

Special Relativity

Newton's laws of motion give us a complete description of the behaviour of moving objects in daily life.

However, subjects moving at very high speed behave differently and no longer abide by Newton's laws!

The trouble is that, when something travels at a speed comparable to the speed of light, we need to take into account of the time for the light to travel between the object and observer. The concept of simultaneity is in doubt. Space and time have to be defined more generally to explain events happening under the circumstances.

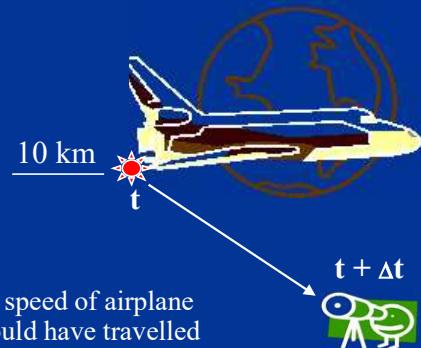
Light speed: $c=3\times 10^8 \text{ m}\cdot\text{s}^{-1}$, Sound speed: $v=350 \text{ m}\cdot\text{s}^{-1}$

If an airplane, travelling at sound speed and 10 km above ground, flashes a light at time t , it takes

$$\Delta t = 10000 / 3\times 10^8 = 3\times 10^{-5} \text{ s}$$

for the light to travel to an observer on the ground.

In 3×10^{-5} s, the airplane travels $350\times 3\times 10^{-5}=0.01$ m. However, if the speed of airplane were 1/3 of the light speed, i.e. $v=1\times 10^8 \text{ m}\cdot\text{s}^{-1}$, then in 3×10^{-5} s, it would have travelled $1\times 10^8\times 3\times 10^{-5}=3000$ m ! (so, the position we see is actually 3000 m away from the real position ! We now have a problem with "simultaneous").



Frames of Reference (參考座標系)

Something, with which you can compare to see if your position is changing.

Physically speaking, reference frame is a coordinate system that allows description of time and position of points relative to a body.

Inertial frames of reference are the ones in which Newton's first law holds. Any frame of reference that is stationary or moves at constant velocity relative to an inertial frame is itself an inertial frame.

There is no such thing as an absolute frame of reference in our universe.

By saying *absolute*, what is actually meant is that there is no place in the universe that is completely stationary. This statement says that since everything is moving, all motion is relative. The earth itself is moving, so even though you are standing still, you are in motion. You are moving through both space and time at all times. Because there is no place or object in the universe that is stationary.

Special Relativity is applied only when the events happened in inertial frames of reference.

Postulates of Special Relativity

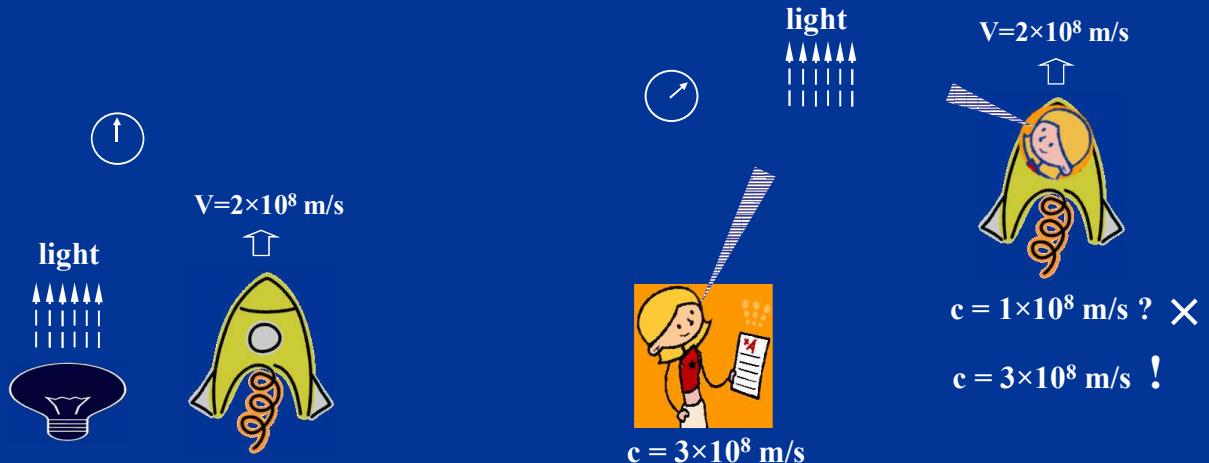
- The first, the principle of relativity, states:

The laws of Physics are the same in all inertial frames of reference.

- The second is based on the results of many experiments and it states:

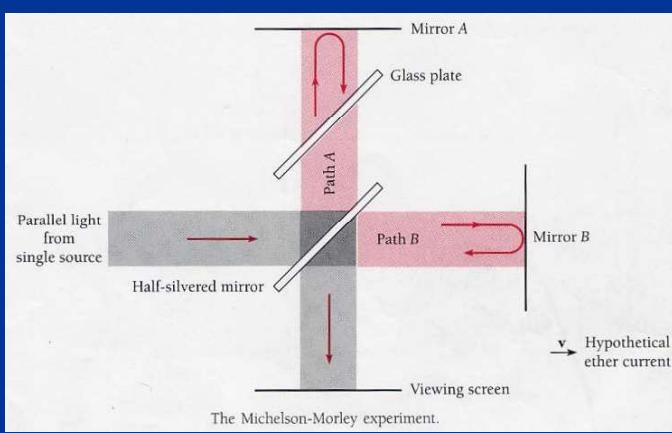
The speed of light in free space has the same value in all inertial frames of reference.

This speed is about 3×10^8 m/s.



The Michelson-Morley experiment

In 19th century, scientists believed there existed a mysterious medium called “ether”, in which light waves were assumed to occur. This experiment was to look for the earth’s motion through “ether”.



The result:

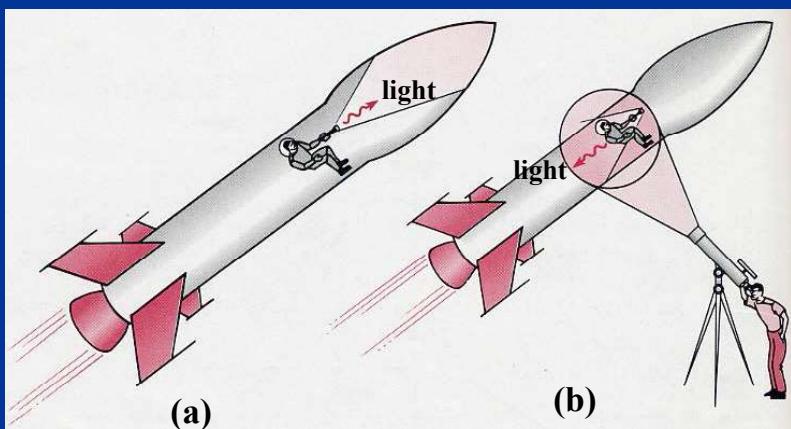
no ether drift was found.

However, the negative result had two consequences:

- It showed that ether does not exist and so there is no such thing as “absolute motion” relative to either.
- It showed that the speed of light is the same for all observers, which is not true of waves that need a material medium in which to occur (like sound and water waves).

The Ultimate Speed Limit

From the two postulates of special relativity, it follows that **nothing can move faster than the speed of light in free space**



A flashlight is switched on in a spacecraft assumed to be moving relative to the earth in a speed faster than light.

- (a) A person in the spacecraft will see the light goes to the front of the spacecraft. (the speed of light in the spacecraft frame is still 3×10^8 m/s — the second postulate)
- (b) A person on the ground will see the light goes to the back of the spacecraft. (the spacecraft is assumed to be moving faster than light, therefore the light is falling behind the spacecraft)

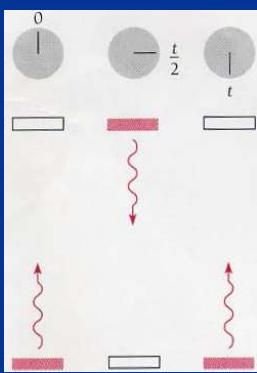
This is against the first postulate that the laws of Physics are the same in all inertial frames of reference, so the speed of light is the ultimate speed limit in free space.

Time dilation (時間擴張)

Measurement of time intervals are affected by the relative motion between an observer and what is observed

A moving clock ticks more slowly than a clock at rest.

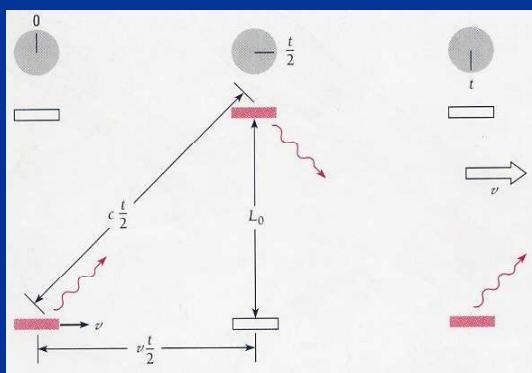
How ?



The light-pulse clock at rest on the ground as seen by an observer on the ground. The dial represent a conventional clock on the ground.

If the time interval between ticks is t_0 ,

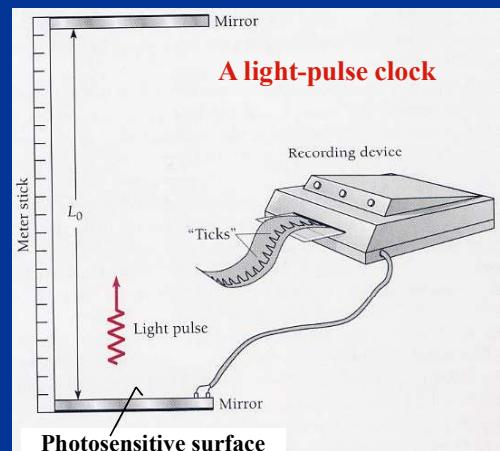
$$\text{then } t_0 = \frac{2L_0}{c}$$



The light-pulse clock in a spacecraft as seen by an observer on the ground. The mirrors are parallel to the direction of motion of the spacecraft. The dial represent a conventional clock on the ground.

If the time interval between ticks is t , the light pulse takes $t/2$ to travel from the bottom to the top mirrors and in this time interval, the light pulse also travels a horizontal distance of $v \cdot (t/2)$ due to the motion of spacecraft.

So, the actual distance of light pulse travels in $t/2$ is: $c \cdot \frac{1}{2}t = \sqrt{L_0^2 + (v \cdot \frac{1}{2}t)^2}$



$$\mathbf{c} \cdot \frac{1}{2} \mathbf{t} = \sqrt{\mathbf{L}_0^2 + (\mathbf{v} \cdot \frac{1}{2} \mathbf{t})^2} \Rightarrow \mathbf{c}^2 \cdot \frac{1}{4} \mathbf{t}^2 = \mathbf{L}_0^2 + \mathbf{v}^2 \cdot \frac{1}{4} \mathbf{t}^2 \Rightarrow \mathbf{t}^2 = \frac{4\mathbf{L}_0^2}{\mathbf{c}^2 - \mathbf{v}^2} \Rightarrow \mathbf{t} = \frac{2\mathbf{L}_0/\mathbf{c}}{\sqrt{1 - \mathbf{v}^2/\mathbf{c}^2}}$$

Substitute $\mathbf{t}_0 = \frac{2\mathbf{L}_0}{\mathbf{c}}$, which is the time interval on clock at rest, into above equation:

$$\text{We have, } \mathbf{t} = \frac{\mathbf{t}_0}{\sqrt{1 - \mathbf{v}^2/\mathbf{c}^2}}$$

t_0 is the time interval on the clock at rest relative to an observer and is called as **proper time** (特徴時間).

t is the time interval on the clock in motion relative to an observer.

v is the speed of relative motion to the observer.

c is the speed of light,

Because $c > v$, $\sqrt{1 - v^2/c^2}$ is always smaller than 1. Therefore: $t > t_0$

—A moving clock ticks more slowly than a clock at rest

Doppler Effect of Light

A verification of time dilation

When the source of a wave is moving, the frequency of the wave changes. In the case of sound, we can hear the change in pitch. This is familiar to us.

$$\text{Doppler effect in sound: } v = v_0 \left(\frac{1 + v/s}{1 - V/s} \right)$$

Here, v = frequency heard by observer, v_0 = source frequency

s = speed of sound

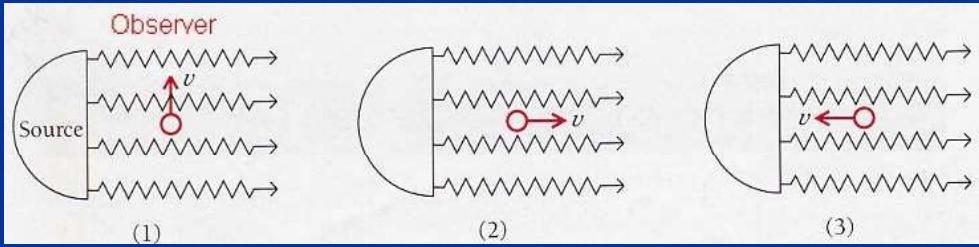
v = speed of observer (+/- for motion towards/away from the source)

V = speed of source (+/- for motion towards/away from the observer)

The Doppler effect in sound depends on whether the source, observer, or both are moving. Sound waves have to travel in a medium such as air or water, and this medium is itself a frame of reference in which the motions of source and observers are both measured.

However, in the case of light, no medium is involved and only the relative motions between the source and observer is meaningful. So we expect something different for Doppler effect in light.

How does the frequency change if there is a relative motion of light source and observer ?



Considering a light source as a clock that ticks ν_0 times per second and emits a wave of light with each click.

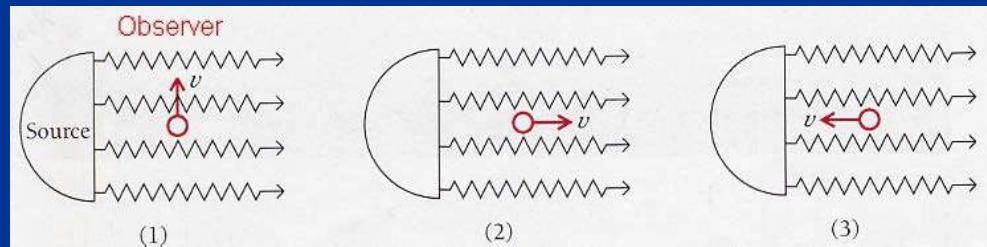
- (1) Observer moving perpendicular to the light

In the reference frame of light source, the interval between ticks is $t_0 = 1/\nu_0$. However, in the reference frame of observer, t_0 corresponds to a period of time $\mathbf{t} = t_0 / \sqrt{1 - \mathbf{v}^2/c^2} = 1/\nu_0 \sqrt{1 - \mathbf{v}^2/c^2}$.

So, the frequency in the observer's frame of reference is:

$$\nu = 1/\mathbf{t} = \nu_0 \sqrt{1 - \mathbf{v}^2/c^2}$$

In the transverse Doppler effect of light, the observed frequency ν is always lower than the source frequency ν_0 .



- (2) Observer moving away from the light source

$$\leftarrow c \cdot t \rightarrow \leftarrow \mathbf{v} \cdot t \rightarrow$$

Now the observer travels a distance $\mathbf{v} \cdot t$ away from the source between the ticks, which means that the light wave from a given tick takes $(\mathbf{v} \cdot t)/c$ longer to reach the observer. Hence, the total time between the arrival of the successive waves is:

$$\mathbf{T} = \mathbf{t} + \mathbf{v} \cdot \mathbf{t} / c = \mathbf{t}(1 + \mathbf{v}/c) = \mathbf{t}_0 \frac{1 + \mathbf{v}/c}{\sqrt{1 - \mathbf{v}^2/c^2}} = \mathbf{t}_0 \frac{\sqrt{1 + \mathbf{v}/c} \sqrt{1 + \mathbf{v}/c}}{\sqrt{1 + \mathbf{v}/c} \sqrt{1 - \mathbf{v}/c}} = \mathbf{t}_0 \sqrt{\frac{1 + \mathbf{v}/c}{1 - \mathbf{v}/c}}$$

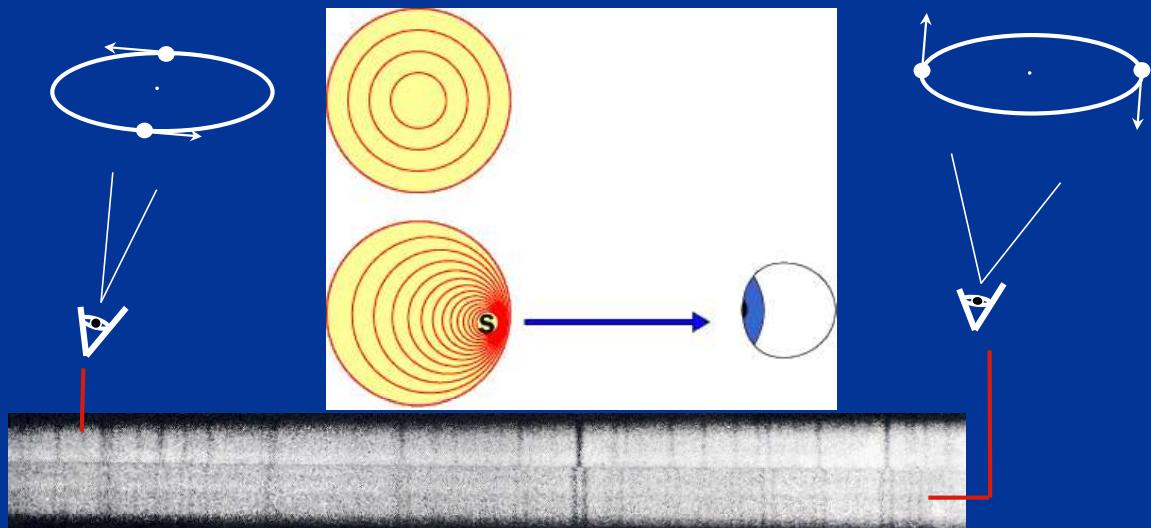
$$\text{The observed frequency } \nu = \frac{1}{\mathbf{T}} = \frac{1}{\mathbf{t}_0} \sqrt{\frac{1 - \mathbf{v}/c}{1 + \mathbf{v}/c}} = \nu_0 \sqrt{\frac{1 - \mathbf{v}/c}{1 + \mathbf{v}/c}}$$

- (3) Observer moving toward the light source

$$\mathbf{T} = \mathbf{t} - \mathbf{v} \cdot \mathbf{t} / c \quad \nu = \nu_0 \sqrt{\frac{1 + \mathbf{v}/c}{1 - \mathbf{v}/c}}$$

In the longitudinal Doppler effect of light

$$v = \begin{cases} v_0 \sqrt{\frac{1-v/c}{1+v/c}} & \text{Moving away from the light source} \\ v_0 \sqrt{\frac{1+v/c}{1-v/c}} & \text{Moving towards the light source} \end{cases}$$



The expanding Universe

The Doppler effect in light is an important tool in astronomy. Stars emit light of characteristic wavelengths called spectral lines, and motion of a star towards or away from the earth shows up as a Doppler shift in its spectrum. All distant galaxies of stars are found to shift towards the lower frequency, i.e. red side of the spectrum, and hence called “red shift”. Such shifts indicate the galaxies are moving away from us and from one another, that is the universe is expanding.

