

# Chapter 42

Atomic Physics



# Atomic Spectra

All objects emit thermal radiation characterized by a continuous distribution of wavelengths.

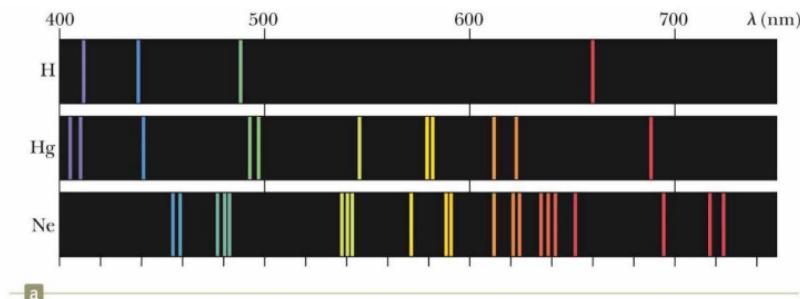
A discrete **line spectrum** is observed when a low-pressure gas is subjected to an electric discharge.

Electric discharge occurs when the gas is subject to a potential difference that creates an electric field greater than the dielectric strength of the gas.

Observation and analysis of these spectral lines is called **emission spectroscopy**.

The simplest line spectrum is that for atomic hydrogen.

Emission Spectra Examples



## Uniqueness of Atomic Spectra

Other atoms exhibit completely different line spectra.

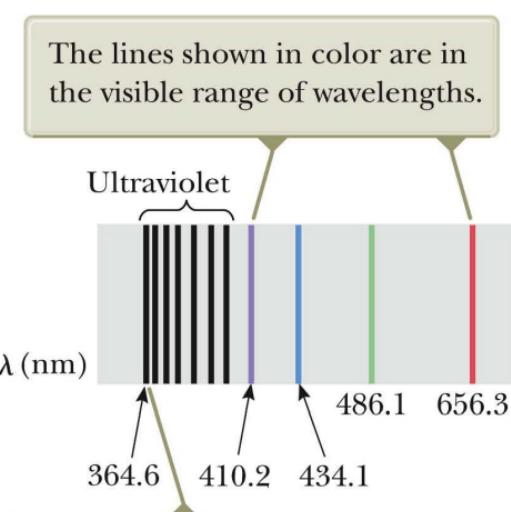
Because no two elements have the same line spectrum, the phenomena represents a practical and sensitive technique for identifying the elements present in unknown samples.

## Balmer Series

In 1885, Johann Balmer found an empirical equation that correctly predicted the four visible emission lines of hydrogen.

- $H_{\alpha}$  is red,  $\lambda = 656.3 \text{ nm}$
- $H_{\beta}$  is green,  $\lambda = 486.1 \text{ nm}$
- $H_{\gamma}$  is blue,  $\lambda = 434.1 \text{ nm}$
- $H_{\delta}$  is violet,  $\lambda = 410.2 \text{ nm}$

The complete set of lines is called the Balmer series.



## Emission Spectrum of Hydrogen – Equation

The wavelengths of hydrogen's spectral lines can be found from

$$\frac{1}{\lambda} = R_H \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$$

- $R_H$  is the Rydberg constant
  - $R_H = 1.097\ 373\ 2 \times 10^7\ \text{m}^{-1}$
- $n$  is an integer,  $n = 3, 4, 5, \dots$
- The spectral lines correspond to different values of  $n$ .
- Values of  $n$  from 3 to 6 give the four visible lines.
- Values of  $n > 6$  give the ultraviolet lines in the Balmer series.

The series limit is the shortest wavelength in the series and corresponds to  $n \rightarrow \infty$ .

