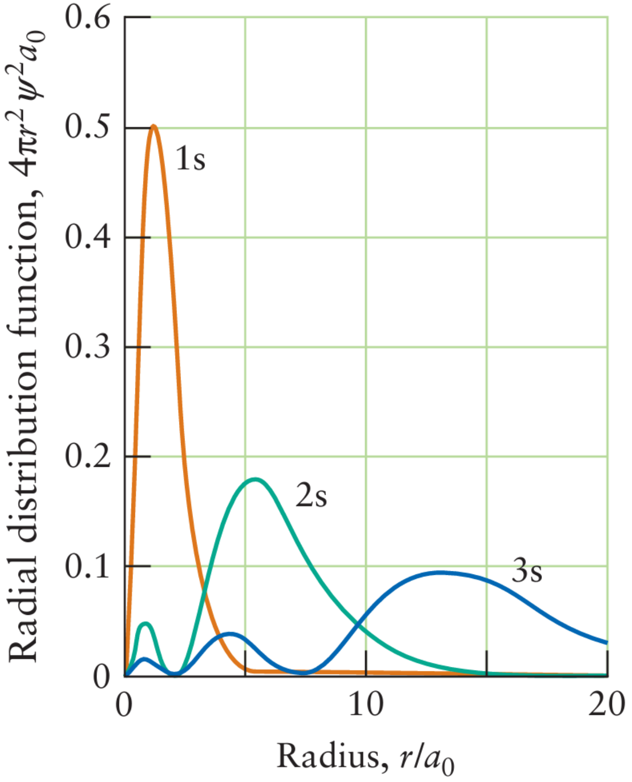
$$P(r) = r^2 R^2(r)$$

- For s-orbitals, $\psi = RY = \frac{R}{2\pi^{\frac{1}{2}}}$, so $R^2 = 4\pi\psi^2$ and this expression is then the same as

$$P(r) = 4\pi r^2 \psi^2(r)$$

This special form applies only to s-orbitals, whereas the previous form applies to all orbitals.

Figure 1D.5



1D.4 The shapes of orbitals

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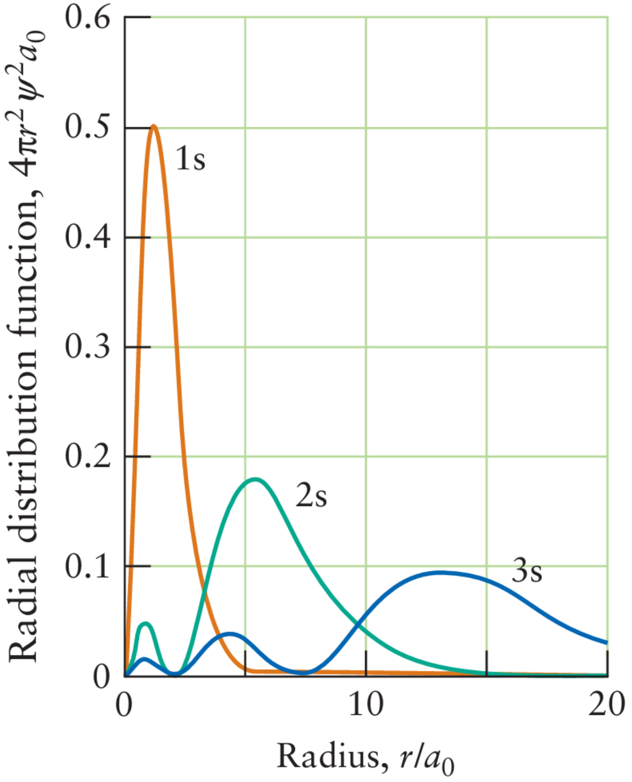
Figure 1D.5

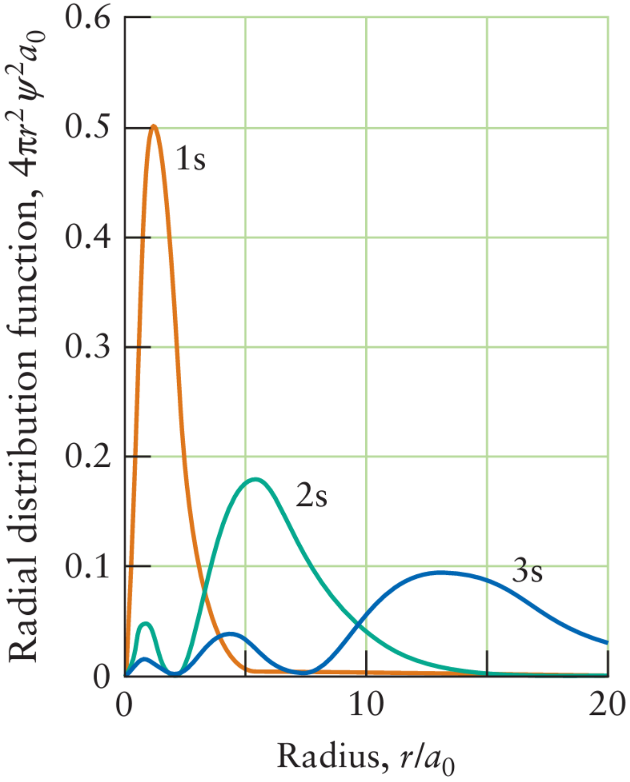


1D.4 The shapes of orbitals

The radial distribution function

- It’s important to **distinguish the radial distribution function** from the wavefunction and its square, the **probability density**:
- The wavefunction itself tells you, through $\psi^2(r,\theta,\phi)\delta V$, the probability of finding the electron in the **small volume δV at a particular location** specified by r, θ, and ϕ.
- The radial distribution function tells you, through $P(r)\delta \mathrm{r}$, the probability of finding the electron anywhere in the **spherical shell** between r and $\mathrm{r} + \delta \mathrm{r}$

