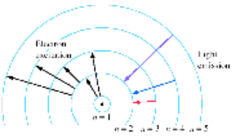
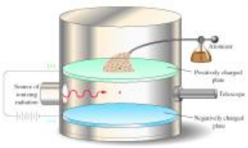
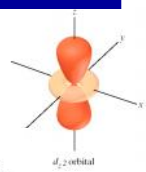
Chapter Seven

Atomic Structure

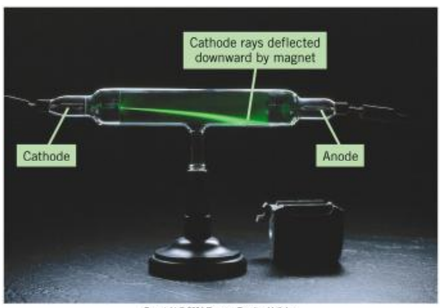






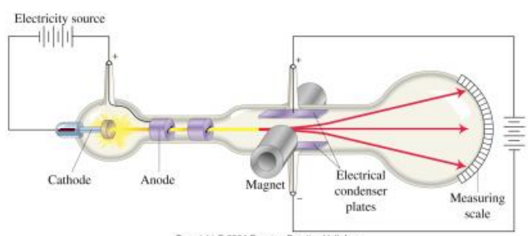
History: The Classic View of Atomic Structure

Cathode Ray Tube



Investigating Cathode Rays

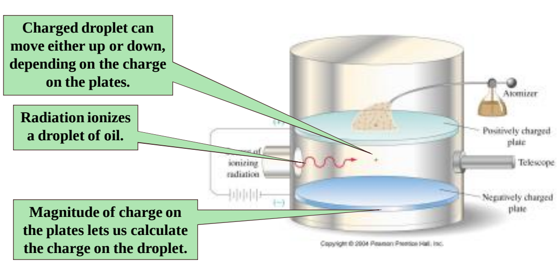
J. J. Thomson used the deflection of cathode rays and the magnetic field strength together, to find the cathode ray particle's ***mass-to-charge ratio***: $m_e/e = -5.686 \times 10^{-12}$ kg/C



Millikan's Oil Drop Experiment

- George Stoney: names the cathode-ray particle the ***electron.***
- Robert Millikan: determines a value for the electron's charge:

$$e = -1.602 \times 10^{-19}\ \text{C}$$



Properties of the Electron

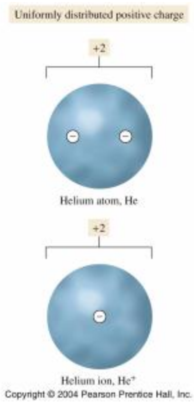
- Thomson determined the mass-to-charge ratio; Millikan found the charge; we can now find the mass of an electron:

$$\mathbf{m_e = 9.109 \times 10^{-31}\ kg/electron}$$

- This is almost *2000 times less* than the mass of a hydrogen atom (1.79×10^{-27} kg)
- Some investigators thought that cathode rays (electrons) were negatively charged ***ions***.
- But the mass of an electron is shown to be *much smaller* than even a hydrogen atom, so an electron cannot be an ion.
- Since electrons are the same regardless of the cathode material, these tiny particles must be a negative part of ***all*** matter.

J. J. Thomson's Model of the Atom

- Thomson proposed an atom with a positively charged sphere containing equally spaced electrons inside.
- He applied this model to atoms with up to 100 electrons.



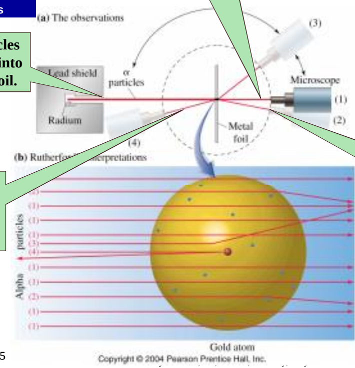
Alpha Scattering Experiment:
Rutherford's observations

Most of the alpha particles passed *through* the foil.