## Other Hydrogen Series

Other lines in the spectrum of hydrogen were also discovered and their wavelengths can be calculated:

Lyman series:  $\frac{1}{\lambda} = R_H \left( 1 - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$

Paschen series:  $\frac{1}{\lambda} = R_H \left( \frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots$

Brackett series:  $\frac{1}{\lambda} = R_H \left( \frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$

# Niels Bohr

1885 – 1962

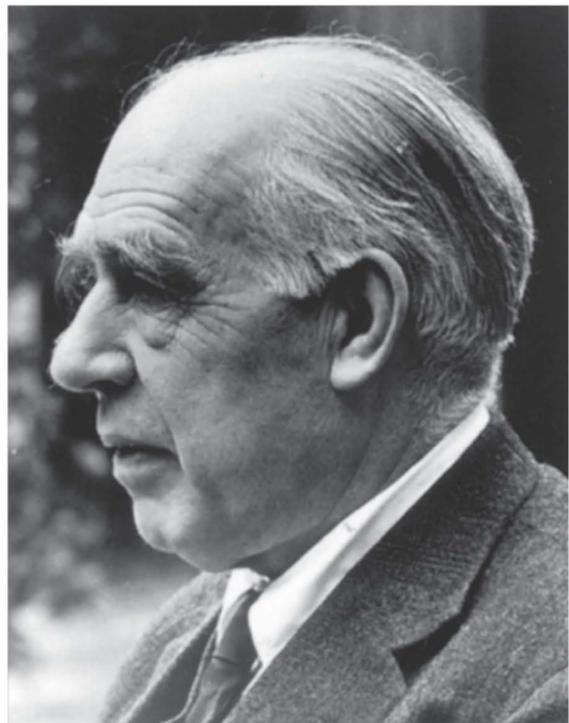
Danish physicist

An active participant in the early development of quantum mechanics

Headed the Institute for Advanced Studies in Copenhagen

Awarded the 1922 Nobel Prize in physics

- For structure of atoms and the radiation emanating from them



## The Bohr Theory of Hydrogen

In 1913 Bohr provided an explanation of atomic spectra that includes some features of the currently accepted theory.

His model includes both classical and non-classical ideas.

He applied Planck's ideas of quantized energy levels.

This model is now considered obsolete.

It has been replaced by a probabilistic quantum-mechanical theory.

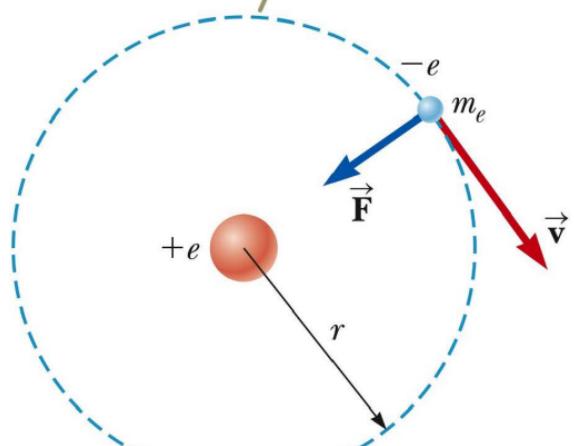
The model can still be used to develop ideas of energy quantization and angular momentum quantization as applied to atomic-sized systems.

## Bohr's Postulates for Hydrogen, 1

The electron moves in circular orbits around the proton under the electric force of attraction.

- The Coulomb force produces the centripetal acceleration.

The orbiting electron is allowed to be only in specific orbits of discrete radii.



## Bohr's Postulates, 2

Only certain electron orbits are stable.

- Bohr called these **stationary states**.
- These are the orbits in which the electron does not emit energy in the form of electromagnetic radiation, even though it is accelerating.
- Therefore, the energy of the atom remains constant and classical mechanics can be used to describe the electron's motion.
- This representation claims the centripetally accelerated electron does not continuously emit energy and therefore does not eventually spiral into the nucleus.

## Bohr's Postulates, 3

Radiation is emitted by the atom when the electron makes a transition from a more energetic initial stationary state to a lower-energy stationary state.

- The transition cannot be treated classically.
- The frequency emitted in the transition is related to the change in the atom's energy.
- The frequency is independent of frequency of the electron's orbital motion.
- The frequency of the emitted radiation is given by
  - $E_i - E_f = hf$
  - If a photon is absorbed, the electron moves to a higher energy level, but only if the photon has an energy that exactly matches the difference in energy between an allowed state of the atom and a higher-energy state.

## Bohr's Postulates, 4

The size of the allowed electron orbits is determined by a condition imposed on the electron's orbital angular momentum.

The allowed orbits are those for which the electron's orbital angular momentum about the nucleus is quantized and equal to an integral multiple of  $\hbar = h/2\pi$ .

$$m_e v r = n \hbar \quad n = 1, 2, 3, \dots$$

where  $m_e$  is the electron mass,  $v$  is the electron's speed in its orbit, and  $r$  is the orbital radius.