Length Contraction

Measurements of lengths are also affected by the relative motion. The length \mathbf{L} of an object in motion with respect to an observer always appears to the observer to be shorter than its length \mathbf{L}_0 when it is at rest. The length \mathbf{L}_0 of an object in its rest frame is called **proper length** of the object.

Here we'll show how this happen according to the time dilation and the principle of relativity.

Facts about muons in cosmic-ray:

- have speeds of about 2.994×10^8 m/s ($0.998c$)
- reach earth's surface (sea level) at 1 per centimeter squared per minute
- unstable with average lifetime of $t_0 = 2.2 \mu s$

In the lifetime of a muon, it can only travel:

$$\mathbf{v} \cdot \mathbf{t} = (2.994 \times 10^8 \text{ m/s}) \times (2.2 \times 10^{-6} \text{ s}) = 0.66 \text{ km}$$

How can the muons reach the earth surface from the sky (~10 km above) ?

To resolve the paradox, we note that the muon lifetime of $t_0 = 2.2 \mu s$ is what an observer at rest with respect to a muon would find. Because the muons are traveling **very rapidly** at the speed of $0.998c$, their lifetimes are extended in our frame of reference (i.e, earth) by time dilation:

$$\mathbf{t} = \frac{\mathbf{t}_0}{\sqrt{1 - \mathbf{v}^2/\mathbf{c}^2}} = \frac{2 \cdot 2 \times 10^{-6}}{\sqrt{1 - (0.998\mathbf{c})^2/\mathbf{c}^2}} = 34.8 \times 10^{-6} \text{ s} = 34.8 \mu s$$

In $34.8 \mu s$, a muon moving at speed of $0.998c$ will travel the distance:

$$\mathbf{v} \cdot \mathbf{t} = (2.994 \times 10^8 \text{ m/s}) \times (34.8 \times 10^{-6} \text{ s}) = 10.4 \text{ km}, \text{ and therefore can reach the earth.}$$

What if somebody were travelling with the muon at $\mathbf{v} = 0.998c$, so that to him/her the muon is at rest? The observer and the muon are now in the same frame of reference and in this frame, the muon's lifetime is only $2.2 \mu s$. To the observer in this frame, muons can travel only 0.66 km before decaying. However, according to the principle of relativity, muons do reach the surface of earth. (because they do in the earth frame of reference.) The only way to account for this is that to the observer in the moving frame of reference, the distance it travels is shortened to 0.66 km, i.e. by a factor of $\sqrt{1 - \mathbf{v}^2/\mathbf{c}^2}$.

So, the length contraction for a moving object at speed \mathbf{v} is:
$$\mathbf{L} = \mathbf{L}_0 \sqrt{1 - \mathbf{v}^2/\mathbf{c}^2}$$

—*Faster means shorter*

Summary of last lecture:

- Two postulates of special relativity
 - The laws of Physics are the same in all inertial frames of reference.
 - The speed of light in free space has the same value in all inertial frames of reference.
- nothing can move faster than the speed of light in free space
- Time dilation
$$t = \frac{t_0}{\sqrt{1 - v^2/c^2}}$$
- Length contraction
$$L = L_0 \sqrt{1 - v^2/c^2}$$
 (only along the direction of motion)

Relativity of Mass

$$\begin{array}{c} F \\ \longrightarrow \\ \text{---} \end{array} \boxed{\text{m}} \longrightarrow V = (F/m) \cdot t \quad V \text{ increases as } t, \text{ at some point there will be } V > c !$$

We have known that c is the speed limit of universe, so the object's speed can not keep increasing in proportion as more work is done to it.

How about the conservation of energy ? (which is still valid in the world of relativity.)

The explanation is: **the mass of moving subject is changing.**

As the speed increase, so does the mass, so that the work done is turning into kinetic energy even though V never exceeds c .

How does this happen?

Consider two small balls A and B in elastic collision:

- A and B are identical and at rest in the reference frame S and S', respectively.

- Frame S' is moving at constant speed \mathbf{v} with respect to frame S.

At the moment that A and B cross each other in x-axis, A is thrown in the +y direction at the speed V_A , and at the same time B is thrown in the -y' direction at the speed V'_B , where

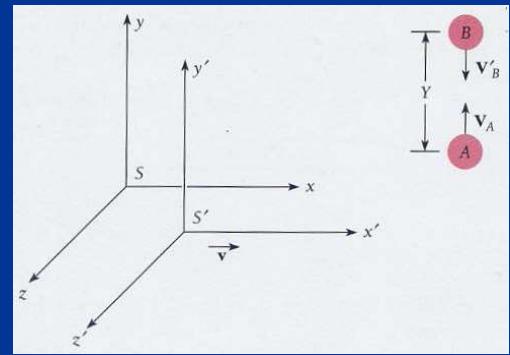
$$V_A = V'_B \quad (1)$$

When A and B collide, A rebounds in the -y direction at the speed V_A , while B rebounds in the +y' direction at the speed V'_B . If A and B are Y apart at beginning, an observer in S finds that the collision occurs at $y=(1/2)Y$. The round-trip time T_0 for A as measured in frame S is therefore:

$$T_0 = \frac{Y}{V_A} \quad (2)$$

The same will be observed for B by someone in S', and

$$T_0 = \frac{Y}{V'_B} \quad (3)$$



If linear momentum is conserved in the S frame, it must be true that

$$m_A V_A = m_B V'_B \quad (4)$$

where m_A and m_B are the mass of A and B, and V_A and V'_B are their speeds as measured in S frame, In S the speed V_B is found from:

$$V_B = \frac{Y}{T} \quad (5)$$

where T is the time for B to make the round-trip as measured in S. But in its own frame S', B's trip time is T_0 , and

$$T = \frac{T_0}{\sqrt{1 - v^2/c^2}} \quad (6)$$

Substitute (6) into (5): $V_B = \frac{Y\sqrt{1 - v^2/c^2}}{T_0} \quad (7)$

From (2), we have $V_A = \frac{Y}{T_0} \quad (8)$

Insert (7) and (8) into (4), i.e. $m_A V_A = m_B V_B$

We have $m_A = m_B \sqrt{1 - v^2/c^2}$, i.e.

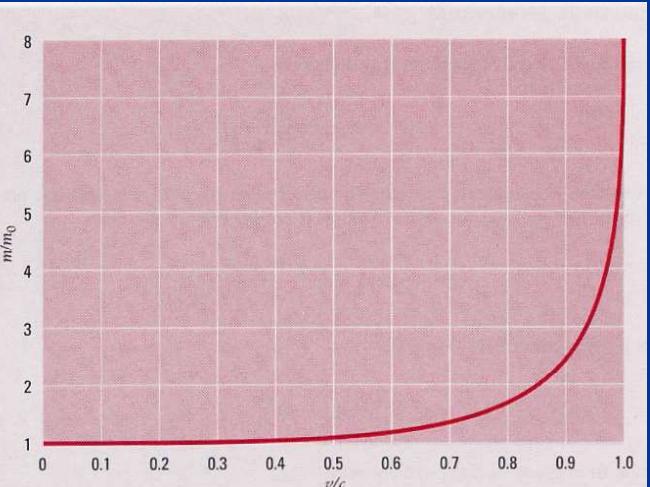
$$m_B = \frac{m_A}{\sqrt{1 - v^2/c^2}}$$

which is the mass of B observed in frame S.

(Note: in its own frame S', $m'_B = m_A$)

If $V_A, V_B \ll v$, we can ignore the motion of A in the frame S and of B in frame S'.

Then, in frame S: $m_A = m_0$ and $m_B = m$ So,



The relativity of mass. Since $m = \infty$ when $v = c$, no material object can equal the speed of light in free space.

$$m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$$

—Rest mass is least

Relativistic momentum

$$p = mv = \frac{m_0 v}{\sqrt{1 - v^2/c^2}}$$

conservation of momentum is valid in special relativity just as in classical physics. However, Newton's second law of motion is correct only in the form

Relativistic second law

$$F = \frac{d}{dt}(mv) = \frac{d}{dt}\left(\frac{m_0 v}{\sqrt{1 - v^2/c^2}}\right)$$

This is *not* equivalent to saying that

$$F = ma = m \frac{dv}{dt}$$

because

$$\frac{d}{dt}(mv) = m \frac{dv}{dt} + v \frac{dm}{dt}$$

and dm/dt does not vanish if the speed of the body varies with time. The resultant force on a body is always equal to the time rate of change of its momentum.

Mass and Energy

$E = mc^2$ is the most famous equation obtained from the postulates of special relativity, which concerns the relation between mass and energy.

Let's see how it works out from what we already learned.

Kinetic energy $KE = \int_0^s F ds$, here $F = \frac{d}{dt}(mv)$, as we just discussed in previous section.

$$\text{So, } KE = \int_0^s \frac{d(mv)}{dt} ds = \int_0^{mv} v d(mv) = \int_0^v v d\left(\frac{m_0 v}{\sqrt{1 - v^2/c^2}}\right)$$

Integrating by parts ($\int x dy = xy - \int y dx$),

$$\begin{aligned} KE &= \frac{m_0 v^2}{\sqrt{1 - v^2/c^2}} - m_0 \int_0^v \frac{v dv}{\sqrt{1 - v^2/c^2}} \\ &= \frac{m_0 v^2}{\sqrt{1 - v^2/c^2}} + \left[m_0 c^2 \sqrt{1 - v^2/c^2} \right]_0^v \\ &= \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} - m_0 c^2 \\ &= mc^2 - m_0 c^2 \end{aligned}$$

$$KE = mc^2 - m_0c^2 = (m - m_0)c^2$$

This result states that the kinetic energy of an object is equal to the increase in its mass due to its relative motion multiplied by the square of the speed of light.

The above equation can be written as:

Total energy $mc^2 = m_0c^2 + KE$

If we interpret mc^2 as the **total energy** E of the object, we see that when it is at rest and $KE = 0$, it nevertheless possesses the energy m_0c^2 . Accordingly m_0c^2 is called the **rest energy** E_0 of something whose mass at rest is m_0 . We therefore have

$$E = E_0 + KE$$

where

Rest energy $E_0 = m_0c^2$

If the object is moving, its total energy is

Total energy $E = mc^2 = \frac{m_0c^2}{\sqrt{1 - v^2/c^2}}$

Kinetic Energy at Low Speeds

When the relative speed v is small compared with c , the formula for kinetic energy must reduce to the familiar $\frac{1}{2}m_0v^2$, which has been verified by experiment at such speeds. Let us see if this is true. The relativistic formula for kinetic energy is

Kinetic energy $KE = mc^2 - m_0c^2 = \frac{m_0c^2}{\sqrt{1 - v^2/c^2}} - m_0c^2 \quad (1.23)$

Since $v^2/c^2 \ll 1$, we can use the binomial approximation $(1 \pm x)^n \approx 1 \pm nx$, valid for $|x| \ll 1$, to obtain

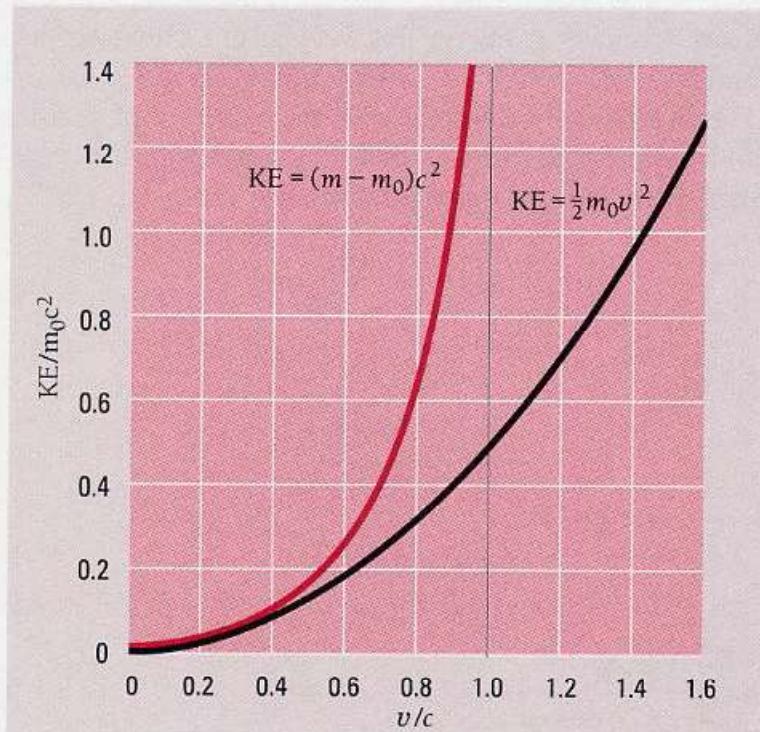
$$\frac{1}{\sqrt{1 - v^2/c^2}} \approx 1 + \frac{1}{2} \frac{v^2}{c^2} \quad v \ll c$$

Thus we have the result

$$KE \approx \left(1 + \frac{1}{2} \frac{v^2}{c^2}\right) m_0c^2 - m_0c^2 \approx \frac{1}{2} m_0v^2 \quad v \ll c$$

At low speeds the relativistic expression for the kinetic energy of a moving object does indeed reduce to the classical one. So far as is known, the correct formulation of mechanics has its basis in relativity, with classical mechanics representing an approximation that is valid only when $v \ll c$.

A comparison between the classical and relativistic formulas for the ratio between kinetic energy KE of a moving body and its rest energy m_0c^2 . At low speeds the two formulas give the same results, but they diverge at speeds approaching that of light. According to relativistic mechanics, a body would need an infinite kinetic energy to travel with the speed of light, whereas in classical mechanics it would need only a kinetic energy of half its rest energy to have this speed.



MASSLESS PARTICLES

Can a massless particle exist? To be more precise, can a particle exist which has no rest mass but which nevertheless exhibits such particlelike properties as energy and momentum? In classical mechanics, a particle must have rest mass in order to have energy and momentum, but in relativistic mechanics this requirement does not hold.

Let us see what we can learn from the relativistic formulas for total energy and linear momentum:

Total energy
$$E = \frac{m_0c^2}{\sqrt{1 - v^2/c^2}} \quad (1)$$

Relativistic momentum
$$p = \frac{m_0v}{\sqrt{1 - v^2/c^2}} \quad (2)$$

When $m_0 = 0$ and $v < c$, it is clear that $E = p = 0$. A massless particle with a speed less than that of light can have neither energy nor momentum. However, when $m_0 = 0$ and $v = c$, $E = 0/0$ and $p = 0/0$, which are indeterminate: E and p can have any values. Thus Eqs. (1) and (2) are consistent with the existence of massless particles that possess energy and momentum *provided that they travel with the speed of light*.

Total energy

$$E = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} \quad (1)$$

Relativistic momentum

$$p = \frac{m_0 v}{\sqrt{1 - v^2/c^2}} \quad (2)$$

From Eq. (1) $E^2 = \frac{m_0^2 c^4}{1 - v^2/c^2}$

From Eq. (2) $p^2 = \frac{m_0^2 v^2}{1 - v^2/c^2} \quad p^2 c^2 = \frac{m_0^2 v^2 c^2}{1 - v^2/c^2}$

Subtracting $p^2 c^2$ from E^2 yields

$$E^2 - p^2 c^2 = \frac{m_0^2 c^4 - m_0^2 v^2 c^2}{1 - v^2/c^2} = \frac{m_0^2 c^4 (1 - v^2/c^2)}{1 - v^2/c^2} = m_0^2 c^4$$

$$E^2 = m_0^2 c^4 + p^2 c^2$$

All particles

$$E = \sqrt{m_0^2 c^4 + p^2 c^2} = \sqrt{E_0^2 + p^2 c^2}$$

All particles

$$E = \sqrt{m_0^2 c^4 + p^2 c^2} = \sqrt{E_0^2 + p^2 c^2}$$

According to this formula, if a particle exists with $m_0 = 0$, the relationship between its energy and momentum must be given by

Massless particles

$$E = pc$$

All the above means not that massless particles necessarily occur, only that the laws of mechanics do not exclude the possibility provided that $v = c$ and $E = pc$ for them. In fact, massless particles of two different kinds—the photon and the neutrino—have indeed been discovered and their behavior is as expected.