Alpha particles were "shot" into thin metal foil.

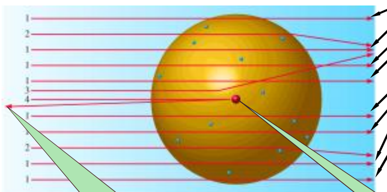
A *very* few "bounced back" to the source!

A few particles were *deflected slightly* by the foil.



Alpha Scattering Experiment:
Rutherford's conclusions

If Thomson's model of the atom was correct, most of the alpha particles should have been deflected a little, like bullets passing through a cardboard target.



Most of the alpha particles passed *through* the foil => An atom must be mostly empty space.

A *very* few alpha particles bounced back => The nucleus must be very small and massive.

The nucleus is *far* smaller than is suggested here.

Protons and Neutrons

- Rutherford's experiments also told him the amount of ***positive*** nuclear charge.
- The positive charge was carried by particles that were named ***protons.***
- The proton charge was the fundamental unit of positive charge.
- The nucleus of a hydrogen atom consists of a single proton.
- Scientists introduced the concept of ***atomic number***, which represents the number of protons in the nucleus of an atom.
- James Chadwick discovered ***neutrons*** in the nucleus, which have nearly the same mass as protons but are uncharged.

Mass Spectrometry

- Research into cathode rays showed that a cathode-ray tube also produced ***positive*** particles.
- Unlike cathode rays, these positive particles *were* ions.
- The metal of the cathode: M → e^- + M^+

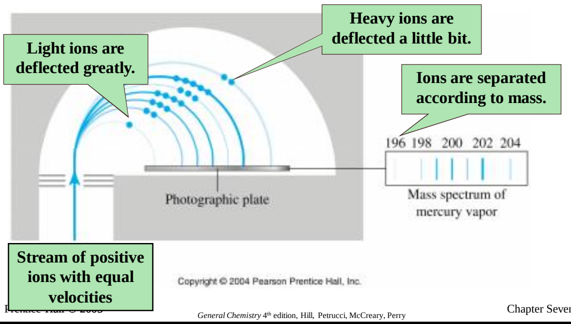
***Positive* particles**

Cathode rays

Mass Spectrometry (cont'd)

- In ***mass spectrometry*** a stream of positive ions having equal velocities is brought into a magnetic field.
- All the ions are deflected from their straight line paths.
- The lightest ions are deflected the most; the heaviest ions are deflected the least.
- The ions are thus separated by ***mass***.
  - Actually, separation is by *mass-to-charge ratio (m/e)*, but the mass spectrometer is designed so that most particles attain a 1+ charge.

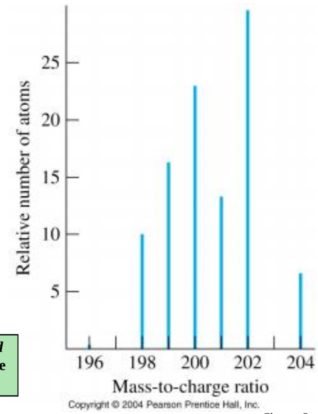
A Mass Spectrometer



A Mass Spectrum for Mercury

Mass spectrum of an *element* shows the abundance of its isotopes. What are the three most abundant isotopes of mercury?

Mass spectrum of a *compound* can give information about the structure of the compound.



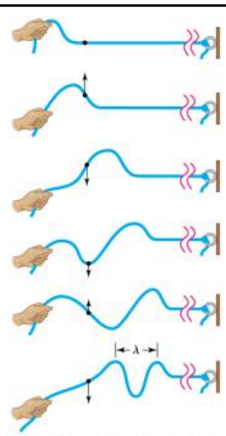
Light and the Quantum Theory

The Wave Nature of Light

- ***Electromagnetic waves*** originate from the movement of electric charges.
- The movement produces fluctuations in electric and magnetic fields.
- Electromagnetic waves require no medium.
- Electromagnetic radiation is characterized by its ***wavelength***, ***frequency***, and ***amplitude***.

