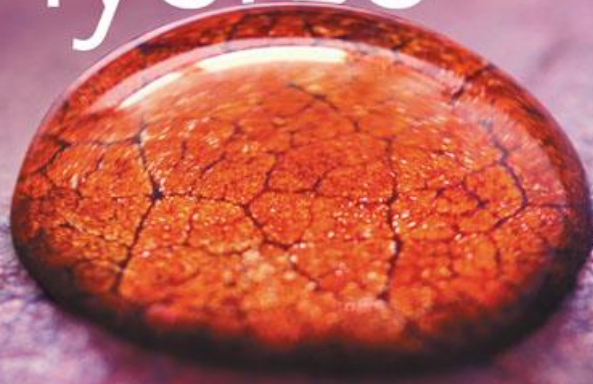


THIRD EDITION

college
physics a strategic approach



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Lecture Presentation

Chapter 29

Atoms and Molecules

Suggested Videos for Chapter 29

- **Prelecture Videos**

- *Atomic Energy Levels and Spectra*
- *Molecules*

- **Class Videos**

- *Fluorescence*

- **Video Tutor Solutions**

- *Atoms and Molecules*

- **Video Tutor Demos**

- *Illuminating Sodium Vapor with Sodium and Mercury Lamps*

Suggested Simulations for Chapter 29

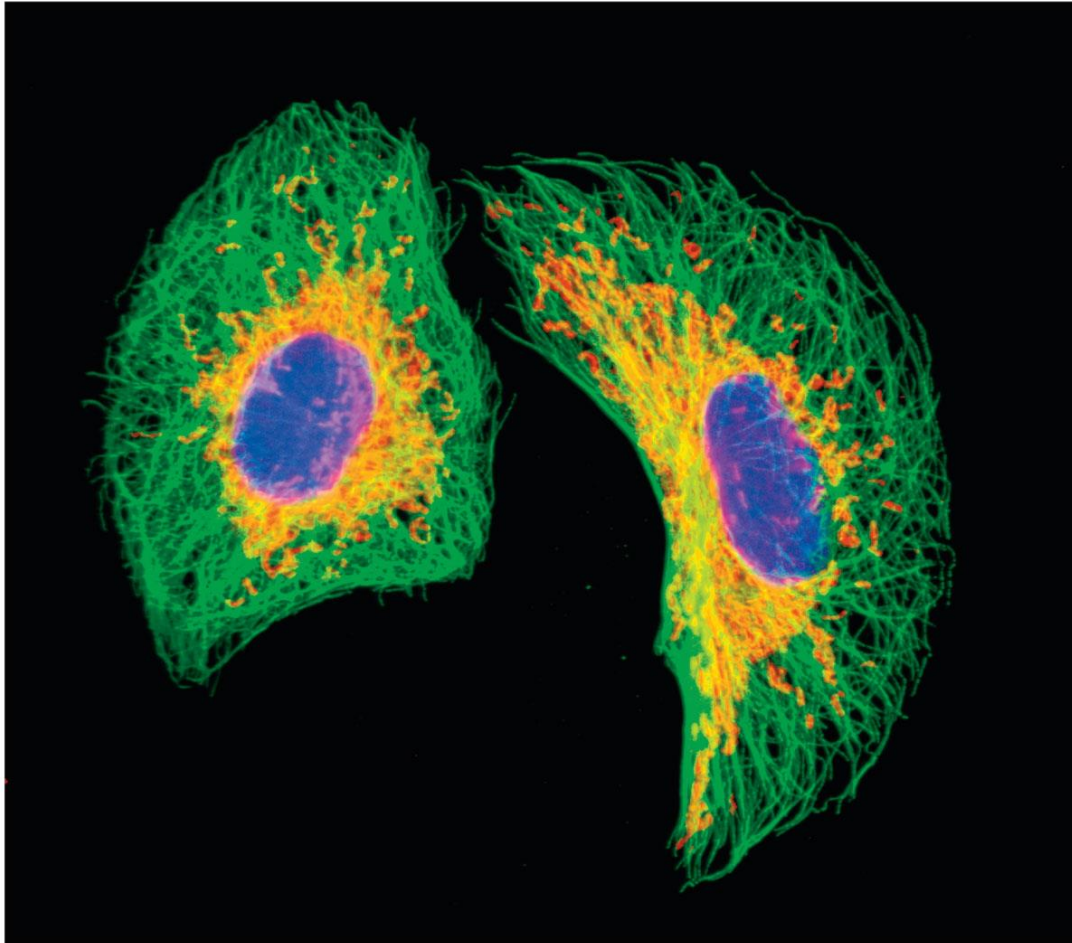
- **ActivPhysics**

- *18.1–18.3*
- *19.1*

- **PhETs**

- *Blackbody Spectrum*
- *Rutherford Scattering*
- *Models of Hydrogen Atom*
- *Neon Lights and Other Discharge Lamps*
- *Stern-Gerlach Experiment*
- *Lasers*

Chapter 29 Atoms and Molecules

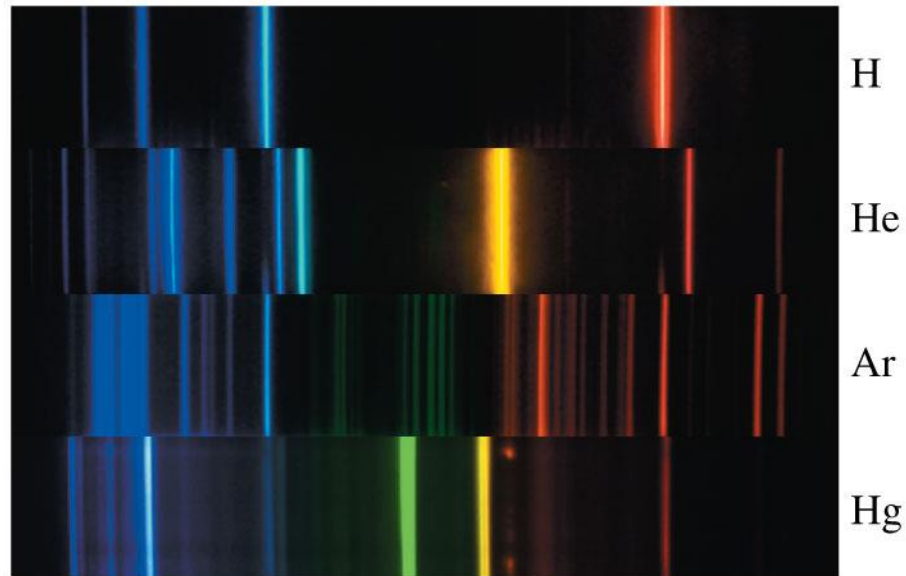


Chapter Goal: To use quantum physics to understand the properties of atoms, molecules, and their spectra.

Chapter 29 Preview

Looking Ahead: Atomic Models

- When light from a glowing gas is dispersed into colors by a diffracting grating, each element emits a unique set of wavelengths.



- You'll learn how these spectra lines are important clues into the nature of the atom.

Chapter 29 Preview

Looking Ahead: Molecules

- Specialized molecules in certain microscopic plankton can emit light. These glowing waves are caused by such *bioluminescent* creatures.



- You'll learn why, unlike atoms, the light given off by molecules contains a broad *band* of wavelengths.

Chapter 29 Preview

Looking Ahead: Lasers

- The intense beams of light as this laser light show result from the **stimulated emission** of photons by atoms.



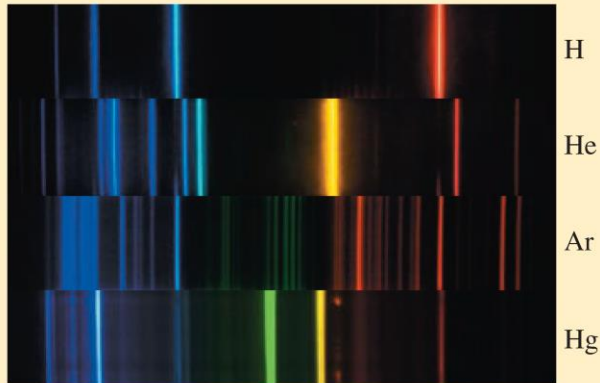
- You'll learn that when atoms give off light, they can stimulate other atoms to emit light of exactly the same wavelength and phase.

Chapter 29 Preview

Looking Ahead

Atomic Models

When light from a glowing gas is dispersed into colors by a diffraction grating, each element emits a unique set of wavelengths.



You'll learn how these **spectral lines** are important clues into the nature of the atom.

Molecules

Specialized molecules in certain microscopic plankton can emit light. These glowing waves are caused by such *bioluminescent* creatures.



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Lasers

The intense beams of light at this laser light show result from the **stimulated emission** of photons by atoms.



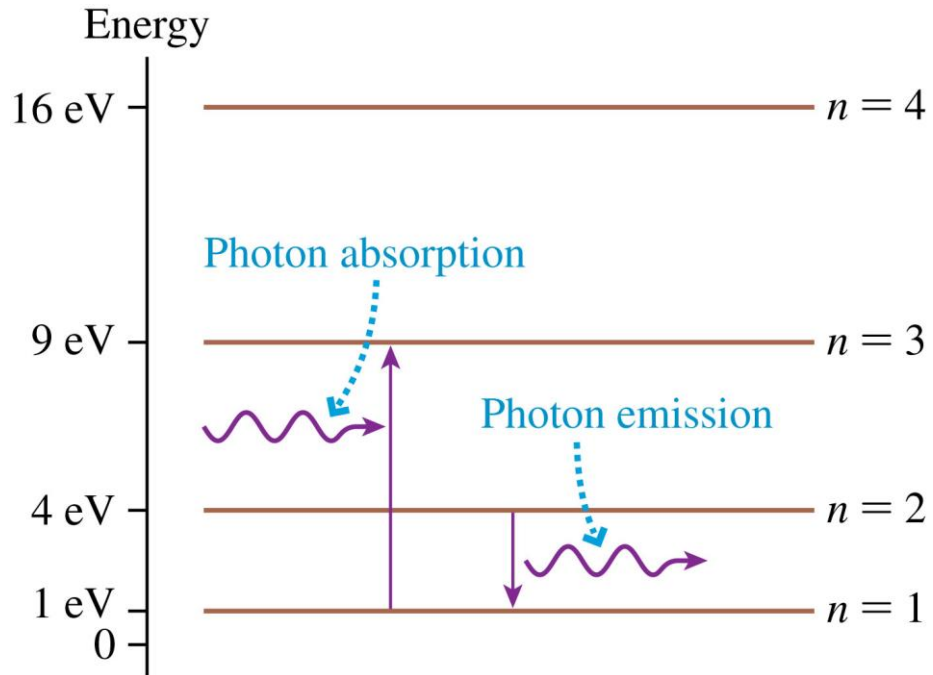
You'll learn that when atoms give off light, they can stimulate other atoms to emit light of exactly the same wavelength and phase.

Text: p. 940

Chapter 29 Preview

Looking Back: Energy-Level Diagrams

- In Sections 28.5 and 28.6 you learned that the energies of atomic-sized systems are *quantized*. The allowed energies of such a system can be represented in an energy-level diagram.
- In this chapter, we'll use the ideas of quantization to understand in detail the energy levels and spectra of atoms and molecules.



Chapter 29 Preview

Stop to Think

After the $n = 1$ to $n = 3$ absorption shown in the energy-level diagram to the left, which is a possible energy of an emitted photon?

- A. 1 eV
- B. 4 eV
- C. 5 eV
- D. 9 eV


Reading Question 29.1

A hot, low-pressure gas emits

- A. A continuous spectrum.
- B. A discrete spectrum.
- C. An absorption spectrum.
- D. A beta spectrum.

Reading Question 29.1

A hot, low-pressure gas emits

-  A. A continuous spectrum.
- B. A discrete spectrum.
- C. An absorption spectrum.
- D. A beta spectrum.


Reading Question 29.2

What is the “Balmer formula” a formula for?

- A. Masses of atomic nuclei of hydrogen isotopes
- B. Wavelengths in the hydrogen emission spectrum
- C. Energies of stationary states of hydrogen
- D. Probabilities of electron position in stationary states of hydrogen

Reading Question 29.2

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- A. Masses of atomic nuclei of hydrogen isotopes
-  B. Wavelengths in the hydrogen emission spectrum
- C. Energies of stationary states of hydrogen
- D. Probabilities of electron position in stationary states of hydrogen

Reading Question 29.3

The results of Rutherford's experiment, in which alpha particles were fired toward thin metal foils, were surprising because

- A. Some of the alpha particles were reflected almost straight backward.
- B. Two alpha particles emerged from the foil for every alpha that entered.
- C. Beta particles were created.
- D. Some alpha particles were destroyed in collisions with the foil.

Reading Question 29.3

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- D. Some alpha particles were destroyed in collisions with the foil.


Reading Question 29.4

Which of the following aspects of the stationary states of hydrogen does Bohr's analysis of the hydrogen atom get *right*?

- A. The existence of a “spin” quantum number
- B. The existence of a “magnetic” quantum number
- C. The shapes of the electron clouds
- D. The energies

Reading Question 29.4

Which of the following aspects of the stationary states of hydrogen does Bohr's analysis of the hydrogen atom get *right*?

- A. The existence of a “spin” quantum number
- B. The existence of a “magnetic” quantum number
- C. The shapes of the electron clouds
-  D. The energies


Reading Question 29.5

During the operation of a laser, as photons interact with atoms inside the laser the photons

- A. Double their energy.
- B. Double their wavelength.
- C. Lose energy to collisions.
- D. Create “clones” of themselves.

Reading Question 29.5

During the operation of a laser, as photons interact with atoms inside the laser the photons

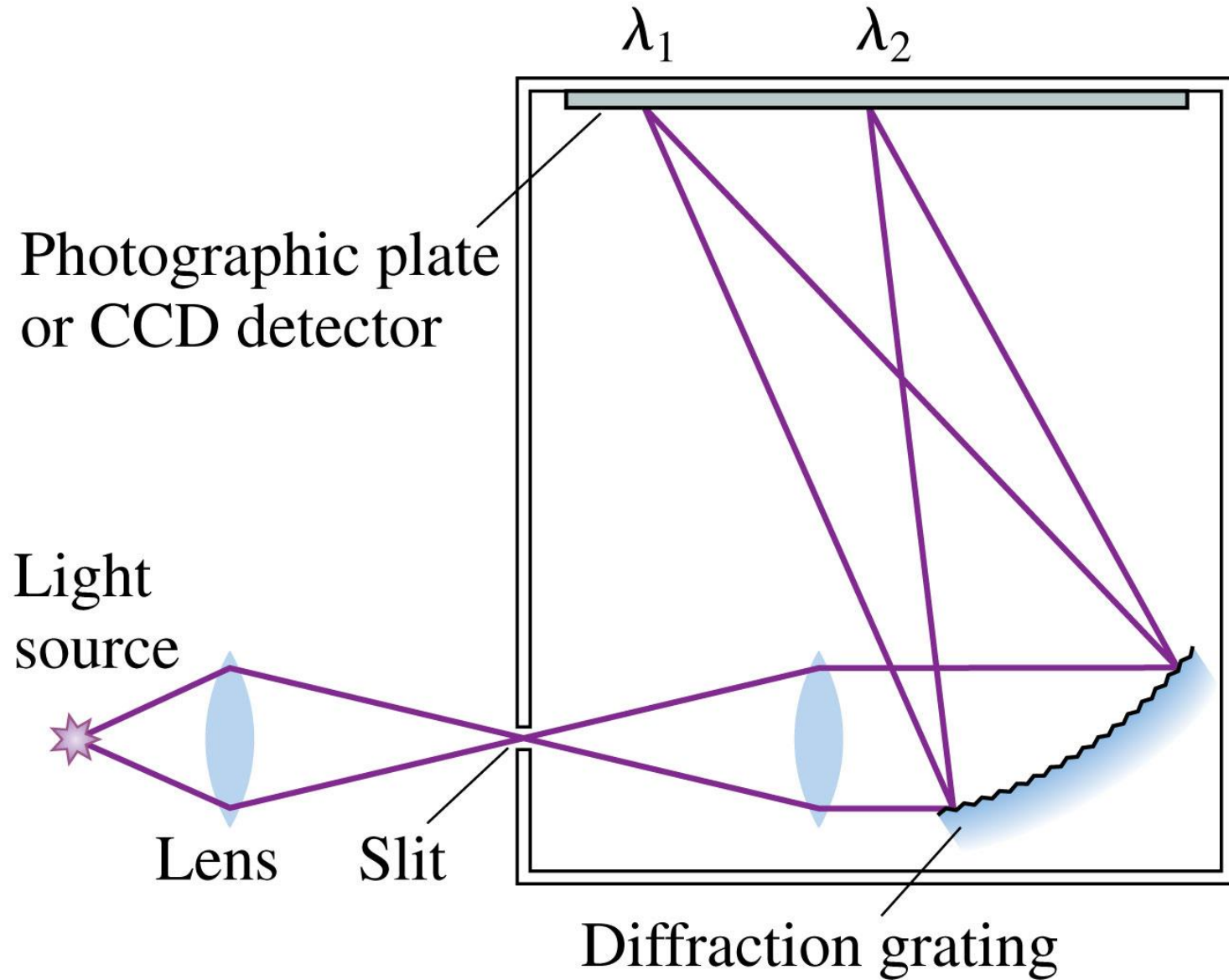
- A. Double their energy.
- B. Double their wavelength.
- C. Lose energy to collisions.
-  D. Create “clones” of themselves.

Section 29.1 Spectroscopy

Spectroscopy

- A **spectrometer** is the primary instrument for measuring the wavelengths of light.
- The spectrometer uses a diffraction grating that causes different wavelengths of light to diffract at different angles.
- A **spectrum** is the distinctive pattern of wavelengths emitted by a source of light and recorded on a detector, like a CCD, in the spectrometer.

Spectroscopy

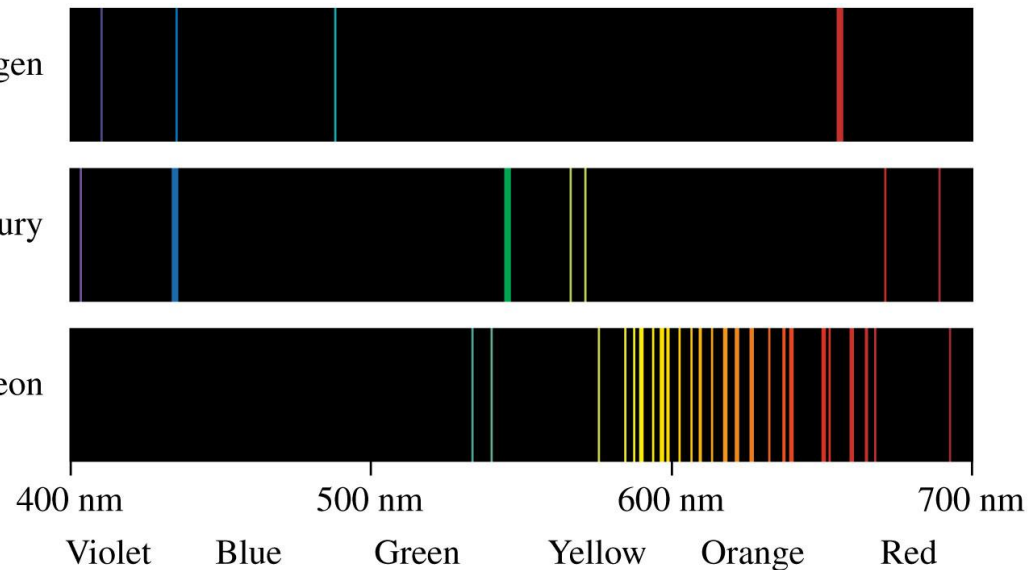


Spectroscopy

- Hot, self-luminous objects, such as the sun or the filament of an incandescent light bulb, emit a **continuous spectrum**.
- The spectrum depends on the object's temperature only.

Spectroscopy

- We can study light emitted and absorbed by individual atoms by applying a voltage to low-pressure gas, causing the gas to glow.
- The emitted light contains only certain discrete, individual wavelengths. Such a spectrum is called a **discrete spectrum**.
- Each line in a discrete spectrum is called a **spectral line** and represents one specific wavelength.



Spectroscopy

- Every element in the periodic table has its own, unique discrete *atomic spectrum*.
- The fact that each element emits a unique spectrum means that the atomic spectra can be used as “fingerprints” to identify elements.
- Atomic spectroscopy is used to analyze the composition of unknown materials, monitor air pollutants, and to study the atmospheres of the earth and other planets.

Spectroscopy

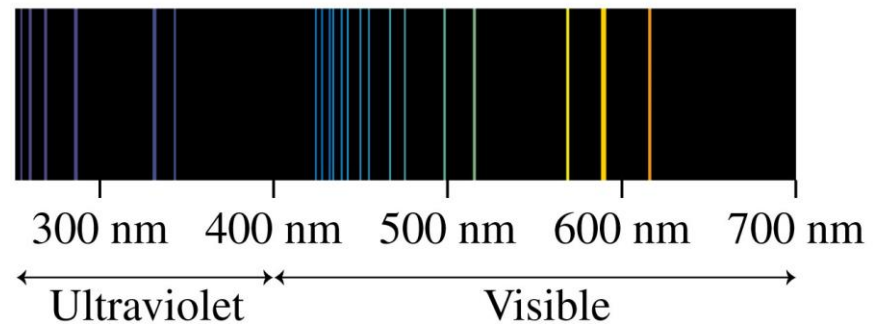
- Gases also absorb discrete wavelengths.
- There is an important difference between the emission spectrum and the absorption spectrum of a gas: **Every wavelength that is absorbed by the gas is also emitted, but *not* every emitted wavelength is absorbed.**

(b) Absorption and emission spectra of sodium

Absorption

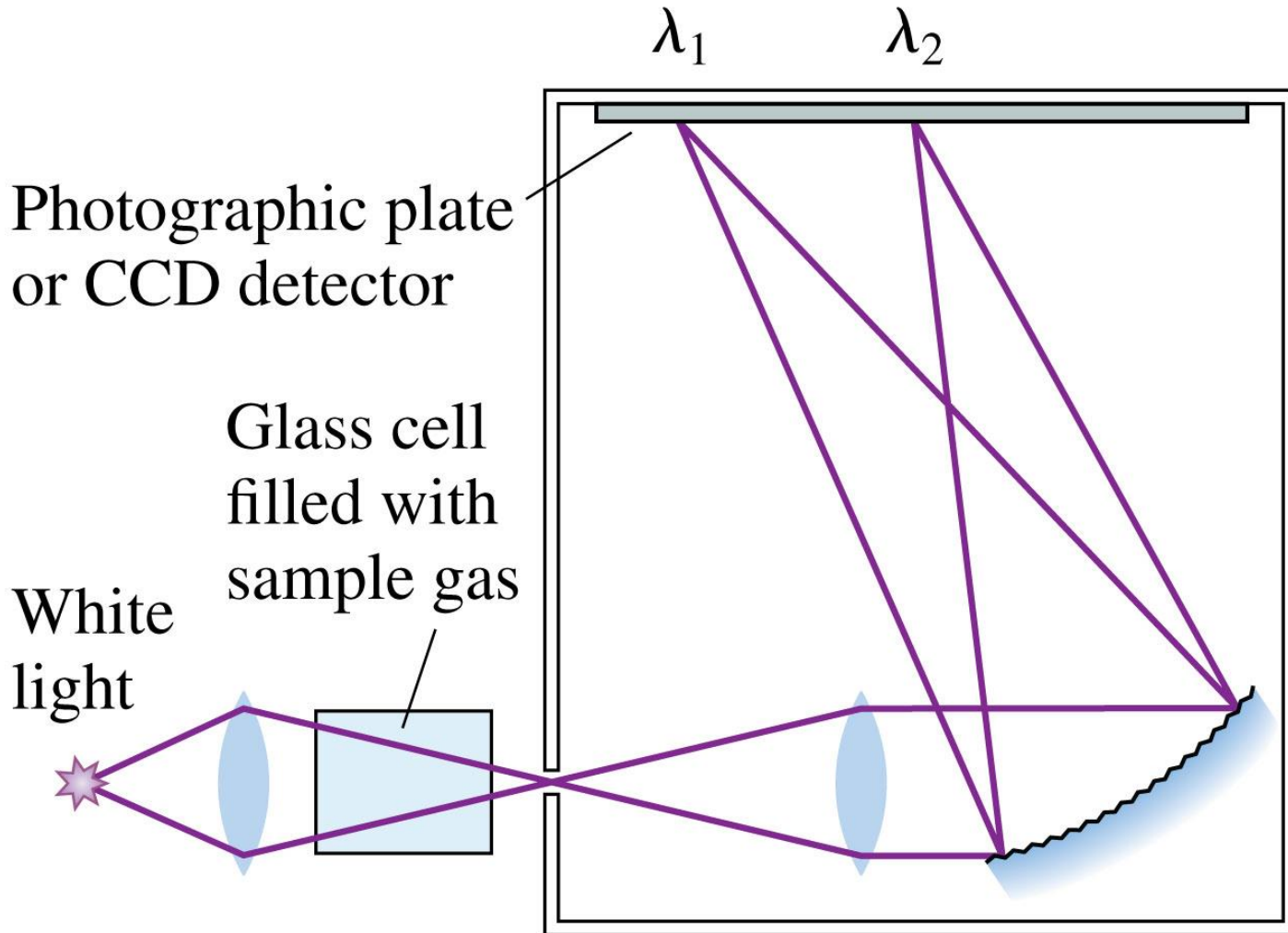


Emission



Spectroscopy

(a) Measuring an absorption spectrum



Spectroscopy

- In 1885 a Swiss school teacher, Johann Balmer, determined that the wavelengths of the spectral lines of hydrogen, which only has 4 lines in the visible spectrum, could be represented by the formula:

$$\lambda = \frac{91.1 \text{ nm}}{\left(\frac{1}{2^2} - \frac{1}{n^2}\right)} \quad n = 3, 4, 5, \dots$$

- Later experimental evidence showed that Balmer's result could be generalized to

$$\lambda = \frac{91.1 \text{ nm}}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)}$$

*m can be 1, 2, 3, ...
n can be any integer greater than m.*

- This is now called the **Balmer formula**.