Figure 1D.5

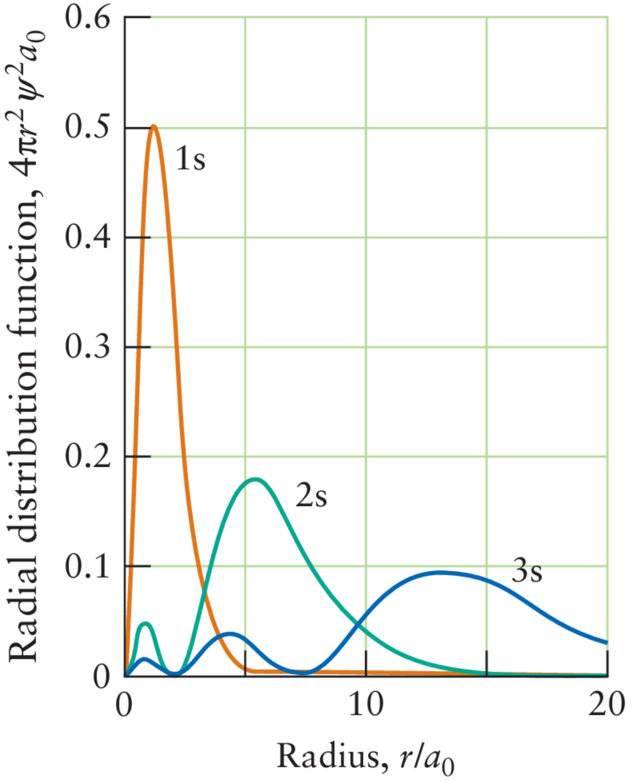


1D.4 The shapes of orbitals

The radial distribution function

- Note that for all orbitals, except s-orbitals, **the radial distribution function $\boldsymbol{P(r)}$ is zero** at the nucleus simply because the region in which the electron is being sought has shrunk to zero size.
- The **probability density for an s-orbital is nonzero a the nucleus**, and in the radial distribution, it is multiplied by a volume, $4\pi r^2\delta r$, which becomes zero at the nucleus, at $r = 0$.
- As r increases, the value of $4\pi r^2$ increases (the **shell is getting bigger**), but for the 1s-orbital, the square of the wavefunction, ψ^2, falls toward zero as r increases.
- As a result, the product of $4\pi r^2$ and ψ^2 starts off at zero, goes through a maximum, and then declines to zero (Figure 1D.5)
- The value of $P(r)$ turns out to be **greatest at $\boldsymbol{a_0}$**, the Bohr radius.
- Therefore the Bohr radius corresponds to the radius at which an electron in a 1s-orbital in a hydrogen atom is **most likely to be found**.

Figure 1D.5



1D.4 The shapes of orbitals

Boundary surface

Instead of drawing an orbital as a cloud, chemists ususally draw a boundary surface:

- A smooth surface that encloses most of the cloud.

+ easier to draw

– does not give the best picture of an atom

- An atom has indefinite, or «fuzzy», edges and is not as smooth as a boundary surface might suggest.
- Boundary surface is useful because an electron is most **likely to be found inside it**.

1D.4 The shapes of orbitals

Boundary surface of the 1s-orbital

- Keep in mind:

  The probability density inside the boundary surface is not uniform.

- An s-orbital has a spherical boundary surface because the electron cloud is spherical.