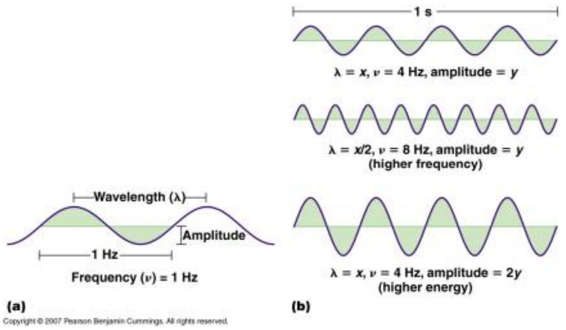
Simple Wave Motion

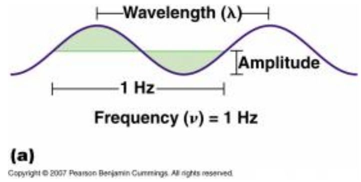
Notice that the rope moves only up-and-down, not from left-to-right.

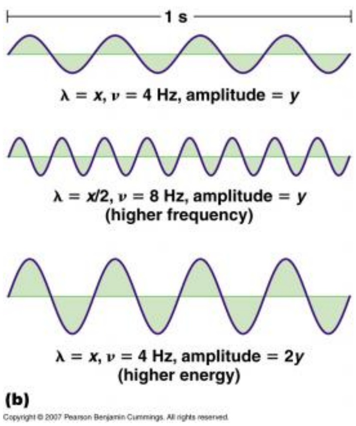


(a) Circular waves

(b) Linear waves

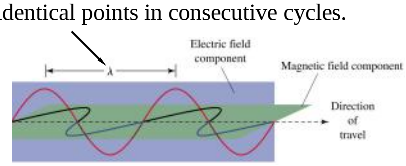






Wavelength and Frequency

- ***Wavelength*** (λ) is the distance between any two identical points in consecutive cycles.



- ***Frequency*** (*ν*) of a wave is the number of cycles of the wave that pass through a point in a unit of time. Unit = waves/s or s^{-1} (***hertz***).

Wavelength and Frequency

The relationship between wavelength and frequency:

$$c = \lambda \nu$$

where *c* is the speed of light (3.00×10^8 m/s)
(2.99792458×10^8)m/s

Example 7.1

Calculate the frequency of an X ray that has a wavelength of 8.21 nm.

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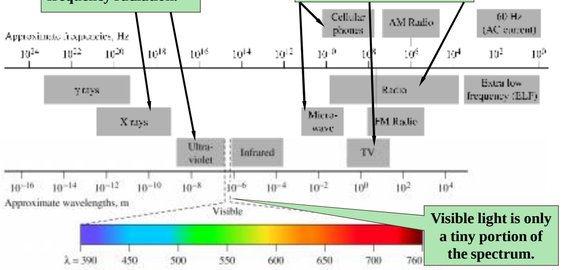
The Electromagnetic Spectrum

UV, X rays are *shorter* wavelength, *higher* frequency radiation.

Communications involve *longer* wavelength, *lower* frequency radiation.



Visible light is only a tiny portion of the spectrum.

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Example 7.2 A Conceptual Example

Which light has the higher frequency: the bright red brake light of an automobile or the faint green light of a distant traffic signal?

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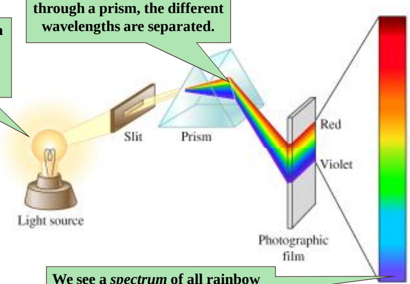
A *Continuous* Spectrum

White light from a lamp contains all wavelengths of visible light.