Electronvolts

In atomic physics the usual unit of energy is the **electronvolt** (eV), where 1 eV is the energy gained by an electron accelerated through a potential difference of 1 volt. Since $W = QV$,

$$1 \text{ eV} = (1.602 \times 10^{-19} \text{ C})(1.000 \text{ V}) = 1.602 \times 10^{-19} \text{ J}$$

The rest energies of elementary particles are often expressed in MeV and GeV and the corresponding rest masses in MeV/c^2 and GeV/c^2 . The advantage of the latter units is that the rest energy equivalent to a rest mass of, say, $0.938 \text{ GeV}/c^2$ (the rest mass of the proton) is just $E_0 = m_0 c^2 = 0.938 \text{ GeV}$. If the proton's kinetic energy is 5.000 GeV, finding its total energy is simple:

$$E = E_0 + KE = (0.938 + 5.000) \text{ GeV} = 5.938 \text{ GeV}$$

$$(1 \text{ MeV} = 10^6 \text{ eV} \quad 1 \text{ GeV} = 10^9 \text{ eV})$$

The Lorentz Transformation

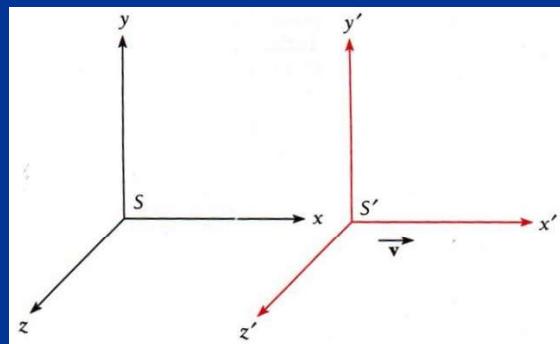
Galilean Transformation

$$x' = x - vt$$

$$y' = y$$

$$z' = z$$

$$t' = t$$



$$v'_x = \frac{dx'}{dt'} = v_x - v$$

$$v'_y = \frac{dy'}{dt'} = v_y$$

$$v'_z = \frac{dz'}{dt'} = v_z$$

Lorentz Transformation

$$x' = A(x - vt), \quad x = A(x' + vt)$$

$$t_0 = t_0' = 0 \Rightarrow x' = c t', \quad x = c t$$

$$x' = A(ct - vt) \begin{cases} = Act(1 - v/c) = ct' \\ = Act'(1 + v/c) = ct \end{cases} \Rightarrow A = \frac{1}{\sqrt{1 - v^2/c^2}}$$

$$c' = c - v \quad ?$$

$$x' = \frac{x - vt}{\sqrt{1 - v^2/c^2}}$$

$$x = A(x' + vt) \\ = A(A(x - vt) + vt)$$

$$\Rightarrow t' = \frac{t - \frac{vx}{c^2}}{\sqrt{1 - v^2/c^2}}$$

Lorentz transformation

$$x' = \frac{x - vt}{\sqrt{1 - v^2/c^2}}$$

$$y' = y$$

$$z' = z$$

$$t' = \frac{t - \frac{vx}{c^2}}{\sqrt{1 - v^2/c^2}}$$

Relativistic velocity transformation

$$x = \frac{x' + vt'}{\sqrt{1 - v^2/c^2}}$$

$$V_x = \frac{dx}{dt} = \frac{dx}{dt'} \cdot \frac{dt'}{dt}$$

$$V_x = \frac{V'_x + v}{1 + \frac{vV'_x}{c^2}}$$

$$V_y = \frac{V'_y \sqrt{1 - v^2/c^2}}{1 + \frac{vV'_x}{c^2}}$$

$$V_z = \frac{V'_z \sqrt{1 - v^2/c^2}}{1 + \frac{vV'_x}{c^2}}$$

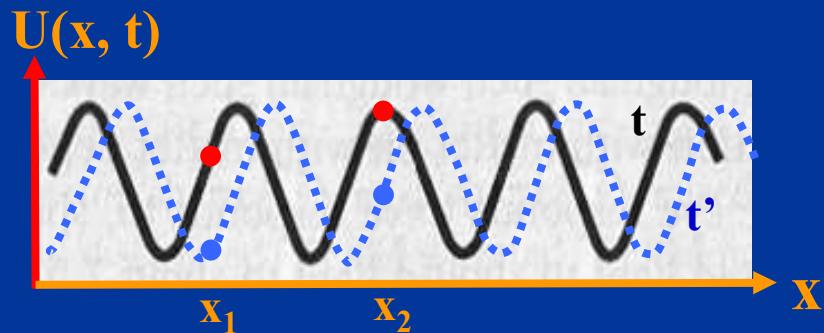
Summary of Special Relativity

- Two postulates of special relativity
 - The laws of Physics are the same in all inertial frames of reference.
 - The speed of light in free space has the same value in all inertial frames of reference.
- nothing can move faster than the speed of light in free space
- Time dilation $t = \frac{t_0}{\sqrt{1 - v^2/c^2}}$
- Length contraction $L = L_0 \sqrt{1 - v^2/c^2}$ (only along the direction of motion)
- Mass of a moving object $m = \frac{m_0}{\sqrt{1 - v^2/c^2}}$
- Energy of matters $E=mc^2$

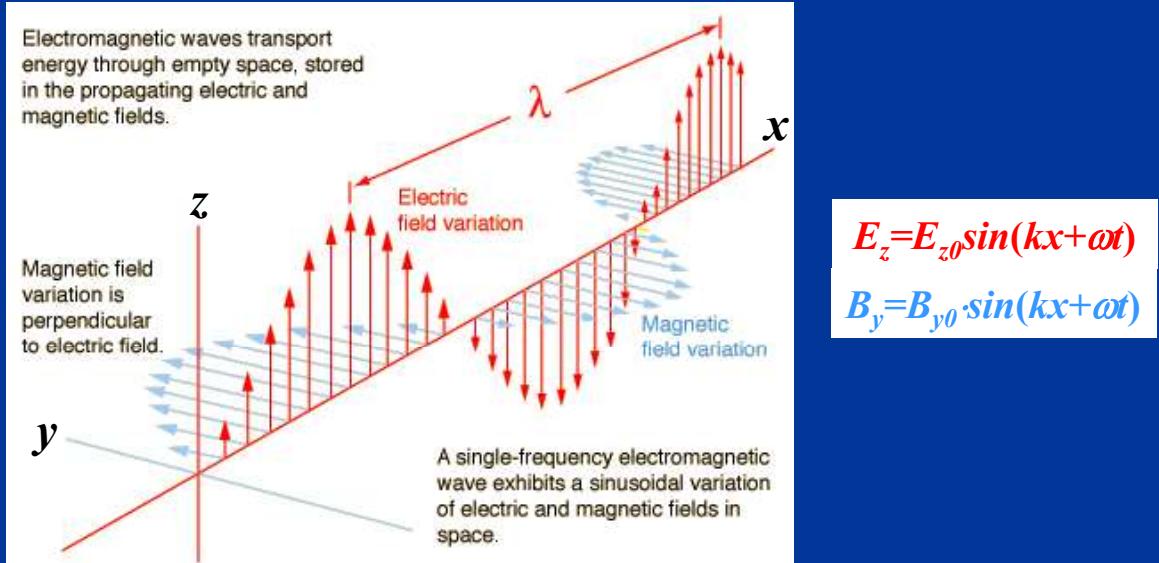
CH2 Particle Properties of Waves

2.1 Electromagnetic waves

Wave — disturbance (e.g. vibration) propagates in space. It is a function of space (location) and time, i.e. $U=U(x, t)$



Electromagnetic waves



Electromagnetic waves are lights — James J Maxwell (~1856)

Why did he think so?

Maxwell's Equations in vacuum (Differential form)

I. Gauss' law for electricity $\nabla \cdot E = 0$

II. Gauss' law for magnetism $\nabla \cdot B = 0$

III. Faraday's law of induction $\nabla \times E = -\frac{\partial B}{\partial t}$

IV. Ampere's law $\nabla \times B = \mu_0 \epsilon_0 \frac{\partial E}{\partial t}$

Do curl to both sides of III:

$$\nabla \times (\nabla \times E) = -\frac{\partial(\nabla \times B)}{\partial t}$$

Substitute with IV:

$$\nabla \times (\nabla \times E) = -\mu_0 \epsilon_0 \frac{\partial^2 E}{\partial t^2}$$

(Here $\epsilon_0 = 8.854 \times 10^{-12}$, or $\epsilon_0 = 1/(4\pi \cdot 9.00 \times 10^9)$ C²/(N·m²) is the permittivity of free space, $\mu_0 = 4\pi \times 10^{-7}$ T·m/A is the permeability of free space)

In one dimensional case, i.e. electrical field along z-axis, propagation along x-axis:

$$\nabla \times (\nabla \times E) = -\frac{\partial^2 E_z}{\partial x^2}$$

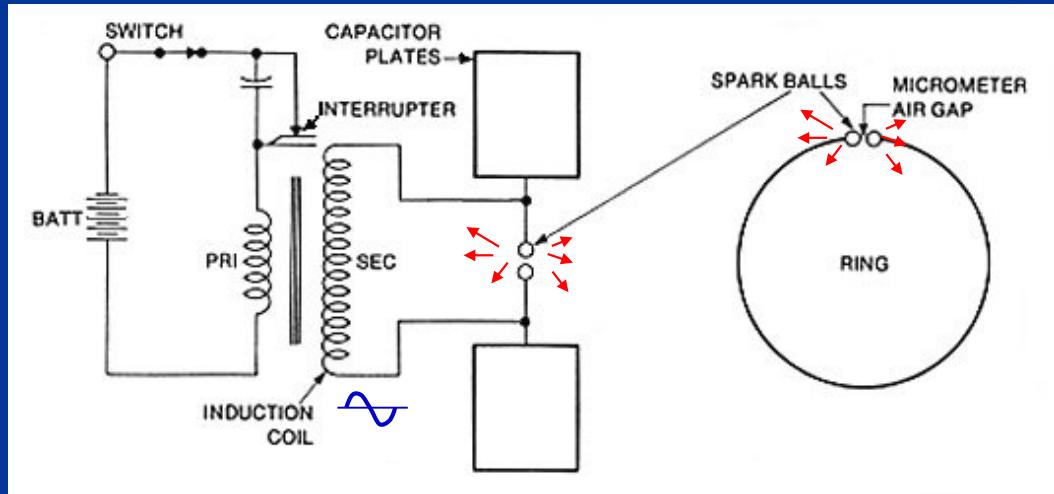
Therefore: $\frac{\partial^2 E_z}{\partial x^2} = \mu_0 \epsilon_0 \frac{\partial^2 E_z}{\partial t^2}$

Compare to general wave equation $\frac{\partial^2 \mathbf{U}(\mathbf{x}, t)}{\partial \mathbf{x}^2} = \frac{1}{V^2} \frac{\partial^2 \mathbf{U}(\mathbf{x}, t)}{\partial t^2}$

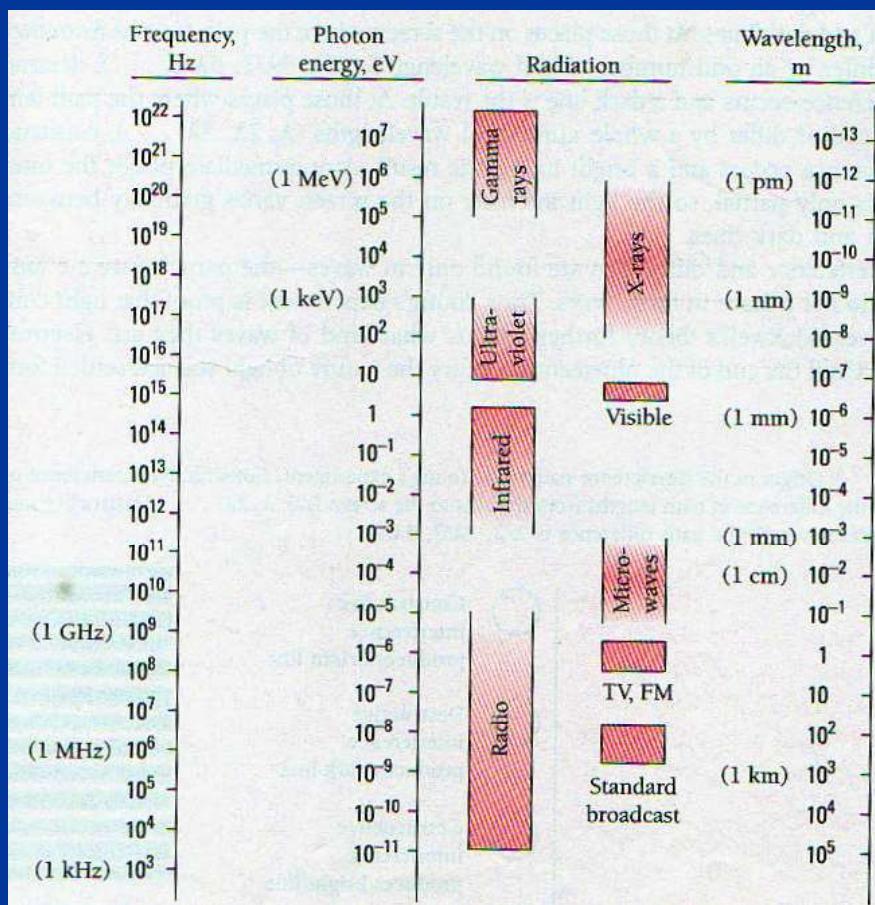
here V is the speed of wave propagation

So, electromagnetic waves travel at speed $\frac{1}{\sqrt{\epsilon_0 \mu_0}} = 3.00 \times 10^8 = c$

In 1888, Hertz designed a brilliant set of experiments tested Maxwell's hypothesis.



Hertz's results showed that electromagnetic waves indeed exist and behave exactly as Maxwell had predicted !



Spectrum of Electromagnetic wave

EM waves visible to eye:

$$f = (4.3 - 7.5) \times 10^{14} \text{ Hz}$$

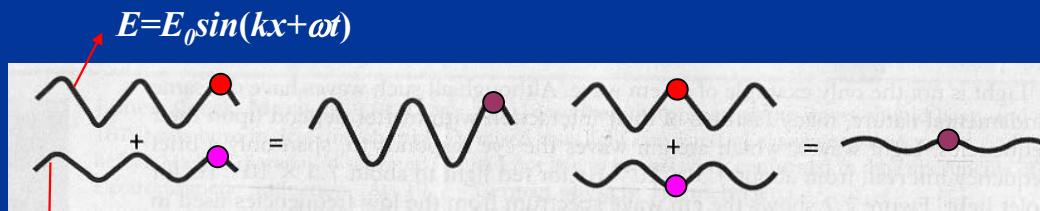
$$\text{Wavelengths, } \lambda = (1/f) \cdot c \\ 698 - 400 \text{ nm}$$

(Sometimes, waves are also described by angular frequency $\omega = 2\pi f$ and wave vector $\mathbf{k} = 2\pi/\lambda$.

$$\text{So, } c = \lambda f = \omega/k$$

A characteristic property of all waves is that they obey the **principle of superposition**:

When two or more waves of the same nature travel past a point at the same time, the instantaneous amplitude there is the sum of the instantaneous amplitudes of the individual waves.



