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):

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

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

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:

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

Compare to previous Rydberg equation:

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

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 $\boldsymbol{n_1 = 1}$

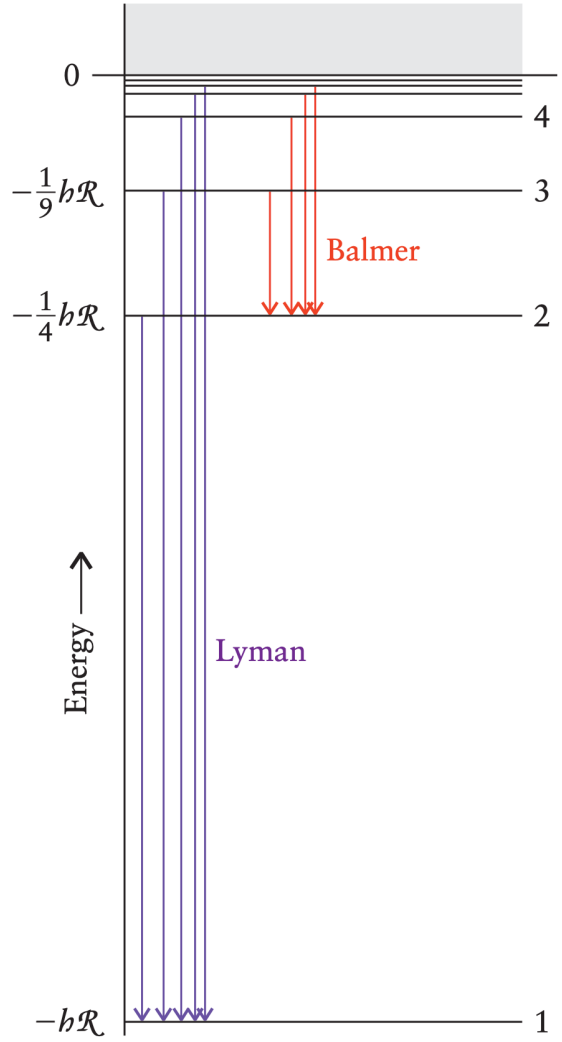


Figure 1D.1

1D.1 Energy levels

Last Tuesday: Finally, it makes sense

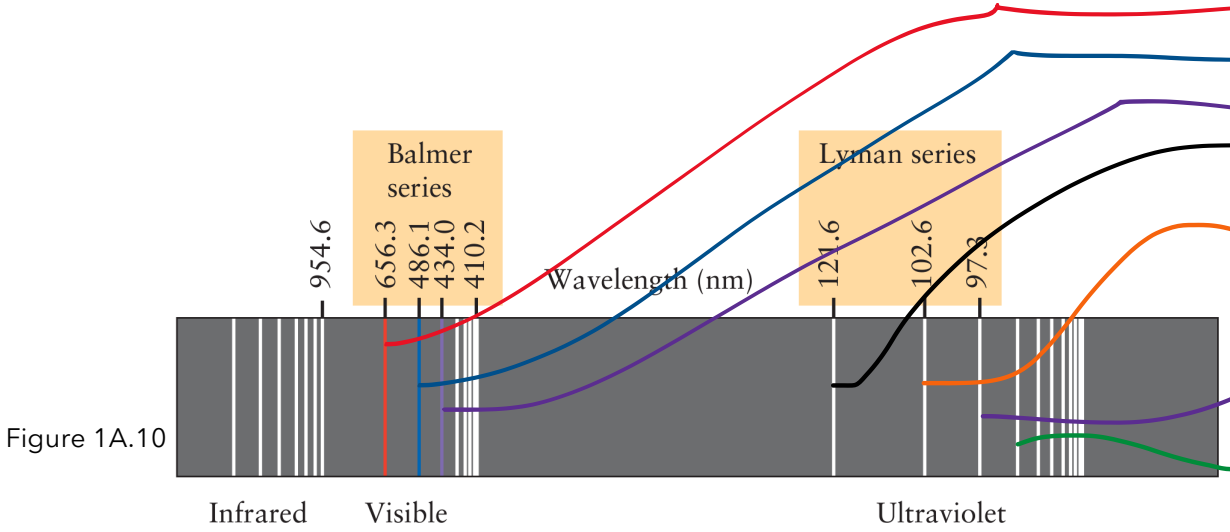


Figure 1A.10

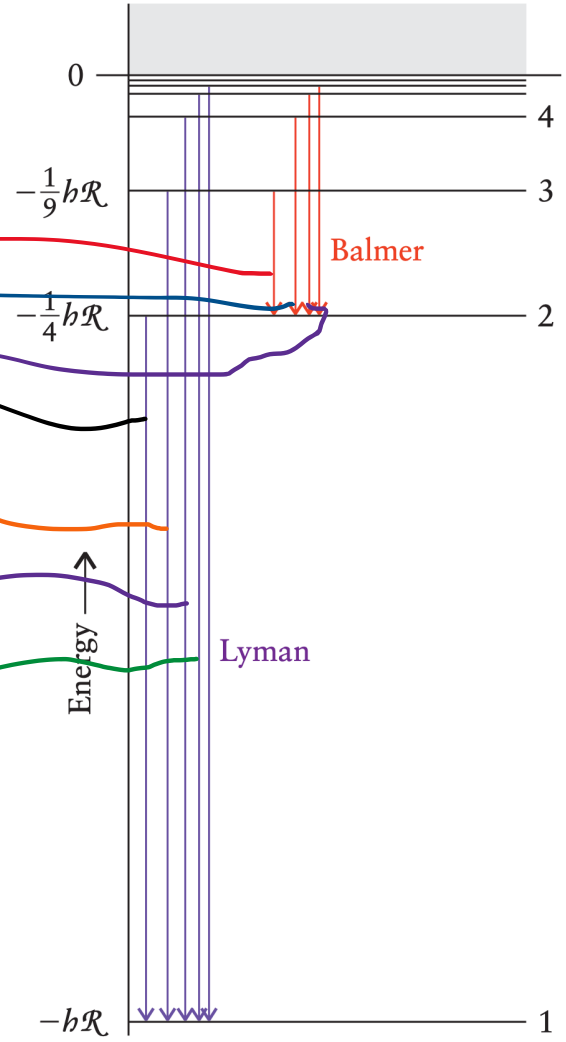


Figure 1D.1

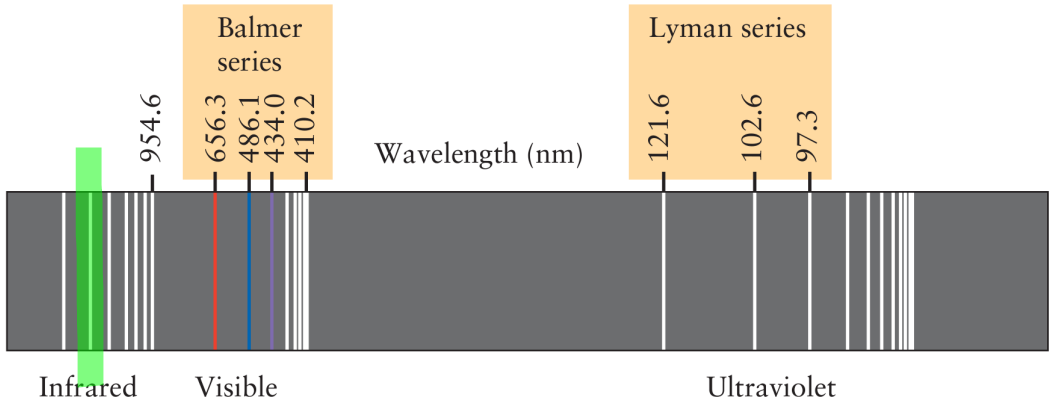
If I wanted to calculate the wavelength of the line highlighted in green, what would be the two values of n_1 and n_2 I would use?