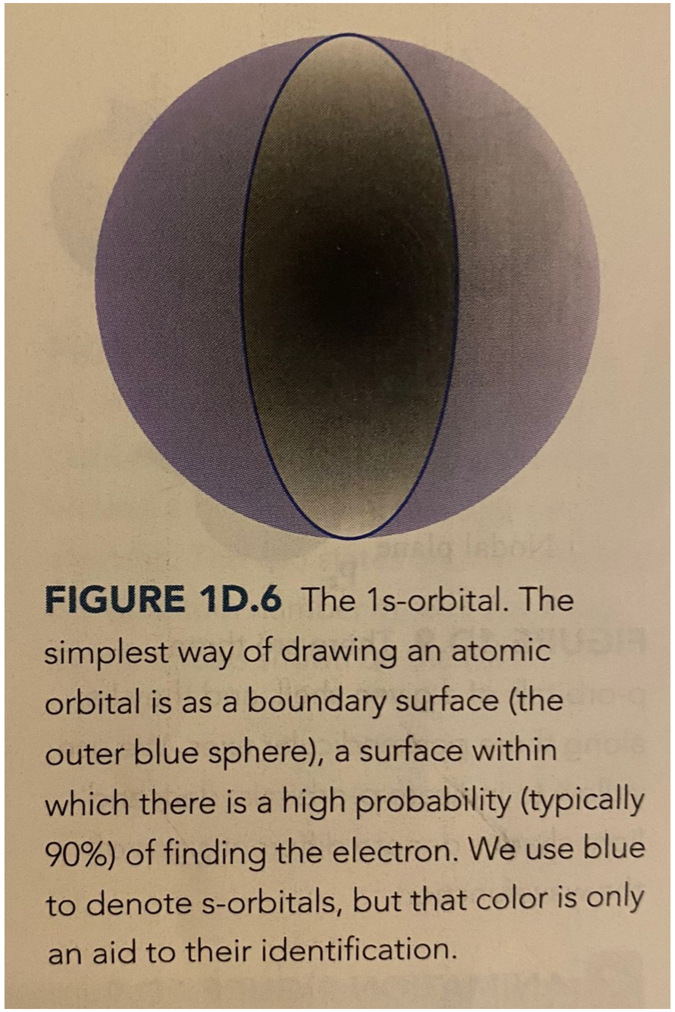


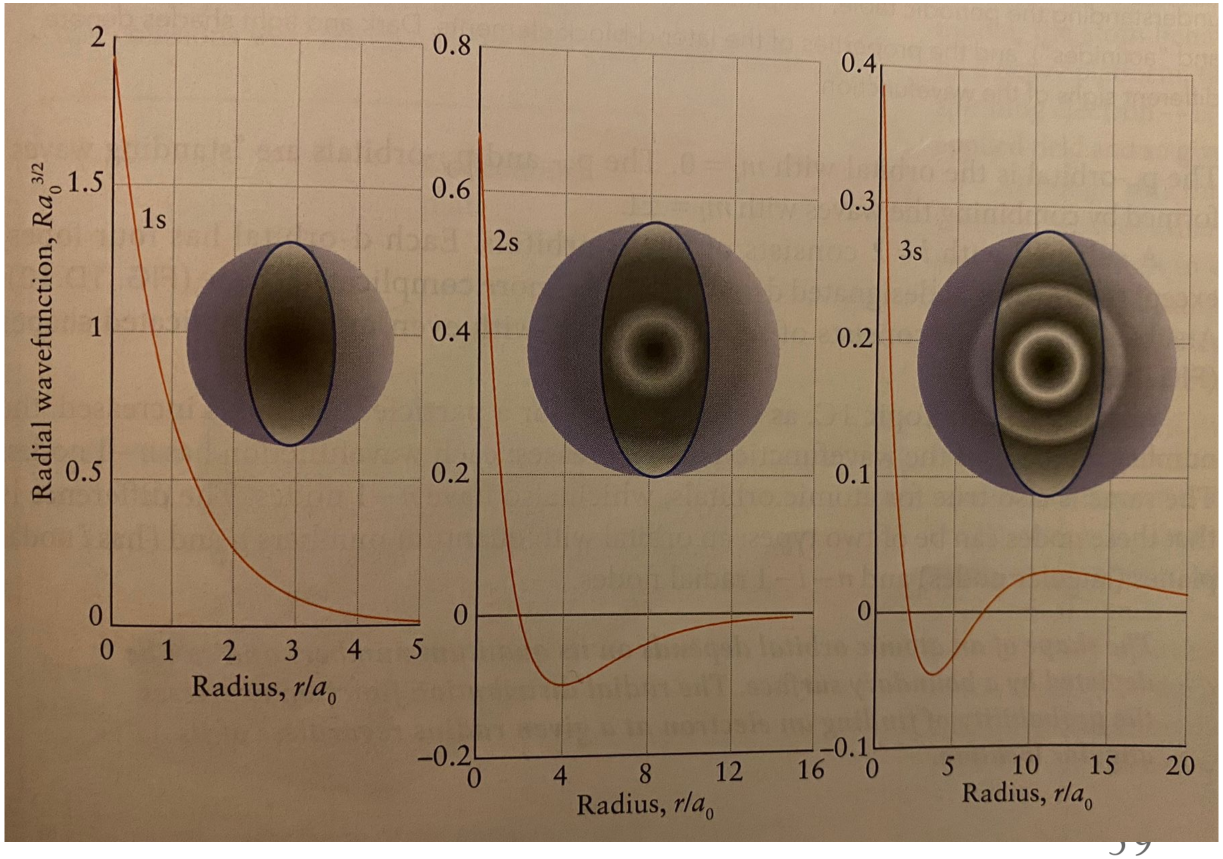
FIGURE 1D.6 The 1s-orbital. The simplest way of drawing an atomic orbital is as a boundary surface (the outer blue sphere), a surface within which there is a high probability (typically 90%) of finding the electron. We use blue to denote s-orbitals, but that color is only an aid to their identification.

1D.3 Quantum numbers, shells, and subshells

Boundary surfaces of higher-order s-orbitals

- The s-orbitals of higher energy have spherical boundary surfaces of greater diameter, **the average distance of the electron** from the nucleus also increases.
- They also have a more complicated radial variation, with **radial nodes**, radii at which the wavefunction passes through zero.