## Mathematics of Bohr's Assumptions and Results

Electron's orbital angular momentum

$$m_e v r = n \hbar \text{ where } n = 1, 2, 3, \dots$$

The total energy of the atom is  $E = K + U = \frac{1}{2} m_e v^2 - k_e \frac{e^2}{r}$

The electron is modeled as a particle in uniform circular motion, so the electrical force on the electron equals the product of its mass and its centripetal acceleration.

$$\frac{k_e e^2}{r^2} = \frac{m_e v^2}{r} \quad \rightarrow \quad v^2 = \frac{k_e e^2}{m_e r}$$

The total energy can also be expressed as  $E = -\frac{k_e e^2}{2r}$ .

- The total energy is negative, indicating a bound electron-proton system.

## Radii and Energy of Orbits

The radii of the Bohr orbits are quantized.

A general expression for the radius of any orbit in a hydrogen atom is

- $r_n = n^2 a_0$
- $a_0 = 0.052\ 9\ \text{nm}$

The energy of any orbit is

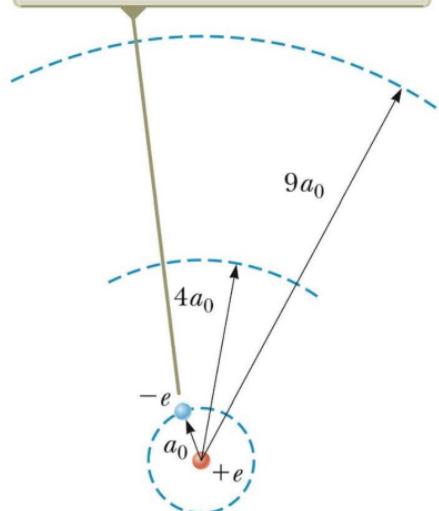
$$E_n = -\frac{k_e e^2}{2a_0} \left( \frac{1}{n^2} \right) \quad n = 1, 2, 3, \dots$$

- This becomes  $E_n = -13.606\ \text{eV} / n^2$

The lowest energy state is called the ground state.

- This corresponds to  $n = 1$  with  $E = -13.606\ \text{eV}$ .

The electron is shown in the lowest-energy orbit, but it could be in any of the allowed orbits.



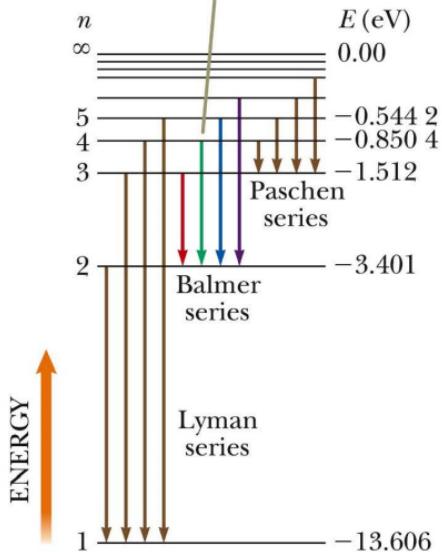
# Energy Level Diagram

Quantum numbers are given on the left and energies on the right.

The uppermost level,  $E = 0$ , represents the state for which the electron is removed from the atom.

- Adding more energy than this amount *ionizes* the atom.
- The uppermost level corresponds to  $n = \infty$  (or  $r = \infty$ ) and  $E = 0$ .

The colored arrows for the Balmer series indicate that this series results in the emission of visible light.



## Frequency and Wavelength of Emitted Photons

The frequency of the photon emitted when the electron makes a transition from an outer orbit to an inner orbit is

$$f = \frac{E_i - E_f}{h} = \frac{k_e e^2}{2a_o h} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

It is convenient to look at the wavelength instead.

The wavelengths are found by

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{k_e e^2}{2a_o h c} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

The value of  $R_H$  from Bohr's analysis is in excellent agreement with the experimental value.

## Extension to Other Atoms

Bohr extended his model for hydrogen to other elements in which all but one electron had been removed.

These systems have the same structure as the hydrogen atom except that the nuclear charge is larger.