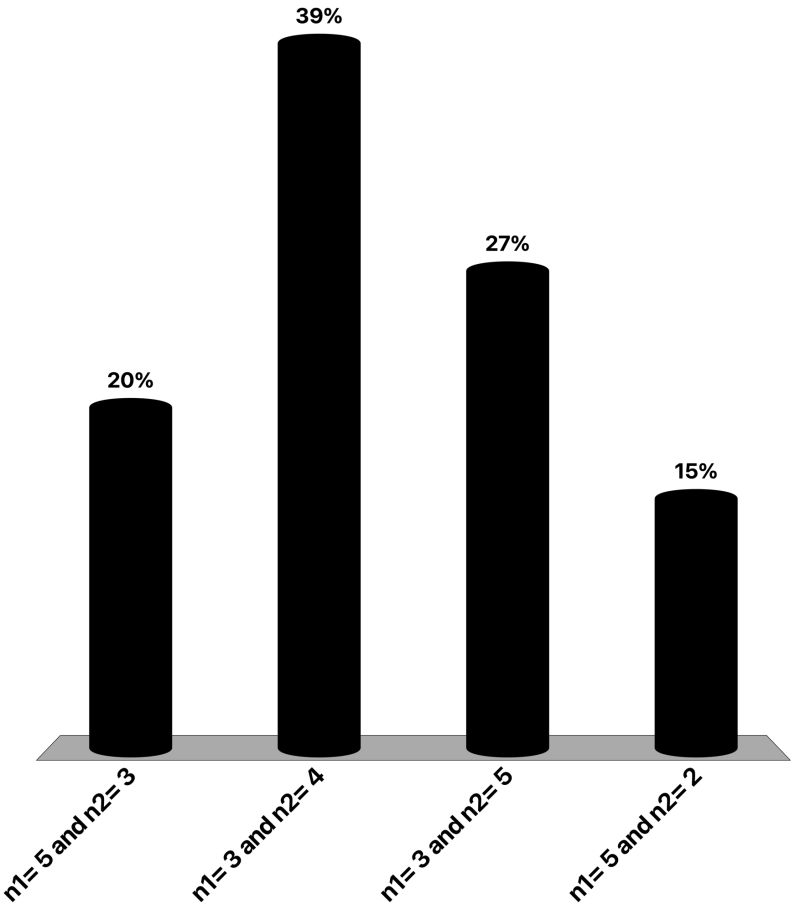
A. n_1= 5 and n_2= 3

B. n_1= 3 and n_2= 4

C. n_1= 3 and n_2= 5 (correct answer)

D. n_1= 5 and n_2= 2





Solution

Paschen Series Overview:

The Paschen series involves transitions where the electron falls to the **third energy level** ($n_1=3$).

The initial energy level (n_2) can be 4,5,6,...

For the Second Line of the Paschen Series:

First Line:

Transition from $n_2=4$ to $n_1=3$ (this corresponds to the first line in the Paschen series).

Second Line:

Transition from $n_2=5$ to $n_1=3$ (this is the second line in the Paschen series).

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:

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

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:

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

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 $m_l = +2, +1, 0, -1, -2$

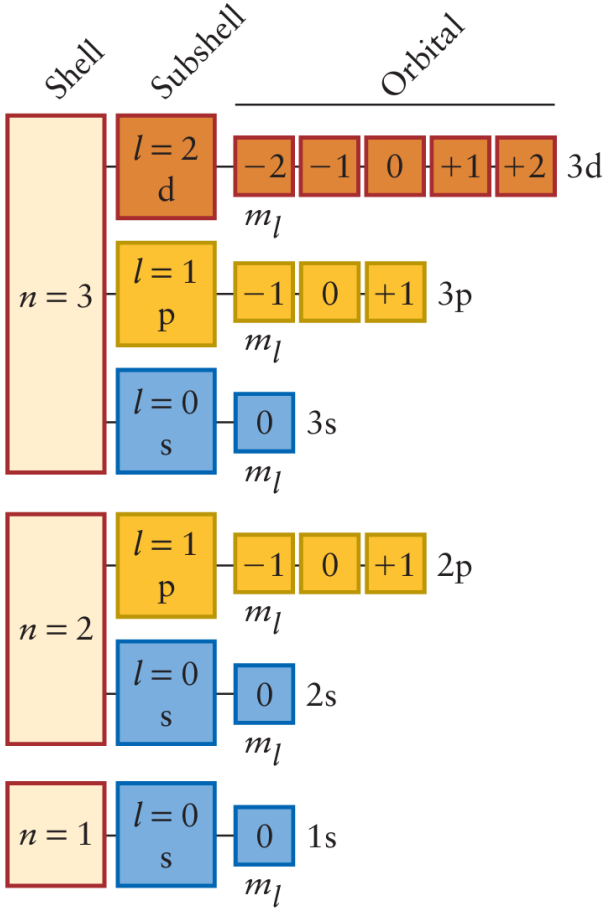


Figure 1D.3

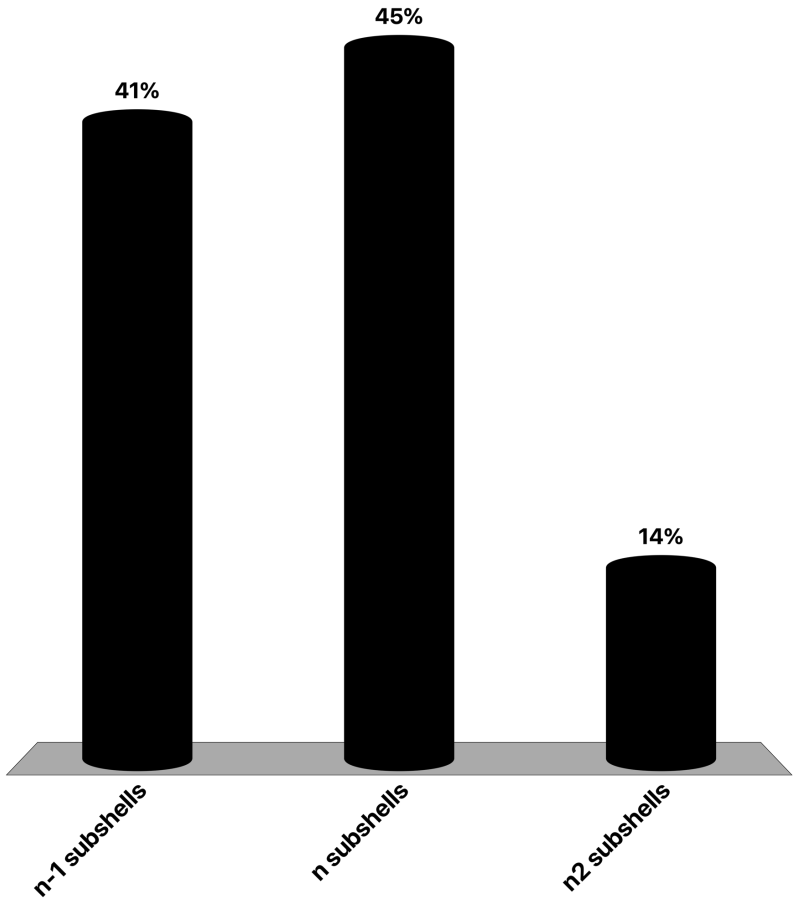
How many subshells are there for quantum number *n*?

A. n-1 subshells

B. n subshells (correct)

C. n^2 subshells

Number of orbitals per shell: n^2



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.

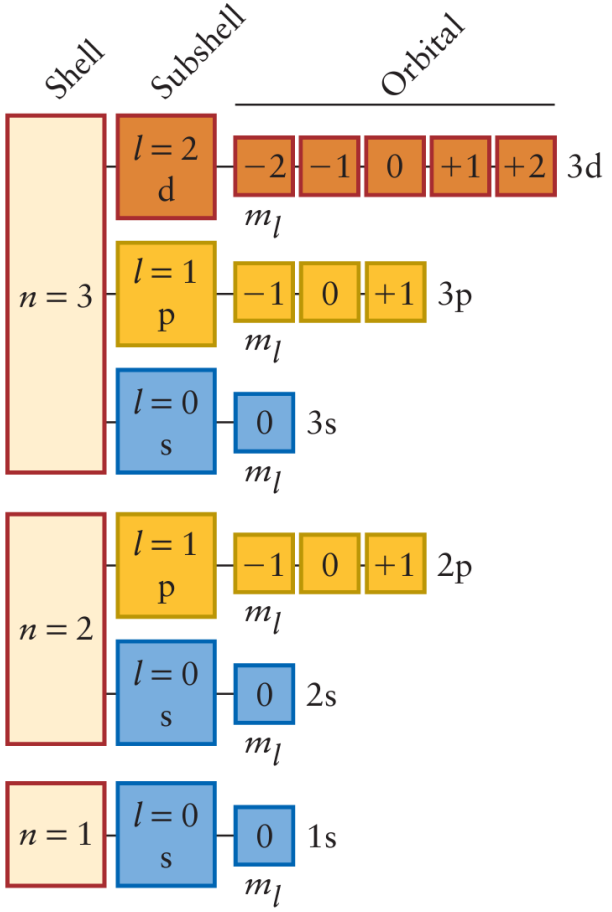


Figure 1D.3

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.