Figure 1D.7

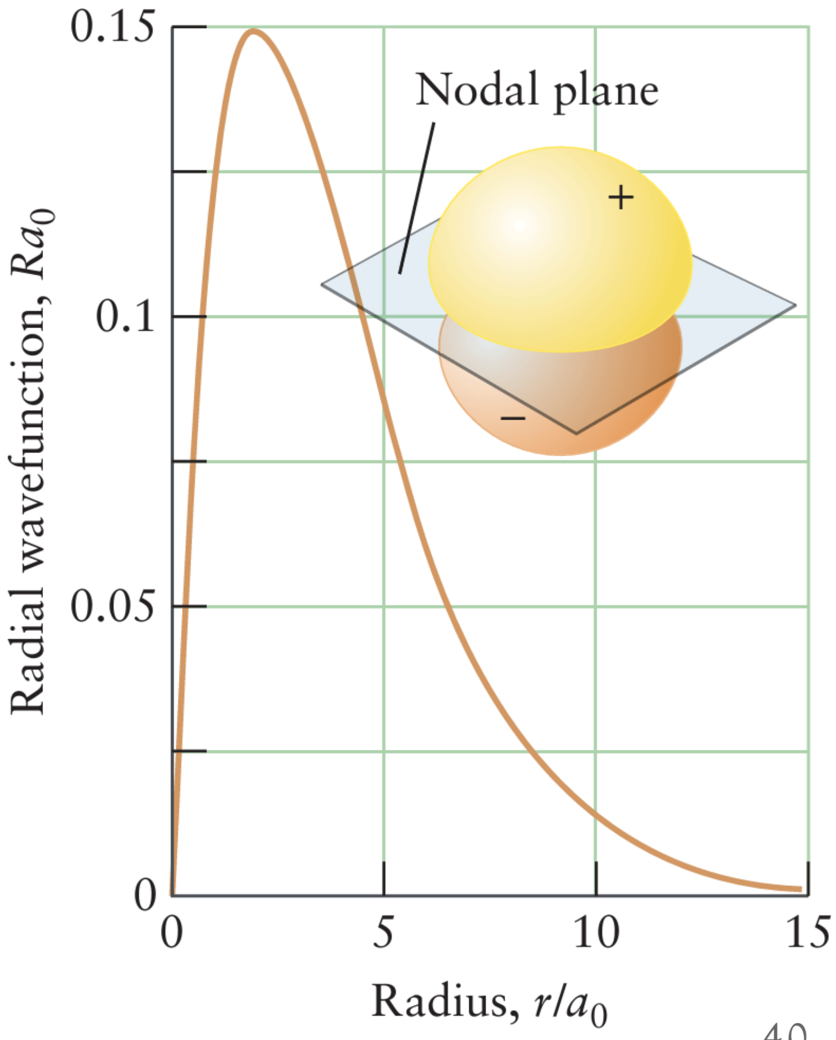


1D.4 The shapes of orbitals

Boundary surfaces of p-orbitals

- Two lobes with signs + and - to signify that wavefunction has two different signs in these two regions
- E.g. $2p_z$ orbital is proportional to $\cos(\theta)$: as θ changes from 0 to π, $\cos(\theta)$ changes from $+1$ through 0 to -1.