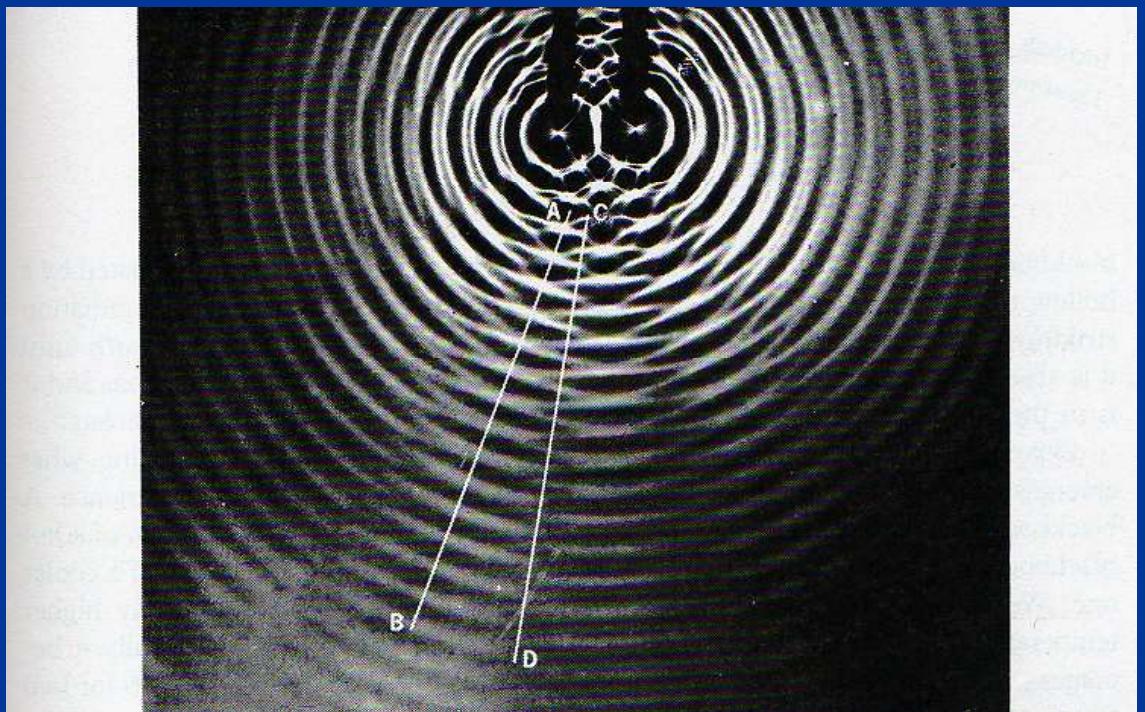
$$E' = E_0' \sin(k'x + \omega't)$$

$$\begin{aligned} kx + \omega t &= \pi/2 \quad E = E_0 \\ k'x + \omega't &= 2\pi + \pi/2 \quad E' = E_0' \end{aligned}$$

$$E + E' = E_0 + E_0'$$

$$\begin{aligned} kx + \omega t &= \pi/2 \quad E = E_0 \\ k'x + \omega't &= \pi + \pi/2 \quad E' = -E_0' \end{aligned}$$

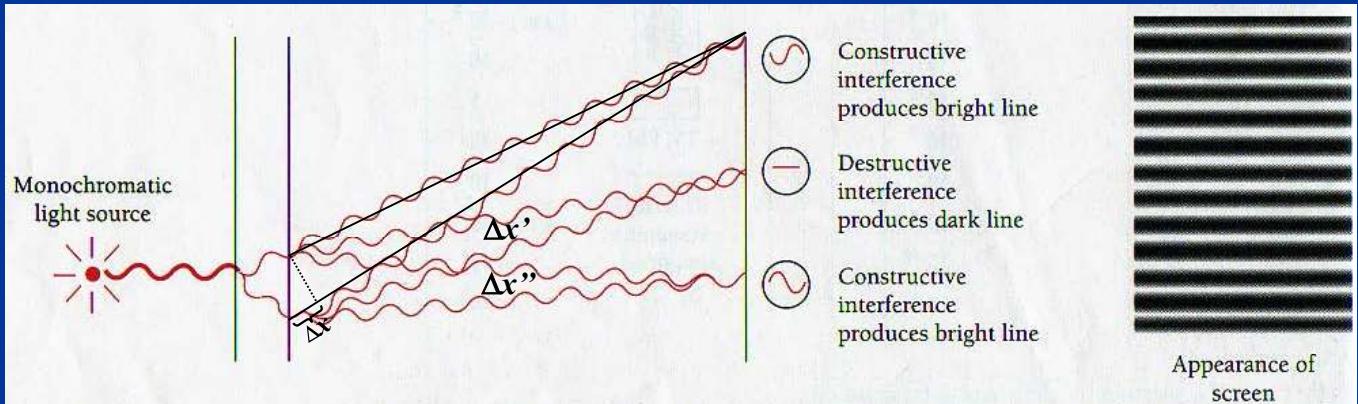
$$E + E' = E_0 - E_0'$$



The interference of water waves. Constructive interference occurs along the line AB and destructive interference occurs along the line CD.

Experiments of light interference

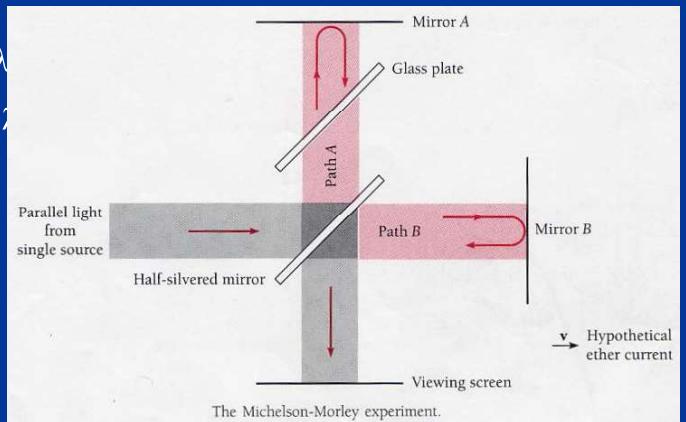
$$E = E_0 \sin(kx + \omega t)$$



Constructive: when light path difference = 0, λ

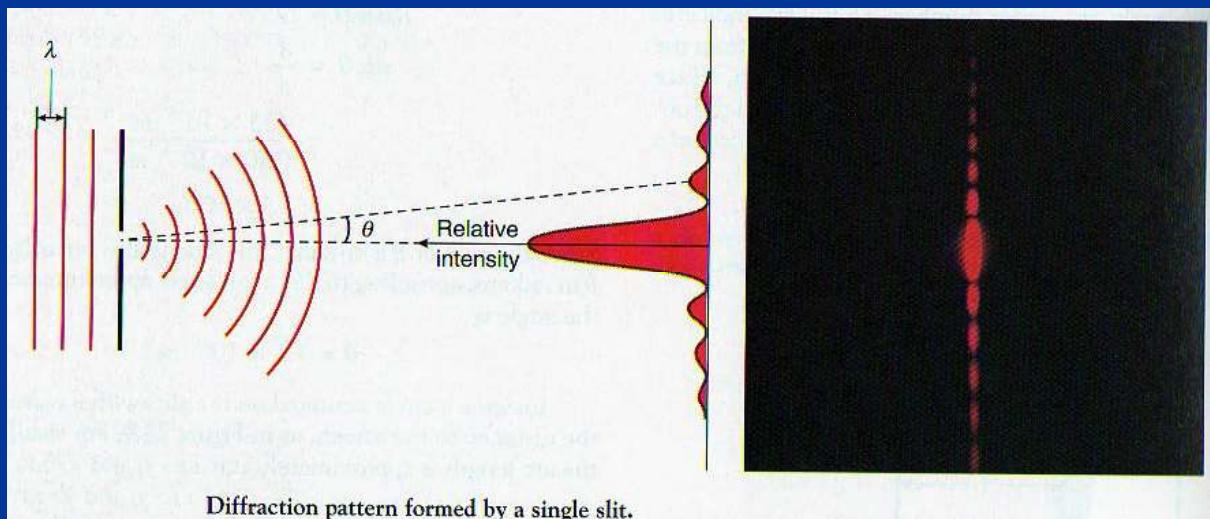
Destructive: when light path difference = 0, $\lambda/2, 3\lambda/2, \dots$

The **Michelson-Morley experiment** we showed in last Chapter is based on the same principle.



In addition to interference, there is another characteristic of waves called **diffraction**.

It happens when waves pass through a small hole whose diameter is comparable to the wavelength.



The interference and diffraction experiments confirmed the wave nature of light.

Thermal radiation

We are all familiar with the glow of a hot piece of metal, which gives off visible light whose colour varies with the temperature of the metal, going from red to yellow to white as it becomes hotter and hotter.

Thermal radiation is the heat transfer by the emission of electromagnetic waves, which carry energy away from the emitting object

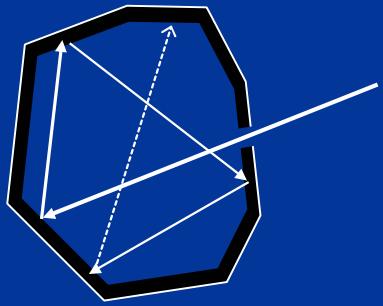
Blackbody Radiation



Under thermal equilibrium:

Absorption = Emission

Hence, blackbody also has maximum emission when being heated up (most efficient emitter)



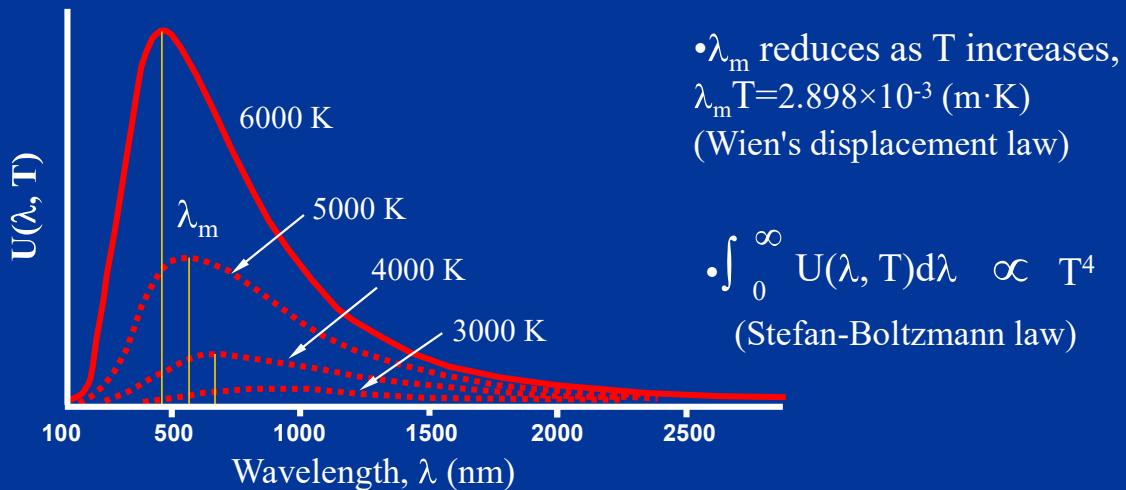
In practical experiments, black-body conditions are met by a cavity with black internal wall and a small opening

Blackbody-radiation or cavity-radiation refers to an object or system which absorbs all radiation incident upon it and re-radiates energy which is characteristic of this radiating system only.

At temperature T, when the cavity reaches thermal equilibrium, the energy density of cavity radiation, $U(v)$, is independent of the shape of cavity and the materials of its wall.

i.e. $U(v)=U(v, T)$

Experimental observations:



Wien's displacement law can be used to estimate the surface temperature of stars:

$$T = \frac{2.898 \times 10^{-3}}{\lambda_m}$$

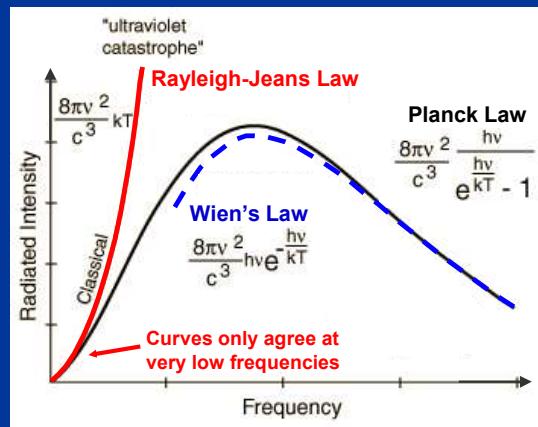
e.g. Sun: $\lambda_m = 500 \text{ nm}$
 $T = 5800 \text{ K}$

Cosmology — 3K Background Radiation (evidence of “Big-Bang Theory”)

A background radiation in microwave region is observed in every part of the sky. It has the same intensity and distribution of frequencies in all direction, independent of celestial objects. It shows the wavelength dependence of a blackbody at 3 K, which is interpreted as the electromagnetic remnant of the primitive fireball, stretched to long wavelengths by the expansion of the universe.

In classic physics, the blackbody emission was described by two contradictory theorems:

- Rayleigh-Jeans radiation law, valid in the low frequency region
- Wien's law, valid in the high frequency region



Classic theory of cavity radiation

(Chapter 9, Section 9.5 in Beiser's book, 5th ed.)

Some starting points:

- Radiation is heat transfer by the emission of electromagnetic waves which carry energy away from the emitting object .
- It can be shown based on the thermodynamic argument that cavity radiation is isotropic, homogeneous, independent of the shape of cavity and the materials of its wall.
- It is not necessary to study the behaviour of the electrons in the walls in detail, instead attention can be focused on the behaviour of electromagnetic waves in the interior of the cavity.

General procedure for calculation of $U(v, T)$

1. Classic electromagnetic theory is used to show the radiation inside the cavity must be exist in the form of **standing waves** with the **nodes on the surface of wall**.
2. Work out the number, N , of the standing waves at frequency v (i.e. density of modes)
3. Work out the average energy, \bar{u} , of the waves at a given temperature
4. The number of modes times average energy, divided by the volume of cavity, gives the energy density:
$$U(v, T) = N \times \bar{u}$$

Think a cavity made of metal

[*<link>*](#)

$E=0$ at $x=0, L$; otherwise there is a current flowing on the wall !

Wave equation for one-dimensional electromagnetic waves:

$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2}$$

The solutions have the plane-wave form:

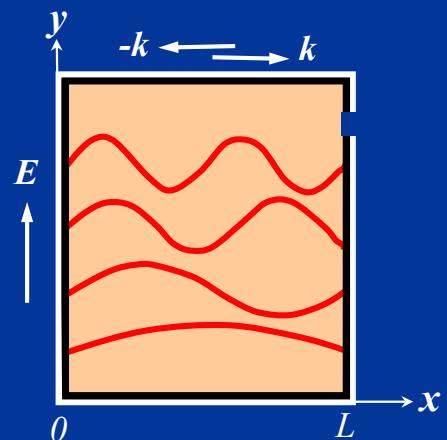
$$E = E_0 \sin(kx) \cdot \sin(\omega t) \quad \text{with } c = \omega/k$$

(here $\omega = 2\pi v$ is the angular frequency, $k = 2\pi/\lambda$ the wave vector)

When $x=L$, $E = E_0 \sin(kL) \cdot \sin(\omega t) = 0$ for any t , hence $kL = n\pi$ ($n=1, 2, 3, \dots$),

i.e.
$$k = n\pi/L$$

So, for the standing waves:
$$E = E_0 \sin(n\pi x/L) \cdot \sin(\omega t)$$



Similarly, for electromagnetic waves in a 3-dimensional cubic cavity:

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2}$$

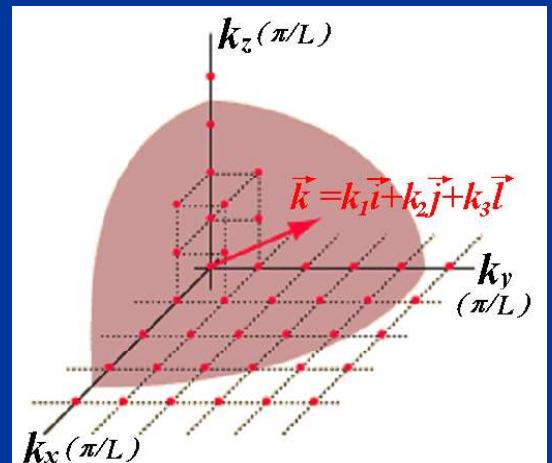
and the solutions for the standing waves are:

$$E = E_0 \sin(k_1 x) \cdot \sin(k_2 y) \cdot \sin(k_3 z) \cdot \sin(\omega t)$$

where, $k_1 = n_1 \pi / L$, $k_2 = n_2 \pi / L$, $k_3 = n_3 \pi / L$
(n_1, n_2, n_3 are integers: 1, 2, 3, ...)

$$\text{and } c = \omega / k \quad \text{with } (k^2 = k_1^2 + k_2^2 + k_3^2)$$

Let $\vec{k} = k_1 \vec{i} + k_2 \vec{j} + k_3 \vec{l}$, which is the 3-dimensional wave-vector.



For each of k , there are many combinations (modes) of k_1, k_2, k_3 to meet $k^2 = k_1^2 + k_2^2 + k_3^2$ and all of them are on the first octant of a sphere with radius of k .

All the modes with k between k and $k + \delta k$ fall inside the shell, whose internal radius is k and external radius $k + \delta k$.

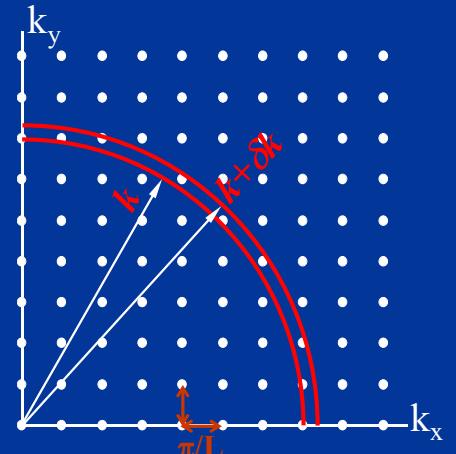
Every mode (i.e. a spot in the picture) take a space of $(\pi/L) \times (\pi/L) \times (\pi/L)$ on average

Hence the number of modes inside the shell is:

$$\delta N = \frac{1}{8} \times \frac{4}{3} \pi (k + \delta k)^3 - \frac{4}{3} \pi k^3 = \frac{L^3}{6\pi^2} [(k + \delta k)^3 - k^3]$$

ignore $(\delta k)^2$ and higher orders, $(k + \delta k)^3 \approx k^3 + 3k^2 \delta k$

$$\text{So } \delta N = \frac{L^3}{2\pi^2} k^2 \delta k, \text{ replace } k \text{ with } k = \omega/c = 2\pi\nu/c, \text{ then } \delta N(\nu) = \frac{4\pi L^3}{c^3} \nu^2 \delta \nu$$



When $\delta \nu \rightarrow 0$, we have the density of modes: $\frac{dN(\nu)}{d\nu} = \frac{4\pi L^3}{c^3} \nu^2$ (i.e. the number of standing waves at a given frequency ν)

If the averaged energy for the standing waves is \bar{u} , then the energy density of blackbody radiation, i.e. energy per unit volume per frequency, is:

$$U(\nu, T) = \frac{dN(\nu)}{d\nu} \times \bar{u} \times 2 \times \frac{1}{L^3} = \frac{8\pi\nu^2}{c^3} \bar{u}$$

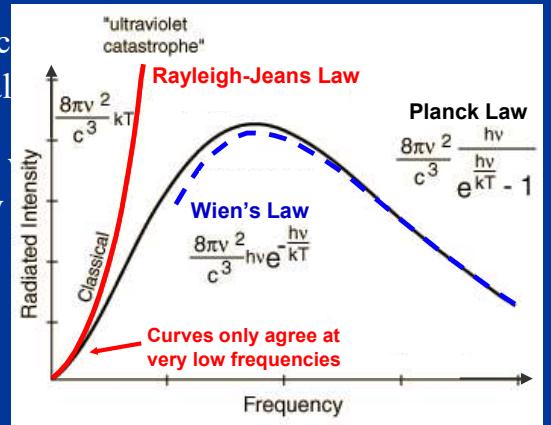
(the factor of 2 is because each electromagnetic wave has two polarisations)

Now we need to work out average energy of the radiation system — \bar{u}

According to classic theory, the energy of each electron u , is the square of its amplitude and can be any value.