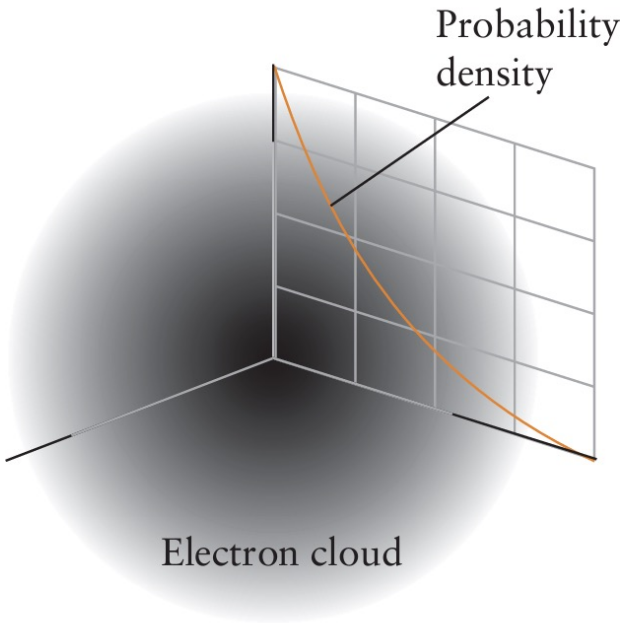
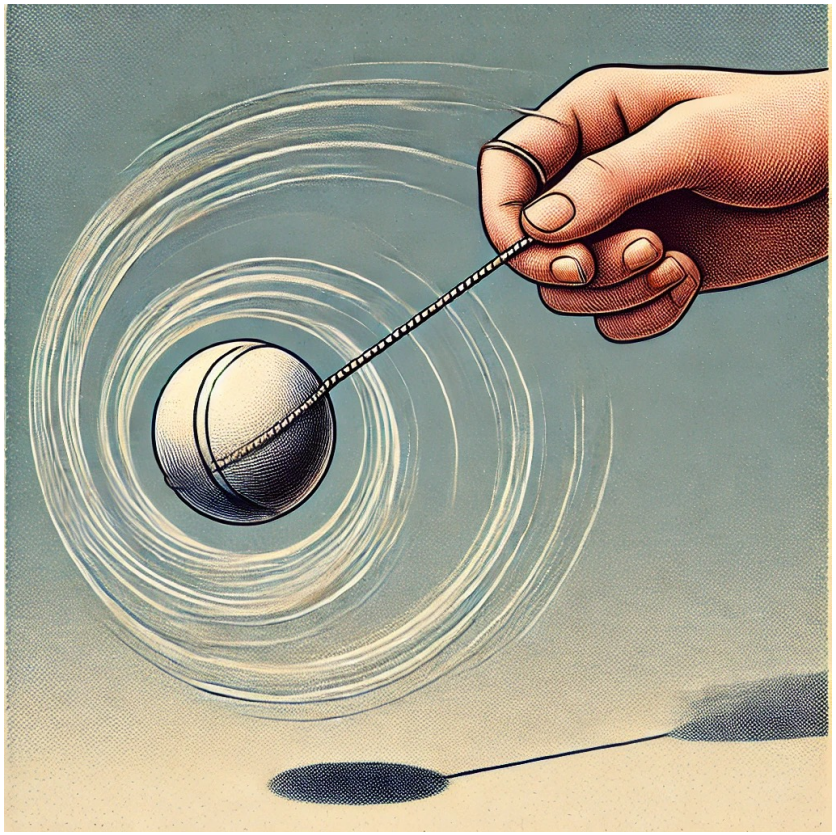


Figure 1D.4

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 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 $\psi(r)$

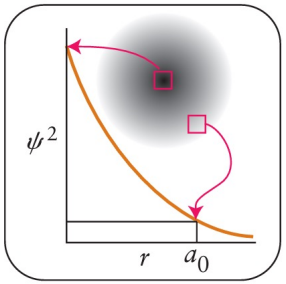
1D.4 The shapes of orbitals

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 $r = 2a_0$:

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

Ratio becomes:

$$e^{-4} = 0.018$$

At $r = 3a_0$:

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

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

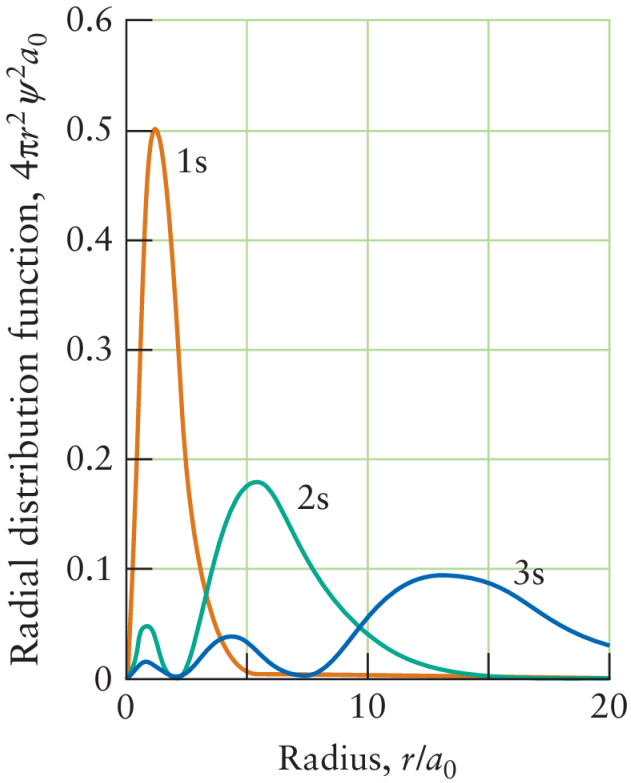
$$P(r) = r^2R^2(r)$$

- For s-orbitals, $\psi = RY = \frac{R}{\frac{1}{2\pi^{\frac{1}{2}}}}$, 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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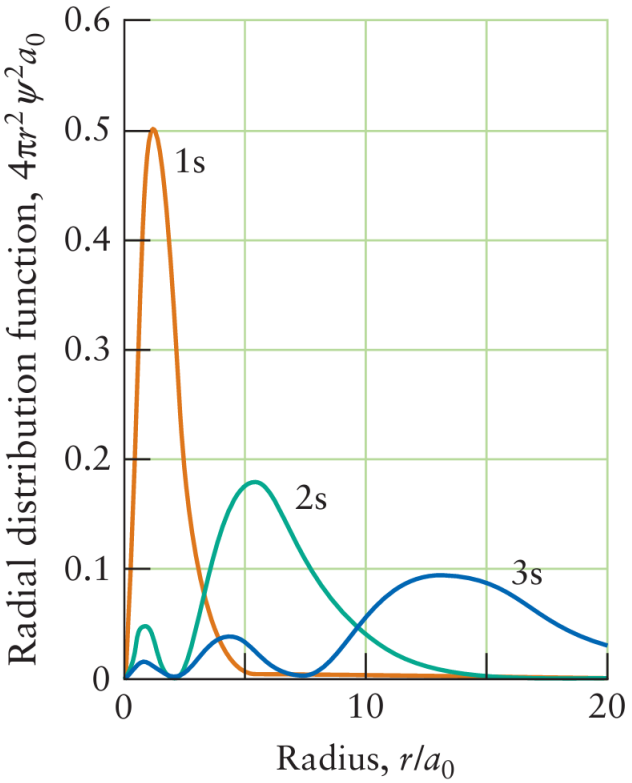
Figure 1D.5