Spectroscopy

TABLE 29.1 Wavelengths of visible lines in the hydrogen spectrum

656 nm

486 nm

434 nm

410 nm

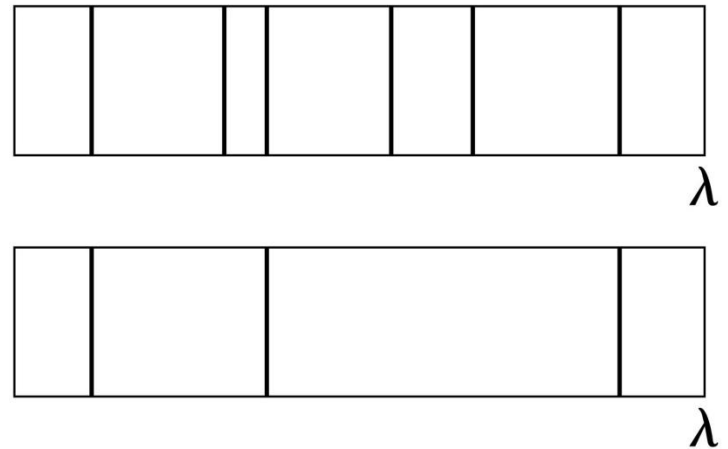
Spectroscopy

- The Balmer formula accurately describes every wavelength in the visible spectrum of hydrogen.
- The Balmer formula is what we call *empirical knowledge*. It is an accurate mathematical representation found through experiments, but it does not rest on any physical principles or laws.
- It took 30 years to understand the physical principles behind the formula.

QuickCheck 29.1

These spectra are from the same element. Which is an emission spectrum, which an absorption spectrum?

- A. Top is emission; bottom absorption.
- B. Top is absorption; bottom emission.
- C. Either could be emission (or absorption), depending on the conditions with which they were made.
- D. Can't tell without knowing the element.



QuickCheck 29.1

These spectra are from the same element. Which is an emission spectrum, which an absorption spectrum?

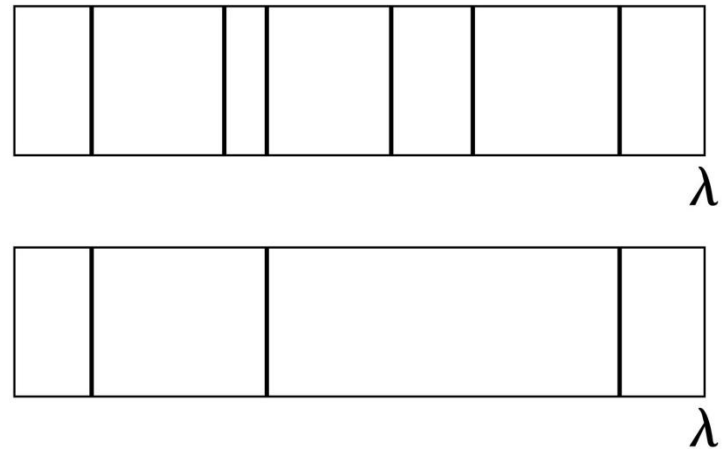


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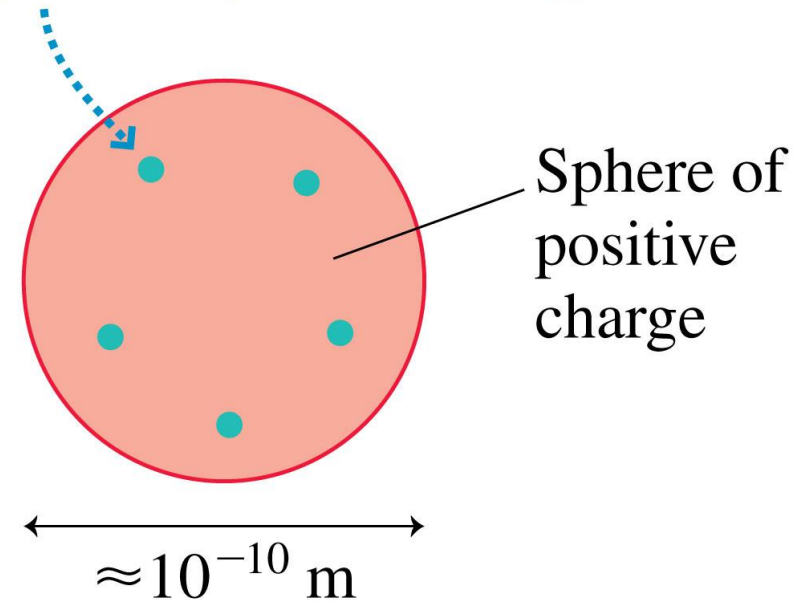


Section 29.2 Atoms

Atoms

- In 1897 J. J. Thomson discovered the first *subatomic* particle: the electron.
- The mass of the electron is much smaller than the mass of the whole atom, so he thought an atom consisted of negatively charged electrons embedded in a more massive cloud of positive charge.
- This model is called the “raisin-cake model.”

Thomson proposed that small negative electrons are embedded in a sphere of positive charge.



Thomson's raisin-cake model of the atom.

Atoms

- Ernest Rutherford, a former student of Thomson, discovered that a uranium crystal can emit two different rays: **Beta rays** and **Alpha rays**.
- Beta rays are high-speed electrons emitted by uranium.
- Alpha rays (now called Alpha particles) consist of helium nuclei, with mass $m = 6.64 \times 10^{-27}$ kg, emitted at high speed from a sample.
- These were the first observations that atoms have an inner structure and that some atoms were not stable and could spit out various kinds of charged particles.

Example 29.1 The speed of an alpha particle

Alpha particles are usually characterized by their kinetic energy in MeV. What is the speed of an 8.3 MeV alpha particle?

Example 29.1 The speed of an alpha particle (cont.)

SOLVE Recall that 1 eV is the energy acquired by an electron accelerating through a 1 V potential difference, with the conversion $1.00 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$. First, we convert the energy to joules:

$$K = 8.3 \times 10^6 \text{ eV} \times \frac{1.60 \times 10^{-19} \text{ J}}{1.00 \text{ eV}} = 1.3 \times 10^{-12} \text{ J}$$

Example 29.1 The speed of an alpha particle (cont.)

Now, using the alpha-particle mass $m = 6.64 \times 10^{-27}$ kg given above, we can find the speed:

$$K = \frac{1}{2}mv^2 = 1.3 \times 10^{-12} \text{ J}$$

$$v = \sqrt{\frac{2K}{m}} = 2.0 \times 10^7 \text{ m/s}$$

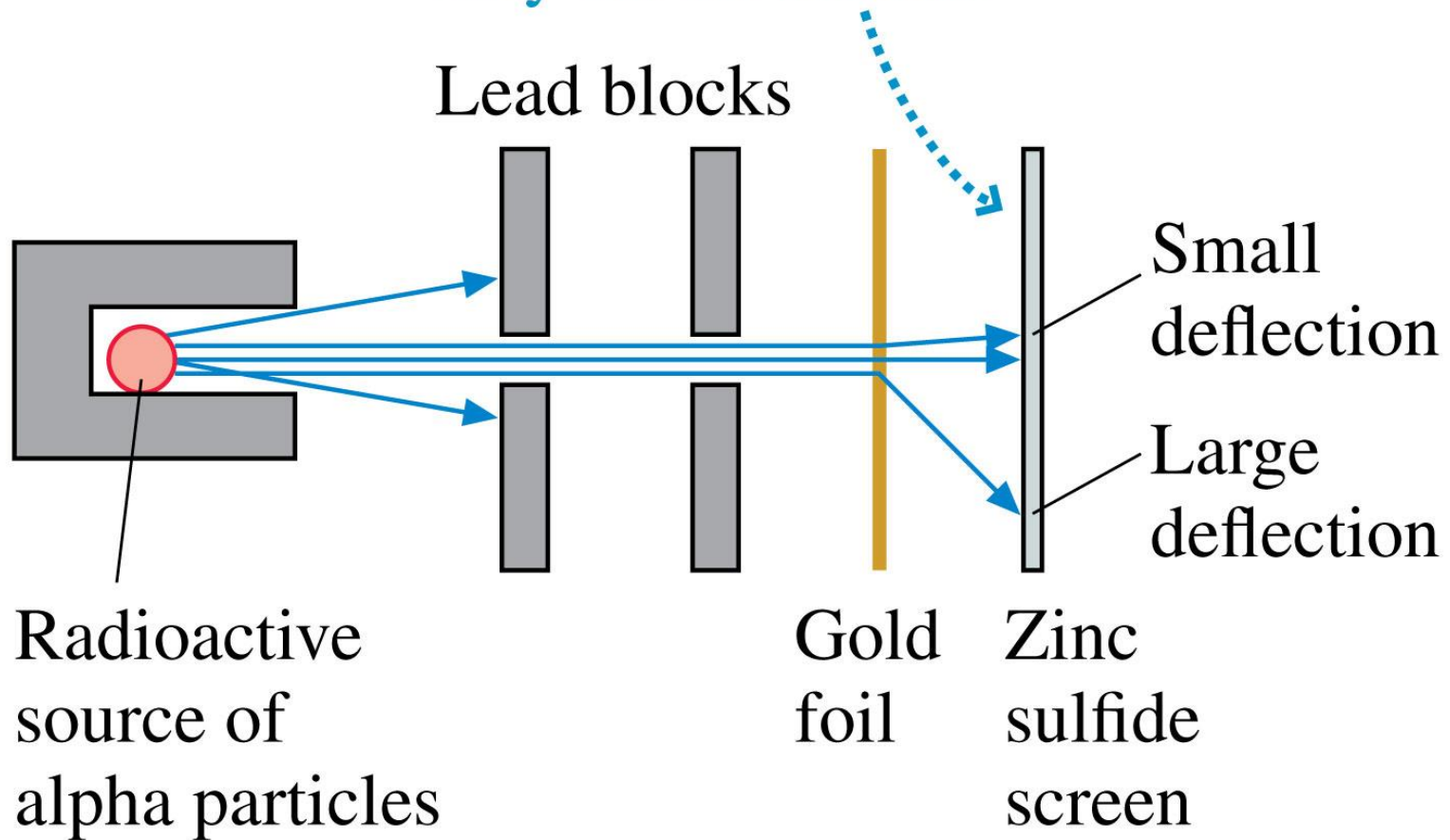
ASSESS This is quite fast, about 7% of the speed of light.

The First Nuclear Physics Experiment

- Rutherford set up an experiment to probe the inside of an atom. He shot high-speed alpha particles through a thin gold foil.
- If the atom's structure were described by Thomson's raisin-cake model, then the forces exerted on the alpha particle by the positive atomic charges should roughly cancel the forces from the negative electrons, causing the particles to experience only slight deflections.

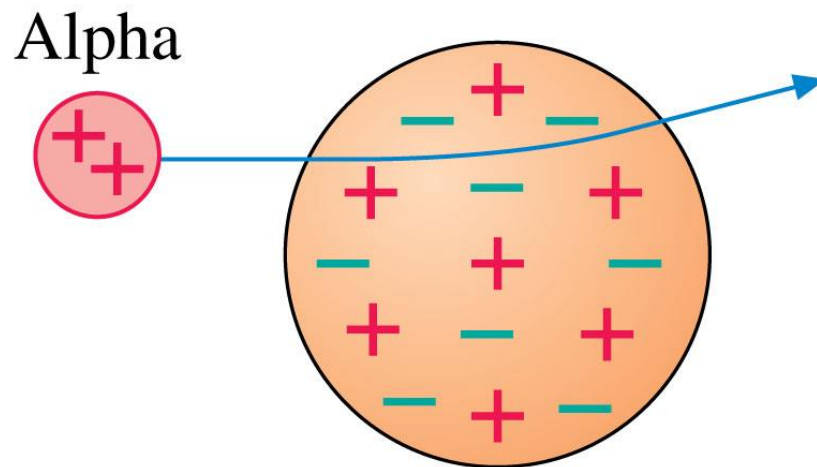
The First Nuclear Physics Experiment

The alpha particles make little flashes of light where they hit the screen.



The First Nuclear Physics Experiment

(a) Thomson model

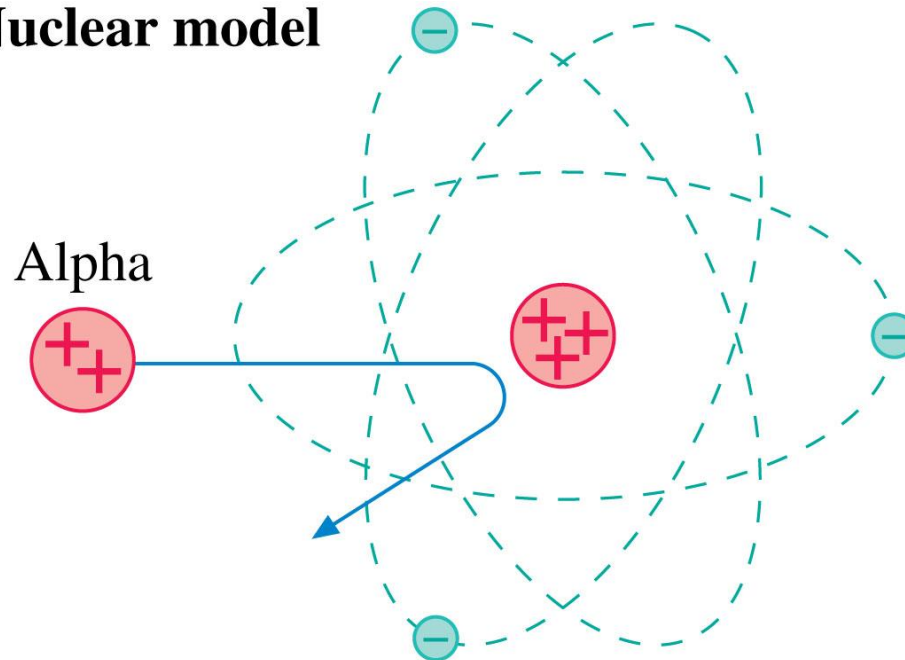


The alpha particle is only slightly deflected by a Thomson atom because forces from the spread-out positive and negative charges nearly cancel.

The First Nuclear Physics Experiment

- Rutherford discovered that some alpha particles were deflected at *large* angles.

(b) Nuclear model



If the atom has a concentrated positive nucleus, some alpha particles will be able to come very close to the nucleus and thus feel a very strong repulsive force.

The First Nuclear Physics Experiment

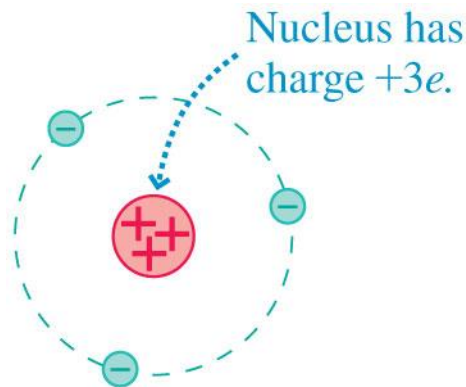
- The discovery of large-angle scattering of alpha particles led Rutherford to envision an atom in which negative electrons orbit a small, massive, positive **nucleus**.
- This is the **nuclear model of the atom**.
- Most of the atom is empty space.

Using the Nuclear Model

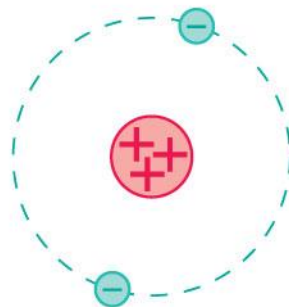
- The **atomic number** of an element indicates its position in the periodic table, is the number of orbiting electrons of a neutral atom, and is the number of units of positive charge in the nucleus.
- The atomic number is represented by Z .
- Hydrogen, with $Z = 1$, has one electron orbiting a nucleus with charge $+1e$. Helium, with $Z = 2$, has two electrons orbiting a nucleus with charge $+2e$.

Using the Nuclear Model

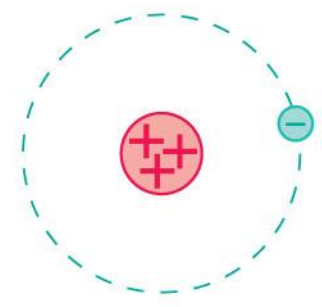
- Orbiting electrons are very light, so a photon or a rapidly moving particle, such as another electron, can knock one of the electrons away, creating a positive *ion*.
- Removing one electron makes a singly charged ion, $q_{\text{ion}} = +e$. Removing two electrons creates a doubly charged ion, $q = +2e$.



Neutral Li



Singly charged Li^+



Doubly charged Li^{++}

Using the Nuclear Model

- The positive charge of the nucleus is associated with a positive subatomic particle called the **proton**.
- The proton's charge is equal but opposite in sign to the electron's charge.
- A proton is about 1800 times more massive than an electron.
- Electrons are more easily transferred than protons because protons are tightly bound in the nucleus.

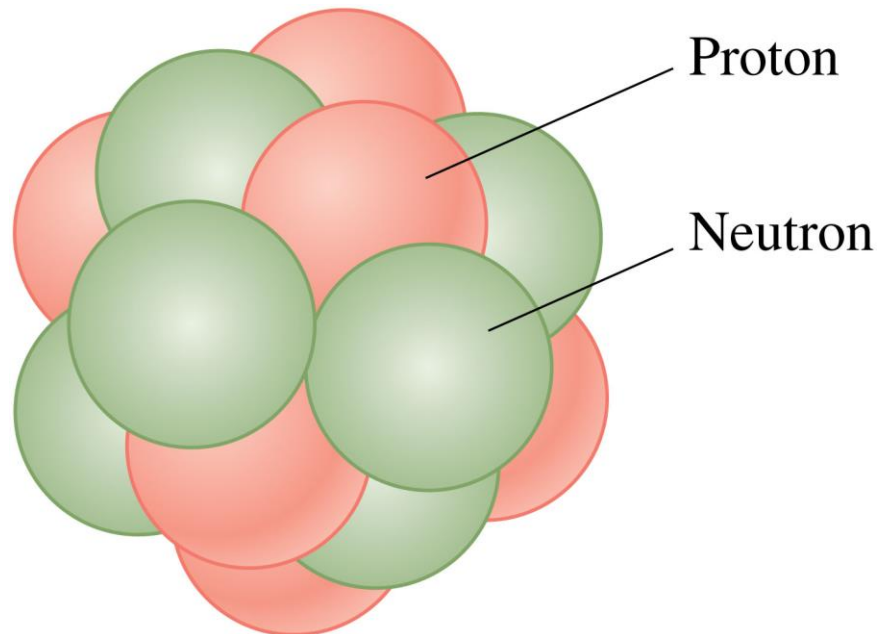
Using the Nuclear Model

- Scientists realized that the sum of the masses of the protons and electrons in a single atom did not equal the mass of the atom. They knew something was still missing.
- In 1932, a third subatomic particle, the **neutron**, was discovered.
- The neutron has essentially the same mass as the proton but *no* electric charge. It resides in the nucleus with the protons.
- Neutrons help provide the “glue” that holds the nucleus together.

Using the Nuclear Model

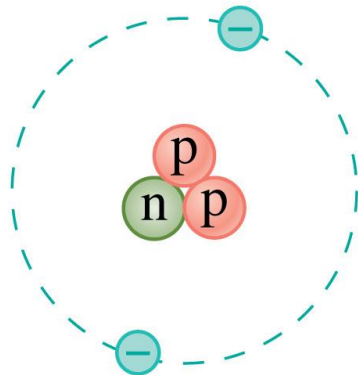
- A nucleus contains Z protons plus N neutrons.
- The atom has a **mass number** $A = Z + N$. It is *approximately* the mass of the atom.
- Proton and neutron masses are $\approx 1\text{u}$:

$$1\text{u} = 1 \text{ atomic mass unit} = 1.66 \times 10^{-27} \text{ kg}$$

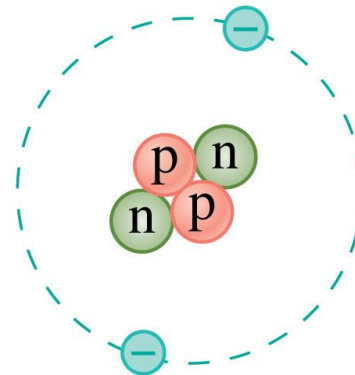


Using the Nuclear Model

- There is a *range* of neutron numbers that can form a nucleus with Z protons.
- Such a series of nuclei are called **isotopes**.
- The notation for isotopes is A_Z , where A is the mass number.



${}^3\text{He}$
 $Z = 2$ $N = 1$
 $A = 3$
0.0001% abundance

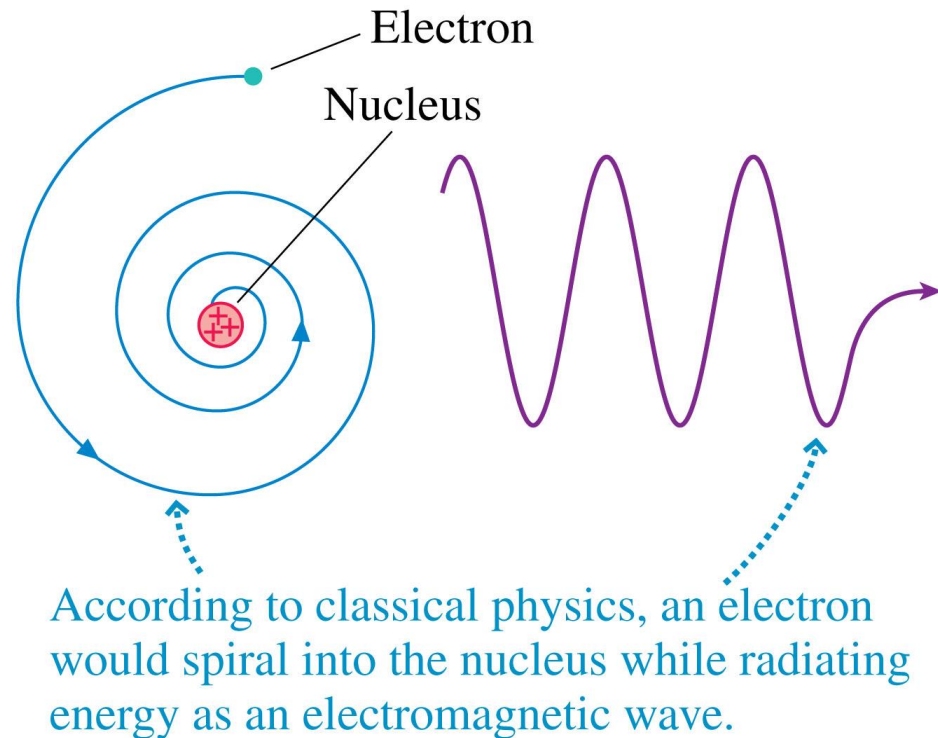


${}^4\text{He}$
 $Z = 2$ $N = 2$
 $A = 4$
99.9999% abundance

Section 29.3 Bohr's Model of Atomic Quantization

Bohr's Model of Atomic Quantization

- According to Maxwell's theory of electricity and magnetism, the electrons orbiting the nucleus should radiate electromagnetic waves.
- The energy carried off by the waves should cause the electrons to spiral into the nucleus.
- It was clear that the Rutherford model was not a complete model for the atom.