To describe a single electron orbiting a fixed nucleus of charge  $+Ze$ , Bohr's theory gives

$$r_n = \left(n^2\right) \frac{a_o}{Z}$$

$$E_n = -\frac{k_e e^2}{2a_o} \left(\frac{Z^2}{n^2}\right) \quad n = 1, 2, 3, \dots$$

- Z is the **atomic number** of the element and is the number of protons in the nucleus.

## Example

(A) The electron in a hydrogen atom makes a transition from the  $n = 2$  energy level to the ground level ( $n = 1$ ). Find the wavelength and frequency of the emitted photon.

( $R_H = 1.097 \times 10^7$ ,  $a_0 = 0.0529 \text{ nm}$ ,  $k_e = 8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2$ ,  $m_e = 9.11 \times 10^{-31} \text{ Kg}$ )

$$\frac{1}{\lambda} = R_H \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3R_H}{4}$$

$$\lambda = \frac{4}{3R_H} = \frac{4}{3(1.097 \times 10^7 \text{ m}^{-1})} = 1.22 \times 10^{-7} \text{ m} = 122 \text{ nm}$$

$$; f = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.22 \times 10^{-7} \text{ m}} = 2.47 \times 10^{15} \text{ Hz}$$

(B) What is the radius of the electron orbit for a Rydberg atom for which  $n = 273$ ?

$$r_{273} = (273)^2 (0.0529 \text{ nm}) = 3.94 \mu\text{m}$$

(C) How fast is the electron moving in a Rydberg atom for which  $n = 273$ ?

$$v = \sqrt{\frac{k_e e^2}{m_e r}} = \sqrt{\frac{(8.99 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2)(1.60 \times 10^{-19} \text{ C})^2}{(9.11 \times 10^{-31} \text{ kg})(3.94 \times 10^{-6} \text{ m})}}$$
$$= 8.01 \times 10^3 \text{ m/s}$$

## The Quantum Model of the Hydrogen Atom

There are three different quantum numbers for each allowed state.

The three different quantum numbers are restricted to integer values.

### Principal Quantum Number

The first quantum number is called the **principal quantum number**.

- It is symbolized by  $n$ .

# Orbital and Orbital Magnetic Quantum Numbers

The **orbital quantum number** is symbolized by  $\ell$ .

- It is associated with the orbital angular momentum of the electron.
- It is an integer.

The **orbital magnetic quantum number** is symbolized by  $m_\ell$ .

- It is also associated with the orbital angular momentum of the electron and is an integer.

**TABLE 42.1** Three Quantum Numbers for the Hydrogen Atom

Quantum Number	Name	Allowed Values	Number of Allowed States
$n$	Principal quantum number	1, 2, 3, ...	Any number
$\ell$	Orbital quantum number	0, 1, 2, ..., $n - 1$	$n$
$m_\ell$	Orbital magnetic quantum number	$-\ell, -\ell + 1, \dots, 0, \dots, \ell - 1, \ell$	$2\ell + 1$

- If  $n = 1$ , then only  $\ell = 0$  and  $m_\ell = 0$  are permitted
- If  $n = 2$ , then  $\ell = 0$  or 1
  - If  $\ell = 0$  then  $m_\ell = 0$
  - If  $\ell = 1$  then  $m_\ell$  may be  $-1, 0$ , or 1

\*The first four of these letters come from early classifications of spectral lines: sharp, principal, diffuse, and fundamental. The remaining letters are in alphabetical order.

## Shells

Historically, all states having the same principle quantum number are said to form a **shell**.

- Shells are identified by letters K, L, M,... for which  $n = 1, 2, 3, \dots$

All states having the same values of  $n$  and  $\ell$  are said to form a **subshell**.