When that light is passed through a prism, the different wavelengths are separated.



We see a *spectrum* of all rainbow colors from red to violet – a *continuous* spectrum.

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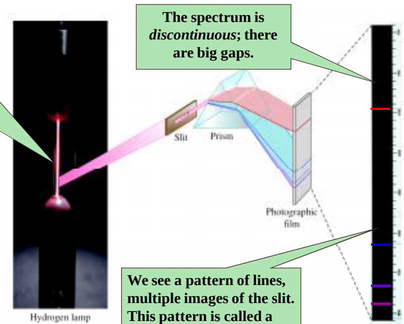
A *Line* Spectrum

Light from an electrical discharge through a gaseous element (e.g., neon light, hydrogen lamp) does *not* contain all wavelengths.

The spectrum is *discontinuous*; there are big gaps.



We see a pattern of lines, multiple images of the slit. This pattern is called a *line spectrum*. (duh!)

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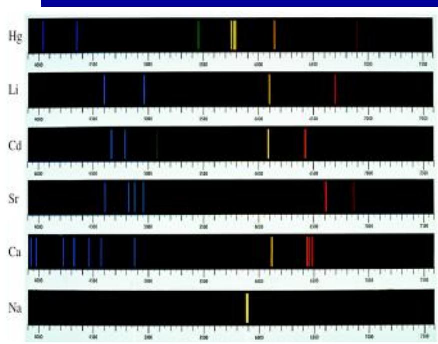
Line Spectra of Some Elements



The line emission spectrum of an element is a "fingerprint" for that element, and can be used to identify the element!

How might you tell if an ore sample contained mercury? Cadmium?

Line spectra are a problem; they can't be explained using classical physics …

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Planck …

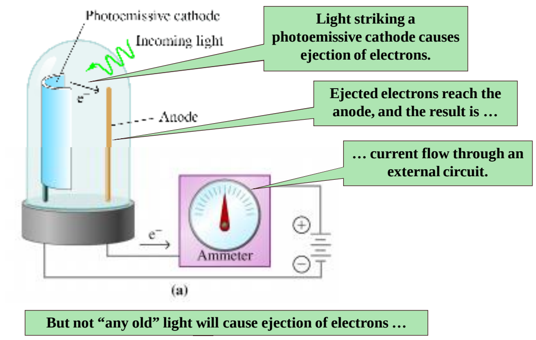
- … proposed that atoms could absorb or emit electromagnetic energy only in ***discrete amounts***.
- The smallest amount of energy, a ***quantum***, is given by:

$$E = h\nu$$

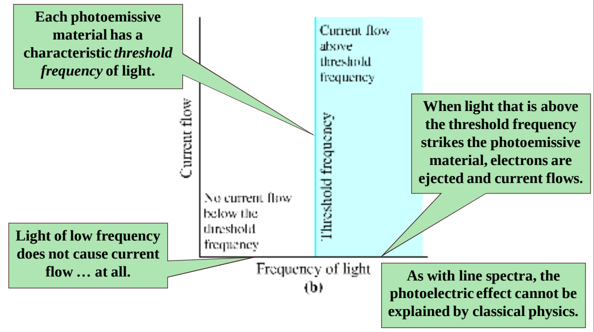
where **Planck's constant,** *h*, has a value of 6.626×10^{-34} J·s.

- Planck's quantum hypothesis states that energy can be absorbed or emitted only as a *quantum* or as *whole multiples* of a quantum, thereby making variations of energy *discontinuous*.
- Changes in energy can occur only in ***discrete*** amounts.
- ***Quantum*** is to ***energy*** as **atomization** is to ***matter***.