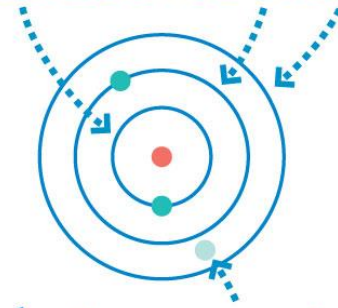
Bohr's Model of Atomic Quantization

- In 1913 Danish physicist Niels Bohr proposed a new model of the atom in which he added quantization to Rutherford's nuclear atom.
- It is called the **Bohr model of the atom.**

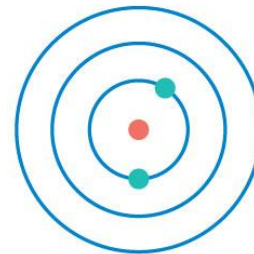
Bohr's Model of Atomic Quantization

- According to Bohr's model, the electrons in an atom can exist in only certain *allowed orbits*. A particular arrangement of electrons in these orbits is called a **stationary state**.

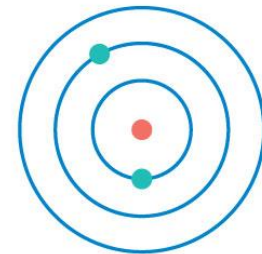
Electrons can exist in only certain allowed orbits.



An electron cannot exist here, where there is no allowed orbit.



This is one stationary state.



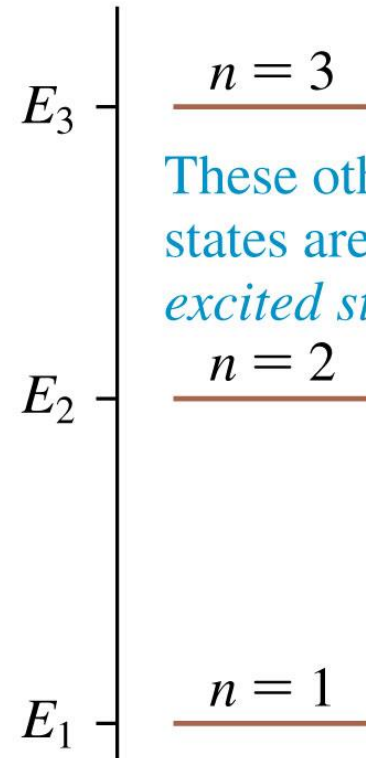
This is another stationary state.

Bohr's Model of Atomic Quantization

- Each stationary state has a discrete, well-defined energy E_n , as the energy-level diagram shows. That is, atomic energies are *quantized*. The stationary states are labeled by the *quantum number n* in order of increasing energy:

$$E_1 < E_2 < E_3 < \dots$$

Energy-level diagram



Stationary states



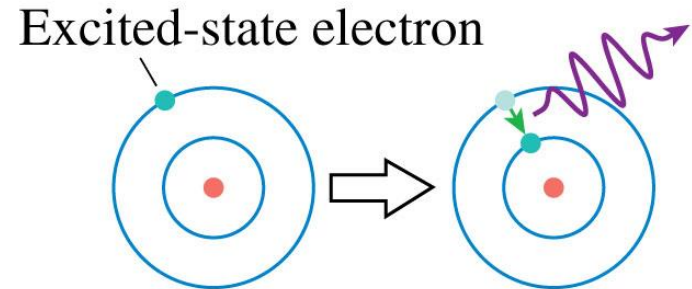
These other states are *excited states*.

This state, with the lowest energy E_1 , is the *ground state*. It is stable and can persist indefinitely.

Bohr's Model of Atomic Quantization

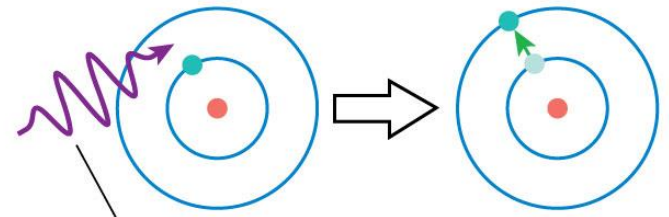
- An atom can undergo a *transition* or *quantum jump* from one stationary state to another by emitting or absorbing a photon whose energy is exactly equal to the energy difference between the two stationary states.

Photon emission



The electron jumps to a lower-energy stationary state and emits a photon.

Photon absorption



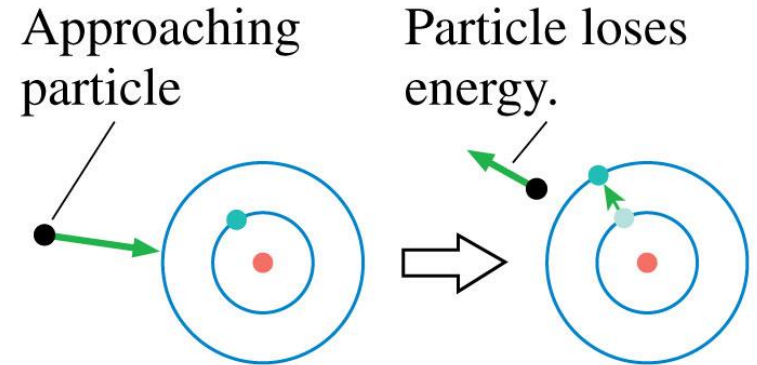
Approaching photon

The electron absorbs the photon and jumps to a higher-energy stationary state.

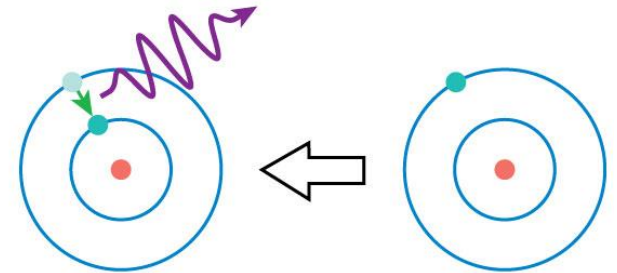
Bohr's Model of Atomic Quantization

- Atoms can also move from a lower-energy state to a higher-energy state by absorbing energy in a collision with an electron or other atom in a process called **collisional excitation**.
- The excited atoms soon jump down to lower states, eventually ending in the stable ground state.

Collisional excitation



The particle transfers energy to the atom in the collision and excites the atom.



An atom in an excited state soon jumps to lower states, emitting a photon at each jump.

Bohr's Model of Atomic Quantization

- The implications of Bohr's model are profound.
 1. **Matter is stable.** Once an atom is in its ground state, there are no states of any lower energy to which it can jump. It can remain in the ground state forever.
 2. **Atoms emit and absorb a *discrete spectrum*.** When an atom jumps from an initial state with energy E_i to a final state with energy E_f , conservation of energy requires that it emit or absorb a photon with energy

$$E_{\text{photon}} = \Delta E_{\text{atom}} = |E_f - E_i|$$

Because $E_{\text{photon}} = hf$, this photon must have frequency $f_{\text{photon}} = \Delta e_{\text{atom}}/h$. Photons of other frequencies cannot be emitted or absorbed without violating energy conservation.

Bohr's Model of Atomic Quantization

3. **Emission spectra can be produced by collisions.**

Energy from collisions can kick an atom up to an excited state. The atom then emits photons in a discrete emission spectrum as it jumps down to lower-energy states.

Bohr's Model of Atomic Quantization

- Absorption wavelengths are a subset of the wavelengths in the emission spectrum.** Recall that all the lines seen in an absorption spectrum are also seen in emission, but many emission lines are *not* seen in absorption. According to Bohr's model, **most atoms, most of the time, are in their lowest energy state.** Thus the absorption spectrum consists of *only* those transitions such as $1 \rightarrow 2$, $1 \rightarrow 3$, ... Transitions such as $2 \rightarrow 3$ are not observed because there are essentially no atoms in $n = 2$ at any instant of time to do the absorbing. Atoms in the $n = 3$ state can emit photons corresponding to transitions $3 \rightarrow 1$ *and* $3 \rightarrow 2$. Thus the wavelengths are seen in both emission and absorption.

Bohr's Model of Atomic Quantization

5. **Each element in the periodic table has a unique spectrum.** The energies of the stationary states are just the energies of the orbiting electrons. Different elements, with different numbers of electrons, have different stable orbits and thus different stationary states. States with different energies will emit and absorb photons of different wavelengths.

QuickCheck 29.2

An atom has the energy levels shown. A photon with a wavelength of 620 nm has an energy of 2.0 eV. Do you expect to see a spectral line with wavelength of 620 nm in this atom's absorption spectrum?

- A. Yes
- B. No
- C. There's not enough information to tell.



QuickCheck 29.2

An atom has the energy levels shown. A photon with a wavelength of 620 nm has an energy of 2.0 eV. Do you expect to see a spectral line with wavelength of 620 nm in this atom's absorption spectrum?

A. Yes

✓ B. No

C. There's not enough information to tell.



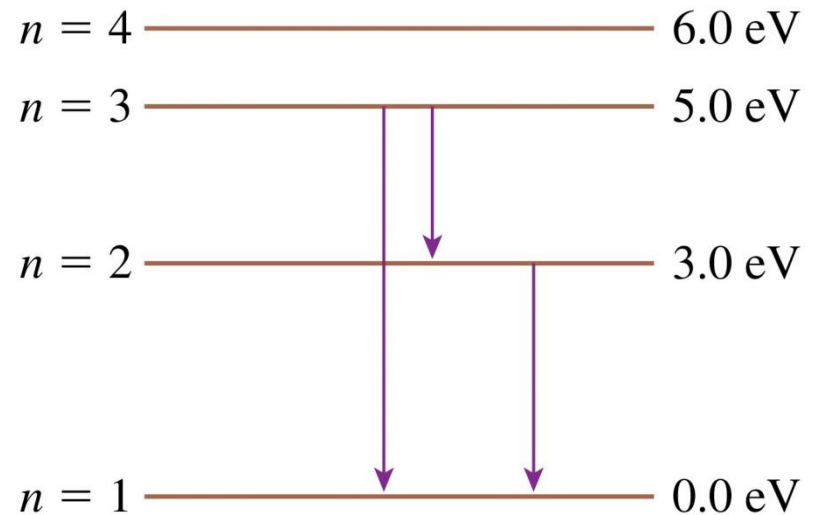
Absorption occurs from the ground state, where nearly all the atoms are.

No quantum jump from the ground state has $\Delta E_{\text{atom}} = 2.0 \text{ eV}$.

QuickCheck 29.3

An atom has the energy levels shown. A beam of electrons with 5.5 eV kinetic energy collides with a gas of these atoms. How many spectral lines will be seen?

- A. 2
- B. 3
- C. 4
- D. 5
- E. 6



QuickCheck 29.3

An atom has the energy levels shown. A beam of electrons with 5.5 eV kinetic energy collides with a gas of these atoms. How many spectral lines will be seen?

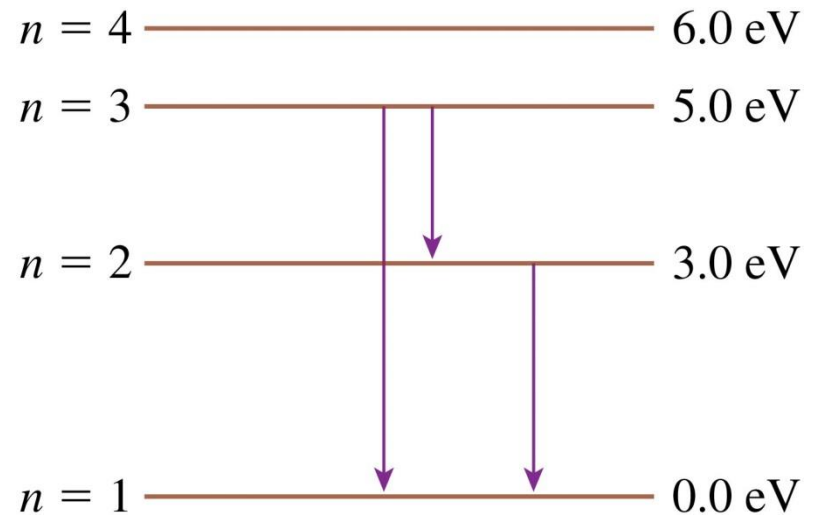
A. 2

B. 3 A 5.5 eV electron can excite either the $n = 2$ or the $n = 3$ energy level.

C. 4

D. 5

E. 6

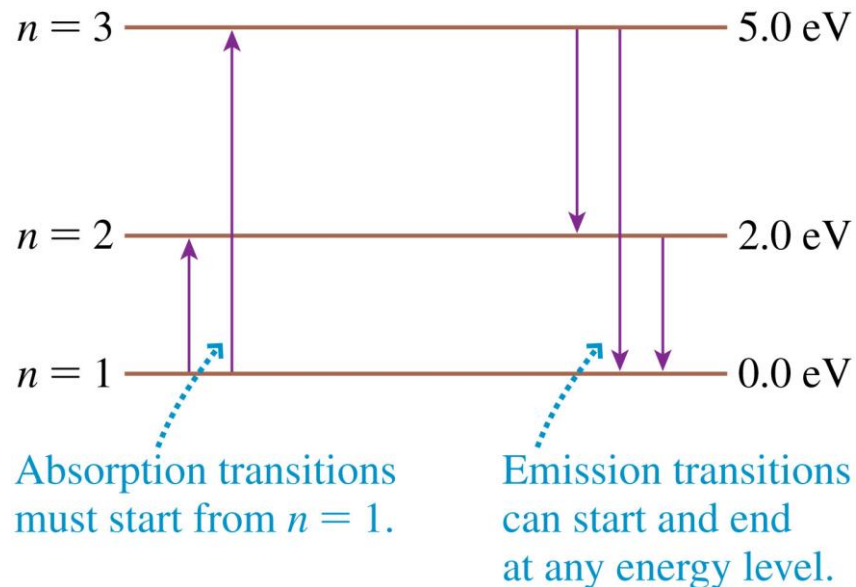


Example 29.3 Wavelengths in emission and absorption spectra

An atom has stationary states $E_1 = 0.0$ eV, $E_2 = 2.0$ eV, and $E_3 = 5.0$ eV. What wavelengths are observed in the absorption spectrum and in the emission spectrum of this atom?

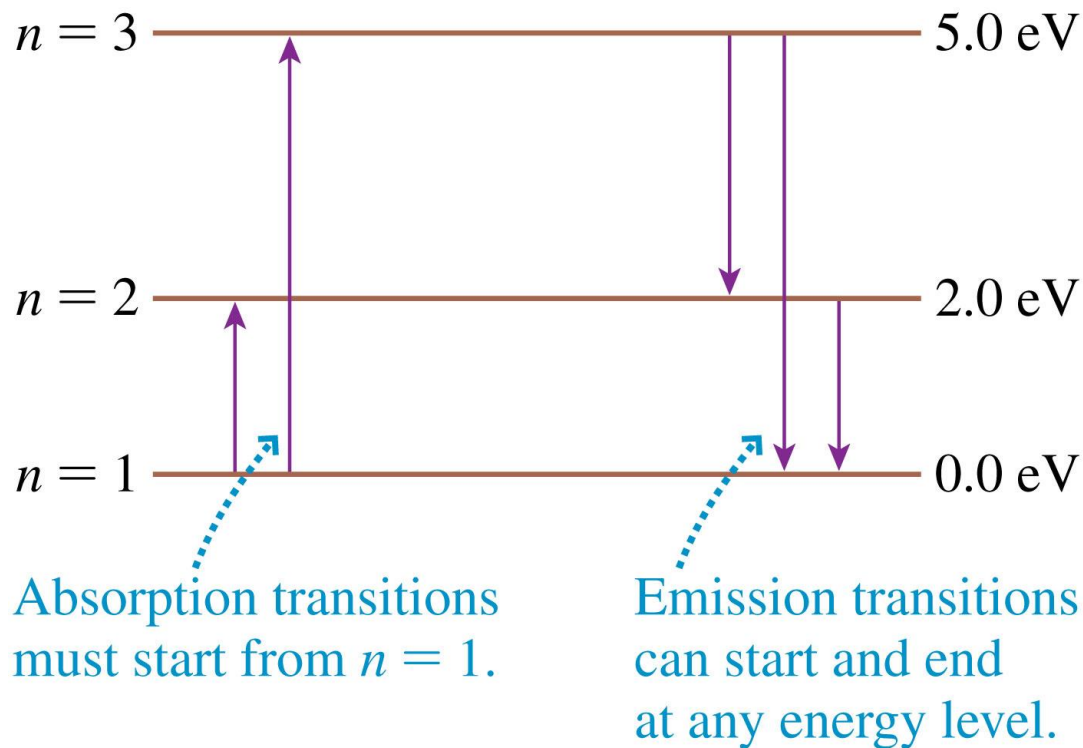
Example 29.3 Wavelengths in emission and absorption spectra (cont.)

PREPARE FIGURE 29.12 shows an energy-level diagram for the atom. Photons are emitted when an atom undergoes a quantum jump from a higher energy level to a lower energy level. Photons are absorbed in a quantum jump from a lower energy level to a higher energy level.



Example 29.3 Wavelengths in emission and absorption spectra (cont.)

However, most of the atoms are in the $n = 1$ ground state, so the only quantum jumps seen in the absorption spectrum start from the $n = 1$ state.



Example 29.3 Wavelengths in emission and absorption spectra (cont.)

SOLVE This atom absorbs photons on the $1 \rightarrow 2$ and $1 \rightarrow 3$ transitions, with $\Delta E_{1 \rightarrow 2} = 2.0 \text{ eV}$ and $\Delta E_{1 \rightarrow 3} = 5.0 \text{ eV}$. From $f_{\text{photon}} = \Delta E_{\text{atom}}/h$ and $\lambda = c/f$, we find that the wavelengths in the absorption spectrum are

$$1 \rightarrow 3 \quad f_{\text{photon}} = 5.0 \text{ eV}/h = 1.2 \times 10^{15} \text{ Hz}$$

$$\lambda = 250 \text{ nm (ultraviolet)}$$

$$1 \rightarrow 2 \quad f_{\text{photon}} = 2.0 \text{ eV}/h = 4.8 \times 10^{14} \text{ Hz}$$

$$\lambda = 620 \text{ nm (orange)}$$

Example 29.3 Wavelengths in emission and absorption spectra (cont.)

The emission spectrum also has the 620 nm and 250 nm wavelengths due to the $2 \rightarrow 1$ and $3 \rightarrow 1$ quantum jumps. In addition, the emission spectrum contains the $3 \rightarrow 2$ quantum jump with $\Delta E_{3 \rightarrow 2} = 3.0 \text{ eV}$ that is *not* seen in absorption because there are too few atoms in the $n = 2$ state to absorb. A similar calculation finds $f_{\text{photon}} = 7.3 \times 10^{14} \text{ Hz}$ and $\lambda = c/f = 410 \text{ nm}$. Thus the emission wavelengths are

$$2 \rightarrow 1 \quad \lambda = 620 \text{ nm (orange)}$$

$$3 \rightarrow 2 \quad \lambda = 410 \text{ nm (blue)}$$

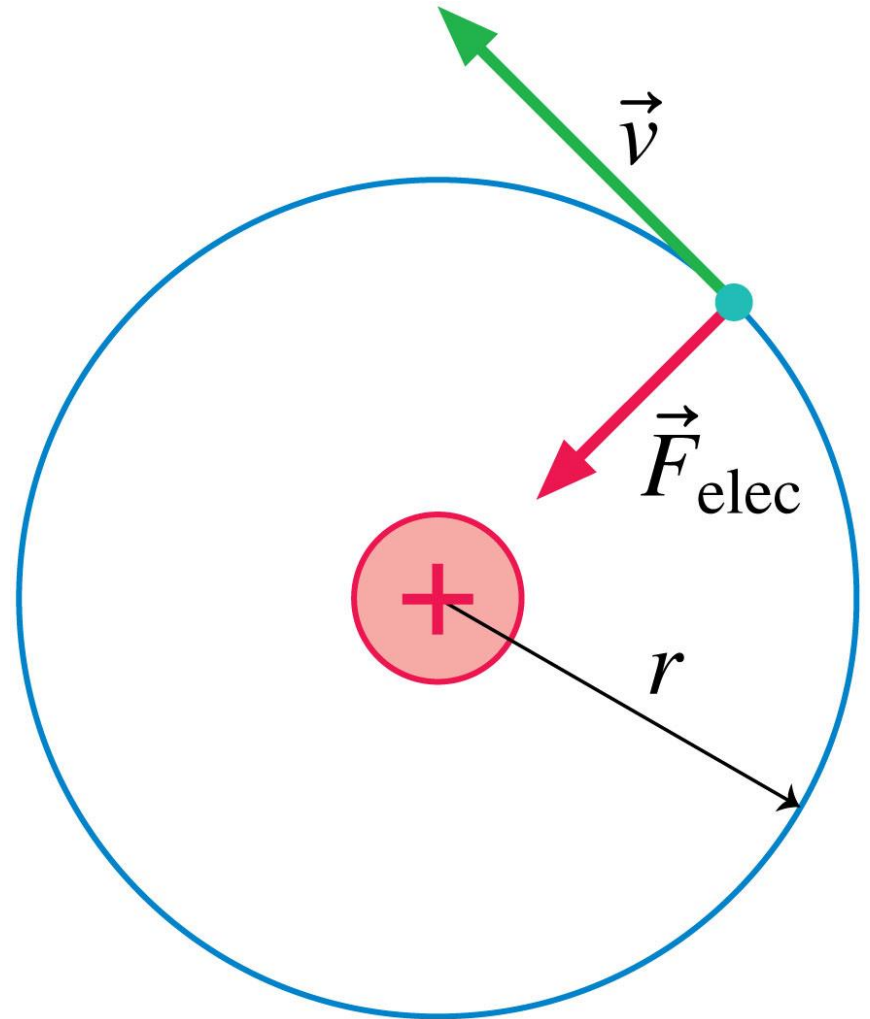
$$3 \rightarrow 1 \quad \lambda = 250 \text{ nm (ultraviolet)}$$

Section 29.4 The Bohr Hydrogen Atom

The Stationary States of the Hydrogen Atom

- The figure shows a Rutherford hydrogen atom, with a single electron orbiting a proton.
- The proton exerts a Coulomb electric force on the electron:

$$\vec{F}_{\text{elec}} = \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}, \text{ toward center} \right)$$



The Stationary States of the Hydrogen Atom

- The centripetal acceleration of the electron moving in a circle of radius r at speed v is v^2/r , so that

$$a_{\text{elec}} = \frac{F_{\text{elec}}}{m} = \frac{e^2}{4\pi\epsilon_0 mr^2} = \frac{v^2}{r}$$

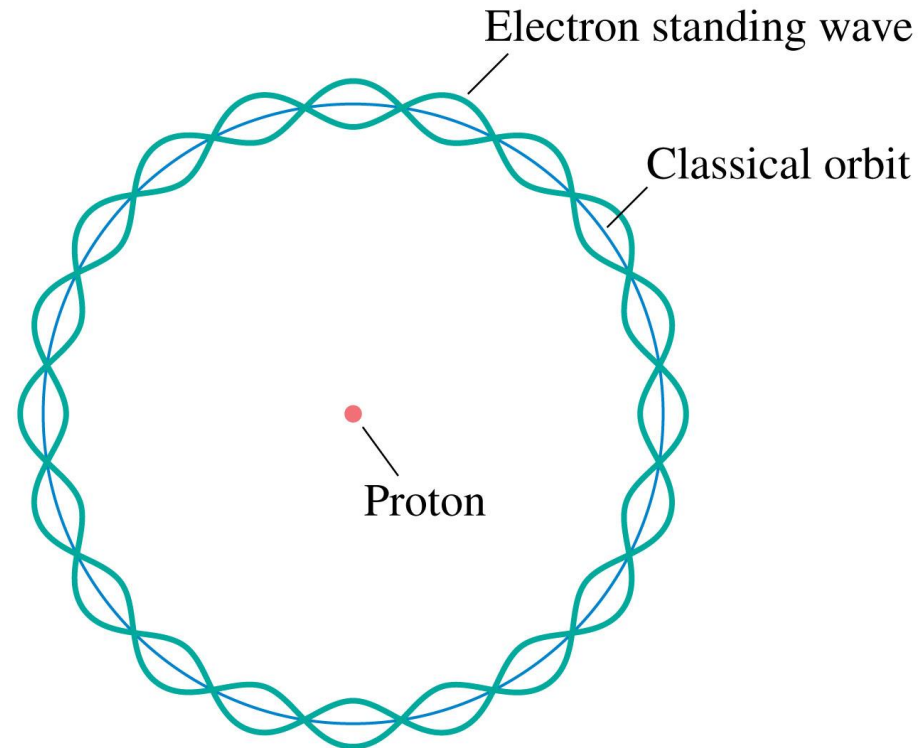
$$v^2 = \frac{e^2}{4\pi\epsilon_0 mr}$$

- This is a *constraint* on the motion of the electron.