The large numbers of the standing electromagnetic waves in the cavity are the entities of a same kind, which follow the distribution: $e^{-\frac{u}{kT}}$

$$\text{Hence the average energy is: } \bar{u} = \frac{\int_0^\infty ue^{-\frac{u}{kT}} du}{\int_0^\infty e^{-\frac{u}{kT}} du}$$



$$\text{Let } x = -u/kT \text{ the denominator: } \int_0^\infty e^{-\frac{u}{kT}} du = kT \int_0^\infty e^{-x} dx = -kTe^{-x} \Big|_0^\infty = kT$$

$$\text{the numerator: } \int_0^\infty ue^{-\frac{u}{kT}} du = (kT)^2 \int_0^\infty xe^{-x} dx = (kT)^2 (xe^{-x} \Big|_0^\infty + \int_0^\infty e^{-x} dx) = (kT)^2$$

$$\text{So, } \bar{u} = \frac{(kT)^2}{kT} = kT, \quad U(\nu, T) = \frac{8\pi\nu^2}{c^3} \bar{u} = \frac{8\pi\nu^2}{c^3} kT \quad \text{Rayleigh-Jeans radiation law}$$

Planck's Assumption (1901):

- The energy exchange between the electrons in the cavity wall and electromagnetic waves only occur in discrete amounts.
- The minimum unit of energy exchange, which is called as “quantum of energy”, is $h\nu$. Here, $h=6.626 \times 10^{-34}$ (J·s) is the Plank's constant, ν the frequency of electromagnetic waves.

$$\text{i.e. } u = nh\nu, \quad n=0, 1, 2, 3, \dots$$

compare to classic

$$\bar{u} = \frac{\int_0^\infty ue^{-\frac{u}{kT}} du}{\int_0^\infty e^{-\frac{u}{kT}} du}$$

So, the average energy is now:

$$\bar{u} = \frac{\sum_{n=0}^{\infty} nh\nu e^{-\frac{n\nu}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{n\nu}{kT}}}$$

Let $Y = \sum_n e^{-nh\nu x}, x = 1/kT$, then

$$\bar{u} = -\frac{d}{dx} \ln Y$$

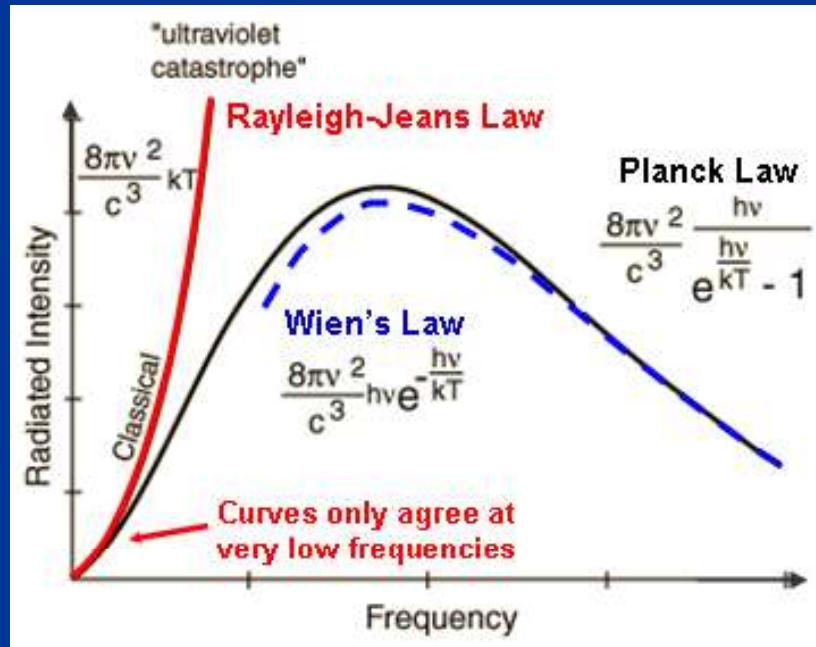
$$Y = \sum_n e^{(-h\nu x)n} = \lim_{n \rightarrow \infty} \frac{1 - e^{(-h\nu x)(n+1)}}{1 - e^{(-h\nu x)}} = \frac{1}{1 - e^{(-h\nu x)}}$$

$$\bar{u} = -\frac{d}{dx} \ln \left[\frac{1}{1 - e^{-h\nu x}} \right] = \frac{d}{dx} \ln(1 - e^{-h\nu x}) = \frac{h\nu e^{-h\nu x}}{1 - e^{-h\nu x}} = \frac{h\nu}{e^{h\nu x} - 1}$$

$$x = 1/kT, \quad \bar{u} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1},$$

$$U(\nu, T) = \frac{8\pi\nu^2}{c^3} \bar{u} = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

Planck Law



$$u = nh\nu, \quad n = 0, 1, 2, 3, \dots$$

Plank's law

$$U(v, T) = \frac{8\pi v^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

Rayleigh-Jeans and Wien's laws are special cases of Plank's law

We know: $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$

If x is small, $e^x \approx 1 + x$, and so for $h\nu/kT \ll 1$ we have

$$\frac{1}{e^{h\nu/kT} - 1} \approx \frac{1}{1 + \frac{h\nu}{kT} - 1} \approx \frac{kT}{h\nu} \quad h\nu \ll kT$$

Thus at low frequencies Planck's formula becomes

$$U(v, T) \approx \frac{8\pi h}{c^3} v^3 \left(\frac{kT}{h\nu} \right) d\nu \approx \frac{8\pi kT}{c^3} v^2$$

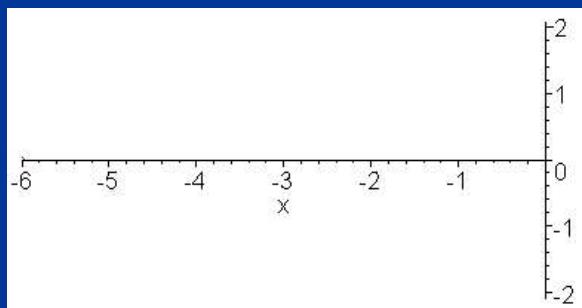
which is the Rayleigh-Jeans formula.

When $h\nu/kT \gg 1$, then

$$e^{h\nu/kT} \gg 1 \quad e^{h\nu/kT} - 1 \approx e^{h\nu/kT}$$

$$\frac{1}{e^{h\nu/kT} - 1} \approx e^{-h\nu/kT} \quad U(v, T) \approx \frac{8\pi v^2}{c^3} h\nu e^{-\frac{h\nu}{kT}}$$

which is Wien's law.



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Photoelectric and Compton Effects

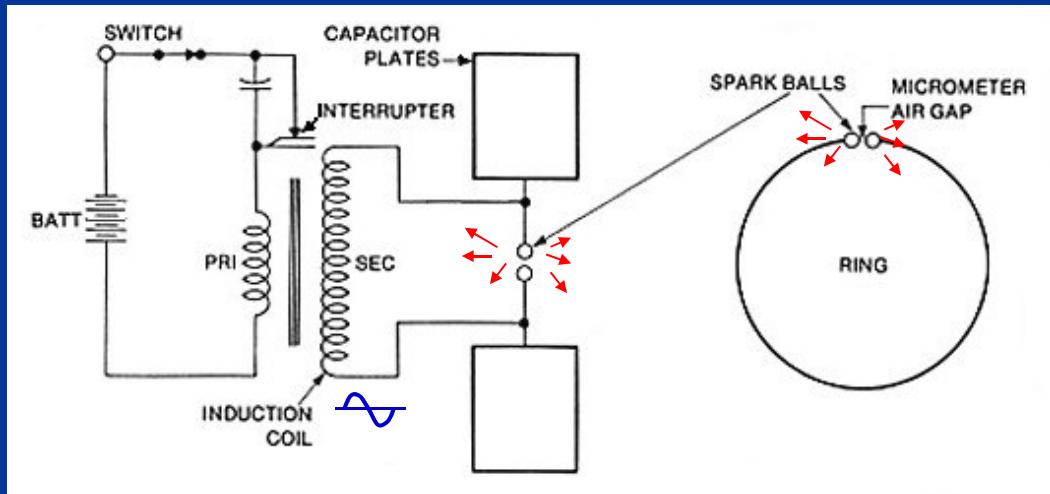
— the particle-like property of light

Photoelectric effect

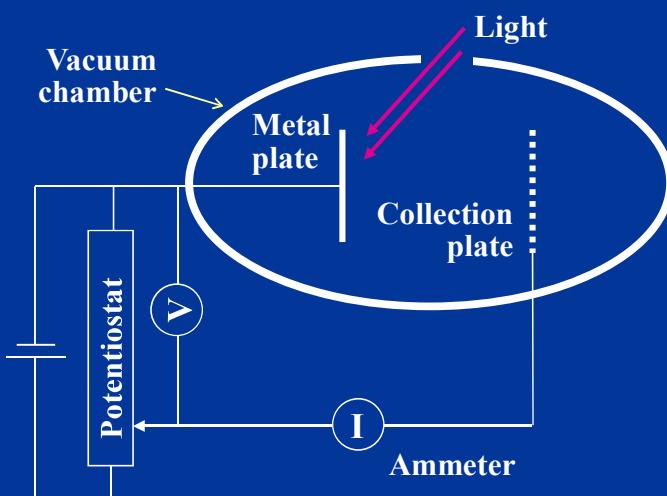
During Hertz's experiment, he noticed that sparks occurred more readily in the air gap when ultraviolet light was directed at one of the metal balls.



Hertz



When ultra-violet (UV) lights impinge on a metal in a vacuum, charged particles are emitted (Hertz 1888), which were later shown to be electrons by J.J. Thomson (1899).



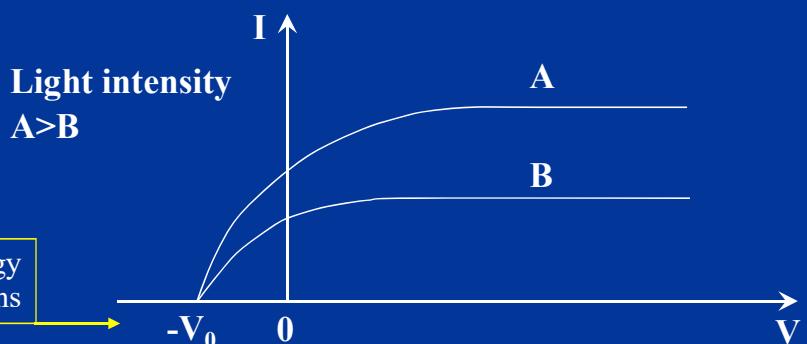
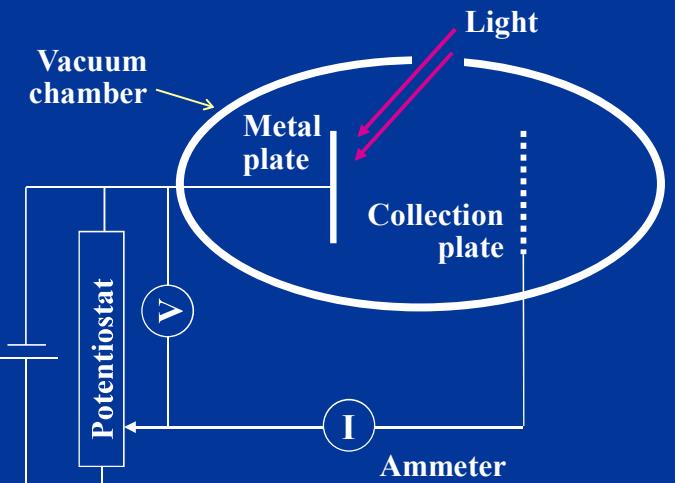
J.J. Thomson

Classical expectations

- Electric field E of light exerts force $F = -eE$ on electrons. As intensity of light increases, force increases, so kinetic energy of ejected electrons should increase.
- Electrons should be emitted whatever the frequency v of the light, so long as E is sufficiently large
- For very low intensities, expect a time lag between light exposure and emission, while electrons absorb enough energy to escape from material

Actual results:

- Maximum kinetic energy of ejected electrons is independent of intensity, but dependent on v
- For $v < v_0$ (i.e. for frequencies below a cut-off frequency) no electrons are emitted
- There is no time lag. However, rate of ejection of electrons depends on light intensity.



Einstein's interpretation (1905):

Light comes in packets of energy (**photons**)

$$E = h\nu$$

An electron absorbs a single photon to leave the material



Einstein



Millikan

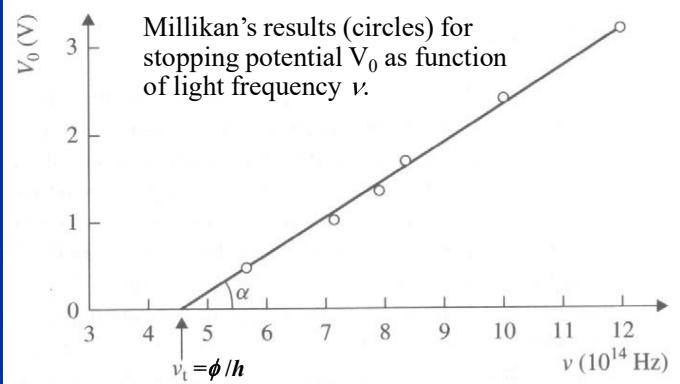
Maximum kinetic energy of an emitted electron is then

$$K_{\max} = h\nu - \phi$$

Planck constant

Work function: minimum energy needed for electron to escape from metal (depends on material, usually 2-5eV)

Verified in detail through experiments by Millikan



$$K_{\max} = h\nu - \phi = eV_0, \text{ so } V_0 = (h/e)\nu - \phi/e \text{ — a linear function of } \nu,$$

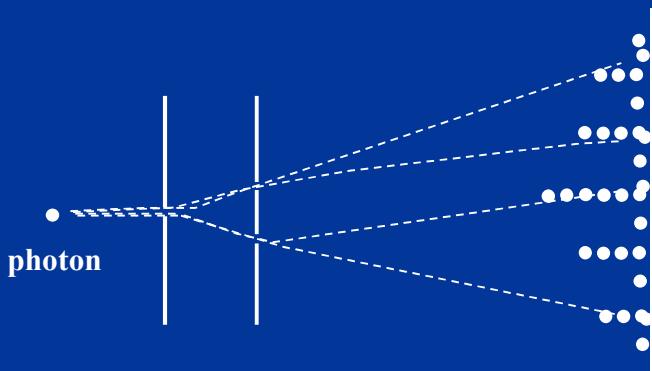
slope = $h/e \rightarrow h = 6.56 \times 10^{-34} \text{ J}\cdot\text{s}$, Millikan's result agreed very well with Planck's result $6.55 \times 10^{-34} \text{ J}\cdot\text{s}$.

What is light ?

Light is wave as well as particle

Light has a dual character !

Each photon can be associated with a wave. The intensity of the wave at a location determines the probability that a photon will arrive there, not the energy. The energy of photon is determined by the frequency of the wave (i.e. $h\nu$).

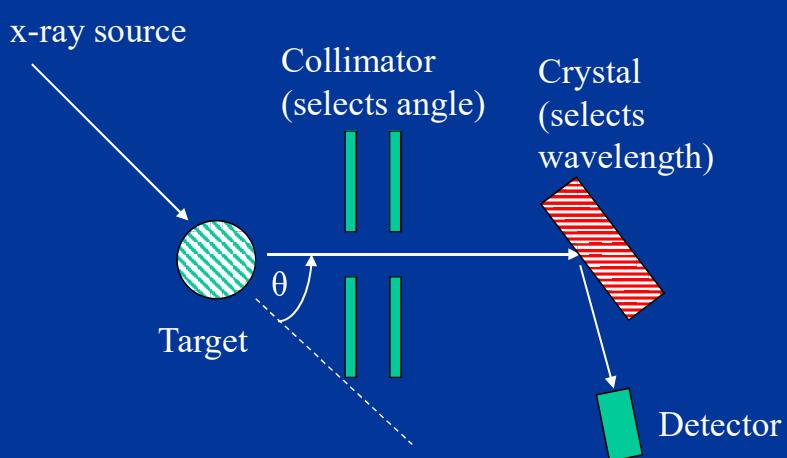


Compton Effect

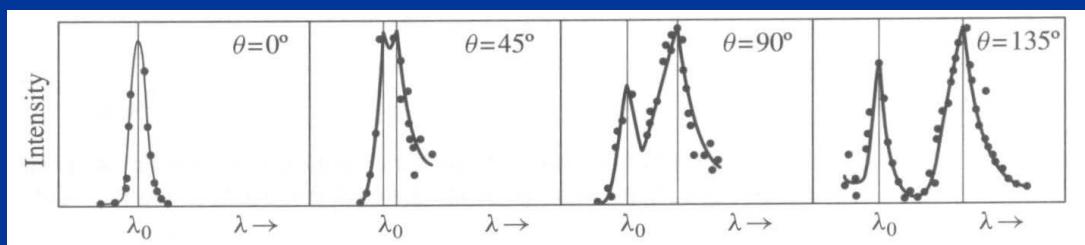
Compton (1923) measured intensity of scattered x-rays (lights with $\lambda \sim 0.1$ nm) from solid target, as function of wavelength for different angles.