The Photoelectric Effect(光電效應)



The Photoelectric Effect (cont'd)



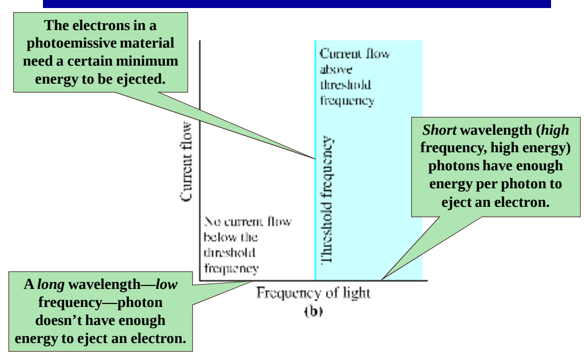
The Photoelectric Effect

- Albert Einstein won the 1921 Nobel Prize in Physics for explaining the photoelectric effect.
- He applied Planck's quantum theory: electromagnetic energy occurs in little "packets" he called ***photons***.

  Energy of a photon (E) = $h\nu$

- The photoelectric effect arises when photons of light striking a surface transfer their energy to surface electrons.
- The energized electrons can overcome their attraction for the nucleus and escape from the surface …
- … but an electron can escape ***only*** if the photon provides ***enough*** energy.

The Photoelectric Effect Explained



Example 7.3

Calculate the energy, in joules, of a photon of violet light that has a frequency of 6.15×10^{14} s^{-1}.

Example 7.4

A laser produces red light of wavelength 632.8 nm. Calculate the energy, in kilojoules, of 1 mol of photons of this red light.

Quantum View of Atomic Structure

Bohr's Hydrogen Atom

- Niels Bohr followed Planck's and Einstein's lead by proposing that electron energy (E_n) was quantized.
- The electron *in an atom* could have only certain allowed values of energy (just as energy itself is quantized).
- Each specified energy value is called an ***energy level*** of the atom:

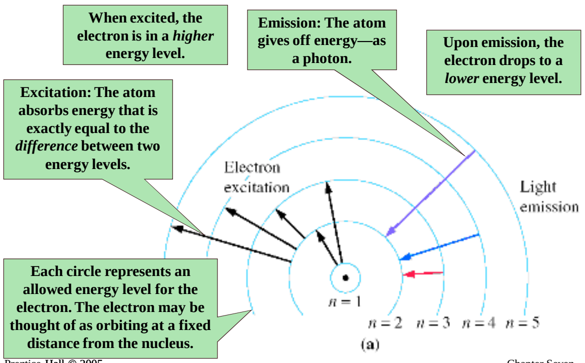
$$E_n = -B/n^2$$

  - n is an integer, and B is a constant (2.179×10^{-18} J)
  - The ***negative*** sign represents force of ***attraction***.
- The energy is zero when the electron is located infinitely far from the nucleus.

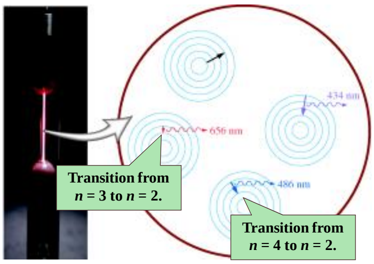
Example 7.5

Calculate the energy of an electron in the second energy level of a hydrogen atom.

The Bohr Model of Hydrogen



Line Spectra Arise Because …



- … each electronic energy level in an atom is quantized.
- Since the ***levels*** are quantized, ***changes*** between levels must ***also*** be quantized.
- A specific change thus represents one specific energy, one specific frequency, and therefore one specific wavelength.

Bohr's Equation …

- … allows us to find the energy change (ΔE_{level}) that accompanies the transition of an electron from one energy level to another.

Initial energy level:

$$E_i = \frac{-B}{n_i^2}$$

Final energy level:

$$E_f = \frac{-B}{n_f^2}$$

- To find the energy *difference*, just subtract:

$$\Delta E_{level} = \frac{-B}{n_f^2} - \frac{-B}{n_i^2} = B\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$

- Together, all the photons having this energy (ΔE_{level}) produce one spectral line.