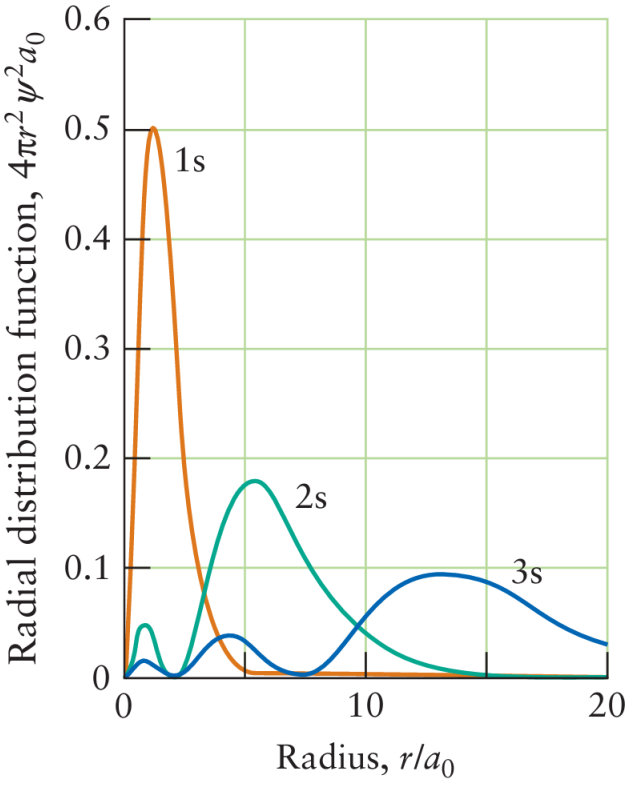


1D.4 The shapes of orbitals

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

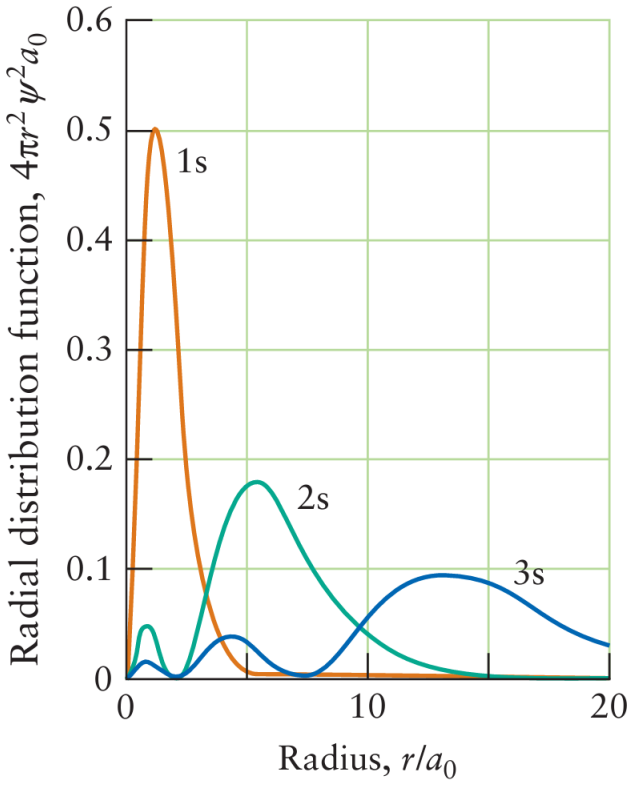


1D.4 The shapes of orbitals

The radial distribution function

- Note that for all orbitals, except s-orbitals, **the radial distribution function $P(r)$ 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 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.