Compton



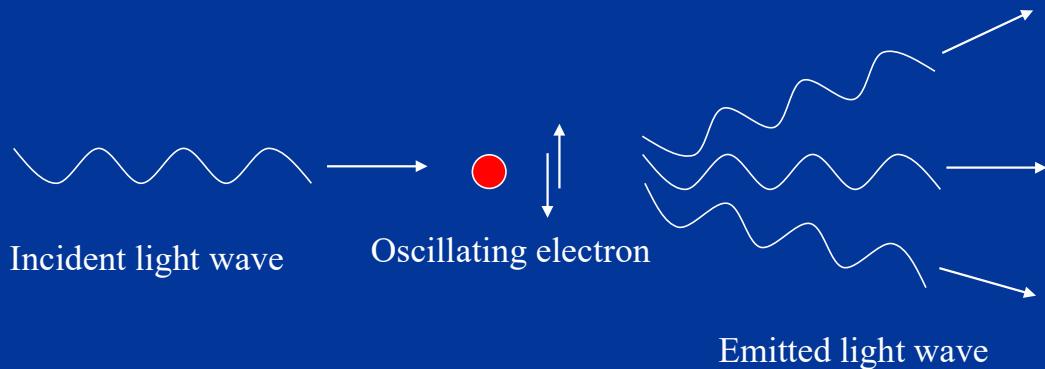
Result: peak in scattered radiation shifts to longer wavelength than source. Amount depends on θ (but not on the target material).



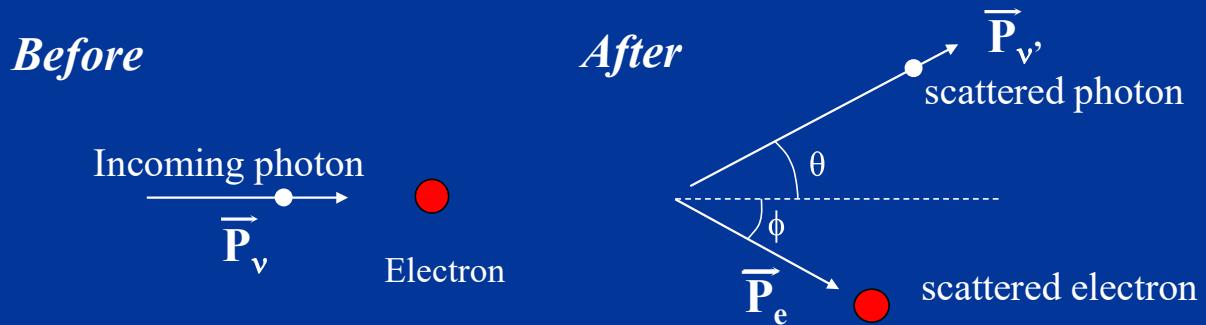
Compton's data (1923) for the scattering of X-rays by graphite

Classical picture: oscillating electromagnetic field causes oscillations in positions of charged particles, which re-radiate in all directions at *same frequency and wavelength* as incident radiation.

Change in wavelength of scattered light is completely unexpected classically



Compton's explanation: “billiard ball” collisions between particles of light (x-ray photons) and electrons in the material



Conservation of energy

$$\begin{aligned} h\nu + m_e c^2 &= h\nu' + \sqrt{p_e^2 c^2 + m_e^2 c^4} \Rightarrow h(\nu - \nu') + m_e c^2 = \sqrt{p_e^2 c^2 + m_e^2 c^4} \Rightarrow \\ [h(\nu - \nu') + m_e c^2]^2 &= p_e^2 c^2 + m_e^2 c^4 \Rightarrow p_e^2 = \frac{h^2}{c^2} (\nu - \nu')^2 + 2m_e h(\nu - \nu') \end{aligned} \quad (1)$$

Conservation of momentum

$$\vec{P}_v = \vec{P}_{v'} + \vec{P}_e \Rightarrow \begin{aligned} p_v &= p_{v'} \cos \theta + p_e \cos \phi \\ 0 &= p_{v'} \sin \theta - p_e \sin \phi \end{aligned} \Rightarrow (p_v - p_{v'} \cos \theta)^2 + p_{v'}^2 \sin^2 \theta = p_e^2$$

$$(p_\nu - p_{\nu'} \cos \theta)^2 + p_{\nu'}^2 \sin^2 \theta = p_e^2 \Rightarrow p_\nu^2 - 2p_\nu p_{\nu'} \cos \theta + p_{\nu'}^2 = p_e^2$$

Photon energy $E = mc^2 = h\nu$, $m = h\nu/c^2$

therefore, photon momentum $p = mc = h\nu/c$

Substitute $p_\nu = h\nu/c$ and $p_{\nu'} = h\nu'/c$ into the above equation

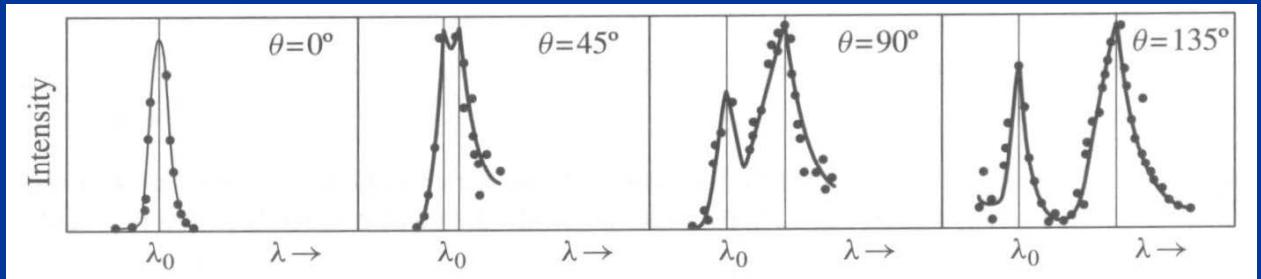
We have

$$p_e^2 = \frac{h^2}{c^2} (\nu^2 + \nu'^2 - 2\nu\nu' \cos \theta) \quad (2)$$

$$\begin{aligned} \text{Put (2) into (1)} \quad p_e^2 &= \frac{h^2}{c^2} (\nu - \nu')^2 + 2m_e h(\nu - \nu') = \frac{h^2}{c^2} (\nu^2 + \nu'^2 - 2\nu\nu' \cos \theta) \\ &(\nu - \nu')^2 + 2m_e c^2 (\nu - \nu') / h = \nu^2 + \nu'^2 - 2\nu\nu' \cos \theta \\ &m_e c^2 (\nu - \nu') / h = \nu\nu' (1 - \cos \theta) \end{aligned}$$

$$\text{so } \frac{\nu - \nu'}{\nu\nu'} = \frac{h}{m_e c^2} (1 - \cos \theta) \quad \text{replace } \nu = c/\lambda, \text{ we finally have:}$$

$$\lambda' - \lambda = \frac{h}{m_e c} (1 - \cos \theta) = \lambda_c (1 - \cos \theta) \geq 0 \quad \lambda_c = \text{Compton wavelength} = \frac{h}{m_e c} = 2.4 \times 10^{-12} \text{ m}$$



Compton's data (1923) for the scattering of X-rays by graphite

$$\lambda' - \lambda = \lambda_c (1 - \cos \theta)$$

$$\theta = 0^\circ, \quad \cos \theta = 1, \quad \lambda' - \lambda = 0$$

$$\theta = 45^\circ, \quad \cos \theta = 0.71, \quad \lambda' - \lambda = 0.39 \lambda_c$$

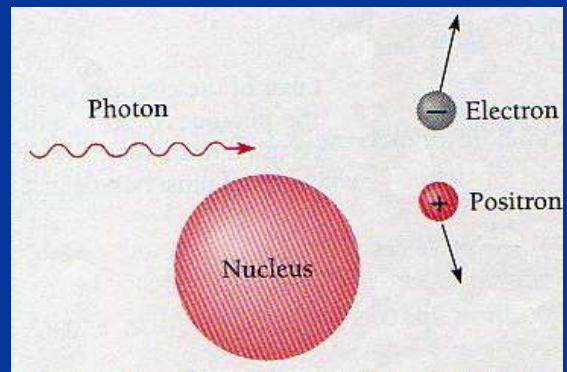
$$\theta = 90^\circ, \quad \cos \theta = 0, \quad \lambda' - \lambda = \lambda_c$$

$$\theta = 135^\circ, \quad \cos \theta = -0.71, \quad \lambda' - \lambda = 1.71 \lambda_c$$

Pair Production

A photon can give an electron all of its energy (as in photoelectric effect) or only a part (as in Compton effect)

A photon can also be materialized into an electron and a positron (positively charged electron)
— pair production

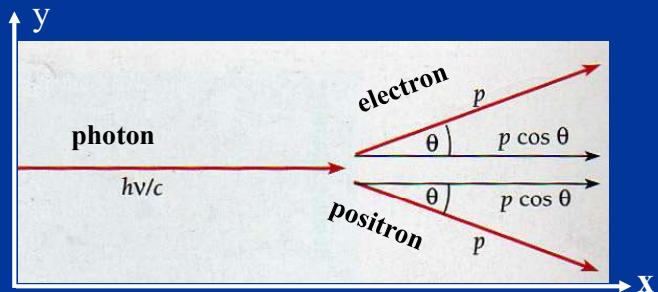


Charge conservation: (photon) $\theta =$ (electron) $e^- +$ (positron) e^+

Energy conservation: $h\nu = 2 \times m_e c^2 + KE_e$

Momentum conservation: $h\nu/c = p_{elect.} + p_{posit.} + P_{nucleus}$
 Needs involvement of nucleus

Why the nucleus has to be involved?



Momentum along x-axis: $h\nu/c = 2p \cdot \cos\theta \rightarrow h\nu = 2pc \cdot \cos\theta$

Energy: $h\nu = 2\sqrt{m_e^2 c^4 + \mathbf{p}^2 c^2}$

$$2pc \cdot \cos\theta = 2\sqrt{m_e^2 c^4 + \mathbf{p}^2 c^2}$$

$$\cos\theta = \frac{\sqrt{m_e^2 c^4 + \mathbf{p}^2 c^2}}{pc} = \sqrt{m_e^2 / \mathbf{p}^2 + 1} > 1$$

There is not such a θ .

Energy and momentum can not both be conserved if pair production were to occur in empty space, so it does not occur there.

$2 \times m_e c^2 = 1.02$ MeV, hence pair production requires a photon energy at least 1.02 MeV, corresponding to the wavelength 1.2×10^{-12} m — **γ-rays**

The inverse of pair production (pair annihilation):



Both electron and positron vanish simultaneously, with the lost mass becoming energy in the form of two **γ-rays** photons.

Unlike pair production, **no nucleus or other particle is needed for pair annihilation.**

X-ray

Photoelectric effect shows that photons of light can transfer energy to electrons.

Is the inverse process possible?

The answer is yes. It was actually discovered before the works of Planck and Einstein, but was not very well understood at the time it was found.

Wilhelm Konrad Roentgen, 1895

When very fast electrons hit on matter, a highly penetrating radiation of unknown nature was generated, which was named as **x-ray**.



Roentgen

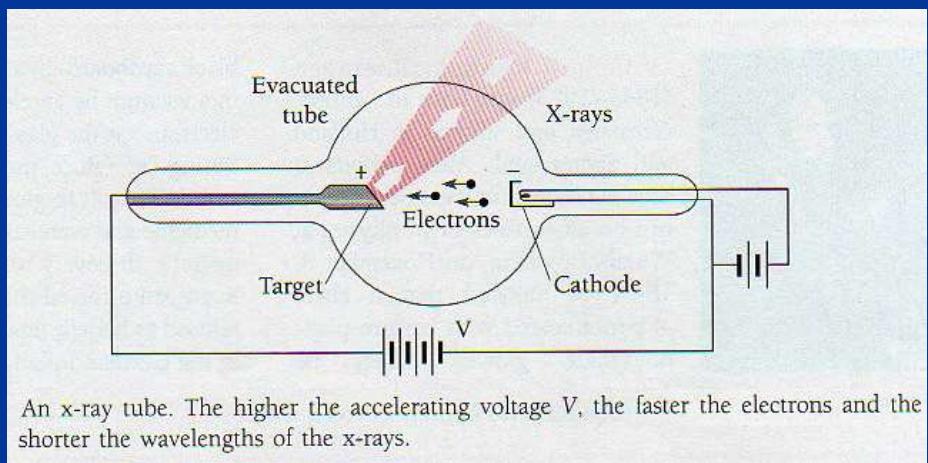
Some properties of x-ray

- travel in straight light
- unaffected by electric and magnetic fields
- readily pass through opaque materials to cause phosphors to glow and to expose photographic plate



An X-ray picture taken by Röntgen

Generation of X-ray



The operating voltage of this modern x-ray tube is 150 kV. Circulating oil carries heat away from the target and releases it to the outside air through a heat exchanger.

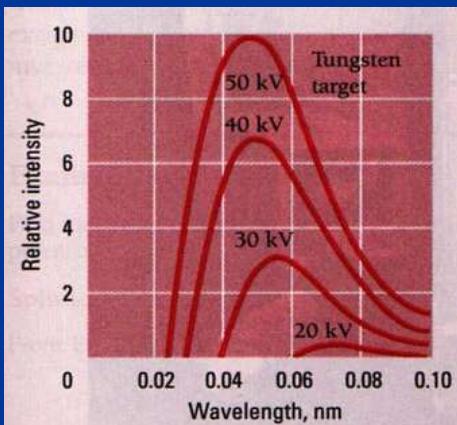
X-ray was soon recognized as electromagnetic waves

Accelerated electric charges will radiate electromagnetic waves
— Maxwell's electromagnetic theory.

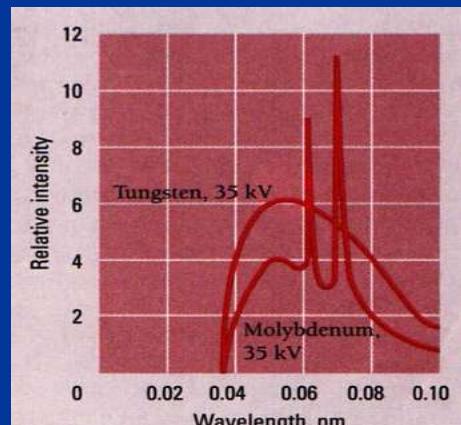
Fast moving electron suddenly brought to rest is certainly accelerated.

So, the generation of x-ray was understandable by classic physics.

But the theory and experiment did not agree very well in certain important respects.



X-ray spectra of tungsten at various accelerating potentials.



X-ray spectra of tungsten and molybdenum at 35 kV accelerating potential.

Two things do not go along with the classic theory

1. Intensity peaks occurred at certain peaks can not be explained.
2. X-rays produced at a given potential V vary in wavelength, but there is a minimum wavelength λ_{\min} . Why?

Increasing V decreases λ_{\min} . At a particular V, λ_{\min} is the same for both targets.

It was found experimentally:
$$\lambda_{\min} = \frac{1.24 \times 10^{-6}}{V} \text{ (V}\cdot\text{m)}$$

How does the quantum theory of radiation explain?

Most of electrons gradually lose their energy by many glancing collisions and turn the energy into heats.

A few electrons lose most or all of their energy in single collision — this is the energy that becomes x-ray

Similar to the photoelectric effect, we can write the energy conservation of the striking electron and the released x-ray photon as:

$$h\nu_{\max} = K + \phi$$

↑ ↑ ↗
 frequency kinetic energy work function
 of x-ray of electron of target

$$K = V \cdot e \gg \phi \quad \text{so} \quad h\nu_{\max} \approx K = V \cdot e \quad \nu_{\max} = V \cdot e / h$$

↑ ↗
 ~ keV ~ 2-5 eV

$$\lambda_{\min} = c / \nu_{\max} = hc / Ve = \frac{1.24 \times 10^{-6}}{V}$$

X-ray diffraction

X-ray is an electromagnetic wave (light), so it should have the common properties that other waves have — **interference and diffraction**

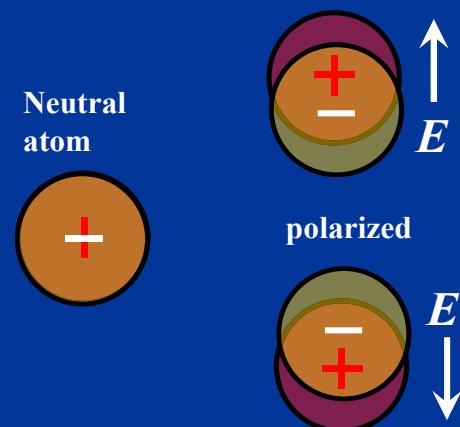
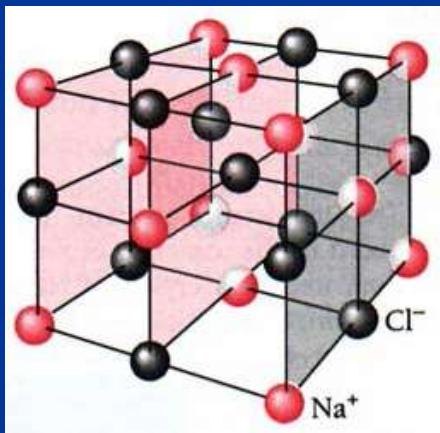
However, the wavelengths of x-rays are so short ($\sim 0.1\text{nm}$) that it is very difficult to find a diffraction grating, which has the line spacing similar to the wavelength of x-ray.



In 1912, Laue realized that the wavelengths of x-ray were comparable to atomic spacing in crystals and proposed to use crystal for x-ray diffraction.