Figure 1D.8

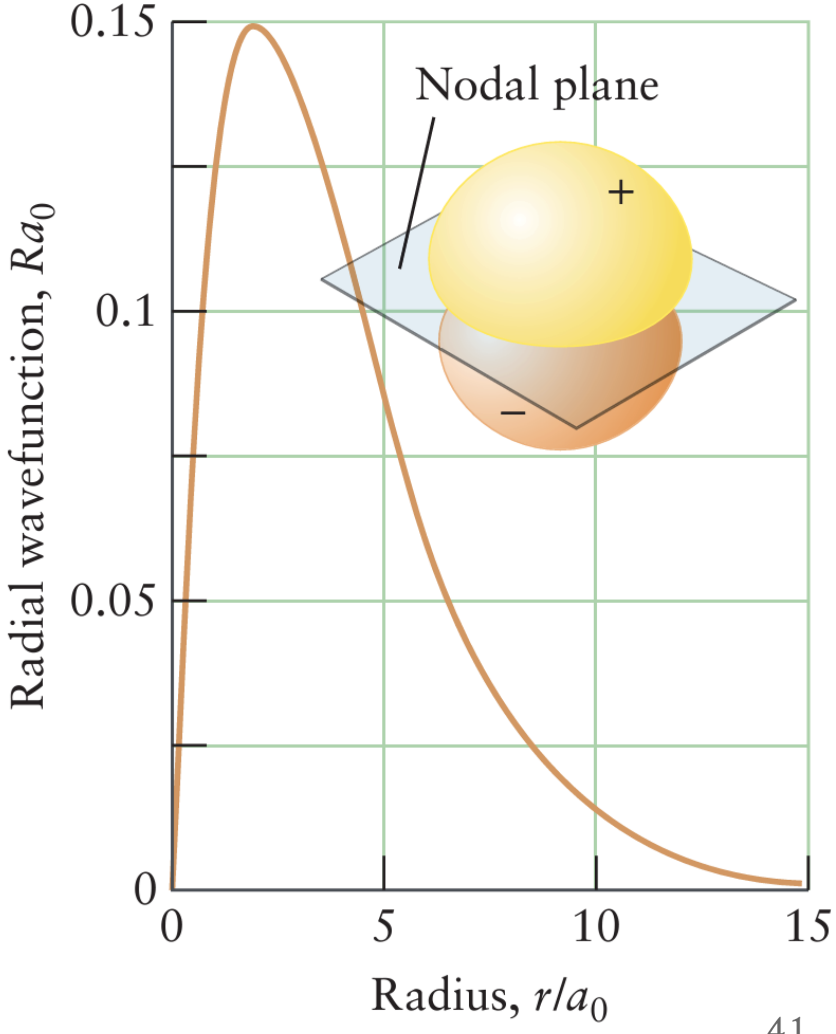


1D.4 The shapes of orbitals

Nodal planes

- The two lobes of a p-orbital are separated by a **nodal plane**, cuts through the nucleus, $\psi = 0$. The wavefunction changes sign **on passing through this plane**.
- Also called **angular nodes** because they occur when the angular wavefunction passes through zero.
- A p-electron will **never be found at the nucleus** because the wavefunction is zero there.
- Electrons in p-orbitals have nonzero angular momentum, which flings them away from the nucleus.

Figure 1D.8

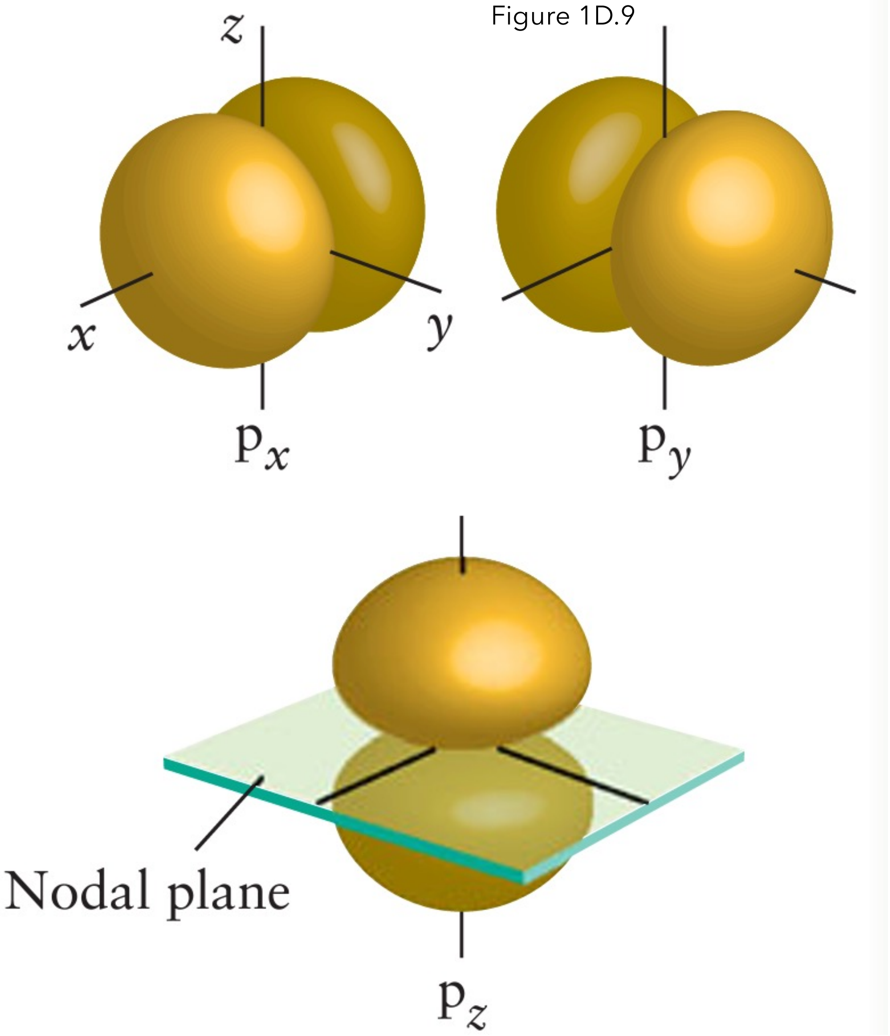


1D.4 The shapes of orbitals

p-orbitals

- Three p-orbitals in each subshell of an atom
- Quantum numbers $m_l = +1, 0, -1$
- Chemists refer to them according to the axes along which the lobes lie: p_x-, p_y-, p_z-orbitals
- p_z-orbital has $m_l = 0$
- p_x-, p_y-orbitals have $m_l = \pm 1$

Figure 1D.9



1D.4 The shapes of orbitals

d-orbitals

- Subshell l = 2 consists of **five d-orbitals**
- Each d-orbital has four lobes, except d_{z^2}