The Stationary States of the Hydrogen Atom

- If we treat the electron as a de Broglie wave, the particle will set up a standing wave, just like the particle in a box, if there are waves traveling in both directions and if the round-trip distance is an integer number of wavelengths.
- The standing circular waves occur when

$$2\pi r = n\lambda \quad n = 1, 2, 3, \dots$$



The Stationary States of the Hydrogen Atom

- The de Broglie wavelength for a particle *has* to be $\lambda = h/p = h/mv$. Thus the standing-wave condition for a de Broglie wave is

$$2\pi r = n \frac{h}{mv}$$

- This condition is true only if the electron's speed is

$$v = \frac{nh}{2\pi mr} \quad n = 1, 2, 3, \dots$$

- The electron cannot have just any speed, only the discrete values given by this equation.

The Stationary States of the Hydrogen Atom

- The quantity $h/2\pi$ occurs so often in quantum physics that we define the quantity

$$\hbar = \frac{h}{2\pi} = 1.05 \times 10^{-34} \text{ J} \cdot \text{s} = 6.58 \times 10^{-16} \text{ eV} \cdot \text{s}$$

- We can rewrite the electron's speed as

$$v = \frac{n\hbar}{mr} \quad n = 1, 2, 3, \dots$$

The Stationary States of the Hydrogen Atom

- The electron can act as both a particle *and* a wave, so both constraints on the velocity must be obeyed.
- Equating the two constraints on velocities gives

$$v^2 = \frac{e^2}{4\pi\epsilon_0 mr} = \frac{n^2\hbar^2}{m^2 r^2}$$

- We solve for the radius r :

$$r_n = n^2 \frac{4\pi\epsilon_0\hbar^2}{me^2} \quad n = 1, 2, 3, \dots$$

- We can group the constants together and define the **Bohr radius** a_B to be

$$a_B = \text{Bohr radius} = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11} \text{ m} = 0.0529 \text{ nm}$$

The Stationary States of the Hydrogen Atom

- The radius of the electron's orbit is

$$r_n = n^2 a_B \quad n = 1, 2, 3, \dots$$

Allowed radii of the Bohr hydrogen atom

- **A hydrogen atom can exist *only* if the radius of the electron's orbit is one of the values given by this equation.**
- Intermediate values of the radius cannot exist because the electron cannot set up a standing wave around the circumference.
- The possible orbits are *quantized*.

Hydrogen Atom Energy Levels

- The energy of a hydrogen atom is the kinetic energy of its electron plus the potential energy of the electron's interactions with the proton:

$$E = K + U = \frac{1}{2}mv^2 + \frac{1}{4\pi\epsilon_0} \frac{q_{\text{elec}}q_{\text{proton}}}{r} = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r}$$

- To find the energies of the stationary states, we first find the possible electron speeds:

$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n} \frac{\hbar}{ma_B} = \frac{v_1}{n} \quad n = 1, 2, 3, \dots$$

- The energies of the stationary states simplifies to

$$E_n = \frac{1}{2}mv_n^2 - \frac{e^2}{4\pi\epsilon_0 r_n} = -\frac{1}{n^2} \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} \right)$$

Hydrogen Atom Energy Levels

- We define

$$E_1 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} = 13.60 \text{ eV}$$

- The energy levels of the stationary states of the hydrogen atom are

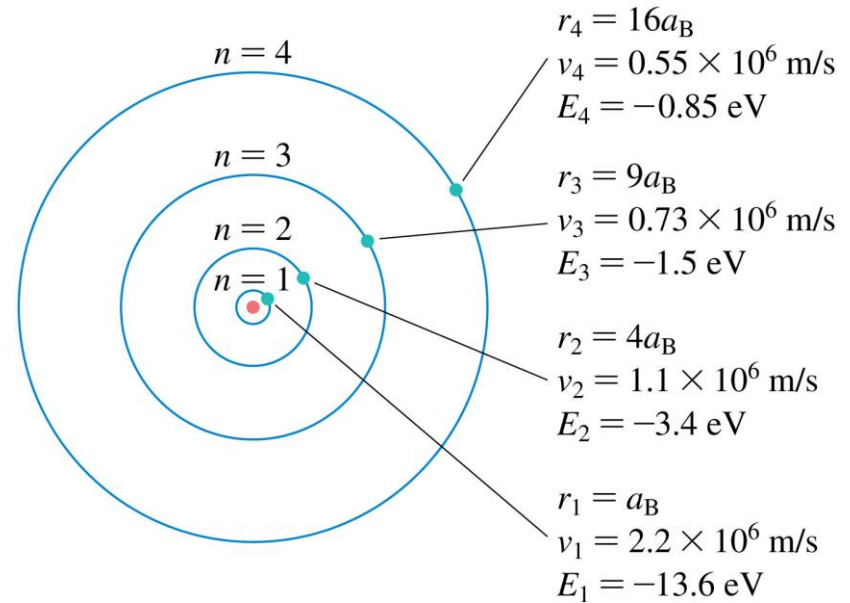
$$E_n = -\frac{E_1}{n^2} = -\frac{13.60 \text{ eV}}{n^2} \quad n = 1, 2, 3, \dots$$

Allowed energies of the Bohr hydrogen atom

Hydrogen Atom Energy Levels

TABLE 29.2 Radii, speeds, and energies for the first four states of the Bohr hydrogen atom

n	r_n (nm)	v_n (m/s)	E_n (eV)
1	0.053	2.19×10^6	-13.60
2	0.212	1.09×10^6	-3.40
3	0.476	0.73×10^6	-1.51
4	0.847	0.55×10^6	-0.85



The first four stationary states, or allowed orbits, of the Bohr hydrogen atom drawn to scale.

QuickCheck 29.4

A hydrogen atom has energy $E = -1.51 \text{ eV} = -13.60/9 \text{ eV}$.
The atom's radius is:

- A. $a_B/9$
- B. $a_B/3$
- C. $3a_B$
- D. $9a_B$
- E. $27a_B$

QuickCheck 29.4

A hydrogen atom has energy $E = -1.51 \text{ eV} = -13.60/9 \text{ eV}$.

The atom's radius is:

|
 $n = 3$ state

A. $a_B/9$

✓ B. $a_B/3$ $r_n = n^2 a_B$

C. $3a_B$

D. $9a_B$

E. $27a_B$

Example 29.4 Possible electron speeds in a hydrogen atom

Can an electron in a hydrogen atom have a speed of 3.60×10^5 m/s? If so, what are its energy and the radius of its orbit? What about a speed of 3.65×10^5 m/s?

PREPARE To be in a stationary state, the electron must have speed $vn = v_1/n$, with $n = v_1/v$ an integer. Only if v_1/v is an integer is v an allowed electron speed.

Example 29.4 Possible electron speeds in a hydrogen atom (cont.)

SOLVE A speed of 3.60×10^5 m/s would require quantum number

$$n = \frac{v_1}{v} = \frac{2.19 \times 10^6 \text{ m/s}}{3.60 \times 10^5 \text{ m/s}} = 6.08$$

This is not an integer, so the electron can *not* have this speed. But if $v = 3.65 \times 10^5$ m/s, then

$$n = \frac{2.19 \times 10^6 \text{ m/s}}{3.65 \times 10^5 \text{ m/s}} = 6$$

Example 29.4 Possible electron speeds in a hydrogen atom (cont.)

This is the speed of an electron in the $n = 6$ excited state. An electron in this state has energy

$$E_6 = -\frac{13.60 \text{ eV}}{6^2} = -0.378 \text{ eV}$$

and the radius of its orbit is

$$r_6 = 6^2 a_B = 6^2 (0.0529 \text{ nm}) = 1.90 \text{ nm}$$

Hydrogen Atom Energy Levels

- When an electron and a proton are completely separated and are at rest, their potential and kinetic energy are zero.
- As the electron moves closer to the proton to form a hydrogen atom, its potential energy *decreases*, becoming negative, while the kinetic energy of the orbiting electron increases.
- The potential energy decreases faster than the kinetic energy increases, leading to an overall negative energy for the atom.

Quantization of Angular Momentum

- The angular momentum of a particle in circular motion, whether it is a planet or an electron, is

$$L = mvr$$

- The condition that a de Broglie wave for an electron set up a standing wave around the circumference was given as

$$2\pi r = n\lambda = n \frac{h}{mv}$$

- If we multiply by mv and divide by 2π we find

$$mvr = n \frac{h}{2\pi} = n\hbar$$

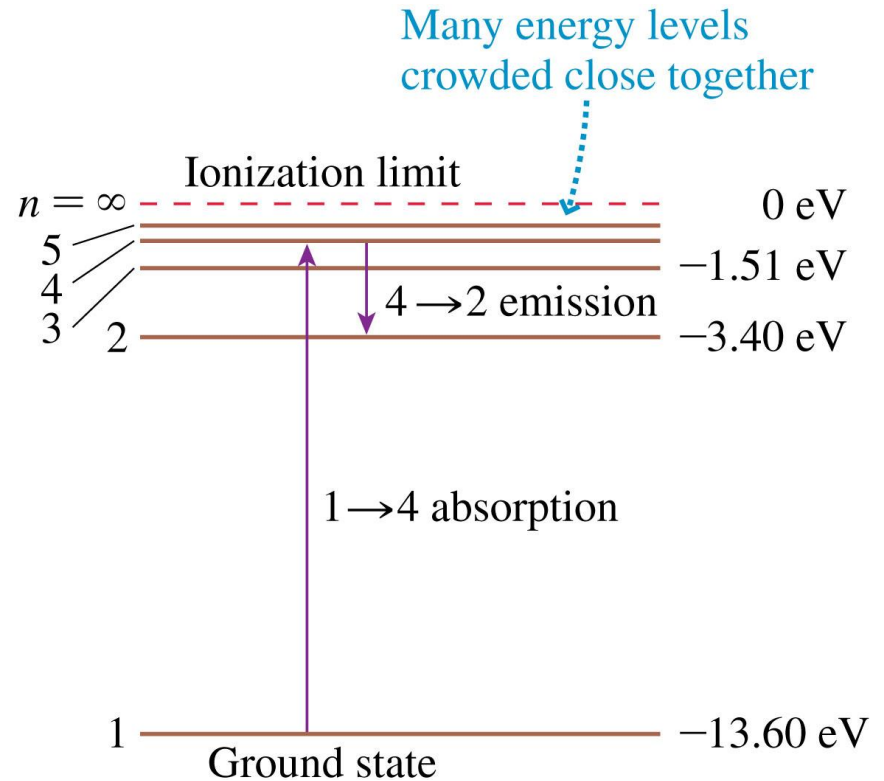
- So the angular momentum is quantized and must satisfy:

$$L = n\hbar \quad n = 1, 2, 3, \dots$$

The Hydrogen Spectrum

- The top rung on the energy-level diagram is called the **ionization limit**.
- According to Bohr's model, the frequency of the photon emitted from the quantum states $n \rightarrow m$ is

$$f_{\text{photon}} = \frac{\Delta E_{\text{atom}}}{h} = \frac{E_n - E_m}{h}$$



The Hydrogen Spectrum

- The wavelength of the photon emitted in an $n \rightarrow m$ quantum jump is

$$\lambda_{n \rightarrow m} = \frac{c}{f_{\text{photon}}} = \frac{\lambda_0}{\left(\frac{1}{m^2} - \frac{1}{n^2} \right)}$$

$$m = 1, 2, 3, \dots$$

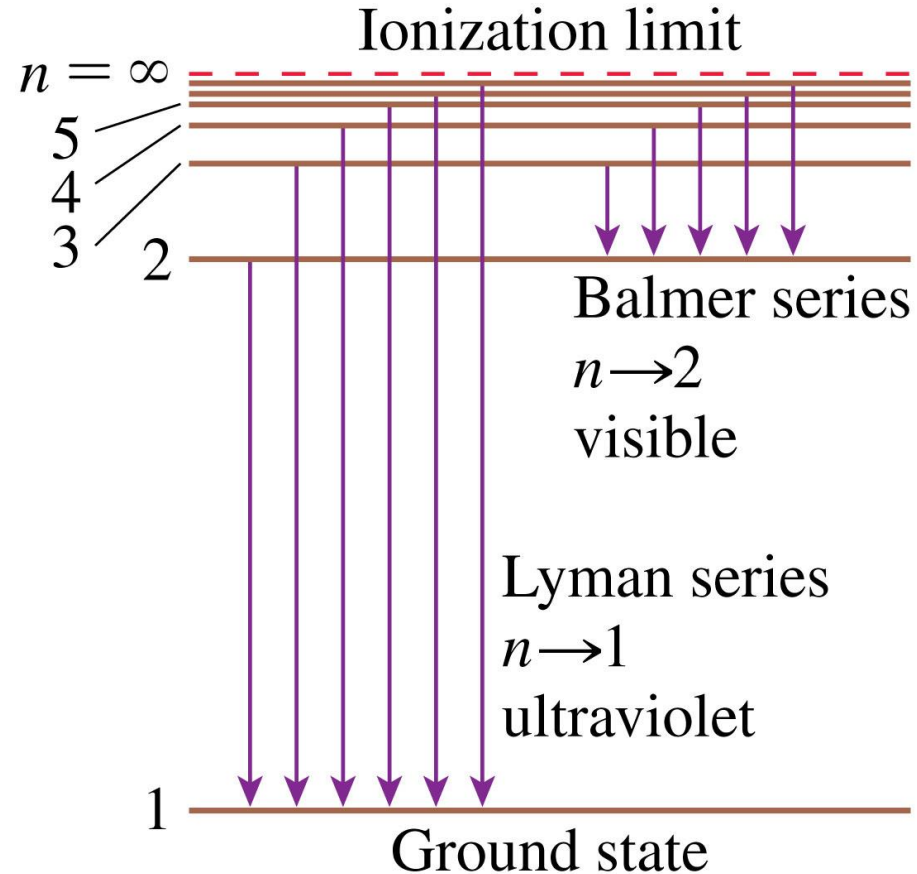
$$n = m + 1, m + 2, \dots$$

with $\lambda_0 = 91.1 \text{ nm}$.

- This is the Balmer formula!
- **The Bohr hydrogen atom correctly predicts the discrete spectrum of the hydrogen atom.**

The Hydrogen Spectrum

- This figure shows two series of transitions that give rise to wavelengths in the spectrum.
- The *Balmer series* consists of transitions ending on the $m = 2$ state and give visible wavelengths.
- The *Lyman series* ends on the $m = 1$ ground state and is in the ultraviolet region of the spectrum.



Example 29.5 Wavelengths in galactic hydrogen absorption

Whenever astronomers look at distant galaxies, they find that the light has been strongly absorbed at the wavelength of the $1 \rightarrow 2$ transition in the Lyman series of hydrogen. This absorption tells us that interstellar space is filled with vast clouds of hydrogen left over from the Big Bang. What is the wavelength of the $1 \rightarrow 2$ absorption in hydrogen?

Example 29.5 Wavelengths in galactic hydrogen absorption (cont.)

SOLVE Equation 29.17 predicts the *absorption* spectrum of hydrogen if we let $m = 1$. The absorption seen by astronomers is from the ground state of hydrogen ($m = 1$) to its first excited state ($n = 2$). The wavelength is

$$\lambda_{1 \rightarrow 2} = \frac{91.1 \text{ nm}}{\left(\frac{1}{1^2} - \frac{1}{2^2} \right)} = 122 \text{ nm}$$

Example 29.5 Wavelengths in galactic hydrogen absorption (cont.)

ASSESS This wavelength is far into the ultraviolet. Groundbased astronomy cannot observe this region of the spectrum because the wavelengths are strongly absorbed by the atmosphere, but with space-based telescopes, first widely used in the 1970s, astronomers see 122 nm absorption in nearly every direction they look.

Section 29.5 The Quantum-Mechanical Hydrogen Atom

The Quantum-Mechanical Hydrogen Atom

- Bohr's model worked well in explaining the hydrogen atom, but it did not work for any other element.
- In 1925 Erwin Schrödinger introduced his theory of *quantum mechanics*, a theory capable of calculating the allowed energy levels of any system.
- The Bohr hydrogen atom was characterized by a single quantum number n . Schrödinger's analysis of the hydrogen atom found that it must be described by *four* quantum numbers.

The Quantum-Mechanical Hydrogen Atom

1. Schrödinger found that the *energy* of the hydrogen atom is given by the same expression found by Bohr:

$$E_n = -\frac{13.60 \text{ eV}}{n^2} \quad n = 1, 2, 3, \dots$$

The integer n is called the **principle quantum number**.

2. The angular momentum L of the electron's orbit must be one of the values

$$L = \sqrt{l(l+1)} \hbar \quad l = 0, 1, 2, 3, \dots, n-1$$

The integer l is called the **orbital quantum number**.

The Quantum-Mechanical Hydrogen Atom

3. The plane of the electron's orbit can be tilted, but only at certain discrete angles. Each allowed angle is characterized by a quantum number m , which must be one of the values

$$m = -l, -l + 1, \dots, 0, \dots, l - 1, l$$

The integer m is the **magnetic quantum number** because it becomes important when the atom is placed in a magnetic field.

The Quantum-Mechanical Hydrogen Atom

4. The electron's *spin* can point only up or down. These two orientations are described by the **spin quantum number** m_s , which must be one of the values

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

Example 29.6 Listing quantum numbers

List all possible states of a hydrogen atom that have energy $E = -3.40 \text{ eV}$.

Example 29.6 Listing quantum numbers (cont.)

SOLVE Energy depends on only the principal quantum number n . From Equation 29.18, states with $E = -3.40$ eV have

$$n = \sqrt{\frac{-13.60 \text{ eV}}{-3.40 \text{ eV}}} = 2$$

Example 29.6 Listing quantum numbers (cont.)

An atom with principal quantum number $n = 2$ could have either $l = 0$ or $l = 1$, but $l \geq 2$ is ruled out. If $l = 0$, the only possible value for the magnetic quantum number m is $m = 0$. If $l = 1$, then the atom could have $m = -1$, $m = 0$, or $m = +1$. For each of these, the spin quantum number could be $m_s = +\frac{1}{2}$ or $m_s = -\frac{1}{2}$.

Example 29.6 Listing quantum numbers (cont.)

Thus the possible sets of quantum numbers are

n	l	m	m_s	n	l	m	m_s
2	0	0	$+\frac{1}{2}$	2	0	0	$-\frac{1}{2}$
2	1	1	$+\frac{1}{2}$	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	$-\frac{1}{2}$

These eight states all have the same energy.

Energy and Angular Momentum Are Quantized

- The hydrogen atom depends on only the principal quantum number n , however for other atoms, the allowed energies depend on n and l .
- We call the ground state of the hydrogen atom, $n = 1$, $l = 0$, the $1s$ state; the $3d$ state has $n = 3$, $l = 2$.

TABLE 29.3 Symbols used to represent quantum number l

l	Symbol
0	s
1	p
2	d
3	f

Energy and Angular Momentum Are Quantized

	l	0	1	2	3
Symbol		s	p	d	f
n	$E = 0$ eV	----- Ionization limit -----			
4	-0.85 eV	<u>4s</u>	<u>4p</u>	<u>4d</u>	<u>4f</u>
3	-1.51 eV	<u>3s</u>	<u>3p</u>	<u>3d</u>	
2	-3.40 eV	<u>2s</u>	<u>2p</u>		

$1 \quad -13.60$ eV 1s Ground state

The energy-level diagram for the hydrogen atom.

Energy and Angular Momentum Are Quantized

- **The electron's orbital angular momentum is quantized.**
- The magnitude of the orbital angular momentum must be one of the discrete values

$$L = \sqrt{l(l+1)}\hbar = 0, \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar, \dots$$

- These predicted angular momentum values agree with experimental data.
- An interesting prediction is that the ground state of hydrogen, with $l = 0$, has *no* angular momentum. A classical particle cannot orbit unless it has angular momentum, but a quantum particle can.

The Electron Spin

- We learned that an electron has an inherent magnetic dipole moment—it acts like a tiny bar magnet.
- It also has an intrinsic *angular momentum* called the *electron spin*.
- The two possible spin quantum numbers, $m_s = \pm 1/2$ means that the electrons' intrinsic magnetic dipole points in the $+z$ -direction or the $-z$ -direction.
- The orientations are called *spin up* and *spin down*.
- It is convenient to picture a little vector that can be drawn \uparrow for a spin-up state and \downarrow for a spin-down state. We will use this notation in the next section.

QuickCheck 29.5

Which state of the hydrogen atom has energy $E = -13.60/9$ eV and angular momentum $L = \sqrt{6}\hbar$?

- A. $2s$
- B. $2p$
- C. $3p$
- D. $3d$
- E. $9d$

QuickCheck 29.5

Which state of the hydrogen atom has energy

$$E = -13.60/9 \text{ eV} \quad \text{and angular momentum } L = \sqrt{6}\hbar?$$

$$\begin{array}{c} | \\ n = 3 \end{array}$$

$$\begin{array}{c} | \\ l = 2 = d\text{-state} \end{array}$$

A. $2s$

B. $2p$

C. $3p$

 D. $3d$

E. $9d$

QuickCheck 29.6

The $3d$ energy level in hydrogen has how many distinct states with different values of the quantum number m ?

- A. 2
- B. 3
- C. 4
- D. 5
- E. 6


QuickCheck 29.6

The $3d$ energy level in hydrogen has how many distinct states with different values of the quantum number m ?