Max von Laue

A crystal consists of a regular array of atoms



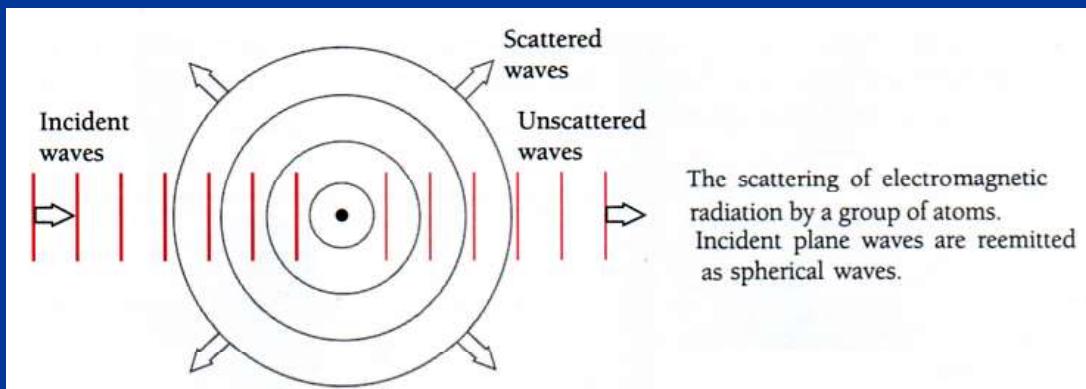
The mechanism of scattering

In a constant electric field, an atom will become polarized (separation of negative and positive centre), forming an electric dipole.

In the alternating electric field of electromagnetic wave, the polarization direction of the dipole will change at the same frequency as the incoming electromagnetic wave v .

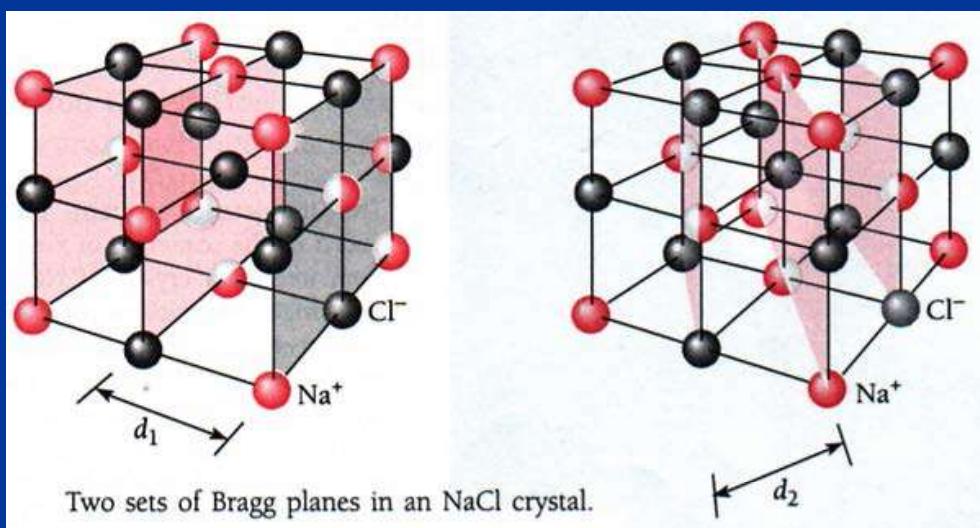
The oscillating dipole will in turn radiate electromagnetic waves of frequency v and the secondary radiation will go out in all direction.

Atoms absorb incoming plane waves and re-emit spherical waves of the same frequency, which will travel in all the directions.

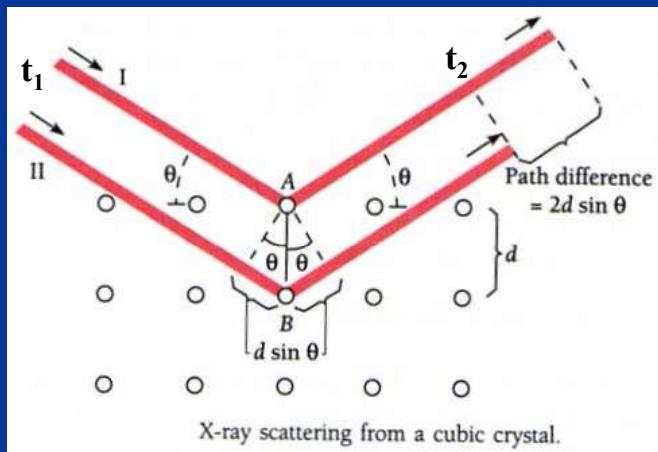


The re-emitted waves from different atoms in the crystal will obey the principle of the superposition. Owing to the regular arrangements of atoms in the crystal, in some directions constructive interference will be observed, while in other directions, destructive interference will be observed.

We can imagine that the 3-dimensional atomic lattice in a crystal is built up by a set of parallel planes of equal spacing. You can choose another set of parallel planes to build the lattice, but the spacing of the planes will be different. Therefore the inter-plane spacing, d , is a characteristic parameter for a particular set of parallel planes. Such planes are called **Bragg planes**.



We can analyze x-ray scattering according to Bragg planes.



Constructive interference occurs when:

- scattered rays are parallel to each other, with the common scattering angle equal to the incident angle θ
- the path difference of scattered rays, ΔL , equals the integral multiples of incident x-ray wavelength, i.e. $n\lambda$.

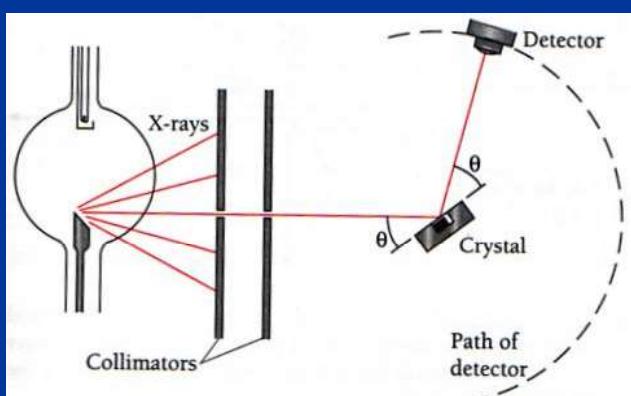
The path difference for the ray I (scattered by the atoms in first plane) and the ray II (scattered by the atoms in the second plane) is:

$$\Delta L = 2d \cdot \sin \theta$$

So, constructive interference happens, when

$$2d \cdot \sin \theta = n\lambda \quad (n = 1, 2, 3, \dots)$$

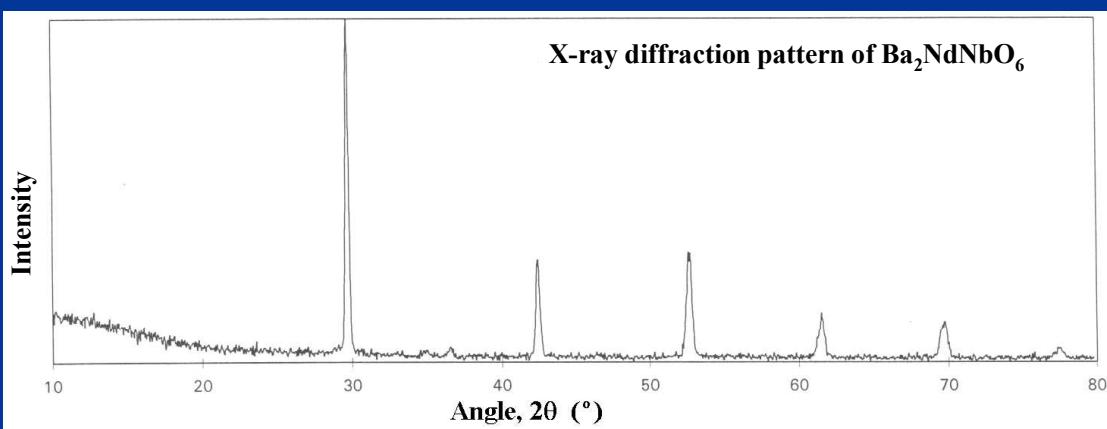
X-ray spectrometer



$$2d \cdot \sin \theta = n\lambda$$

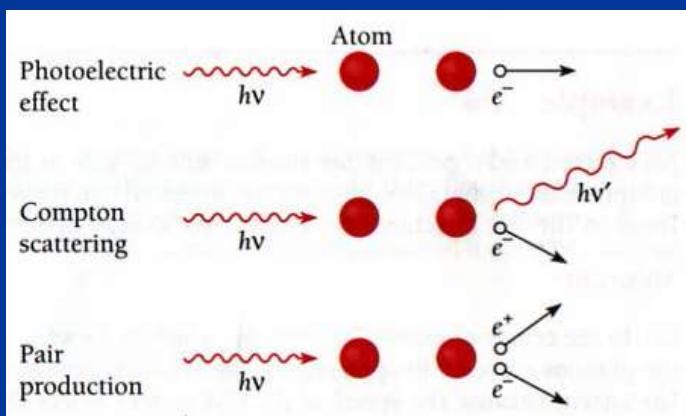
If the spacing d is known, the x-ray wavelength, λ , can be calculated.

For x-ray, λ falls between 0.01–10nm



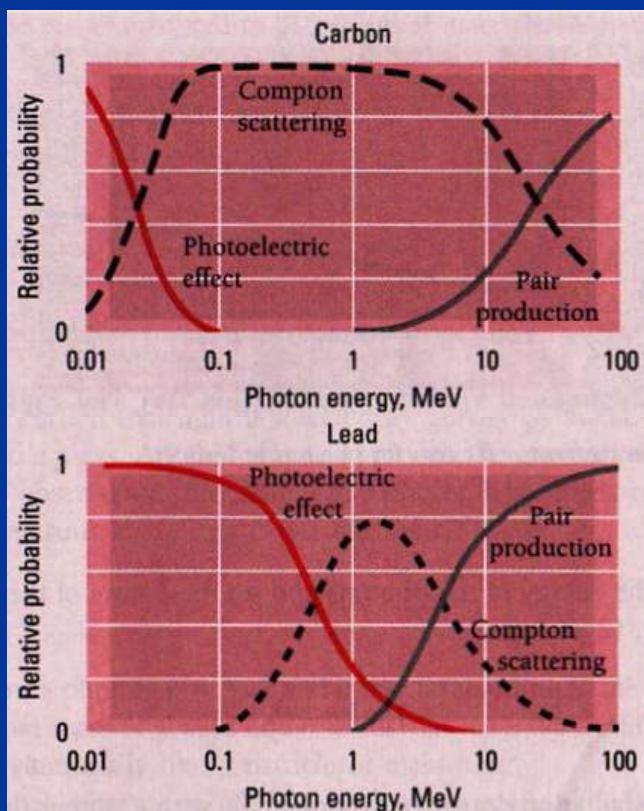
Photon Absorption

Photons of high-energy radiations (x-ray & γ -ray) interact with matters in three chief ways



Importance of energy loss mechanism

photon energy low	photoelectric	Compton (10s keV)	pair-production (>1.02 MeV)	photon energy high
heavier absorber	Remains significant for higher energy photons	Not happen until 1 MeV	Take over at lower energy (4MeV for heaviest, 10 MeV for lighter ones)	



The relative probabilities of photoelectric effect, Compton scattering, and pair production as functions of photon energy in carbon (a light element) and lead (a heavy element).

Linear Absorption

The intensity of x- or γ -ray beam is defined as the rate at which it transports energy per unit cross-sectional area of the beam.

The fractional energy – dI/I lost by the beam in passing a thickness dx of a matter is found to be proportional to dx , i.e.

$$-\frac{dI}{I} = \mu dx$$

The proportional constant μ is called the **linear attenuation coefficient** and its value depends on the energy of the photons as well as the nature of the matter.

Integrating above equation gives:

$$I = I_0 e^{-\mu \cdot x}$$

We can use the above equation to work out the thickness of absorbing material required to reduce the intensity of x- or γ -ray to a specific value:

$$x = \frac{\ln(I_0/I)}{\mu}$$

Wave Properties of Particles

De Broglie waves

A moving body behaves in certain way as though it has a wave nature.



Louis de Broglie

A photon of light of frequency ν has the momentum :
$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \quad (\lambda\nu = c)$$

The wavelength of a photon can therefore be specified by its momentum :
$$\lambda = \frac{h}{p} \quad (3.1)$$

De Broglie: the above equation is a completely general one that applies to other particles as well as photons

De Broglie wavelength:
$$\lambda = \frac{h}{p} = \frac{h}{m\mathbf{v}}, \text{ here } m = \frac{m_0}{\sqrt{1 - \mathbf{v}^2/c^2}} \quad (3.2)$$

A moving body has both particle and wave properties, which set of properties is most obvious depends on how its de Broglie wavelength compares with its dimensions and dimensions of whatever it interacts with.

Example

Find the de Broglie wavelengths of (a) a 46-g golf ball with a velocity of 30 m/s, and (b) an electron with a velocity of 10^7 m/s.

Solution

(a) Since $v \ll c$, we can let $m = m_0$. Hence

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(0.046 \text{ kg})(30 \text{ m/s})} = 4.8 \times 10^{-34} \text{ m}$$

The wavelength of the golf ball is so small compared with its dimensions that we would not expect to find any wave aspects in its behavior.

(b) Again $v \ll c$, so with $m = m_0 = 9.1 \times 10^{-31} \text{ kg}$, we have

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.1 \times 10^{-31} \text{ kg})(10^7 \text{ m/s})} = 7.3 \times 10^{-11} \text{ m}$$

The dimensions of atoms are comparable with this figure—the radius of the hydrogen atom, for instance, is $5.3 \times 10^{-11} \text{ m}$. It is therefore not surprising that the wave character of moving electrons is the key to understanding atomic structure and behavior.

WAVES OF WHAT? *Waves of probability*

In water waves, the quantity that varies periodically is the height of the water surface. In sound waves, it is pressure. In light waves, electric and magnetic fields vary. What is it that varies in the case of matter waves?

The quantity whose variations make up matter waves is called the **wave function**, symbol Ψ (the Greek letter psi). The value of the wave function associated with a moving body at the particular point x, y, z in space at the time t is related to the likelihood of finding the body there at the time.

The wave function Ψ itself, however, has no direct physical significance. There is a simple reason why Ψ cannot be interpreted in terms of an experiment. The probability that something be in a certain place at a given time must lie between 0 (the object is definitely not there) and 1 (the object is definitely there). An intermediate probability, say 0.2, means that there is a 20% chance of finding the object. But the amplitude of any wave is negative as often as it is positive, and a negative probability, say -0.2 , is meaningless. Hence Ψ by itself cannot be an observable quantity.

This objection does not apply to $|\Psi|^2$, the square of the absolute value of the wave function, which is known as **probability density**:

The probability of experimentally finding the body described by the wave function Ψ at the point x, y, z , at the time t is proportional to the value of $|\Psi|^2$ there at t .

DESCRIBING A WAVE

A general formula for waves

How fast do de Broglie waves travel? Since we associate a de Broglie wave with a moving body, we expect that this wave has the same velocity as that of the body. Let us see if this is true.

If we call the de Broglie wave velocity v_p , we can apply the usual formula

$$v_p = \nu\lambda$$

to find v_p . The wavelength λ is simply the de Broglie wavelength $\lambda = h/mv$. To find the frequency, we equate the quantum expression $E = h\nu$ with the relativistic formula for total energy $E = mc^2$ to obtain

$$\begin{aligned} h\nu &= mc^2 \\ \nu &= \frac{mc^2}{h} \end{aligned}$$

The de Broglie wave velocity is therefore

De Broglie phase velocity $v_p = \nu\lambda = \left(\frac{mc^2}{h}\right)\left(\frac{h}{mv}\right) = \frac{c^2}{v}$ (3.3)

Because the particle velocity v must be less than the velocity of light c , the de Broglie waves always travel faster than light! In order to understand this unexpected result, we must look into the distinction between **phase velocity** and **group velocity**. (Phase velocity is what we have been calling wave velocity.)

Wave formula

Let us begin by reviewing how waves are described mathematically. For simplicity we consider a string stretched along the x axis whose vibrations are in the y direction, as in Fig. 3.1, and are simple harmonic in character. If we choose $t = 0$ when the displacement y of the string at $x = 0$ is a maximum, its displacement at any future time t at the same place is given by the formula

$$y = A \cos 2\pi\nu t \quad (3.4)$$

where A is the amplitude of the vibrations (that is, their maximum displacement on either side of the x axis) and ν their frequency.

Equation (3.4) tells us what the displacement of a single point on the string is as a function of time t . A complete description of wave motion in a stretched string, however, should tell us what y is at *any* point on the string at *any* time. What we want is a formula giving y as a function of both x and t .

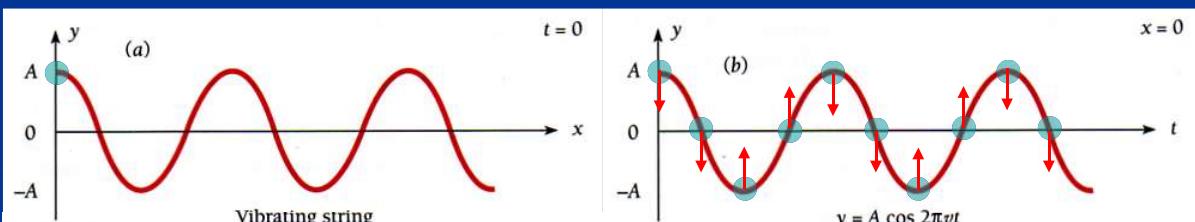


Figure 3.1 (a) The appearance of a wave in a stretched string at a certain time. (b) How the displacement of a point on the string varies with time.