- The letters s, p, d, f, g, h, .. are used to designate the subshells for which  $\ell = 0, 1, 2, 3, \dots$

**TABLE 42.2**

*Atomic Shell Notations*

<i>n</i>	Shell Symbol
1	K
2	L
3	M
4	N
5	O
6	P

**TABLE 42.3**

*Atomic Subshell Notations*

$\ell$	Subshell Symbol
0	s
1	p
2	d
3	f
4	g
5	h

## Example

For a hydrogen atom, determine the allowed states corresponding to the principal quantum number  $n = 2$  and calculate the energies of these states.

$$\ell = 0 \rightarrow m_\ell = 0$$

$$\ell = 1 \rightarrow m_\ell = -1, 0, \text{ or } 1$$

Hence, we have one state, designated as the  $2s$  state, that is associated with the quantum numbers  $n = 2$ ,  $\ell = 0$ , and  $m_\ell = 0$ , and we have three states, designated as  $2p$  states, for which the quantum numbers are  $n = 2$ ,  $\ell = 1$ , and  $m_\ell = -1$ ;  $n = 2$ ,  $\ell = 1$ , and  $m_\ell = 0$ ; and  $n = 2$ ,  $\ell = 1$ , and  $m_\ell = 1$ .

The energy for all four of these states with  $n = 2$

$$E_2 = -\frac{13.606 \text{ eV}}{2^2} = -3.401 \text{ eV}$$

## Physical Interpretation of $\ell$

The magnitude of the angular momentum of an electron moving in a circle of radius  $r$  is

$$L = m_e v r$$

The direction of the angular momentum vector is perpendicular to the plane of the circle.

- The direction is given by the right hand rule.

According to quantum mechanics, an electron in a state whose principle quantum number is  $n$  can take on the following discrete values of the magnitude of the orbital angular momentum:

$$L = \sqrt{\ell(\ell+1)}\hbar \quad \ell = 0, 1, 2, \dots, n-1$$

## Physical Interpretation of $m_\ell$

The atom possesses an orbital angular momentum.

There is a sense of rotation of the electron around the nucleus, so that a magnetic moment is present due to this angular momentum.

There are distinct directions allowed for the magnetic moment vector with respect to the magnetic field vector.

Because the magnetic moment  $\vec{\mu}$  of the atom can be related to the angular momentum vector,  $\vec{L}$ , the discrete direction of the magnetic moment vector translates into the fact that the direction of the angular momentum is quantized.

Therefore,  $L_z$ , the projection of  $\vec{L}$  along the z axis, can have only discrete values.

## Physical Interpretation of $m_\ell$ , cont.

The orbital magnetic quantum number  $m_\ell$  specifies the allowed values of the z component of orbital angular momentum.

$$L_z = m_\ell \hbar$$

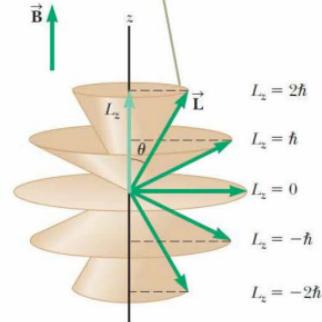
The quantization of the possible orientations of  $\vec{L}$  with respect to an external magnetic field is often referred to as **space quantization**.

$\vec{L}$  does not point in a specific direction

Imagine that  $\vec{L}$  must lie anywhere on the surface of a cone that makes an angle  $\theta$  with the z axis. ( $\theta$  is also quantized)

$$\cos \theta = \frac{L_z}{L} = \frac{m_\ell}{\sqrt{\ell(\ell + 1)}}$$

Because the x and y components of the orbital angular momentum vector are not quantized, the vector  $\vec{L}$  lies on the surface of a cone.



## Spin Quantum Number $m_s$

Additional quantum states can be explained by requiring a fourth quantum number for each state.

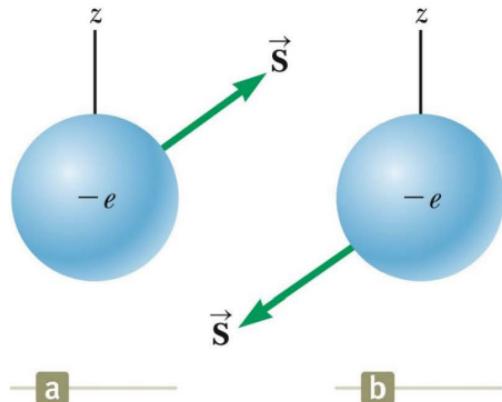
This fourth quantum number is the spin magnetic quantum number  $m_s$ .

## Electron Spins

Only two directions exist for electron spins.

The electron can have spin up (a) or spin down (b).