A. 2

B. 3

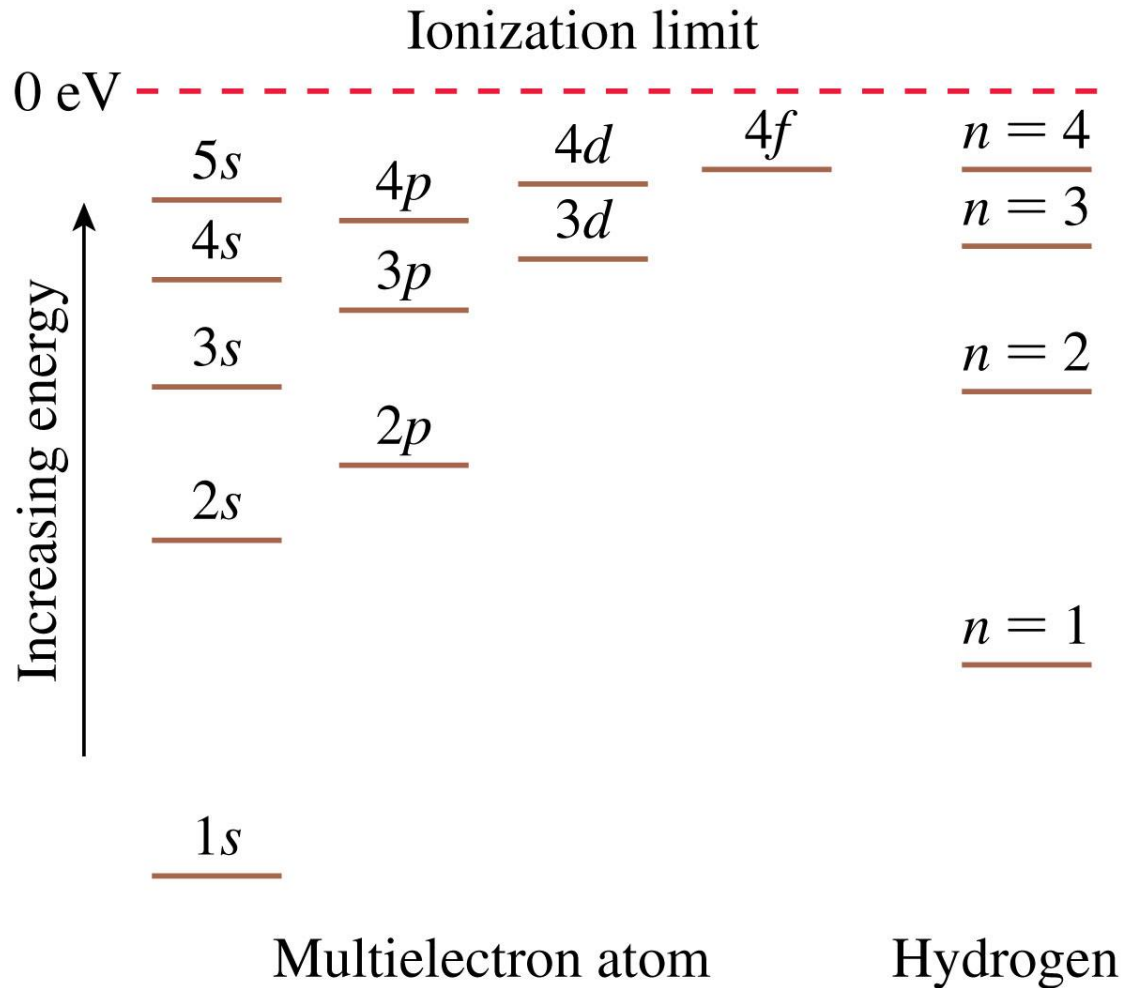
C. 4

 D. 5 *d* state means $l = 2$.
Then $m = -2, -1, 0, 1, \text{ or } 2$.

E. 6

Section 29.6 Multielectron Atoms

Multielectron Atoms



An energy-level diagram for electrons in a multielectron atom.

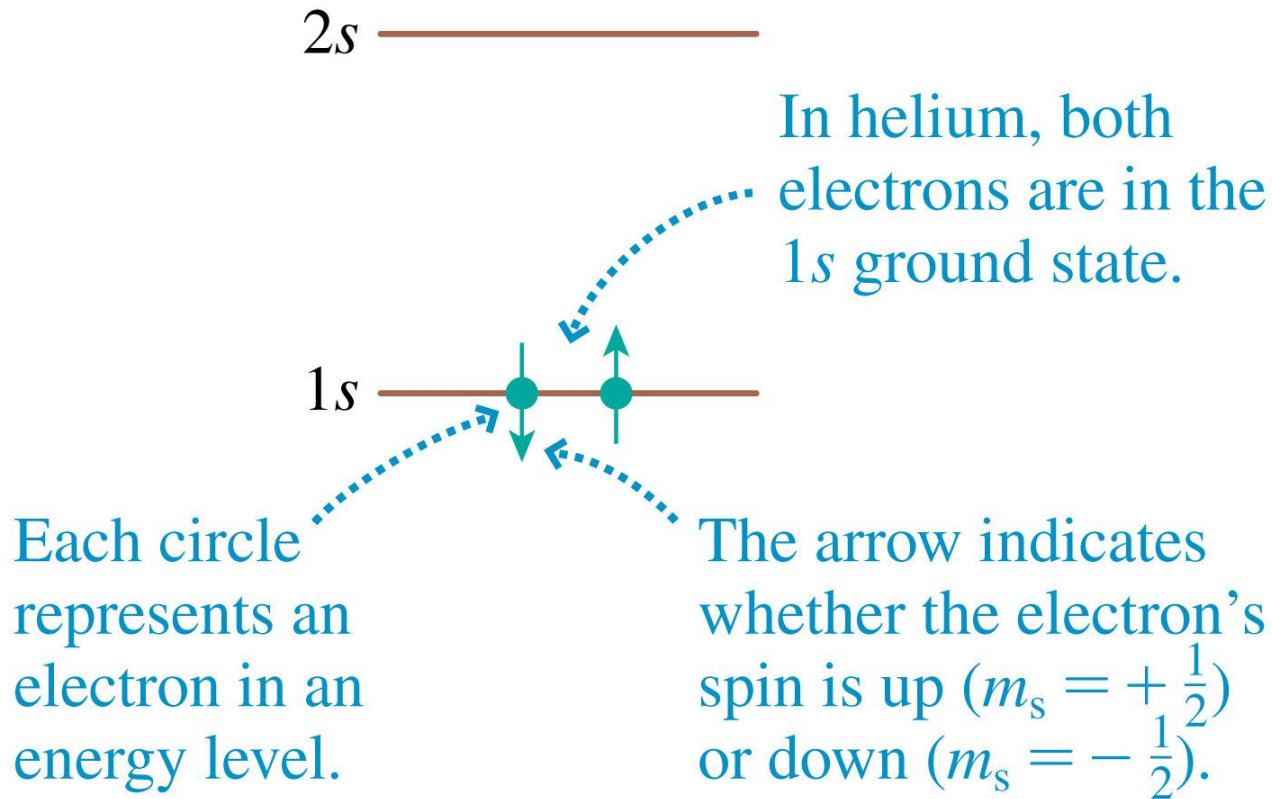
Multielectron Atoms

- For multielectron atoms we find:
 1. For each n , the energy increases as l increases until the maximum- l state has an energy very nearly that of the same n in hydrogen. States with small values of l are significantly lower in energy than the corresponding state in hydrogen.
 2. As the energy increases, states with different n begin to alternate in energy. For example, the $3s$ and $3p$ states have lower energy than a $4s$ state, but the energy of an electron in a $3d$ state is slightly higher. This will have important implications for the structure of the periodic table.

The Pauli Exclusion Principle

- In 1925, the Austrian physicist Wolfgang Pauli hypothesized that no two electrons in a quantum system can be in the same quantum state.
- That is, **no two electrons can have exactly the same set of quantum numbers (n, l, m, m_s)**.
- This is called the **Pauli exclusion principle**.

The Pauli Exclusion Principle

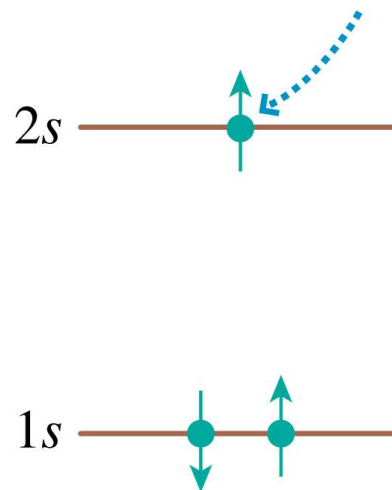


- The Pauli exclusion principle does not prevent both electrons of helium from being in the 1s state as long as they have opposite values of m_s .

The Pauli Exclusion Principle

- A list of an atom's occupied energy levels is called its **electron configuration**.
- The electron configuration of the helium ground state is written $1s^2$, where 2 indicates two electrons in the $1s$ energy level.
- When all the possible states in an energy level are filled, the electron configuration is called a **closed shell**.

The $1s$ state can hold only two electrons, so the third electron in lithium must be in the $2s$ state.

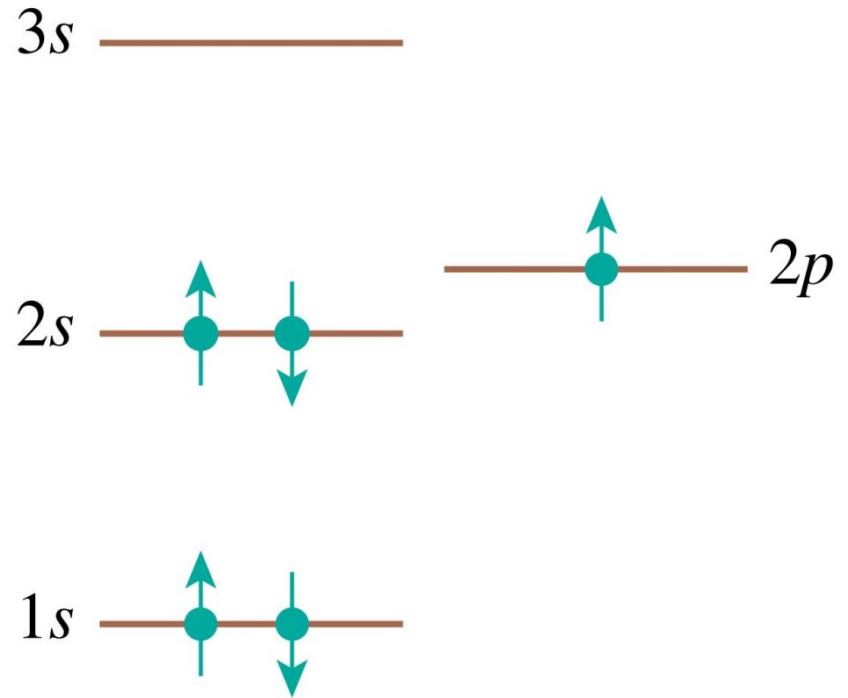


The ground state of lithium.

QuickCheck 29.7

Is this the ground state, an excited state, or a not allowed (impossible) state of an atom?

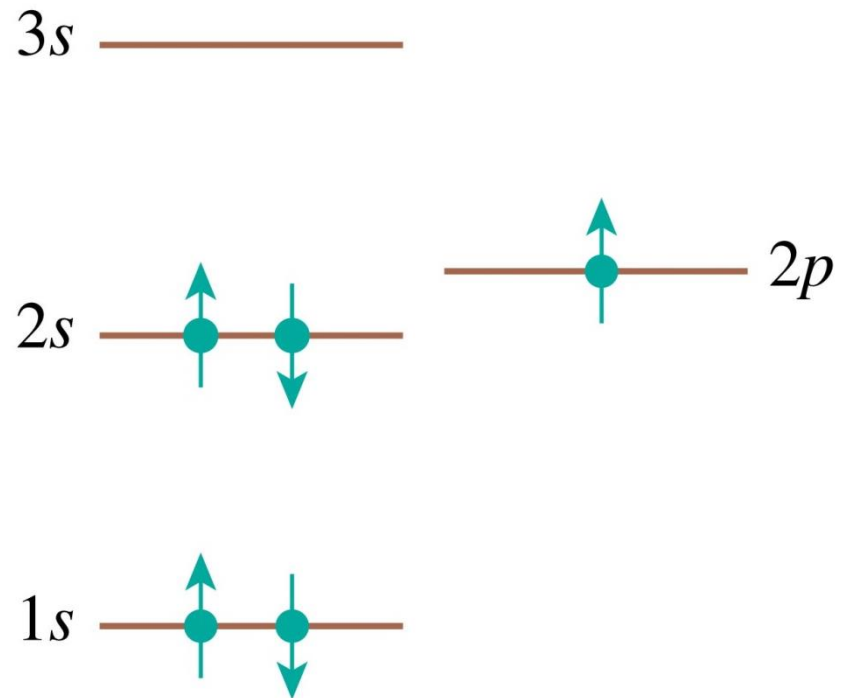
- A. Ground state
- B. Excited state
- C. Impossible state



QuickCheck 29.7

Is this the ground state, an excited state, or a not allowed (impossible) state of an atom?

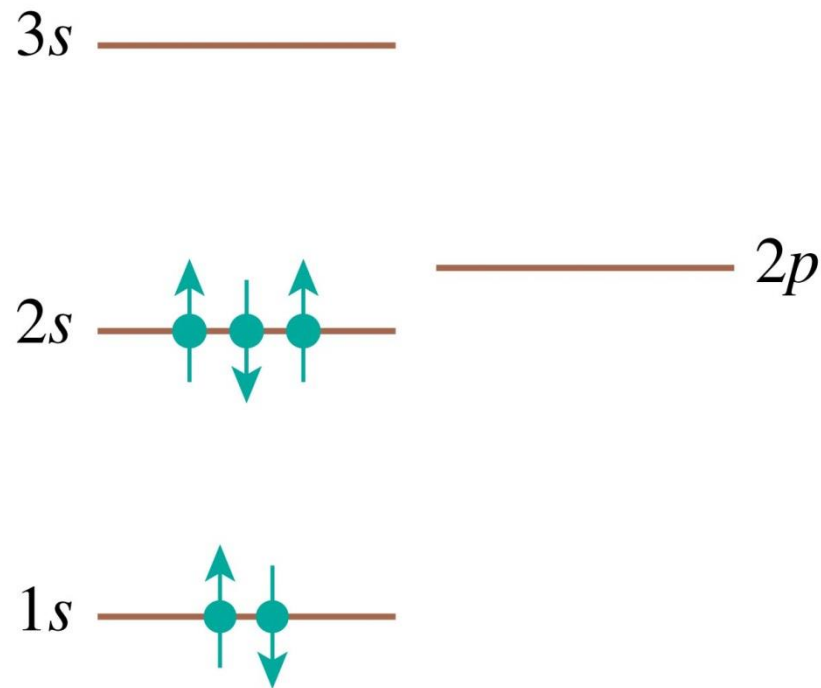
- ✓ A. Ground state
- B. Excited state
- C. Impossible state



QuickCheck 29.8

Is this the ground state, an excited state, or a not allowed (impossible) state of an atom?

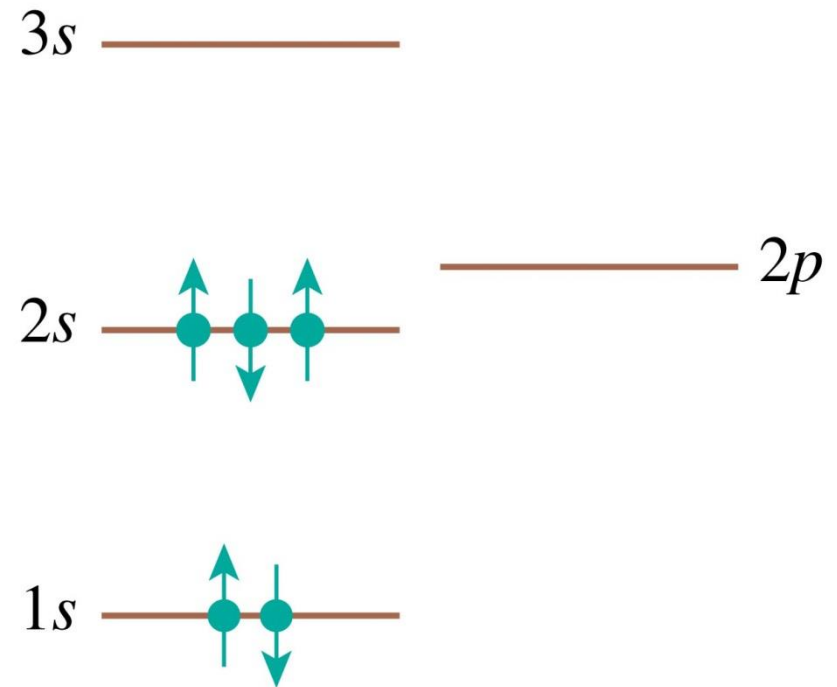
- A. Ground state
- B. Excited state
- C. Impossible state



QuickCheck 29.8

Is this the ground state, an excited state, or a not allowed (impossible) state of an atom?

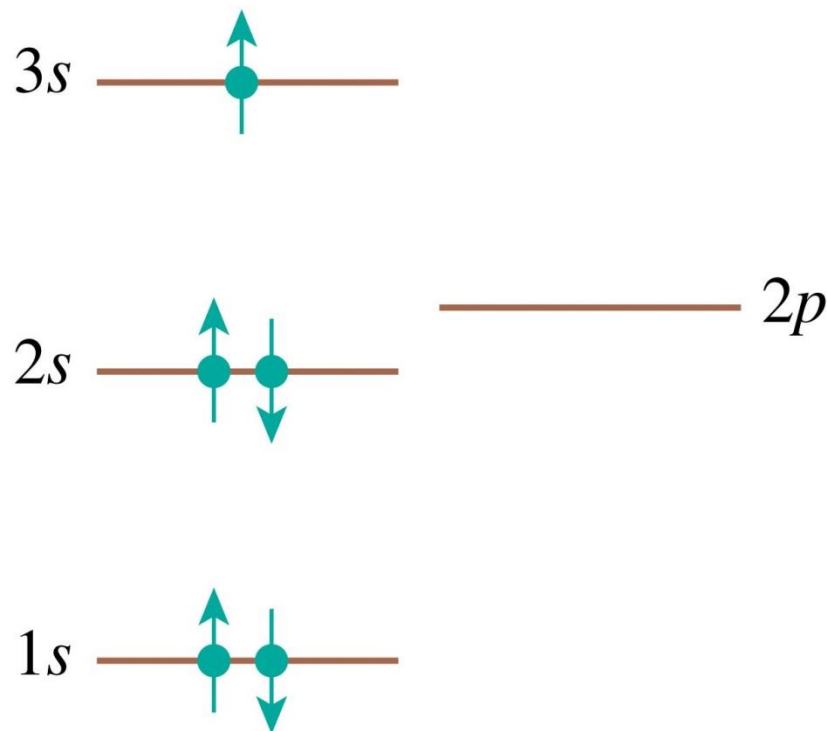
- A. Ground state
- B. Excited state
- ✓ C. Impossible state



QuickCheck 29.9

Is this the ground state, an excited state, or a not allowed (impossible) state of an atom?

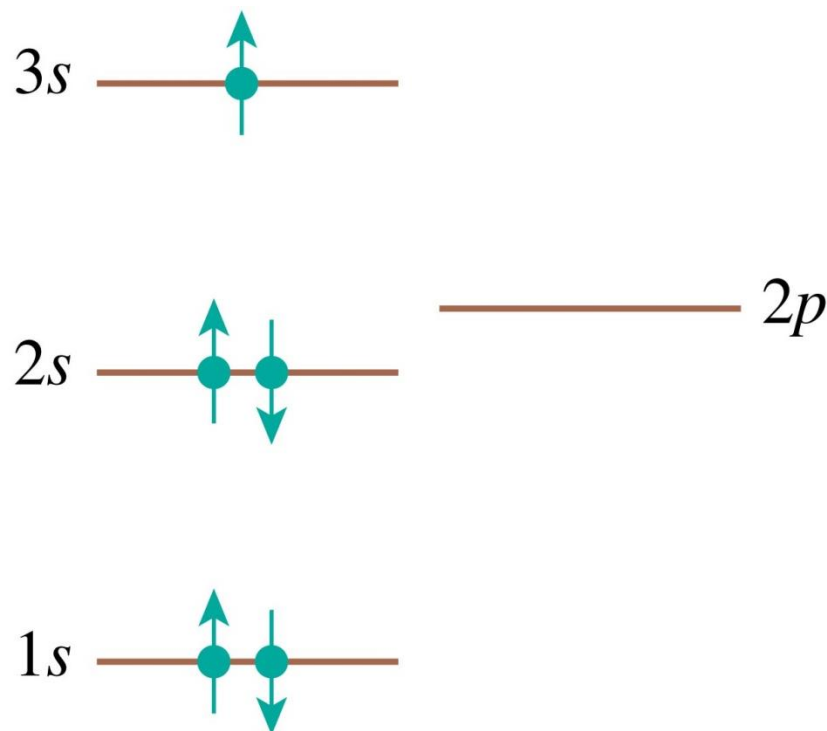
- A. Ground state
- B. Excited state
- C. Impossible state



QuickCheck 29.9

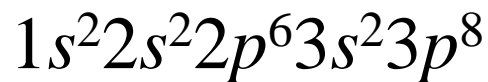
Is this the ground state, an excited state, or a not allowed (impossible) state of an atom?

- A. Ground state
- ✓ B. Excited state
- C. Impossible state



QuickCheck 29.10

Is the electron configuration

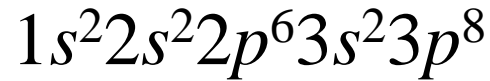


the ground state, an excited state, or a not allowed (impossible) state of an atom?

- A. Ground state
- B. Excited state
- C. Impossible state

QuickCheck 29.10

Is the electron configuration



the ground state, an excited state, or a not allowed (impossible) state of an atom?

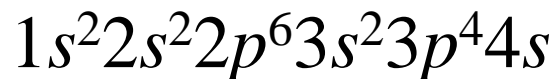
A. Ground state

B. Excited state

 C. Impossible state

QuickCheck 29.11

Is the electron configuration

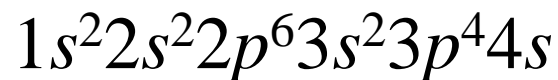


the ground state, an excited state, or a not allowed (impossible) state of an atom?

- A. Ground state
- B. Excited state
- C. Impossible state

QuickCheck 29.11

Is the electron configuration



the ground state, an excited state, or a not allowed (impossible) state of an atom?

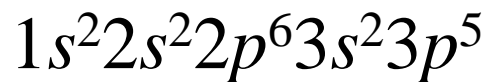
A. Ground state

 B. Excited state

C. Impossible state

QuickCheck 29.12

Is the electron configuration

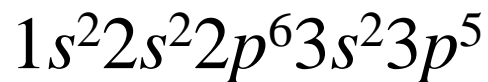


the ground state, an excited state, or a not allowed (impossible) state of an atom?


- A. Ground state
- B. Excited state
- C. Impossible state

QuickCheck 29.12

Is the electron configuration



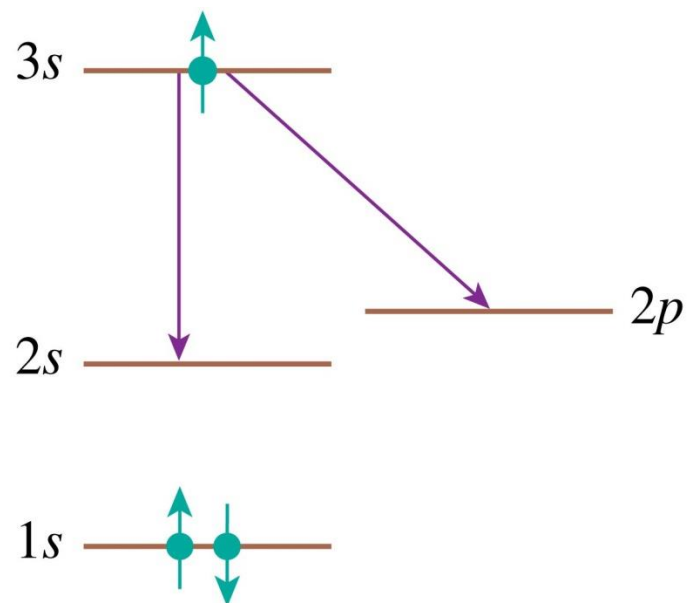
the ground state, an excited state, or a not allowed (impossible) state of an atom?