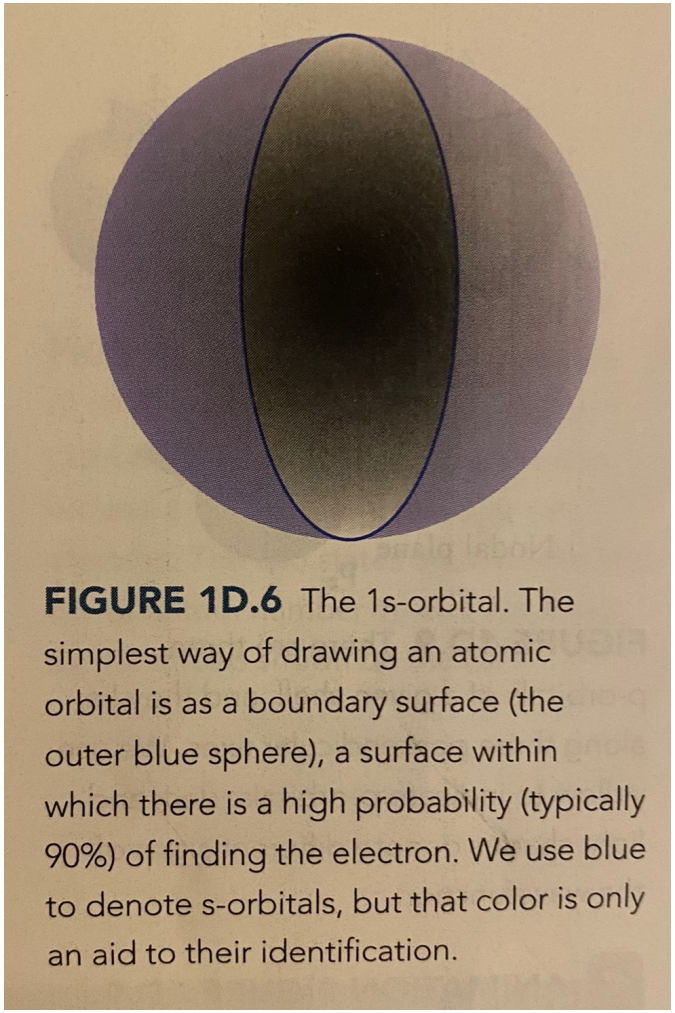


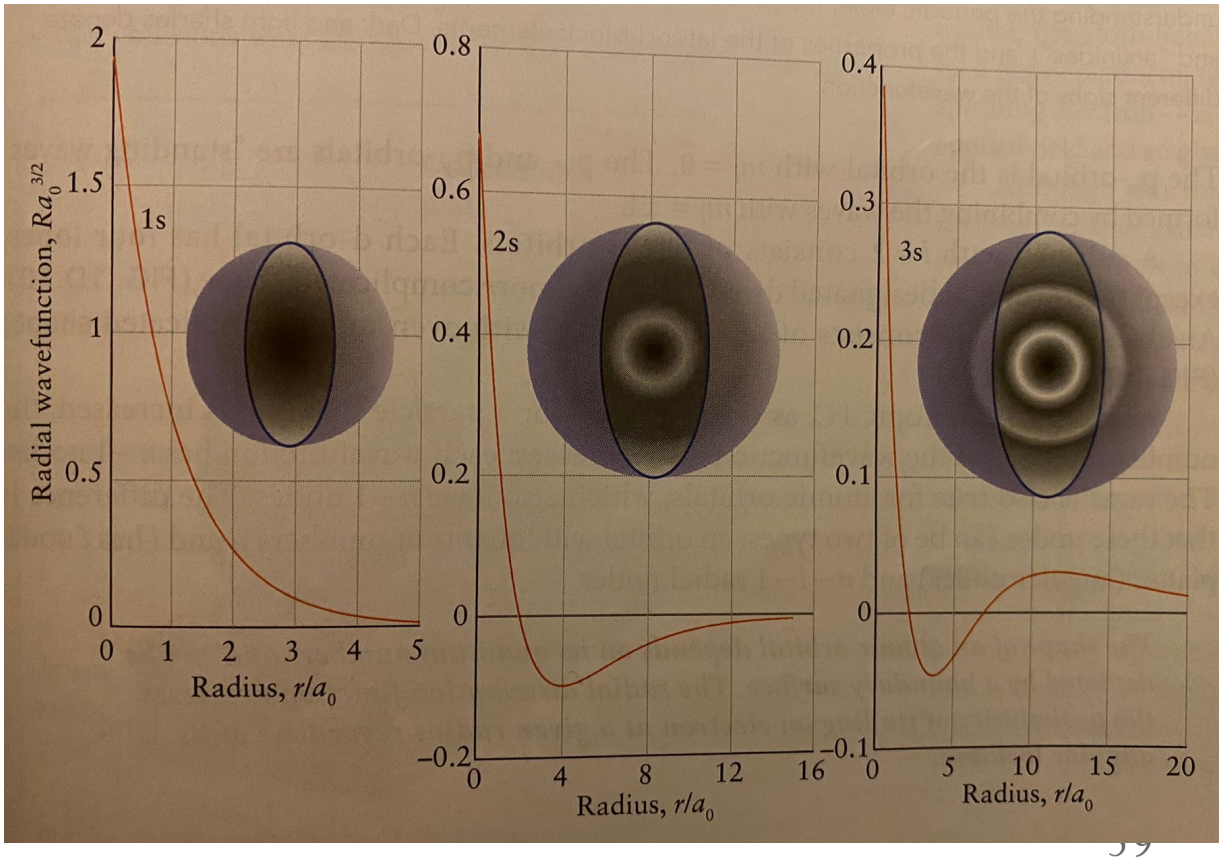
FIGURE 1D.6 The 1s-orbital. The simplest way of drawing an atomic orbital is as a boundary surface (the outer blue sphere), a surface within which there is a high probability (typically 90%) of finding the electron. We use blue to denote s-orbitals, but that color is only an aid to their identification.