In the presence of a magnetic field, the energy of the electron is slightly different for the two spin directions and this produces doublets in spectra of certain gases.



The concept of a spinning electron is conceptually useful.

The electron is a point particle, without any spatial extent.

Therefore the electron cannot be considered to be actually spinning.

The experimental evidence supports the electron having some intrinsic angular momentum that can be described by  $m_s$ .

## Spin Angular Momentum

The total angular momentum of a particular electron state contains both an orbital contribution  $\vec{L}$  and a spin contribution  $\vec{S}$ .

Electron spin can be described by a single quantum number  $s$ , whose value can only be  $s = \frac{1}{2}$ .

The spin angular momentum of the electron never changes.

Because spin is a form of angular momentum, it must follow the same quantum rules as orbital angular momentum. The magnitude of the spin angular momentum is

$$S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

The spin angular momentum can have two orientations relative to a z axis, specified by the spin quantum number  $m_s = \pm \frac{1}{2}$ .

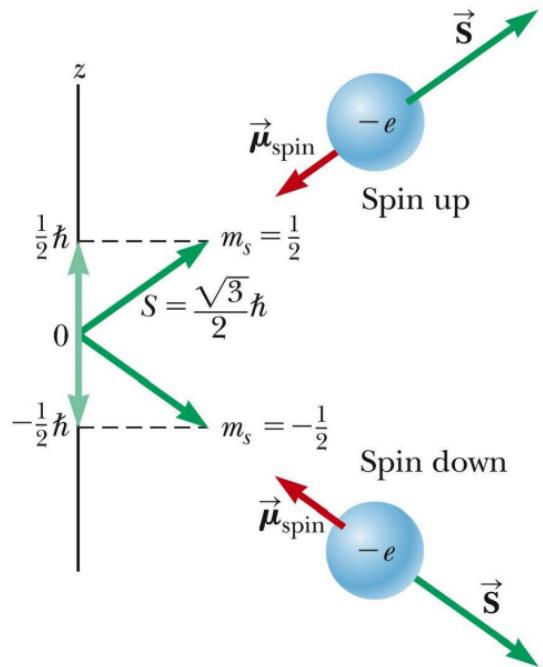
- $m_s = +\frac{1}{2}$  corresponds to the spin up case.
- $m_s = -\frac{1}{2}$  corresponds to the spin down case.

## Spin Angular Momentum, cont.

The  $z$  component of spin angular momentum is

$$S_z = m_s \hbar = \pm \frac{1}{2} \hbar$$

Spin angular momentum is quantized.



## Quantum States

There are eight quantum states corresponding to  $n = 2$ .

- These states depend on the addition of the possible values of  $m_s$ .
- Table 42.4 summarizes these states.

**TABLE 42.4** Quantum Numbers for the  $n = 2$  State of Hydrogen

$n$	$\ell$	$m_\ell$	$m_s$	Subshell	Shell	Number of States in Subshell
2	0	0	$\frac{1}{2}$	2s	L	2
2	0	0	$-\frac{1}{2}$			
2	1	1	$\frac{1}{2}$	2p	L	6
2	1	1	$-\frac{1}{2}$			
2	1	0	$\frac{1}{2}$			
2	1	0	$-\frac{1}{2}$			
2	1	-1	$\frac{1}{2}$			
2	1	-1	$-\frac{1}{2}$			

## Example

Consider the hydrogen atom in the  $\ell = 3$  state. Calculate the magnitude of  $\vec{L}$ , the allowed values of  $L_z$ , and the corresponding angles  $\theta$  that  $\vec{L}$  makes with the z axis.

Calculate the magnitude of the orbital angular momentum

$$L = \sqrt{\ell(\ell + 1)}\hbar = \sqrt{3(3 + 1)}\hbar = 2\sqrt{3}\hbar$$

Calculate the allowed values of  $L_z$  with  $m_\ell = -3, -2, -1, 0, 1, 2, 3$

$$L_z = -3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar$$

Calculate the allowed values of  $\cos \theta$

$$\cos \theta = \frac{\pm 3}{2\sqrt{3}} = \pm 0.866 \quad \cos \theta = \frac{\pm 2}{2\sqrt{3}} = \pm 0.577$$

$$\cos \theta = \frac{\pm 1}{2\sqrt{3}} = \pm 0.289 \quad \cos \theta = \frac{0}{2\sqrt{3}} = 0 \quad \theta = 30.0^\circ, 54.7^\circ, 73.2^\circ, 90.0^\circ, 107^\circ, 125^\circ, 150^\circ$$