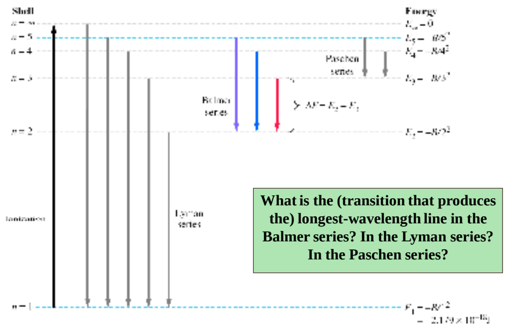
Example 7.6

Calculate the energy change, in joules, that occurs when an electron falls from the $n_i = 5$ to the $n_f = 3$ energy level in a hydrogen atom.

Example 7.7

Calculate the frequency of the radiation released by the transition of an electron in a hydrogen atom from the $n = 5$ level to the $n = 3$ level, the transition we looked at in Example 7.6.

Energy Levels and Spectral Lines for Hydrogen



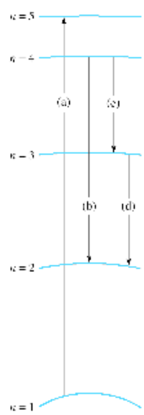
What is the (transition that produces the) longest-wavelength line in the Balmer series? In the Lyman series? In the Paschen series?

Ground States and Excited States

- When an atom has its electrons in their lowest possible energy levels, the atom is in its ***ground state.***
- When an electron has been promoted to a higher level, the electron (and the atom) is in an ***excited state.***
- Electrons are promoted to higher levels through an electric discharge, heat, or some other source of energy.
- An atom in an excited state eventually emits a photon (or several) as the electron drops back down to the ground state.

Example 7.8
A Conceptual Example

Without doing detailed calculations, determine which of the four electron transitions shown in Figure 7.19 produces the shortest-wavelength line in the hydrogen emission spectrum.



De Broglie's Equation

- Louis de Broglie's hypothesis stated that an object in motion behaves as both *particles* and *waves*, just as light does.
- A particle with mass *m* moving at a speed *v* will have a wave nature consistent with a wavelength given by the equation:

$$\lambda = h/mv$$

- This wave nature is of importance only at the microscopic level (tiny, tiny *m*).
- De Broglie's prediction of matter waves led to the development of the electron microscope.

Example 7.9

Calculate the wavelength, in meters and nanometers, of an electron moving at a speed of 2.74×10^6 m/s. The mass of an electron is 9.11×10^{-31} kg, and 1 J = 1 kg m^2 s^{-2}.

Uh oh …

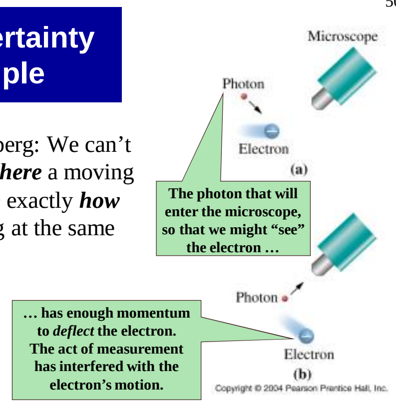
- de Broglie just messed up the Bohr model of the atom.
- Bad: An electron can't orbit at a "fixed distance" if the electron is a wave.
  - An ocean wave doesn't have an exact location—neither can an electron wave.
- Worse: We can't even talk about "where the electron is" if the electron is a wave.
- Worst: The wavelength of a moving electron is roughly the size of an atom! How do we describe an electron that's too big to be "in" the atom??

Wave Functions

- Erwin Schrödinger: We can describe the electron *mathematically*, using ***quantum mechanics*** (wave mechanics).
- Schrödinger developed a ***wave equation*** to describe the hydrogen atom.
- An acceptable solution to Schrödinger's wave equation is called a ***wave function.***
- A wave function represents an energy state of the atom.

The Uncertainty Principle

Werner Heisenberg: We can't know exactly ***where*** a moving particle is AND exactly ***how fast*** it is moving at the same time.