-  A. Ground state
- B. Excited state
- C. Impossible state

QuickCheck 29.13

This is an excited state of lithium. Which transition or transitions will generate spectral lines in lithium's emission spectrum?

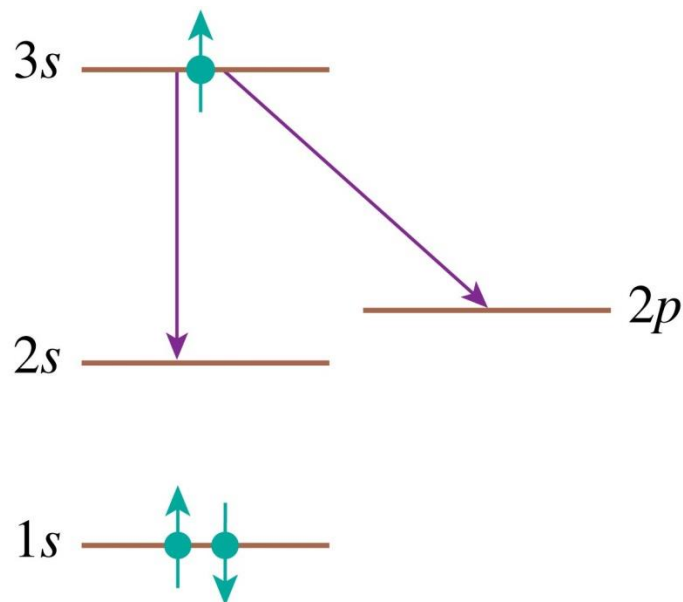
- A. Only the $3s \rightarrow 2s$ transition
- B. Only the $3s \rightarrow 2p$ transition
- C. Both
- D. Neither



QuickCheck 29.13

This is an excited state of lithium. Which transition or transitions will generate spectral lines in lithium's emission spectrum?

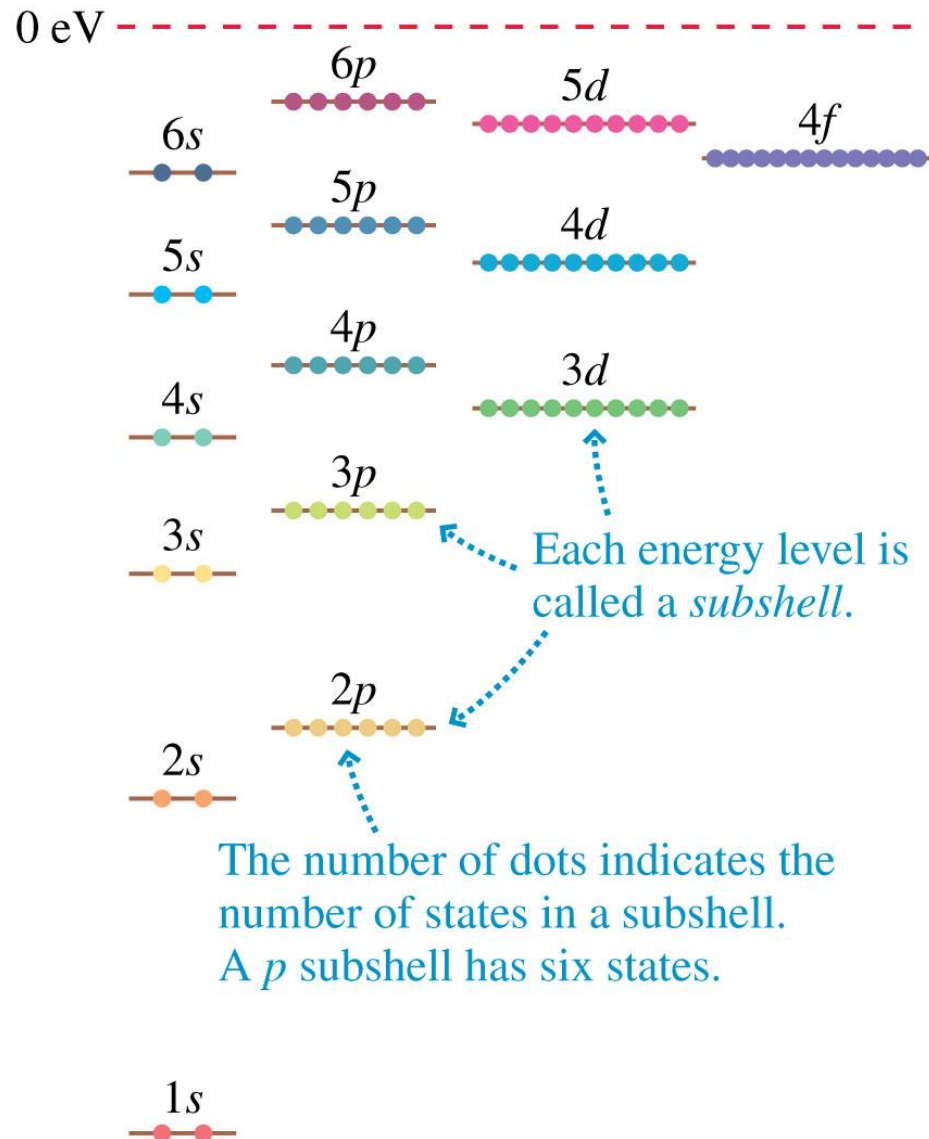
- A. Only the $3s \rightarrow 2s$ transition
- ✓ B. Only the $3s \rightarrow 2p$ transition
- C. Both $\Delta l = \pm 1$ selection rule
- D. Neither



The Periodic Table of the Elements

- In 1867 the Russian chemist Dmitri Mendelée \acute{e} v was the first to propose a *periodic* arrangement of the elements based on the regular recurrence of chemical properties.
- He was able to predict properties of elements that had not yet been discovered, verifying his organizational scheme, which is now known as the *periodic table of the elements*.
- The structure of the energy-level diagram explains the structure of the periodic table.

The Periodic Table of the Elements



The Periodic Table of the Elements

- The s state can hold two electrons, one spin up and the other spin down.
- The higher-angular-momentum states can hold more than two electrons.
- For each value of l , there are $2l + 1$ possible values of the magnetic quantum number m , and for each of those, two values of the spin quantum number m_s . Therefore each energy *level* is actually $2(2l + 1)$ different *states*, that taken together are called a *subshell*.

The Periodic Table of the Elements

TABLE 29.4 Number of states in each subshell of an atom

Subshell	l	Number of states
s	0	2
p	1	6
d	2	10
f	3	14

The Periodic Table of the Elements

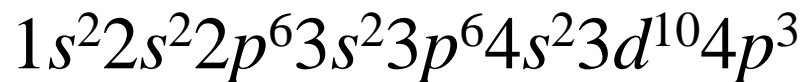
1 1s H																	2 1s He
3 Li 2s	4 Be											5 B	6 C	7 N 2p	8 O	9 F	10 Ne
11 Na 3s	12 Mg	Transition elements										13 Al	14 Si	15 P 3p	16 S	17 Cl	18 Ar
19 K 4s	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn 3d	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As 4p	34 Se	35 Br	36 Kr
37 Rb 5s	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc 4d	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb 5p	52 Te	53 I	54 Xe
55 Cs 6s	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re 5d	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi 6p	84 Po	85 At	86 Rn
87 Fr 7s	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh 6d	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn						
Lanthanides		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu 4f	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
Actinides		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am 5f	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		
		Inner transition elements															

- The entire periodic table can be built up using our knowledge of the energy-level diagram of a multielectron atom along with the Pauli exclusion principle.

Example 29.7 The ground state of arsenic

Predict the ground-state electron configuration of arsenic.

SOLVE The periodic table shows that arsenic (As) has $Z = 33$, so we must identify the states of 33 electrons. Arsenic is in the fourth row, following the first group of transition elements. Argon ($Z = 18$) filled the $3p$ subshell, then calcium ($Z = 20$) filled the $4s$ subshell. The next 10 elements, through zinc ($Z = 30$), filled the $3d$ subshell. The $4p$ subshell starts filling with gallium ($Z = 31$), and arsenic is the third element in this group, so it will have three $4p$ electrons. Thus the ground-state configuration of arsenic is



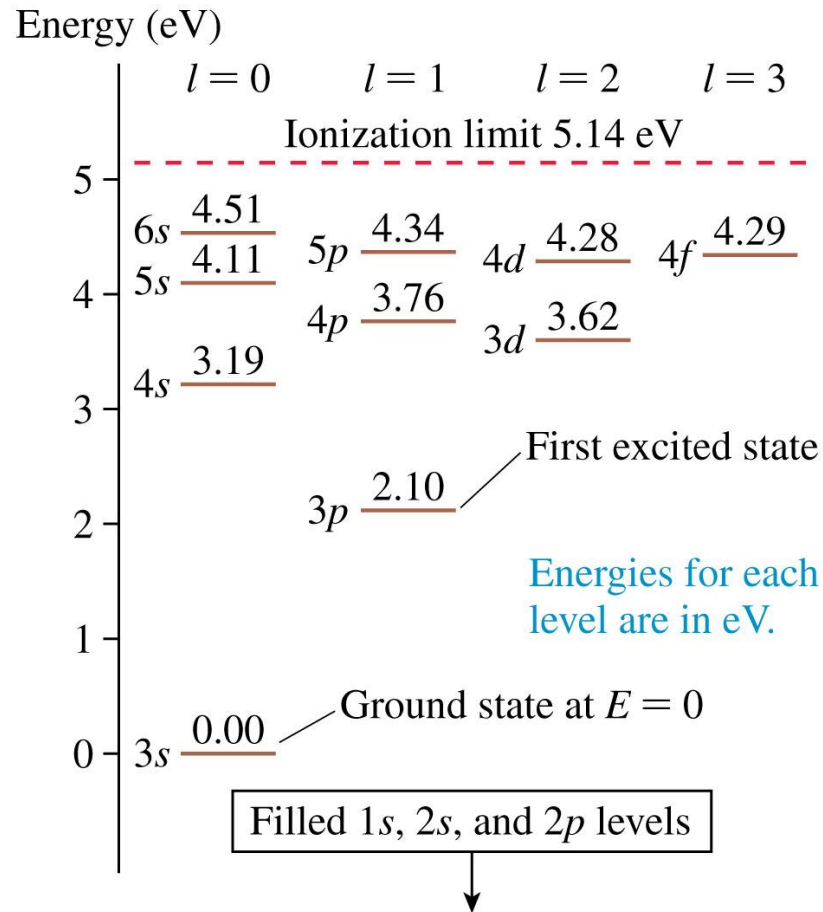
Section 29.7 Excited States and Spectra

Excited States and Spectra

- The *ground states* of electrons are important because most atoms spend most of the time in their ground states.
- The excited states hold the key to understanding atomic spectra.
- If we consider a sodium ($Z = 11$) atom, its ground-state electron configuration is $1s^2 2s^2 2p^6 3s$. The first ten electrons fill the subshells, creating a neon core with tightly bound electrons. The $3s$ electron is a valence electron and can easily be excited to higher energy levels.
- If the valence electron were excited to the $3p$ state, the electron configuration would be $1s^2 2s^2 2p^6 3p$.

Excited States and Spectra

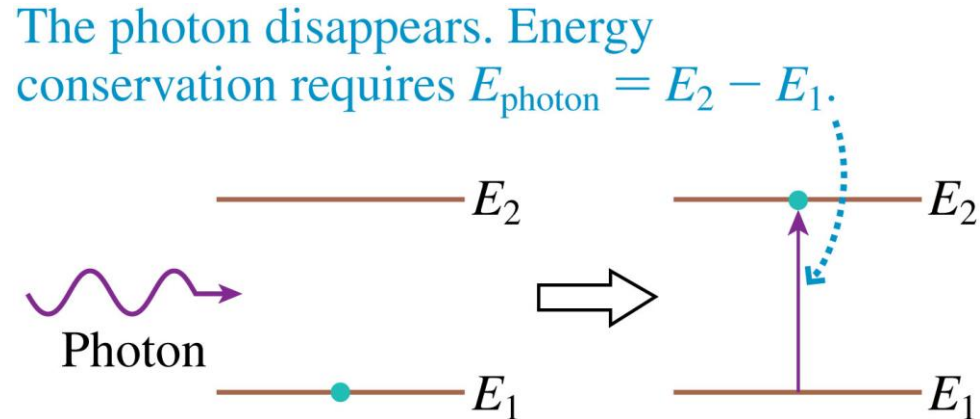
- This figure shows the $3s$ ground state of a sodium atom and some of the excited states.



Excitation by Absorption

- **Excitation** is the process of getting an atom into an excited state.
- The Bohr model says that an atom can jump into a higher-energy state by absorbing a photon with frequency $f_{\text{photon}} = \Delta E_{\text{atom}}/h$.
- In terms of wavelength:

$$\lambda = \frac{c}{f_{\text{photon}}} = \frac{hc}{\Delta E_{\text{atom}}} = \frac{1240 \text{ eV} \cdot \text{nm}}{\Delta E_{\text{atom}}}$$



Excitation by Absorption

- Not every quantum jump is actually allowed. It must also satisfy the **selection rule**: Transitions (either absorption or emission) from a state with orbital quantum number l can occur to only another state whose orbit quantum number differs from the original state by ± 1 :

$$\Delta l = l_2 - l_1 = \pm 1$$

Selection rule for emission and absorption

Example 29.8 Analyzing absorption in sodium

What are the two longest wavelengths in the absorption spectrum of sodium? What are the transitions?

PREPARE Absorption transitions always start from the ground state. Only transitions for which l changes by ± 1 are allowed.

Example 29.8 Analyzing absorption in sodium (cont.)

SOLVE As Figure 29.24 shows, the sodium ground state is $3s$. Starting from an s state ($l = 0$), the selection rule permits quantum jumps only to p states ($l = 1$). The lowest excited state is the $3p$ state and $3s \rightarrow 3p$ is an allowed transition ($\Delta l = 1$), so this will be the longest wavelength.

Example 29.8 Analyzing absorption in sodium (cont.)

You can see from the data in Figure 29.24 that

$\Delta E_{\text{atom}} = 2.10 \text{ eV} - 0.00 \text{ eV} = 2.10 \text{ eV}$ for this transition.

The corresponding wavelength is

$$\lambda = \frac{1240 \text{ eV} \cdot \text{nm}}{2.10 \text{ eV}} = 590 \text{ nm}$$

(Because of rounding, the calculation gives $\lambda = 590 \text{ nm}$. The experimental value is actually 589 nm .)

Example 29.8 Analyzing absorption in sodium (cont.)

- The next excited state is $4s$, but a $3s \rightarrow 4s$ transition is not allowed by the selection rule. The next allowed transition is $3s \rightarrow 4p$, with $\Delta E_{\text{atom}} = 3.76 \text{ eV}$. The wavelength of this transition is

$$\lambda = \frac{1240 \text{ eV} \cdot \text{nm}}{3.76 \text{ eV}} = 330 \text{ nm}$$

Example 29.8 Analyzing absorption in sodium (cont.)

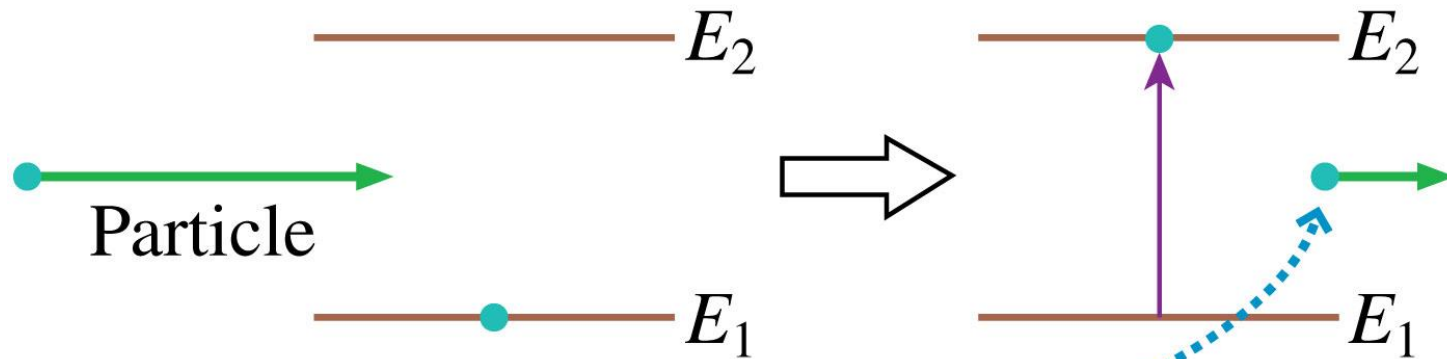
ASSESS If you look at the sodium spectrum shown earlier in Figure 29.3b, you will see that 589 nm and 330 nm are, indeed, the two longest wavelengths in the absorption spectrum.

Collisional Excitation

- **Collisional excitation** of an atom is the process in which a high-speed particle collides with an atom, giving a portion of its energy to excite the atom to a higher state.
- Collisional excitation differs from excitation by absorption because in absorption, the photon disappears. In collisional excitation, the particle is still present after the collision and it does *not* have to transfer its entire energy.

Collisional Excitation

- To excite an atom through collisional excitation, the incident energy of the electron (or any other matter particle) merely has to *exceed* ΔE_{atom} .
- Collisional excitation by electrons is the predominant method of excitation in neon signs and street lights.



The particle carries away energy.

Energy conservation requires $E_{\text{particle}} \geq E_2 - E_1$.

Conceptual Example 29.9 Possible excitation of hydrogen?

Can an electron with a kinetic energy of 11.4 eV cause a hydrogen atom to emit the prominent red spectral line ($\lambda = 656 \text{ nm}$, $E_{\text{photon}} = 1.89 \text{ eV}$) in the Balmer series?

Conceptual Example 29.9 Possible excitation of hydrogen? (cont.)

REASON The electron must have sufficient energy to excite the upper state of the transition. The electron's energy of 11.4 eV is significantly greater than the 1.89 eV energy of a photon with wavelength 656 nm, but don't confuse the energy of the photon with the energy of the excitation.

Conceptual Example 29.9 Possible excitation of hydrogen? (cont.)

The red spectral line in the Balmer series is emitted in an $n = 3 \rightarrow 2$ quantum jump with $\Delta E_{\text{atom}} = 1.89 \text{ eV}$, but to cause this emission, the electron must excite an atom from its *ground state*, with $n = 1$, up to the $n = 3$ level. From Figure 29.16, the necessary excitation energy is

$$\Delta E_{\text{atom}} = E_3 - E_1 = (-1.51 \text{ eV}) - (-13.60 \text{ eV}) = 12.09 \text{ eV}$$

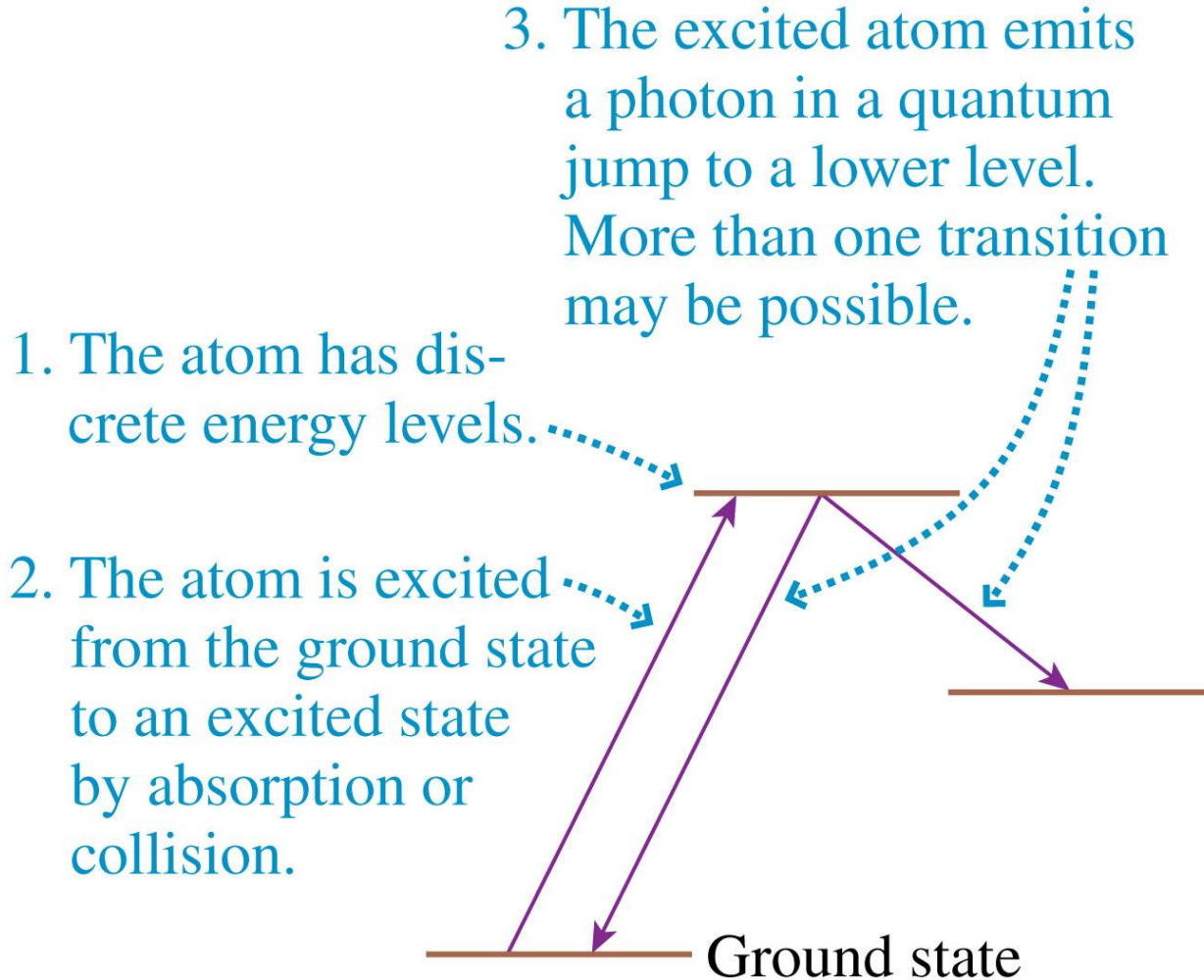
The electron does *not* have sufficient energy to excite the atom to the state from which the emission would occur.

Conceptual Example 29.9 Possible excitation of hydrogen? (cont.)

ASSESS As our discussion of absorption spectra showed, almost all excitations of atoms begin from the ground state. Quantum jumps down in energy, however, can begin and end at any two states allowed by selection rules.

Emission Spectra

- This figure explains the generation of an emission spectrum.