# Wolfgang Pauli

1900 – 1958

Austrian physicist

Important review article on relativity

- At age 21

Discovery of the exclusion principle

Explanation of the connection between  
particle spin and statistics

Relativistic quantum electrodynamics

Neutrino hypothesis

Hypotheses of nuclear spin



## The Exclusion Principle

The four quantum numbers discussed so far can be used to describe all the electronic states of an atom regardless of the number of electrons in its structure.

The **exclusion principle** states that no two electrons can ever be in the same quantum state.

- Therefore, no two electrons in the same atom can have the same set of quantum numbers.

If the exclusion principle was not valid, an atom could radiate energy until every electron was in the lowest possible energy state and the chemical nature of the elements would be modified.

## Filling Subshells

The electronic structure of complex atoms can be viewed as a succession of filled levels increasing in energy.

Once a subshell is filled, the next electron goes into the lowest-energy vacant state.

- If the atom were not in the lowest-energy state available to it, it would radiate energy until it reached this state.

## Orbitals

An *orbital* is defined as the atomic state characterized by the quantum numbers  $n$ ,  $\ell$  and  $m_\ell$ .

From the exclusion principle, it can be seen that only two electrons can be present in any orbital.

- One electron will have spin up and one spin down.

Each orbital is limited to two electrons, the number of electrons that can occupy the various shells is also limited.

**TABLE 42.5** Allowed Quantum States for an Atom Up to  $n = 3$

Shell	$n$	1	2				3								
Subshell	$\ell$	0	0	1			0	1			2				
Orbital	$m_\ell$	0	0	1	0	-1	0	1	0	-1	2	1	0	-1	-2
	$m_s$	$\uparrow\downarrow$													

In general, each shell can accommodate up to  $2n^2$  electrons.

## Hund's Rule

Hund's Rule states that when an atom has orbitals of equal energy, the order in which they are filled by electrons is such that a maximum number of electrons have unpaired spins.

- Some exceptions to the rule occur in elements having subshells that are close to being filled or half-filled.

## Configuration of Some Electron States

The filling of electron states must obey both the exclusion principle and Hund's rule.

Atom	1s	2s	2p	Electronic configuration	
Li					 1s <sup>2</sup> 2s <sup>1</sup>
Be					 1s <sup>2</sup> 2s <sup>2</sup>
B					 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>
C					 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>
N					 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>
O					 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>
F					 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>
Ne					 1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>

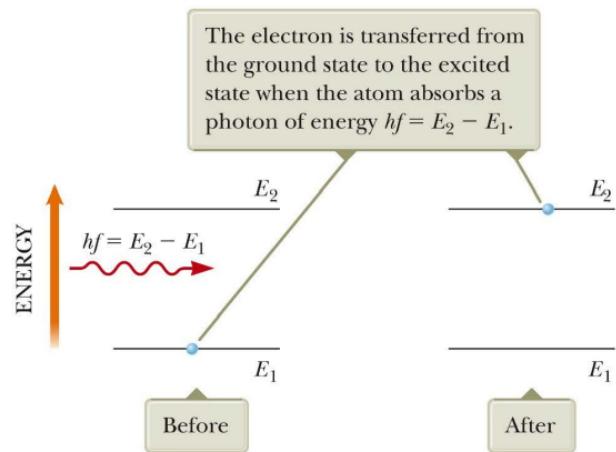
## Stimulated Absorption

When a photon has energy  $hf$  equal to the difference in energy levels, it can be absorbed by the atom.

This is called **stimulated absorption** because the photon stimulates the atom to make the upward transition.

At ordinary temperatures, most of the atoms in a sample are in the ground state.

The absorption of the photon causes some of the atoms to be raised to excited states.



# Spontaneous Emission

Once an atom is in an excited state, the excited atom can make a transition to a lower energy level.

This process is known as **spontaneous emission**.

- Because it happens naturally without requiring an event to trigger the transition. Typically, an atom remains in an excited state for only about  $10^{-8}$  s.