The Uncertainty Principle

- A wave function doesn't tell us where the electron ***is***. The uncertainty principle tells us that we ***can't*** know where the electron is.
- However, the square of a wave function gives the ***probability*** of finding an electron at a given location in an atom.
- Analogy: We can't tell where a single leaf from a tree will fall. But (by viewing all the leaves under the tree) we can describe where a leaf is ***most likely*** to fall.

Quantum Numbers(量子數) and Atomic Orbitals(原子軌域)

- The wave functions for the hydrogen atom contain three parameters called ***quantum numbers*** that must have specific integral values.
- A wave function with a given set of these three quantum numbers is called an ***atomic orbital***.
- These orbitals allow us to visualize the region in which the electron "spends its time."

Quantum Numbers: *n*

When values are assigned to the three quantum numbers, a specific atomic orbital has been defined.

The ***principal quantum number (n)***:主量子數

- Is independent of the other two quantum numbers.
- Can only be a positive integer ($n = 1, 2, 3, 4, \ldots$)
- The ***size*** of an orbital and its electron energy depend on the value of *n.*
- Orbitals with the same value of *n* are said to be in the same ***principal shell***.主層

Quantum Numbers: *l*

The ***orbital angular momentum quantum number (l)***:第二量子數；角動量量子數

- Determines the ***shape*** of the orbital.
- Can have positive integral values from 0, 1, 2, … ($n - 1$)
- Orbitals having the same values of *n* and of *l* are said to be in the same ***subshell***.次層

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

- Each orbital designation represents a different region of space and a different shape.

Quantum Numbers: m_l

The ***magnetic quantum number (m_l)***:磁量子數

- Determines the ***orientation*** in space of the orbitals of any given type in a subshell.
- Can be any integer from $-l$ to $+l$
- The number of possible values for m_l is $(2l + 1)$, and this determines the number of orbitals in a subshell.

Table 7.1 Electronic Shells, Orbitals, and Quantum Numbers

Principal Shell	First	Second				Third								
n	1	2	2	2	2	3	3	3	3	3	3	3	3	3
l	0	0	1	1	1	0	1	1	1	2	2	2	2	2
m_l	0	0	−1	0	+1	0	−1	0	−1	−2	−1	0	+1	+2
Subshell and orbital designation	1s	2*s*	2*p*	2*p*	2*p*	3s	3*p*	3*p*	3*p*	3*d*	3*d*	3*d*	3*d*	3*d*
Number of orbitals in the subshell	1	1		3		1		3				5		

Notice: **one** *s* orbital in each principal shell

three *p* orbitals in the second shell (and in higher ones)

five *d* orbitals in the third shell (and in higher ones)

Example 7.10

Considering the limitations on values for the various quantum numbers, state whether an electron can be described by each of the following sets. If a set is not possible, state why not.

(a) $n = 2, l = 1, m_l = -1$ **(c)** $n = 7, l = 3, m_l = +3$

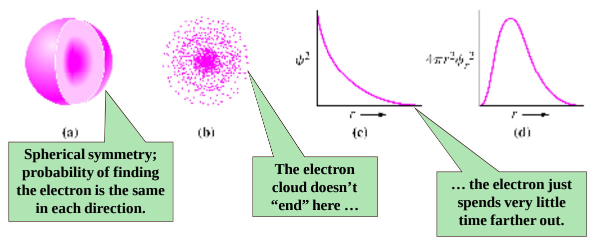
(b) $n = 1, l = 1, m_l = +1$ **(d)** $n = 3, l = 1, m_l = -3$