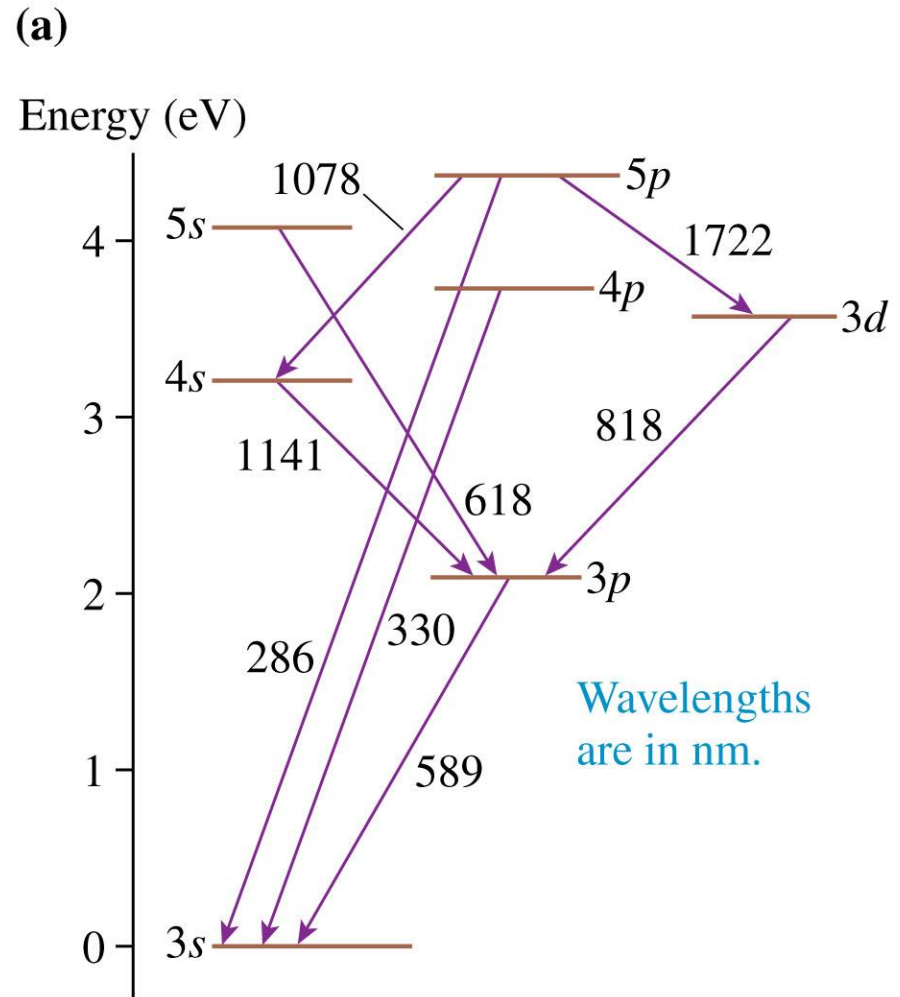


Emission Spectra

- The uncertainty principle does not allow us to know for how long an atom will be in an excited state.
- However, the *average* time an atom spends in the excited state is called the **lifetime** of the state and is typically just a few nanoseconds.

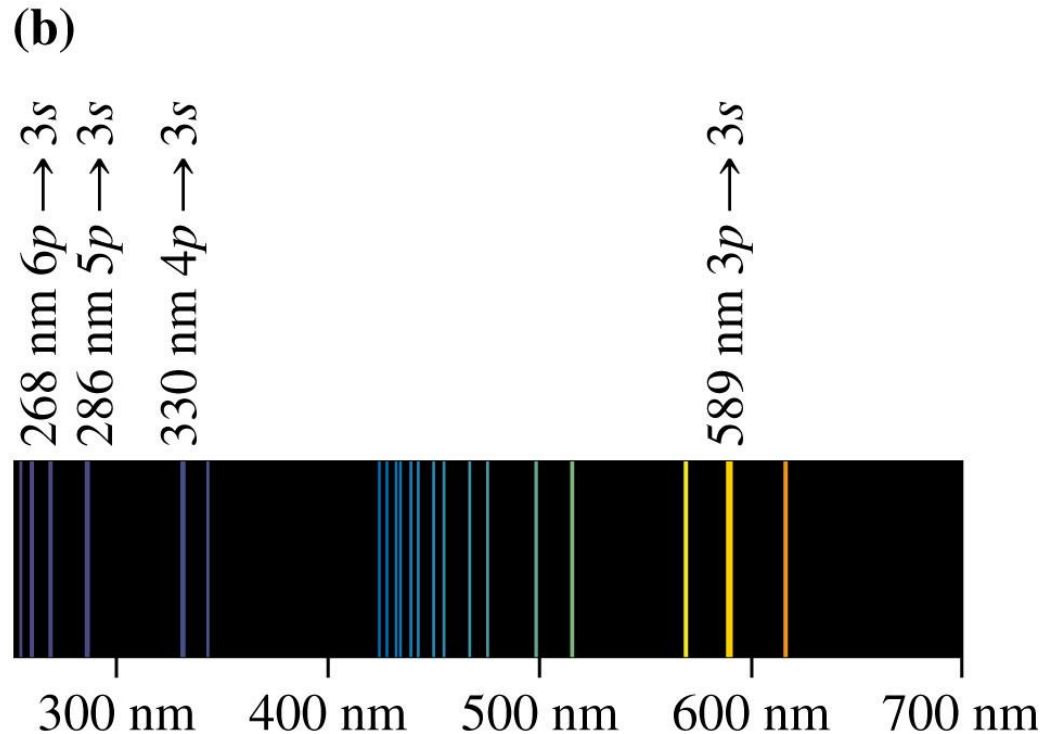
Emission Spectra

- This diagram shows some of the transitions and wavelengths observed in the emission spectrum of sodium.
- Notice that the selection rule prevents $5p$ levels from undergoing quantum jumps to $3p$ and $4p$.



Emission Spectra

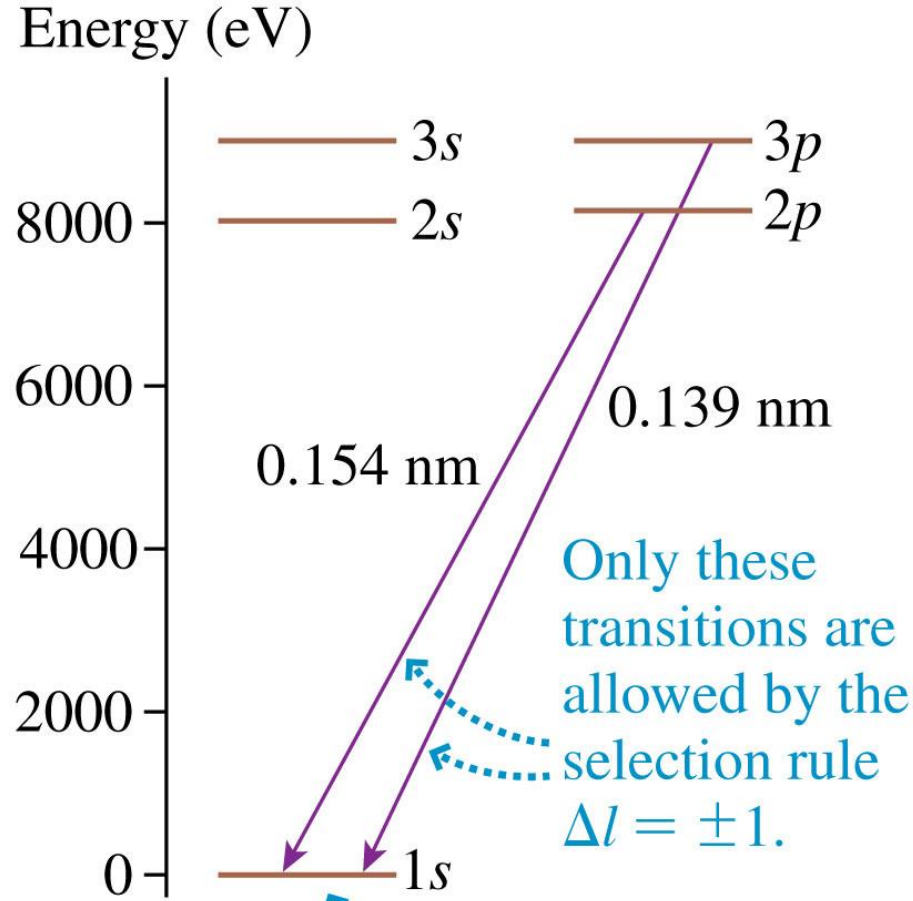
- This figure shows the emission spectrum of sodium as it would be recorded by a spectrometer.
- The *series* of emission lines near 300 nm is due to all the possible $np \rightarrow 3s$ transitions.



X Rays

- Very-high-speed particles are capable of knocking inner-shell electrons out of the target atoms, producing an *inner shell vacancy*.
- The vacancy is filled when an electron from a higher shell undergoes a quantum jump into the vacancy, creating a photon in the process.
- In heavy elements, like copper or iron, the energy difference between inner and outer shells is very large. Therefore the emitted photon has a very high energy and a very small wavelength $\lambda \approx 0.1 \text{ nm}$: an x-ray photon.

X Rays



The 1s state has a vacancy because one of its electrons was knocked out by a high-speed electron.

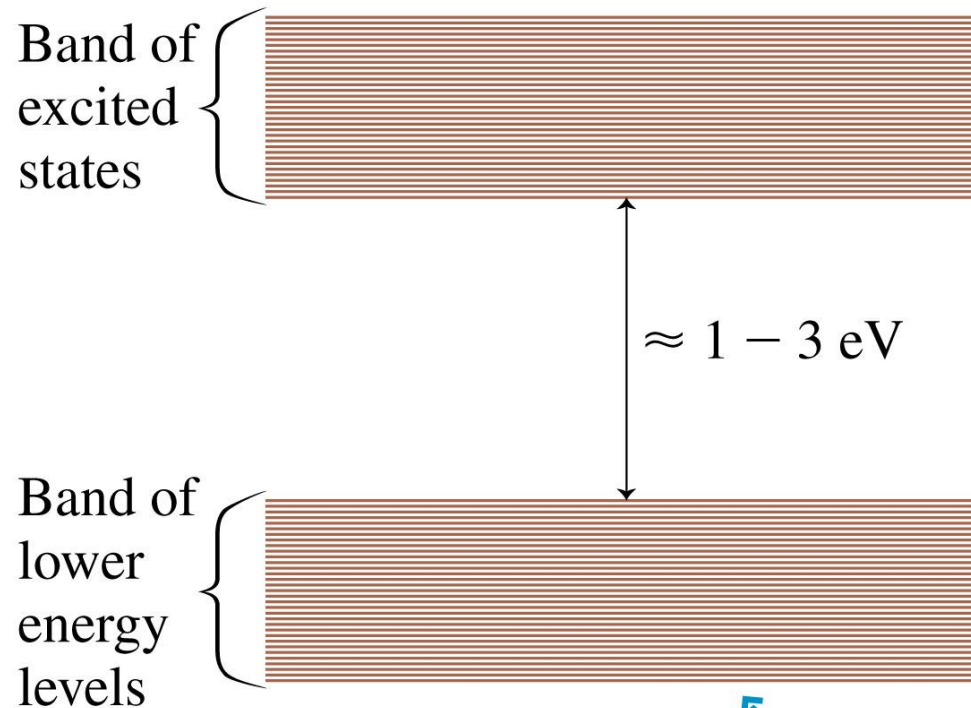
Section 29.8 Molecules

Molecules

- A quantum-mechanical analysis of molecules finds the following general results:
 - The energy is quantized. Electrons can exist in only certain allowed energy levels.
 - The number of energy levels is so extraordinarily high, and the energy levels are jammed so close together, that for all practical purposes the energy levels group into *bands* of allowed energy.
 - In thermal equilibrium, nearly all molecules are in the very lowest energy levels.

Molecules

- A generic molecular energy-level diagram for a medium-size molecule shows that it has broad bands of energy levels.



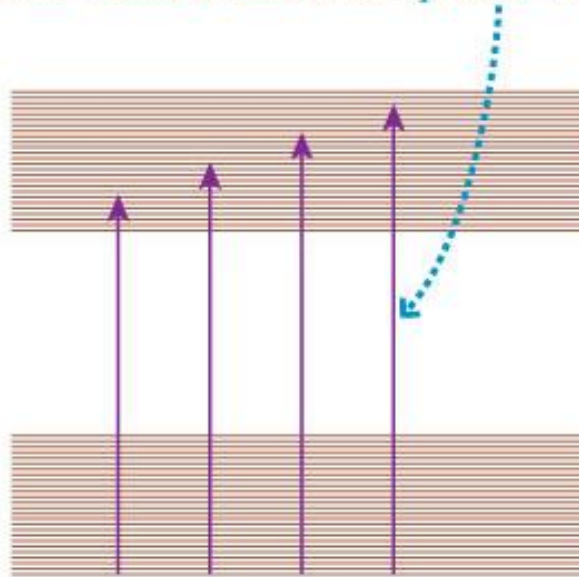
In thermal equilibrium,
nearly all molecules are in
the lowest few energy levels.

Molecules

- The absorption spectrum of an atom consists of discrete spectral lines, but a molecule has a continuous *absorption band*.
- **Fluorescence** is the absorption of light at higher frequency followed by the emission of light at lower frequency. It occurs in molecules, but not atoms, because molecules can transform some of the absorbed energy into vibrational energy of the atoms, increasing the thermal inertia of the molecules.

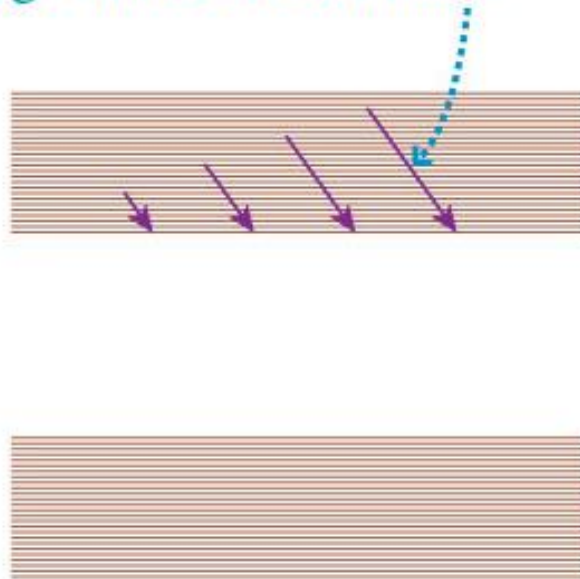
Molecules

The molecules can absorb light over a range of wavelengths. This makes an *absorption band*.



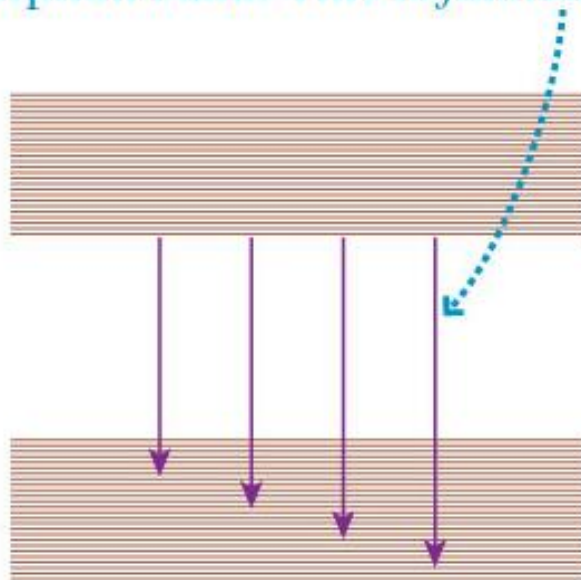
Molecules

The molecules rapidly transform some of the absorbed energy into molecular vibrations, causing the molecules to fall to the bottom edge of the excited band.

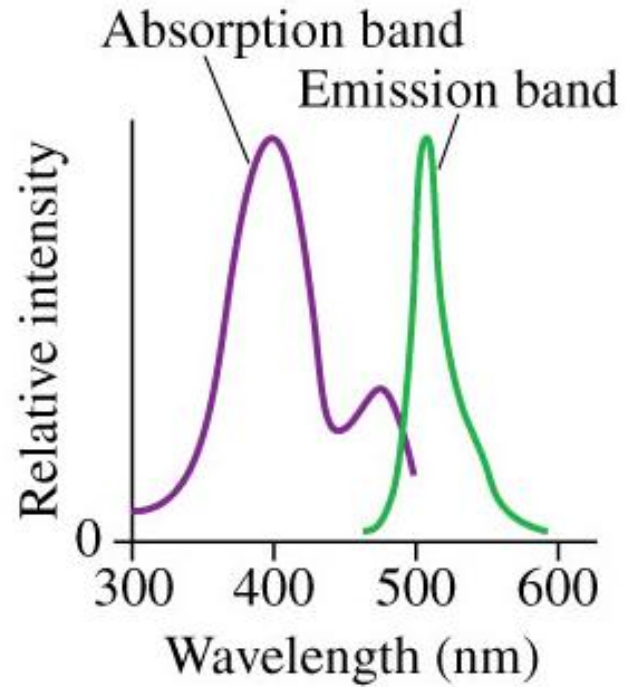


Molecules

Quantum jumps back to the lower band have less energy than the original jumps up. Thus the *emission band* is at longer wavelength than the absorption band. This is *fluorescence*.



Molecules



Molecules

- Many biological molecules are fluorescent. When illuminated by blue or ultraviolet light, chlorophyll fluoresces a dark red color. Marine biologists use this to measure the concentration of phytoplankton in seawater.
- Scientists isolated a fluorescent protein in jellyfish that fluoresces green when illuminated with ultraviolet light. The *green fluorescent gene* (GFG) can be fused to a gene of interest. It will fluoresce when the gene is active, and can therefore be studied.

QuickCheck 29.14

Which of the following is not a possible fluorescence process?

- A. Absorption of red light and emission of green light
- B. Absorption of ultraviolet light and emission of infrared light
- C. Absorption of ultraviolet light and emission of green light
- D. Absorption of blue light and emission of red light

QuickCheck 29.14

Which of the following is not a possible fluorescence process?

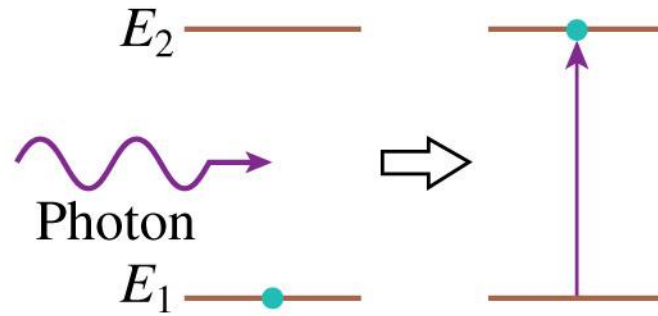
- ✓ A. Absorption of red light and emission of green light
- B. Absorption of ultraviolet light and emission of infrared light
- C. Absorption of ultraviolet light and emission of green light
- D. Absorption of blue light and emission of red light

Section 29.9 Stimulated Emission and Lasers

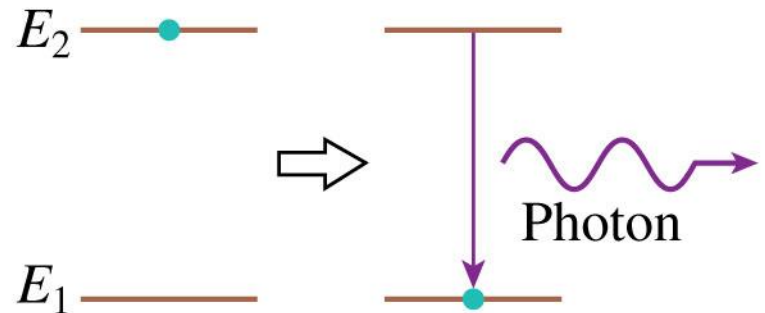
Stimulated Emission and Lasers

- An atom can jump from a lower-energy level to a higher-energy level by absorbing a photon.
- The atom emits a photon of the same energy as it jumps back down.
- This transition occurs spontaneously and is therefore called **spontaneous emission**.

(a) Absorption



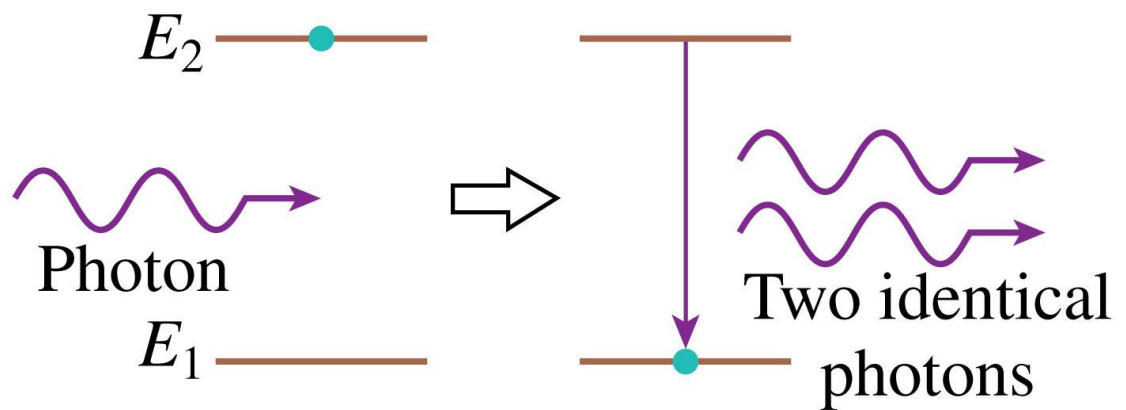
(b) Spontaneous emission



Stimulated Emission and Lasers

- If the energy of a photon is exactly equal to the energy difference $E_2 \rightarrow E_1$, the incoming photon can *induce* an atom to make the $2 \rightarrow 1$ transition, emitting a photon in a process called **stimulated emission**.
- The incident photon is not absorbed and **the stimulated emission produces a second photon that is an exact clone of the first**.

(c) Stimulated emission



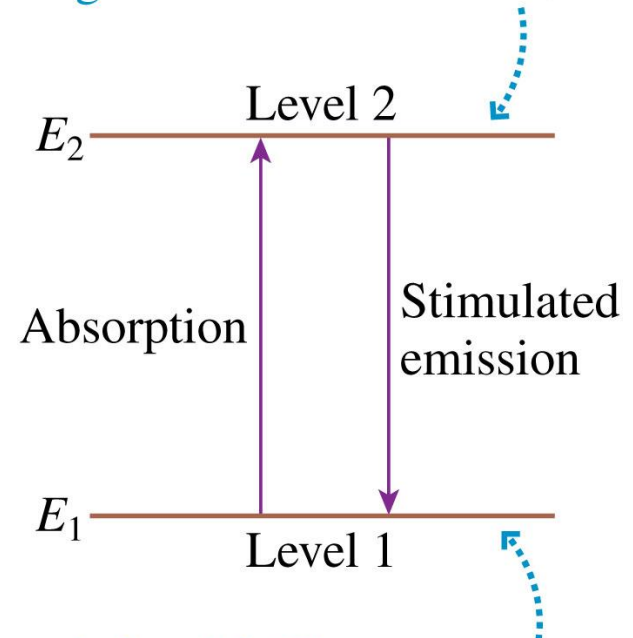
Lasers

- The word **laser** is an acronym for the phrase *light amplification by the stimulated emission of radiation*.
- A laser is a device that produces a beam of highly *coherent* and monochromatic light as a result of stimulated emission.
- **Coherent** light is light in which all electromagnetic waves have the same phase, direction, and amplitude.

Lasers

- A photon with frequency $f = (E_2 - E_1)/h$ incident on a group of atoms can be absorbed or it could cause stimulated emission.
- Ordinarily $N_2 \ll N_1$, so absorption events outnumber stimulated emission events.

N_2 atoms in level 2. Photons of energy $E_{\text{photon}} = E_2 - E_1$ can cause these atoms to undergo stimulated emission.

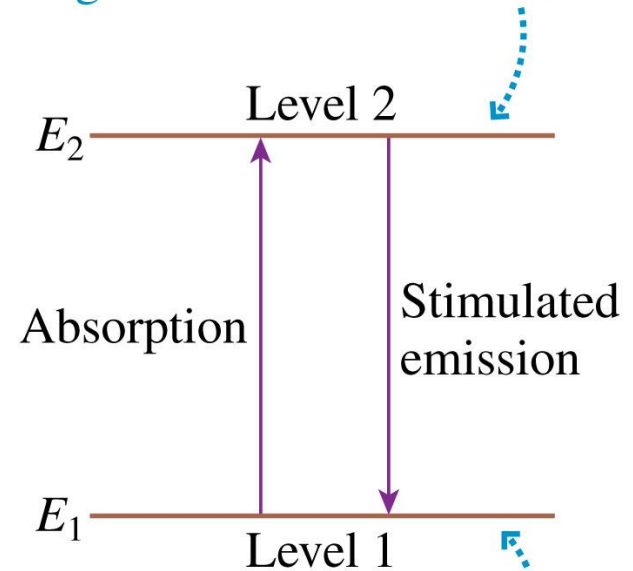


N_1 atoms in level 1. These atoms can absorb photons of energy $E_{\text{photon}} = E_2 - E_1$.