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

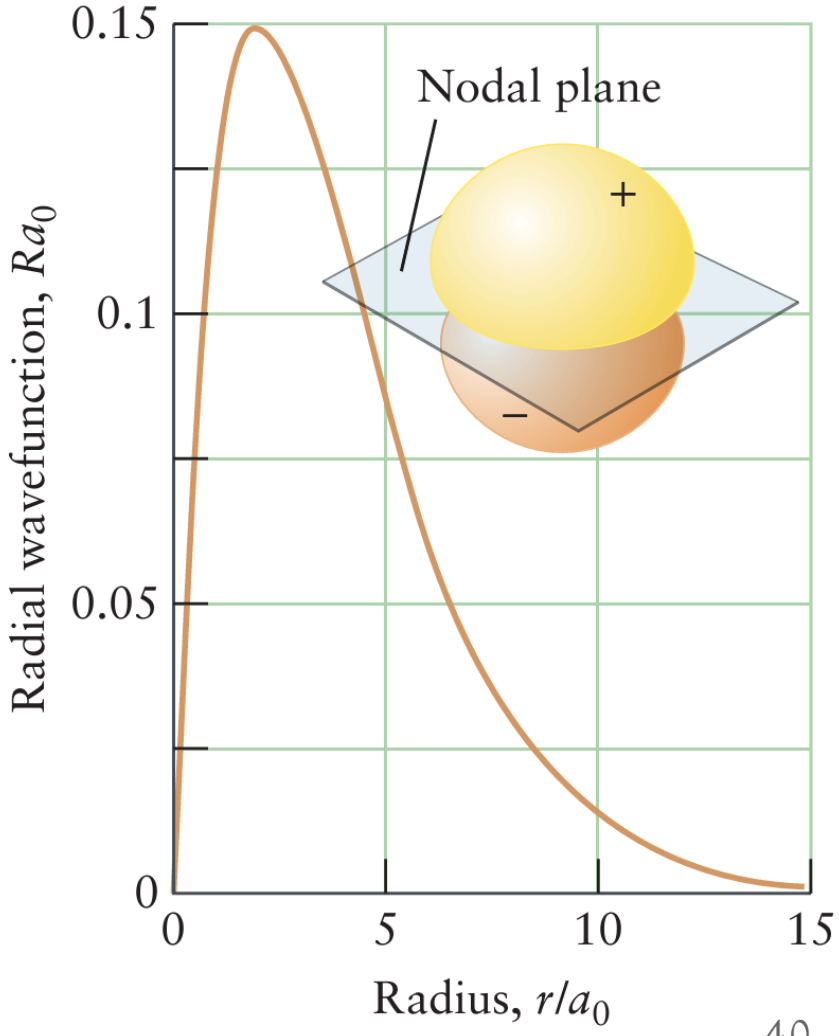


1D.4 The shapes of orbitals

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

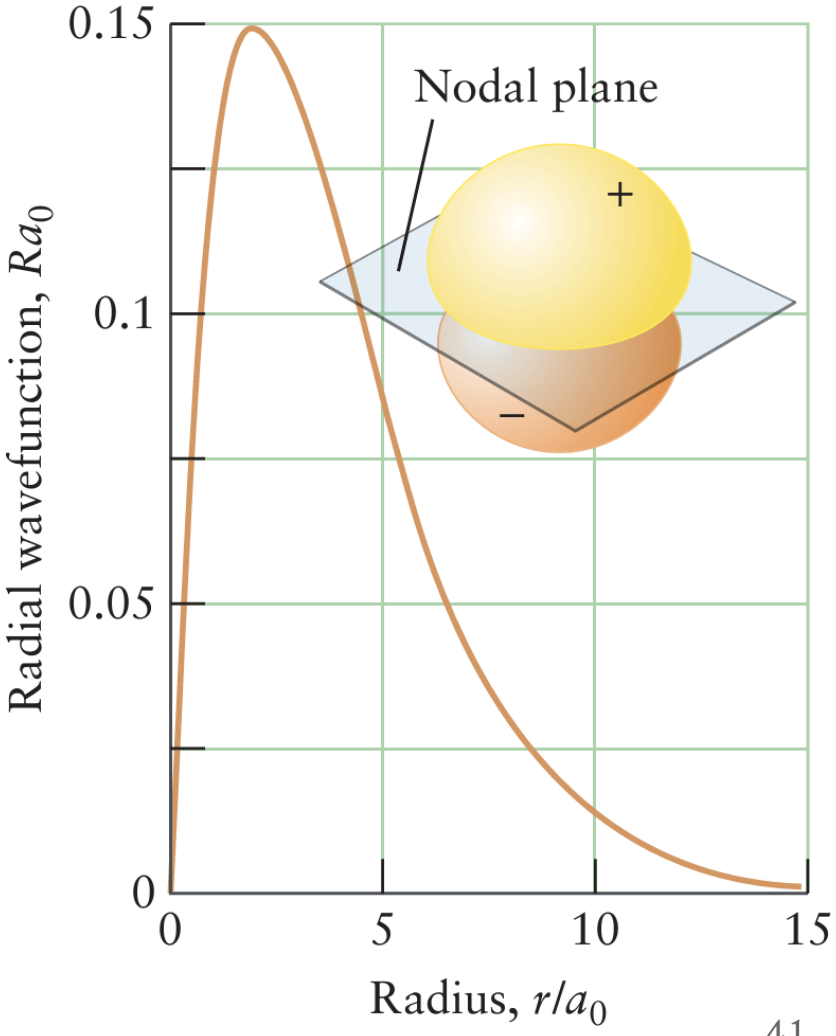


1D.4 The shapes of orbitals

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