Example 7.11

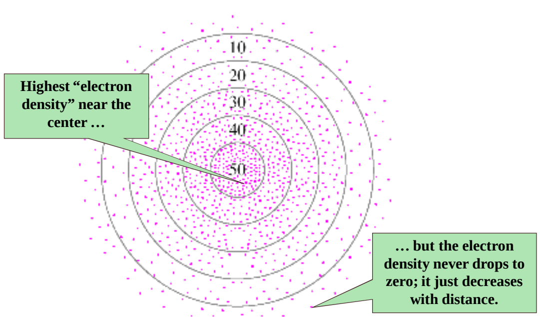
Consider the relationship among quantum numbers and orbitals, subshells, and principal shells to answer the following. **(a)** How many orbitals are there in the 4*d* subshell? **(b)** What is the first principal shell in which *f* orbitals can be found? **(c)** Can an atom have a 2*d* subshell? **(d)** Can a hydrogen atom have a 3*p* subshell?

The 1s Orbital

- The 1*s* orbital ($n = 1$, $l = 0$, $m_l = 0$) has *spherical* symmetry.
- An electron in this orbital spends most of its time near the nucleus.

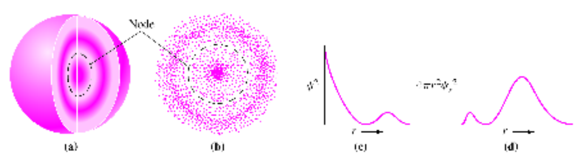


Analogy to the 1s Orbital

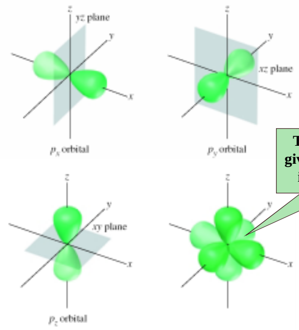


The 2s Orbital

- The 2*s* orbital has two concentric, spherical regions of high electron probability.
- The region near the nucleus is separated from the outer region by a ***node***—a region (a spherical shell in this case) in which the electron probability is zero.

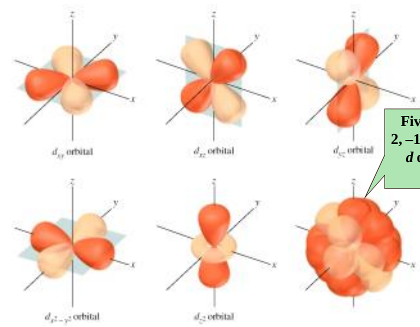


The Three *p* Orbitals



Three values of m_l gives three *p* orbitals in the *p* subshell.

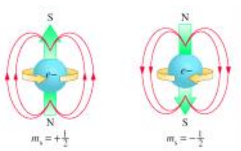
The Five *d* Orbitals



Five values of m_l (–2, –1, 0, 1, 2) gives five *d* orbitals in the *d* subshell.

Electron Spin: m_s

- The ***electron spin quantum number (m_s)* 旋量子數**, explains some of the finer features of atomic emission spectra.
- The number can have two values: +½ and –½.

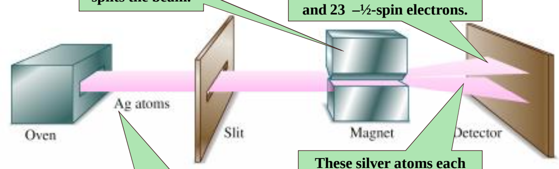


- The spin refers to a magnetic field induced by the moving electric charge of the electron as it spins.
- The magnetic fields of two electrons with opposite spins cancel one another; there is no net magnetic field for the pair.

The Stern-Gerlach Experiment Demonstrates Electron Spin

The magnet splits the beam.

These silver atoms each have 24 +½-spin electrons and 23 –½-spin electrons.



Silver has 47 electrons (odd number). On average, 23 electrons will have one spin, 24 will have the opposite spin.

These silver atoms each have 23 +½-spin electrons and 24 –½-spin electrons.

CUMULATIVE EXAMPLE

Which will produce more energy per gram of hydrogen: H atoms undergoing an electronic transition from the level $n = 4$ to the level $n = 1$, or hydrogen gas burned in the reaction:

$$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)?$$