Lasers

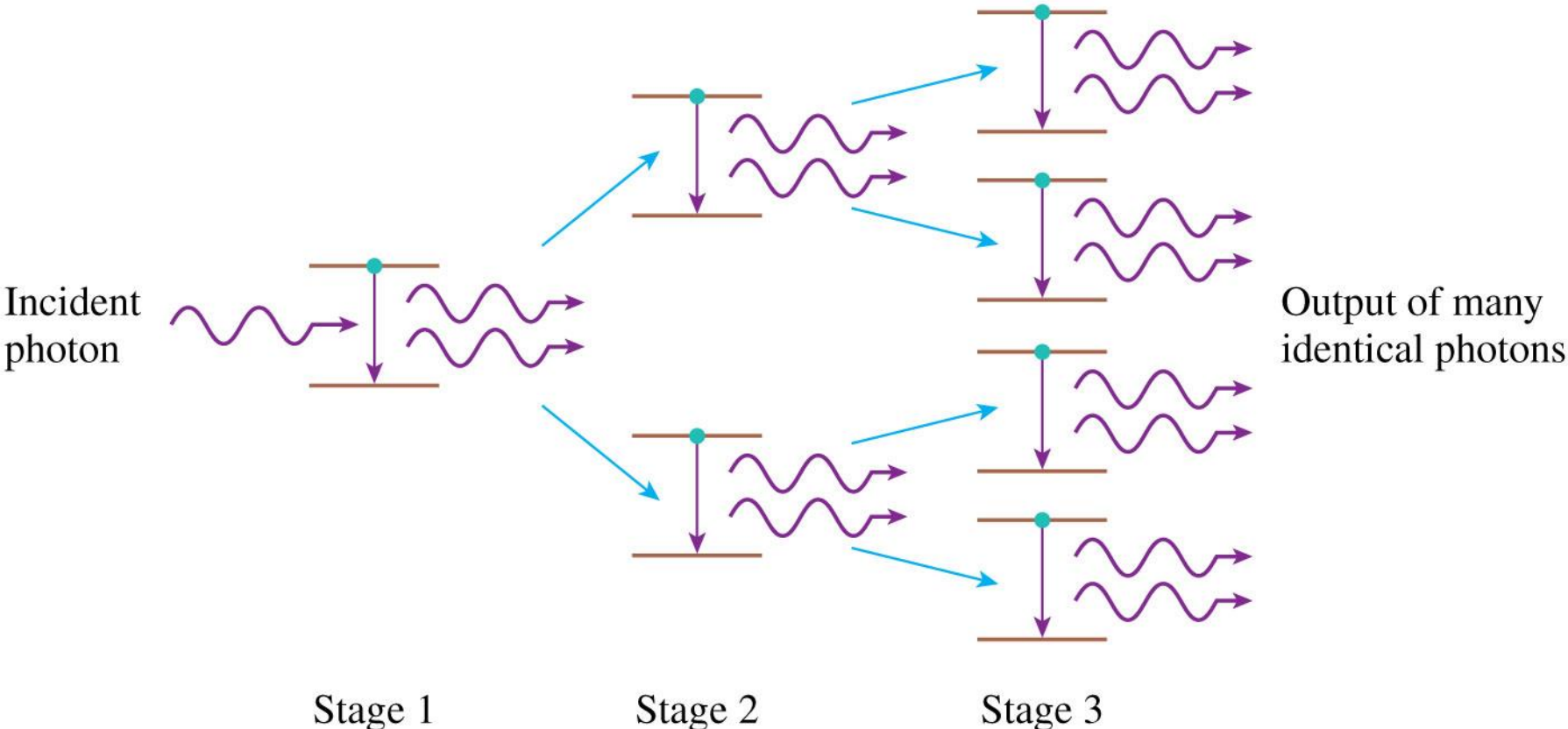
- If we could arrange to place all of the atoms in level 2, then an incident photon will cause stimulated emission. Now there are two photons, which can cause more stimulated emission.
- There will be a chain reaction of stimulated emission.

N_2 atoms in level 2. Photons of energy $E_{\text{photon}} = E_2 - E_1$ can cause these atoms to undergo stimulated emission.



N_1 atoms in level 1. These atoms can absorb photons of energy $E_{\text{photon}} = E_2 - E_1$.

Lasers

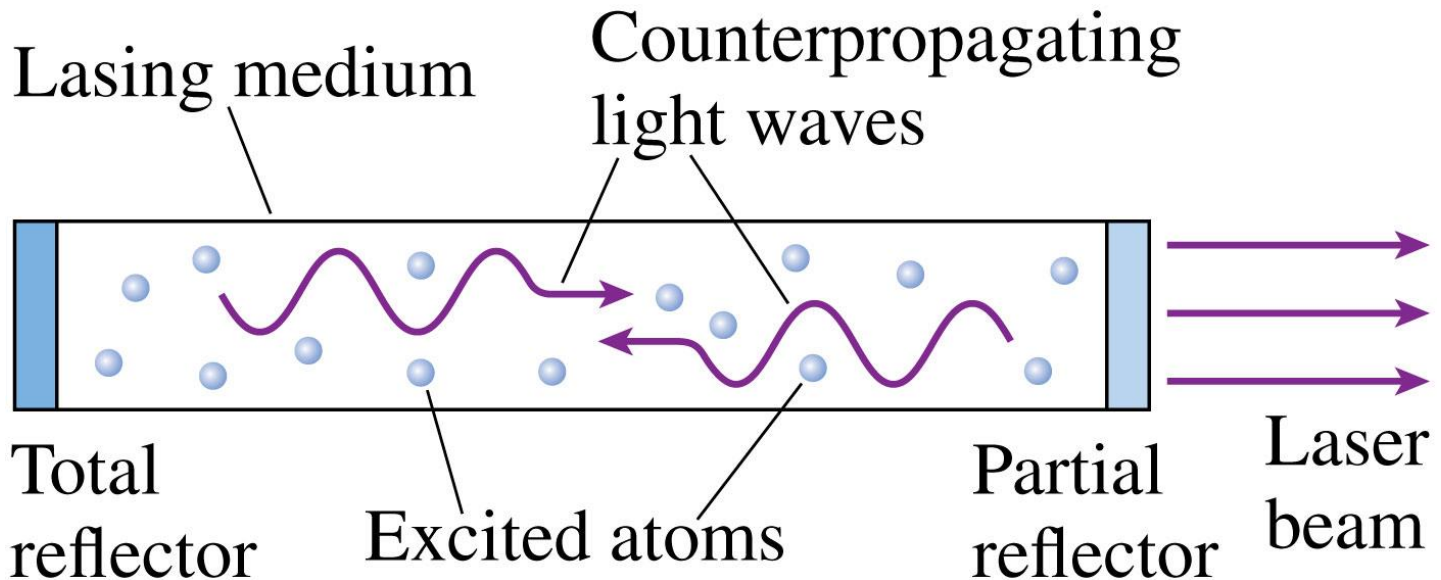


Lasers

- The chain reaction created by stimulated emission will create *identical* photons, all traveling together in the same direction and same phase.
- In order to create the chain reaction, *all* of the atoms do not need to be in level 2, just the majority of them so that stimulated emission exceeds absorption.
- This situation is called an **population inversion**.

Lasers

- The stimulated emission is sustained by placing a *lasing medium* in an **optical cavity** consisting of two facing mirrors.
- If one of the mirrors is partially transmitting, some of the light emerges as a *laser beam*.



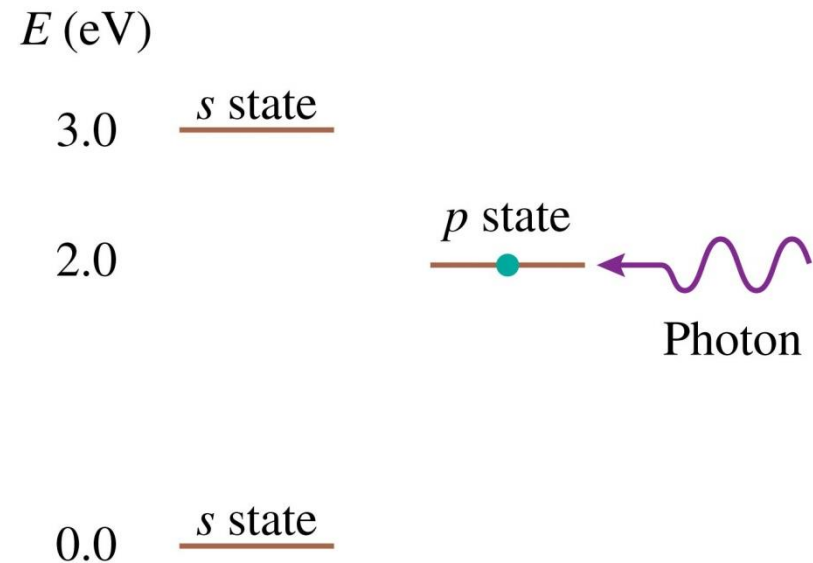
Lasers in Medicine

- Laser surgery is very precise and generally has less blood loss than conventional surgery because the heat of the laser seals the blood vessels and capillaries.
- One common use of lasers is to remove plaque from artery walls, reducing the risk of stroke or heart attack. In this procedure, an optical fiber is threaded through arteries to reach the site. A powerful laser beam is then fired through the fiber to carefully vaporize the plaque.

QuickCheck 29.15

A photon with energy 2.0 eV is incident on an atom that is in the p state. Which can happen?

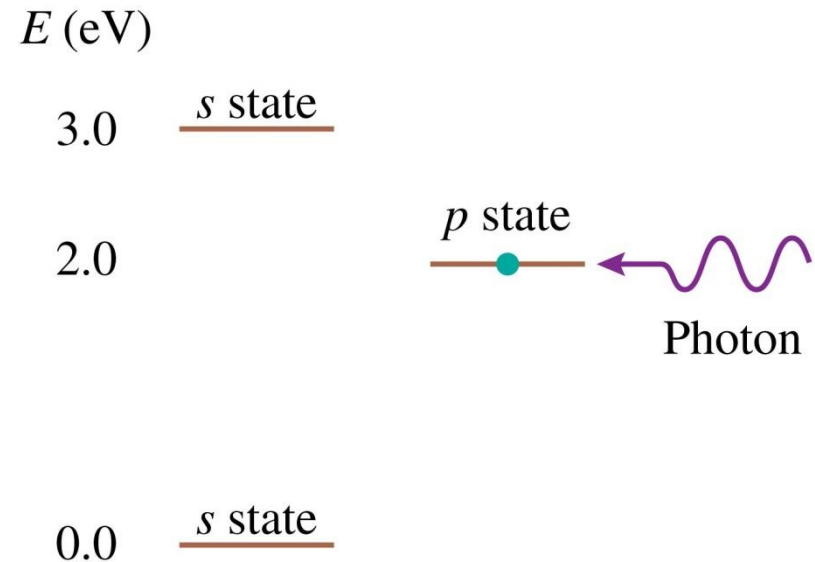
- A. Absorption
- B. Stimulated emission
- C. Both
- D. Neither
- E. Not enough information to tell



QuickCheck 29.15

A photon with energy 2.0 eV is incident on an atom that is in the p state. Which can happen?

- A. Absorption
- ✓ B. Stimulated emission
- C. Both
- D. Neither
- E. Not enough information to tell

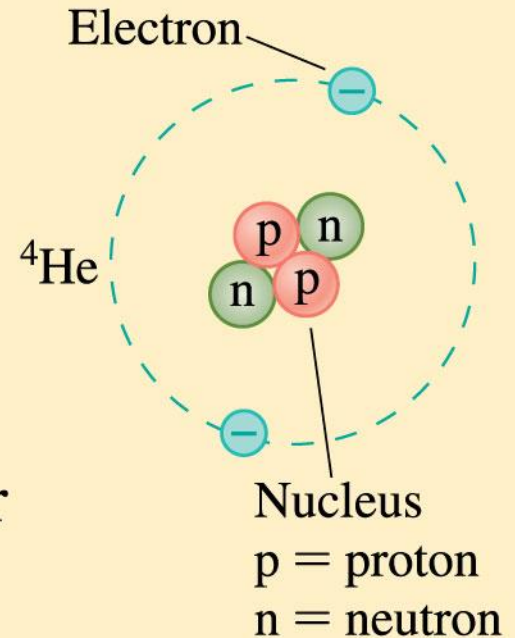


Summary: Important Concepts

The Structure of an Atom

An atom consists of a very small, positively charged nucleus, surrounded by orbiting electrons.

- The number of protons is the atom's **atomic number Z** .
- The **atomic mass number A** is the number of protons + the number of neutrons.



Text: p. 968

Summary: Important Concepts

The Bohr Atom

In Bohr's model,

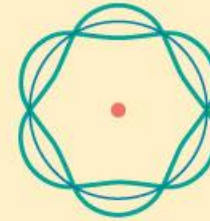
- The atom can exist in only certain **stationary states**. These states correspond to different electron orbits. Each state is numbered by **quantum number** $n = 1, 2, 3, \dots$.
- Each state has a discrete, well-defined energy E_n .
- The atom can change its energy by undergoing a **quantum jump** between two states by emitting or absorbing a photon of energy $E_{\text{photon}} = \Delta E_{\text{atom}} = |E_f - E_i|$.

Text: p. 968

Summary: Important Concepts

The Hydrogen Atom

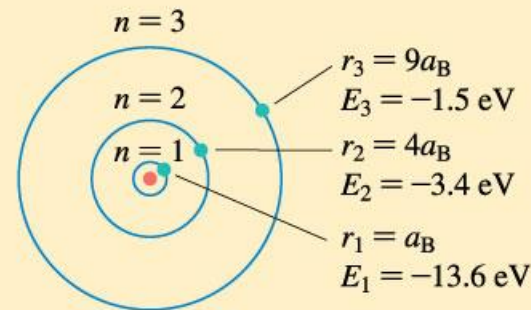
In **Bohr's model of the hydrogen atom** the stationary states are found by requiring an integer number of de Broglie wavelengths to fit around the circumference of the electron's orbit: $2\pi r = n\lambda$. The integer n is the *principal quantum number*.



This leads to energy quantization with

$$E_n = -\frac{13.60 \text{ eV}}{n^2}$$

and orbit radii $r_n = n^2 a_B$, where $a_B = 0.053 \text{ nm}$ is the **Bohr radius**.



The wavelengths of light in the hydrogen atom spectrum are given by the **Balmer formula**:

$$\lambda_{n \rightarrow m} = \frac{91.1 \text{ nm}}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)} \quad \begin{array}{l} m = 1, 2, 3, \dots \\ n = m + 1, m + 2, \dots \end{array}$$

Text: p. 968

Summary: Important Concepts

Beyond the Bohr model, quantum mechanics adds other quantized parameters, each with its own quantum number:

- The *orbital angular momentum*, quantum number l :

$$L = \sqrt{l(l+1)}\hbar \quad l = 0, 1, 2, 3, \dots, n-1$$

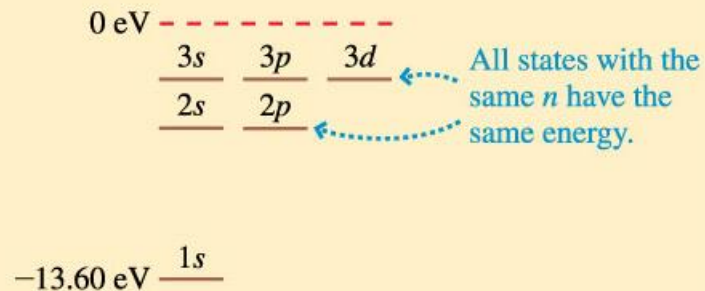
- The *angle of the electron's orbit*, quantum number m :

$$m = -l, -l+1, \dots, 0, \dots, l-1, l$$

- The *direction of the electron spin*, quantum number m_s :

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

The energy of a hydrogen atom depends only on n :



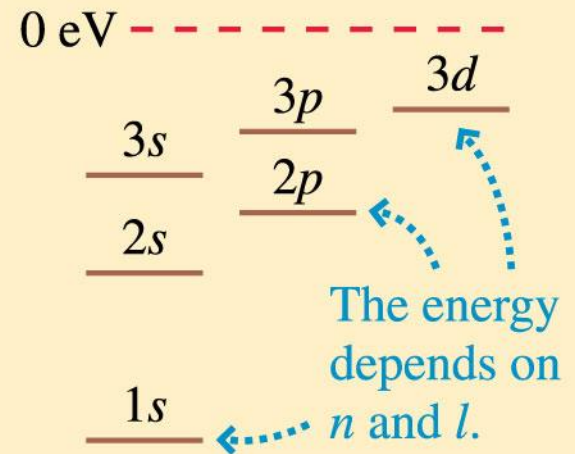
Text: p. 968

Summary: Important Concepts

Multielectron atoms

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The **Pauli exclusion principle** states that no more than one electron can occupy each quantum state.

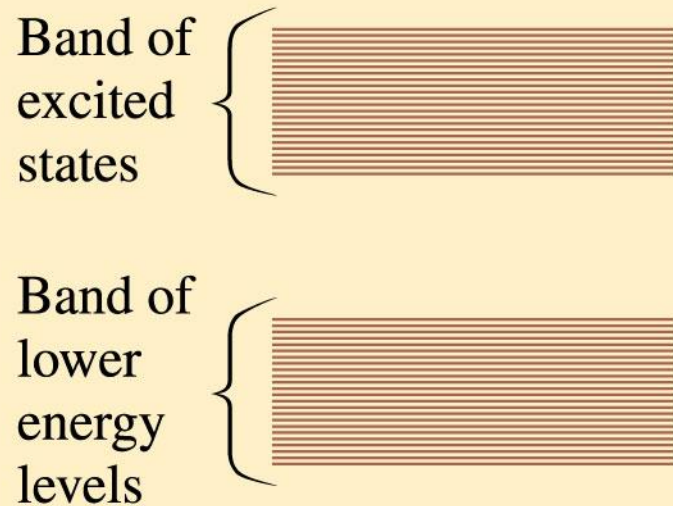


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Summary: Important Concepts

Molecules

In molecules, the states are spaced very closely into **bands** of states. Because electrons can be excited to and from many states, the spectra of molecules are broad, not discrete.

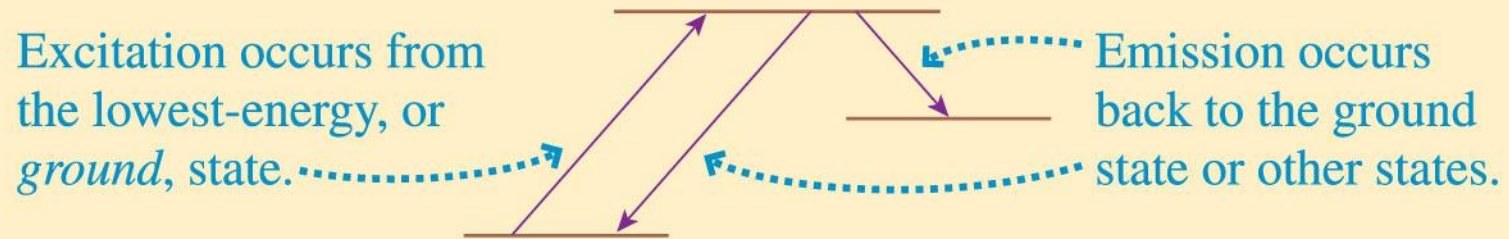


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Summary: Applications

Atomic emission spectra are generated by excitation followed by a photon-emitting quantum jump.

- **Excitation** occurs by absorption of a photon or by collision.
- A quantum jump can occur only if $\Delta l = \pm 1$.
- Quantized energies give rise to a **discrete spectrum**.



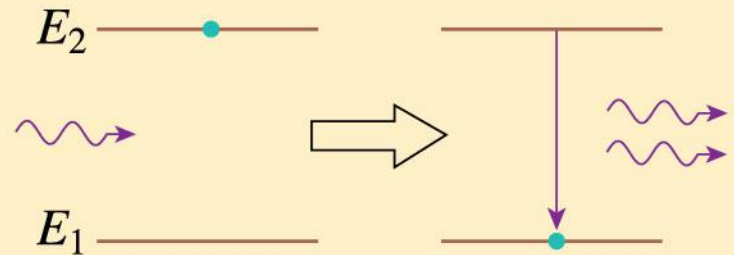
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Summary: Applications

Lasers

A photon with energy $E_{\text{photon}} = E_2 - E_1$ can induce **stimulated emission** of a second photon identical to the first. These

photons can then induce more atoms to emit photons. If more atoms are in state 2 than in state 1, this process can rapidly build up an intense beam of identical photons. This is the principle behind the laser.



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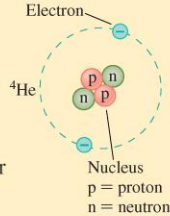
Summary

IMPORTANT CONCEPTS

The Structure of an Atom

An atom consists of a very small, positively charged nucleus, surrounded by orbiting electrons.

- The number of protons is the atom's **atomic number Z** .
- The **atomic mass number A** is the number of protons + the number of neutrons.



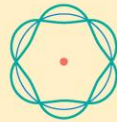
The Bohr Atom

In Bohr's model,

- The atom can exist in only certain **stationary states**. These states correspond to different electron orbits. Each state is numbered by **quantum number $n = 1, 2, 3, \dots$** .
- Each state has a discrete, well-defined energy E_n .
- The atom can change its energy by undergoing a **quantum jump** between two states by emitting or absorbing a photon of energy $E_{\text{photon}} = \Delta E_{\text{atom}} = |E_f - E_i|$.

The Hydrogen Atom

In **Bohr's model of the hydrogen atom** the stationary states are found by requiring an integer number of de Broglie wavelengths to fit around the circumference of the electron's orbit: $2\pi r = n\lambda$. The integer n is the **principal quantum number**.



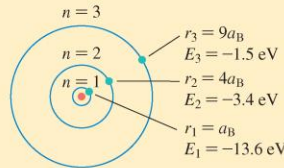
This leads to energy quantization with

$$E_n = -\frac{13.60 \text{ eV}}{n^2}$$

and orbit radii $r_n = n^2 a_B$, where $a_B = 0.053 \text{ nm}$ is the **Bohr radius**.

The wavelengths of light in the hydrogen atom spectrum are given by the **Balmer formula**:

$$\lambda_{n \rightarrow m} = \frac{91.1 \text{ nm}}{\left(\frac{1}{m^2} - \frac{1}{n^2}\right)} \quad \begin{matrix} m = 1, 2, 3, \dots \\ n = m + 1, m + 2, \dots \end{matrix}$$

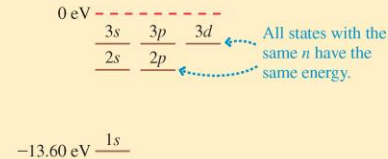


Beyond the Bohr model, quantum mechanics adds other quantized parameters, each with its own quantum number:

- The **orbital angular momentum**, quantum number l :
$$L = \sqrt{l(l+1)}\hbar \quad l = 0, 1, 2, 3, \dots, n-1$$
- The **angle of the electron's orbit**, quantum number m :
$$m = -l, -l+1, \dots, 0, \dots, l-1, l$$
- The **direction of the electron spin**, quantum number m_s :

$$m_s = -\frac{1}{2} \text{ or } +\frac{1}{2}$$

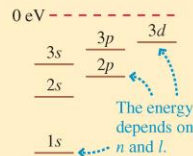
The energy of a hydrogen atom depends only on n :



Multielectron atoms

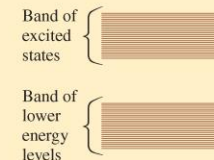
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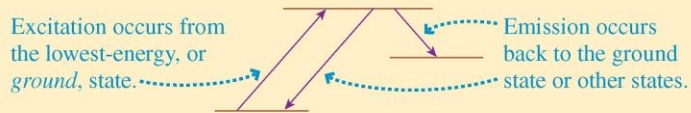
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Summary

APPLICATIONS

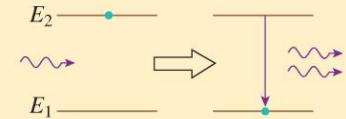
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