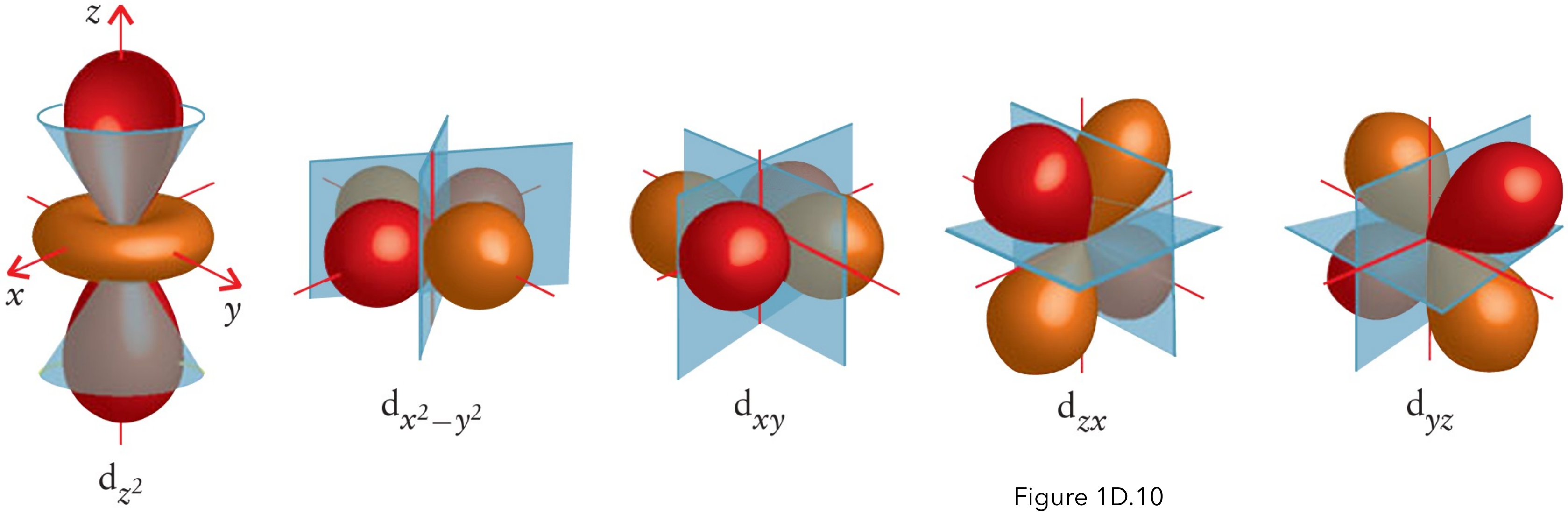


Figure 1D.10

1D.4 The shapes of orbitals

f-orbitals

- Subshell $l = 3$ consists of **seven f-orbitals**.
- Very **complex** appearance.
- Detailed form will not be discussed again in this course.
- Their existence is important for **understanding the periodic table**, the presence of the lanthanoids and actinoids and the properties of the later d-block elements.

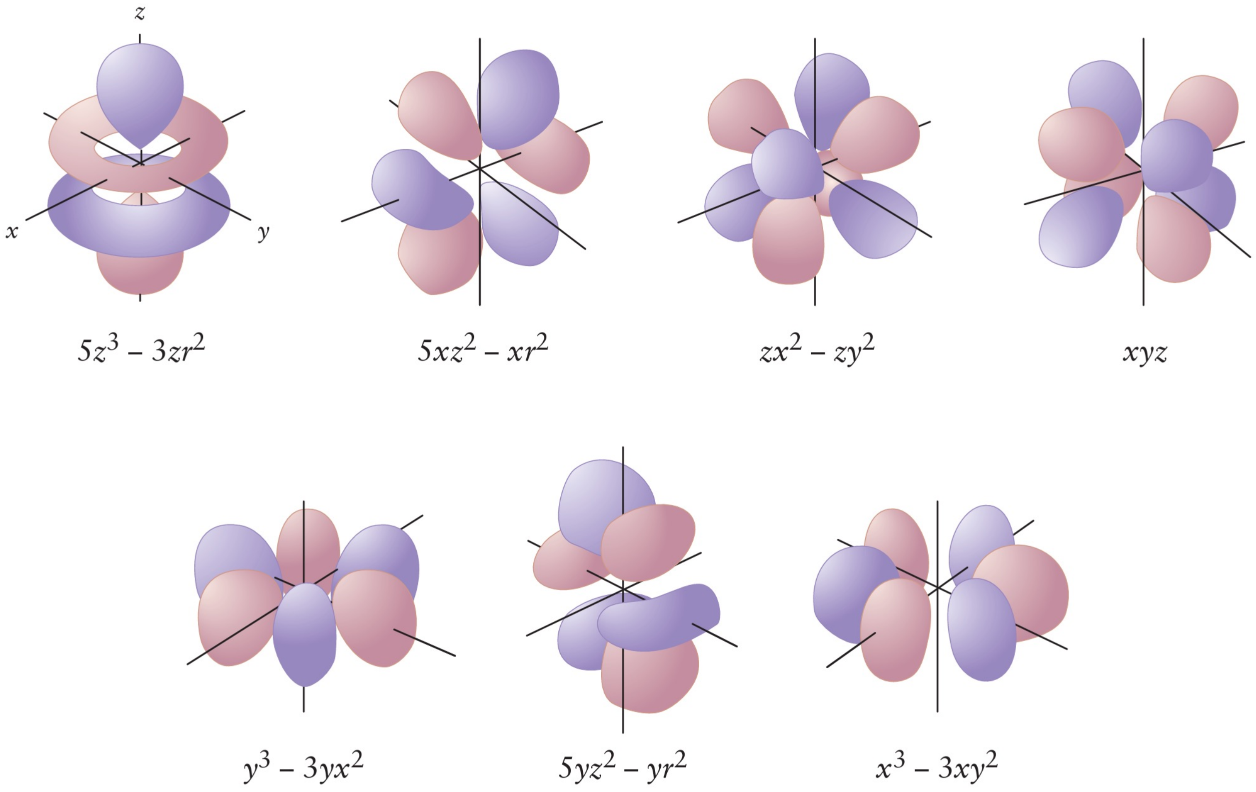


Figure 1D.11

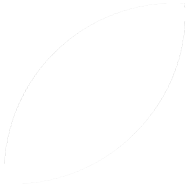
1D.4 The shapes of orbitals

Summary

The shape of an atomic orbital depends on its quantum numbers and can be depicted by a boundary surface. The radial distribution function expresses the probability of finding an electron at a given radius regardless of its angular momentum.