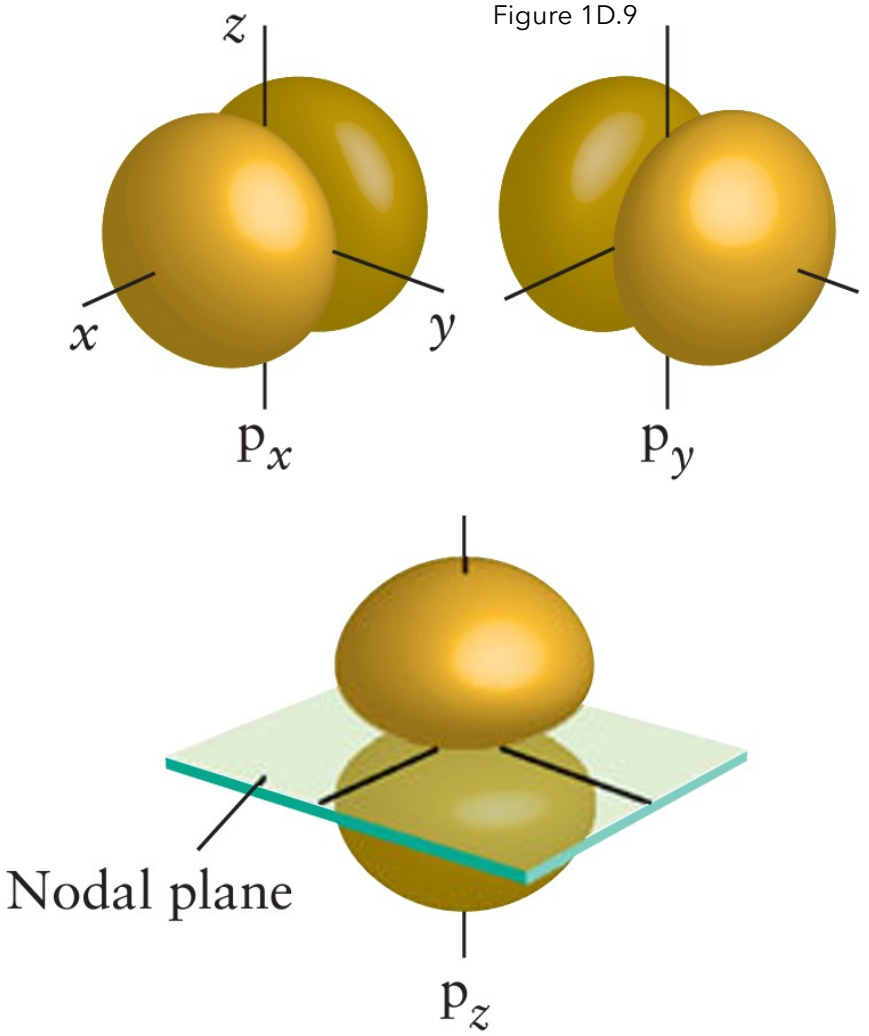


1D.4 The shapes of orbitals

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}

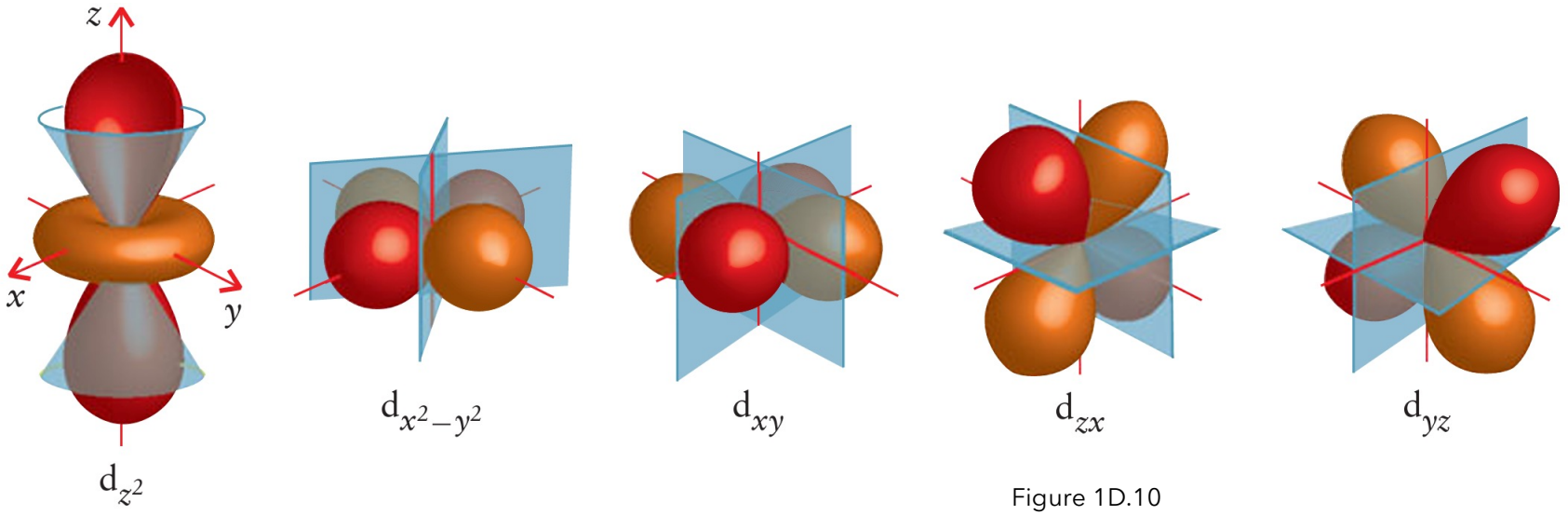


Figure 1D.10

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.

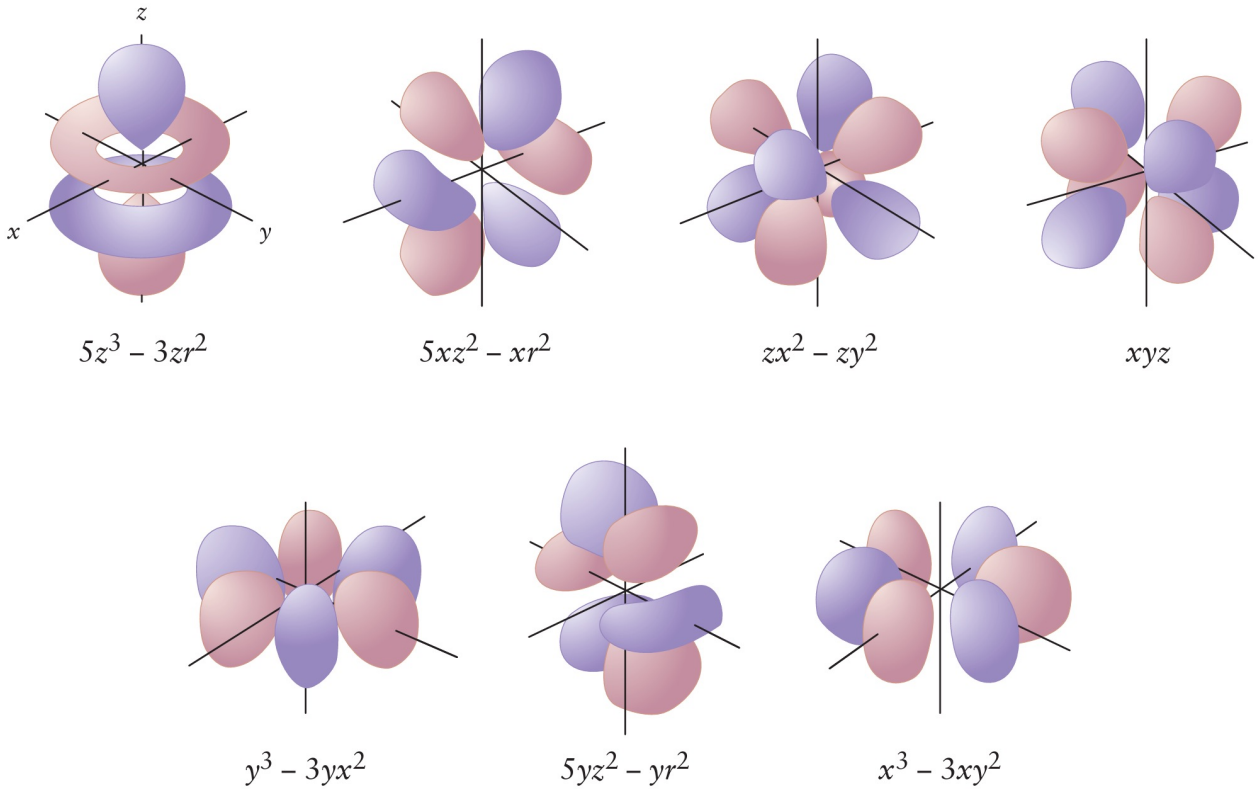


Figure 1D.11

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.