Electron Spin

Topic 1D.5



1D.5 Electron spin

A spinning sphere

Tiny discrepancies were observed in the atomic spectrum of hydrogen.

Goudsmit and Uhlenbeck proposed these differences are due to the fact that an electron behaves like a spinning sphere (like a planet rotating around its axis).

This property is called spin.

Schrödinger’s theory did not account for spin, and it emerged naturally when the British physicist Paul Dirac found a way (in 1928) to combine Einstein’s theory of relativity with Schrödinger’s approach.

According to quantum mechanics, an electron has two spin states represented by the **arrows ↑ and ↓** or the Greek letters α and β.

1D.5 Electron spin

Spin ↑ and ↓

Think of an electron as being able to spin counterclockwise (the ↑ state) and clockwise (the ↓ state) at exactly the same rate.

These two spins are distinguished by a **fourth quantum number**, the spin magnetic quantum number, m_s.

This quantum number can have only one of two values: $+\frac{1}{2}$ (↑) and $-\frac{1}{2}$ (↓).

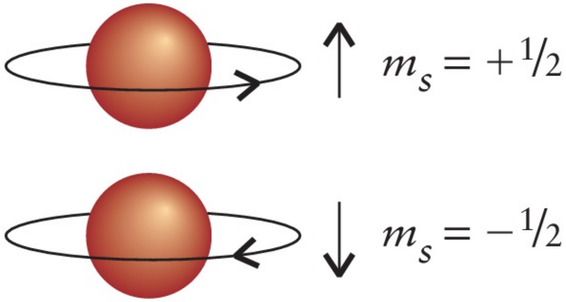


Figure 1D.12

1D.5 Electron spin

Summary

An electron has the property of spin;

the spin is described by the quantum number $m_s = \pm\frac{1}{2}$.

The Electronic Structure of Hydrogen: A Summary

Topic 1D.6

1D.6 The electronic structure of hydrogen: a summary

1) In the **ground state of hydrogen**:

$$n = 1, l = 0, m_l = 0, m_s = \pm\frac{1}{2}$$

Both values of m_s are possible, spin orientation does not affect energy.

This is an s-electron with specified spin.

2) When an atom **acquires enough energy** (by absorbing a photon) for its electron to reach n=2:

It can occupy any of the four orbitals in that shell: one 2s and three 2p orbitals (in hydrogen, they all have the same energy): 2s- or 2p-electron

Average distance of electron from nucleus increases with increasing *n*: atom is «swelling up» as it is excited energetically.

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3) Atom acquires **even more energy**:

Electron can move to n = 3 shell

Atom is now even larger

Nine orbitals available (3s, 3p, 3d)

4) More energy still:

Electron can move to n = 4 shell with 16 available orbitals

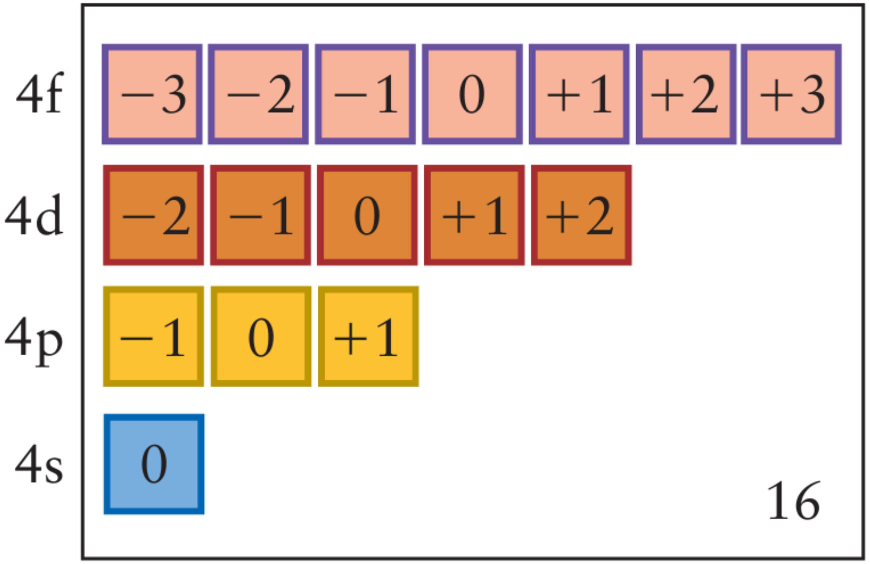

Figure 1D.13

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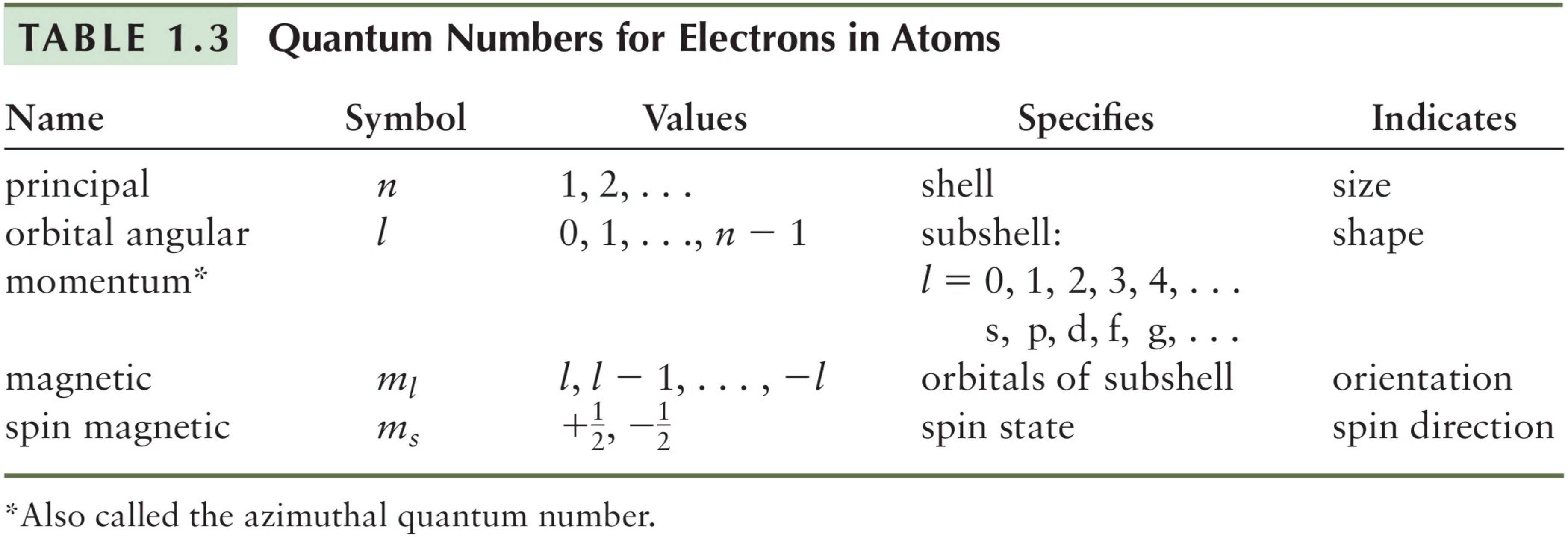

TABLE 1.3 **Quantum Numbers for Electrons in Atoms**

Name	Symbol	Values	Specifies	Indicates
principal	n	1, 2, . . .	shell	size
orbital angular momentum*	l	0, 1, . . ., $n - 1$	subshell: l = 0, 1, 2, 3, 4, . . . s, p, d, f, g, . . .	shape
magnetic	m_l	$l, l - 1, \ldots, -l$	orbitals of subshell	orientation
spin magnetic	m_s	$+\frac{1}{2}, -\frac{1}{2}$	spin state	spin direction

*Also called the azimuthal quantum number.

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Summary

The state of an electron in a hydrogen atom is defined by the four quantum numbers n, l, m_l and m_s; as the value of n increases, the size of the atom increases.

The skills you have mastered are the ability to

- ☐ Assess the relative probability of finding an electron at a given distance from the nucleus of an atom.
- ☐ Name and explain the relation of each of the four quantum numbers to the properties and relative energies of atomic orbitals.
- ☐ Describe the properties of electron spin.
- ☐ Describe the state of a hydrogen atom in ist ground and excited states.

Summary: You have learned that an electron in a hydrogen atom is described by wavefunctions called atomic orbitals and that each orbital is specified by three quantum numers: n, l, and m_l. You now know that the shape and energy of a given orbital is found by solving the Schrödinger equation for an electron attracted to a nucleus. You also now know that transitions between the allowed energy levels account for the observed patterns of spectroscopic lines. You have also encountered the property of "electron spin" and know that electron spin may have either of two orientations.

	Particle in a box	**Hydrogen atom**
Dimension of space	1D	3D
Walls	Physical walls	No physical walls, and electrons are confined by pull of the nucleus
Quantization	Energy quantized	
Potential energy	Potential energy inside the box is zero	Potential energy governed by Coulomb potential
Wave function shape	Sinusoidal functions (sine or cosine)	Wave functions (called **orbitals**) are more complex, often **spherical** or **lobed** in shape (spherical harmonics), with both radial and angular components.
Quantum numbers	One quantum number, *n*, which represents the energy level and is related to the number of nodes in the wave function.	Three quantum numbers: ***n***: principal quantum number (energy level), ***l***: angular momentum quantum number (shape of the orbital), m_l: magnetic quantum number (orientation of the orbital).
Degeneracy	No degeneracy: each energy level corresponds to one unique state.	Degeneracy in energy levels: for a given principal quantum number *n*, multiple different orbitals (characterized by *l* and m_l) have the same energy.
Boundary conditions	The wave function must go to **zero at the walls** of the box.	The wave function must go to zero at infinity, far from the nucleus.
Physical interpretation	The particle is **free** inside the box but cannot escape due to infinite potential at the walls.	The electron is **bound** to the nucleus due to the attractive Coulomb force, which confines the electron.