To obtain such a formula, let us imagine that we shake the string at $x = 0$ when $t = 0$, so that a wave starts to travel down the string in the $+x$ direction (Fig. 3.2). This wave has some speed v_p that depends on the properties of the string. The wave travels the distance $x = v_p t$ in the time t , so the time interval between the formation of the wave at $x = 0$ and its arrival at the point x is x/v_p . Hence the displacement y of the string at x at any time t is exactly the same as the value of y at $x = 0$ at the earlier time $t - x/v_p$. By simply replacing t in Eq. (3.4) with $t - x/v_p$, then, we have the desired formula giving y in terms of both x and t :

Wave formula

$$y = A \cos 2\pi\nu \left(t - \frac{x}{v_p} \right) \quad (3.5)$$

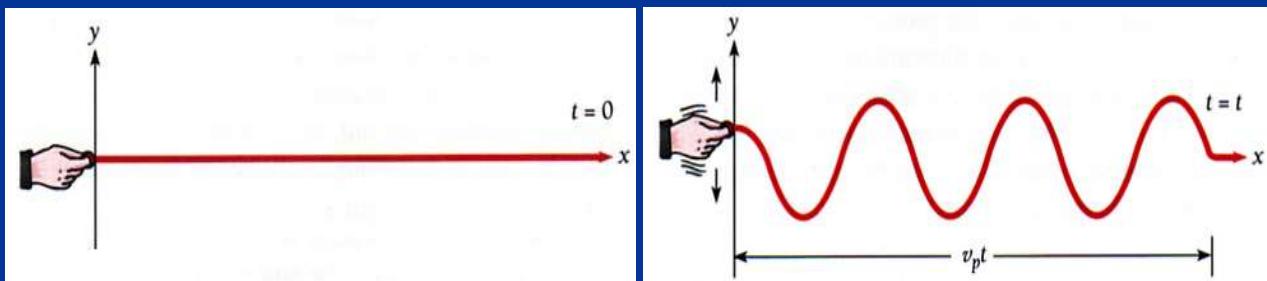


Fig. 3.2 Wave propagation

Equation (3.5) may be rewritten $y = A \cos 2\pi \left(\nu t - \frac{\nu x}{v_p} \right)$

Since the wave speed v_p is given by $v_p = \nu\lambda$ we have

Wave formula $y = A \cos 2\pi \left(\nu t - \frac{x}{\lambda} \right) \quad (3.6)$

Equation (3.6) is often more convenient to use than Eq. (3.5).

Perhaps the most widely used description of a wave, however, is still another form of Eq. (3.5). The quantities **angular frequency** ω and **wave number** k are defined by the formulas

Angular frequency

$$\omega = 2\pi\nu \quad (3.7)$$

Wave number

$$k = \frac{2\pi}{\lambda} = \frac{\omega}{v_p} \quad (3.8)$$

The unit of ω is the radian per second and that of k is the radian per meter. Angular frequency gets its name from uniform circular motion, where a particle that moves around a circle ν times per second sweeps out $2\pi\nu$ rad/s. The wave number is equal to the number of radians corresponding to a wave train 1 m long, since there are 2π rad in one complete wave.

In terms of ω and k , Eq. (3.5) becomes

Wave formula

$$y = A \cos (\omega t - kx) \quad (3.9)$$

In three dimensions k becomes a vector \mathbf{k} normal to the wave fronts and x is replaced by the radius vector \mathbf{r} . The scalar product $\mathbf{k} \cdot \mathbf{r}$ is then used instead of kx in Eq. (3.9).

$$u(\mathbf{r}, t) = \cos (\omega t - \mathbf{k} \cdot \mathbf{r})$$

PHASE AND GROUP VELOCITIES

A group of waves need not have the same velocity as the waves themselves

The amplitude of the de Broglie waves that correspond to a moving body reflects the probability that it will be found at a particular place at a particular time. It is clear that de Broglie waves cannot be represented simply by a formula resembling Eq. (3.9), which describes an indefinite series of waves all with the same amplitude A . Instead, we expect the wave representation of a moving body to correspond to a **wave packet**, or **wave group**, like that shown in Fig. 3.3, whose waves have amplitudes upon which the likelihood of detecting the body depends.

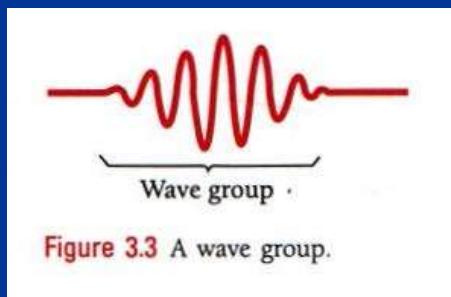


Figure 3.3 A wave group.

A familiar example of how wave groups come into being is the case of **beats**. When two sound waves of the same amplitude but of slightly different frequencies are produced simultaneously, the sound we hear has a frequency equal to the average of the two original frequencies and its amplitude rises and falls periodically. The amplitude fluctuations occur as many times per second as the difference between the two original frequencies. If the original sounds have frequencies of, say, 440 and 442 Hz, we will hear a fluctuating sound of frequency 441 Hz with two loudness peaks, called beats, per second. The production of beats is illustrated in Fig. 3.4.

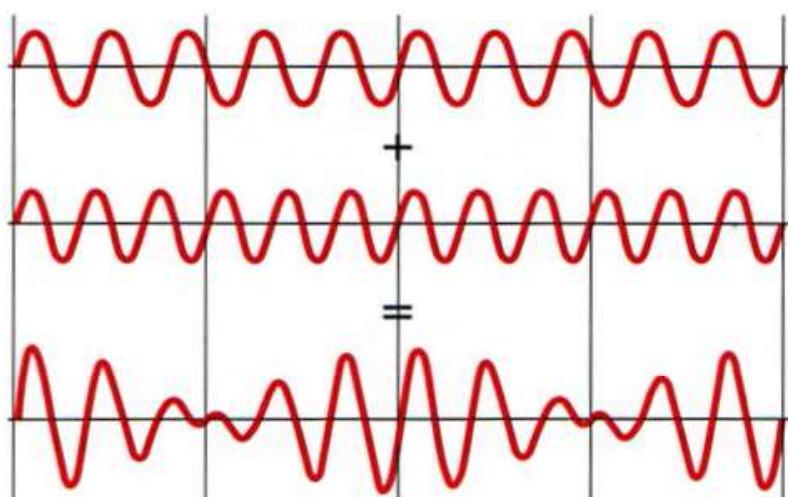


Figure 3.4 Beats are produced by the superposition of two waves with different frequencies.

PHASE AND GROUP VELOCITIES

A way to mathematically describe a wave group, then, is in terms of a superposition of individual waves of different wavelengths whose interference with one another results in the variation in amplitude that defines the group shape. If the velocities of the waves are the same, the velocity with which the wave group travels is the common phase velocity. However, if the phase velocity varies with wavelength, an effect called **dispersion**, the different individual waves do not proceed together. As a result the wave group has a velocity different from the phase velocities of the waves that make it up. This is the case with de Broglie waves.

It is not hard to find the velocity v_g with which a wave group travels. Let us suppose that the wave group arises from the combination of two waves that have the same amplitude A but differ by an amount $\Delta\omega$ in angular frequency and an amount Δk in wave number. We may represent the original waves by the formulas

$$y_1 = A \cos(\omega t - kx)$$
$$y_2 = A \cos[(\omega + \Delta\omega)t - (k + \Delta k)x]$$

The resultant displacement y at any time t and any position x is the sum of y_1 and y_2 . With the help of the identity

$$\cos \alpha + \cos \beta = 2 \cos \frac{1}{2}(\alpha + \beta) \cos \frac{1}{2}(\alpha - \beta)$$

and the relation

$$\cos(-\theta) = \cos \theta$$

we find that

$$y = y_1 + y_2$$
$$= 2A \cos \frac{1}{2}[(2\omega + \Delta\omega)t - (2k + \Delta k)x] \cos \frac{1}{2}(\Delta\omega t - \Delta k x)$$

Since $\Delta\omega$ and Δk are small compared with ω and k respectively,

$$2\omega + \Delta\omega \approx 2\omega$$

$$2k + \Delta k \approx 2k$$

and so

Beats $y = 2A \cos(\omega t - kx) \cos \left(\frac{\Delta\omega}{2} t - \frac{\Delta k}{2} x \right)$ (3.10)

Beats

$$y = 2A \cos(\omega t - kx) \cos\left(\frac{\Delta\omega}{2}t - \frac{\Delta k}{2}x\right) \quad (3.10)$$

Equation (3.10) represents a wave of angular frequency ω and wave number k that has superimposed upon it a modulation of angular frequency $\frac{1}{2}\Delta\omega$ and of wave number $\frac{1}{2}\Delta k$.

The effect of the modulation is thus to produce successive wave groups, as in Fig. 3.4. The phase velocity v_p is

Phase velocity

$$v_p = \frac{\omega}{k} \quad (3.11)$$

and the velocity v_g of the wave groups is

Group velocity

$$v_g = \frac{\Delta\omega}{\Delta k} \quad (3.12)$$

When ω and k have continuous spreads instead of the two values in the preceding discussion, the group velocity is instead given by

Group velocity

$$v_g = \frac{d\omega}{dk} \quad (3.13)$$

Depending on how phase velocity varies with wave number in a particular situation, the group velocity may be less or greater than the phase velocities of its member waves. If the phase velocity is the same for all wavelengths, as is true for light waves in empty space, the group and phase velocities are the same.

The angular frequency and wave number of the de Broglie waves associated with a body of rest mass m_0 moving with the velocity v are

**Angular frequency
of de Broglie
waves**

$$\begin{aligned} \omega &= 2\pi\nu = \frac{2\pi mc^2}{h} \\ &= \frac{2\pi m_0 c^2}{h\sqrt{1 - v^2/c^2}} \end{aligned} \quad (3.14)$$

**Wave number of
de Broglie waves**

$$\begin{aligned} k &= \frac{2\pi}{\lambda} = \frac{2\pi mv}{h} \\ &= \frac{2\pi m_0 v}{h\sqrt{1 - v^2/c^2}} \end{aligned} \quad (3.15)$$

Both ω and k are functions of the body's velocity v .

The group velocity v_g of the de Broglie waves associated with the body is

$$v_g = \frac{d\omega}{dk} = \frac{d\omega/dv}{dk/dv}$$

Now $\frac{d\omega}{dv} = \frac{2\pi m_0 v}{h(1 - v^2/c^2)^{3/2}}$ $\frac{dk}{dv} = \frac{2\pi m_0}{h(1 - v^2/c^2)^{3/2}}$

and so the group velocity turns out to be

**De Broglie group
velocity**

$$v_g = v \quad (3.16)$$

The de Broglie wave group associated with a moving body travels with the same velocity as the body.

The phase velocity v_p of de Broglie waves is, as we found earlier,

**De Broglie phase
velocity**

$$v_p = \frac{\omega}{k} = \frac{c^2}{v} \quad (3.3)$$

This exceeds both the velocity of the body v and the velocity of light c , since $v < c$. However, v_p has no physical significance because it is the motion of the wave group, not the motion of the individual waves that make up the group, that corresponds to the motion of the body, and $v_g < c$ as it should be. The fact that $v_p > c$ for de Broglie waves therefore does not violate special relativity.

PARTICLE DIFFRACTION

An experiment that confirms the existence of de Broglie waves

A wave effect with no analog in the behavior of newtonian particles is diffraction. In 1927 Clinton Davisson and Lester Germer in the United States and G. P. Thomson in England independently confirmed de Broglie's hypothesis by demonstrating that electron beams are diffracted when they are scattered by the regular atomic arrays of crystals.

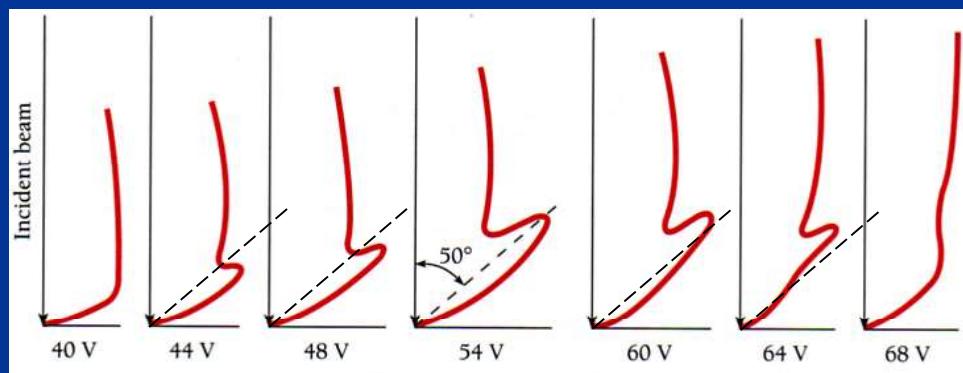
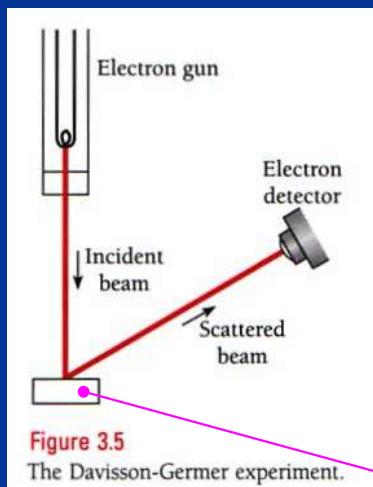


Figure 3.6 Results of the Davisson-Germer experiment. (after baking Ni)

Initially, continuous variations of intensity were observed, but after heating Ni, peaks appeared.

What is the reason for this new effect?

Why did it not appear until after the nickel target was baked?

De Broglie's hypothesis suggested that electron waves were being diffracted by the target, much as x-rays are diffracted by planes of atoms in a crystal. This idea received support when it was realized that heating a block of nickel at high temperature causes the many small individual crystals of which it is normally composed to form into a single large crystal, all of whose atoms are arranged in a regular lattice.

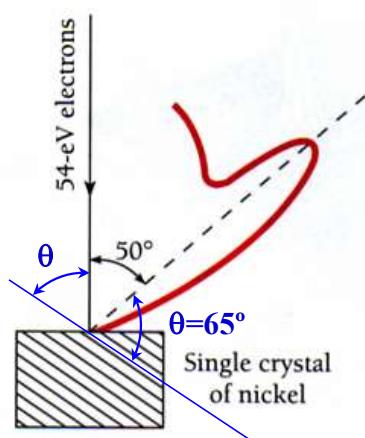


Figure 3.7 The diffraction of the de Broglie waves by the target is responsible for the results of Davisson and Germer.

The Bragg equation for maxima in the diffraction pattern is

$$n\lambda = 2d \sin \theta \quad (2.13)$$

Here $d = 0.091 \text{ nm}$ (measured from x-ray diffraction) and $\theta = 65^\circ$.

For $n = 1$ the de Broglie wavelength λ of the diffracted electrons is

$$\lambda = 2d \sin \theta = (2)(0.091 \text{ nm})(\sin 65^\circ) = \underline{0.165 \text{ nm}}$$

Now we use the de Broglie formula $\lambda = h/mv$ to find the expected wavelength of the electrons.

The electron kinetic energy of 54 eV in this experiment is small compared to its rest energy $m_0 c^2$ (which is 0.51 MeV), so we can ignore relativistic effect and the kinetic energy of electron can be written as:

$$KE = \frac{1}{2}mv^2$$

the electron momentum mv is

$$\begin{aligned} mv &= \sqrt{2mKE} \quad (KE = \frac{1}{2}mv^2) \\ &= \sqrt{(2)(9.1 \times 10^{-31} \text{ kg})(54 \text{ eV})(1.6 \times 10^{-19} \text{ J/eV})} \\ &= 4.0 \times 10^{-24} \text{ kg} \cdot \text{m/s} \end{aligned}$$

The electron wavelength is therefore

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{4.0 \times 10^{-24} \text{ kg} \cdot \text{m/s}} = 1.66 \times 10^{-10} \text{ m} = \underline{0.166 \text{ nm}}$$

which agrees well with the observed wavelength of 0.165 nm. The Davisson-Germer experiment thus directly verifies de Broglie's hypothesis of the wave nature of moving bodies.

Electron Microscopes

The wave nature of moving electrons is the basis of the electron microscope, the first of which was built in 1932. The resolving power of any optical instrument, which is limited by diffraction, is proportional to the wavelength of whatever is used to illuminate the specimen. In the case of a good microscope that uses visible light, the maximum useful magnification is about $500 \times$; higher magnifications give larger images but do not reveal any more detail. Fast electrons, however, have wavelengths very much shorter than those of visible light and are easily controlled by electric and magnetic fields because of their charge. X-rays also have short wavelengths, but it is not (yet?) possible to focus them adequately.

In an electron microscope, current-carrying coils produce magnetic fields that act as lenses to focus an electron beam on a specimen and then produce an enlarged image on a fluorescent screen or photographic plate (Fig. 3.8). To prevent the beam from being scattered and thereby blurring the image, a thin specimen is used and the entire system is evacuated.

The technology of magnetic "lenses" does not permit the full theoretical resolution of electron waves to be realized in practice. For instance, 100-keV electrons have wavelengths of 0.0037 nm, but the actual resolution they can provide in an electron microscope may be only about 0.1 nm. However, this is still a great improvement on the ~ 200 -nm resolution of an optical microscope, and magnifications of over $1,000,000 \times$ have been achieved with electron microscopes.

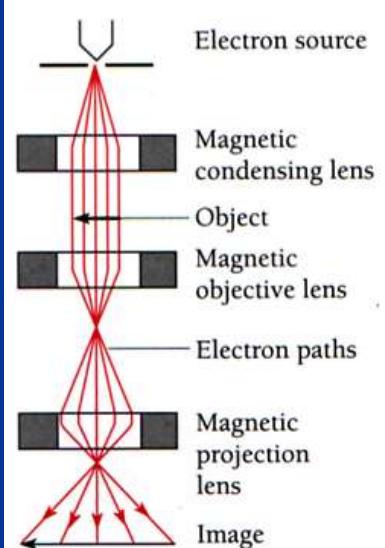


Figure 3.8 Because the wavelengths of the fast electrons in an electron microscope are shorter than those of the light waves in an optical microscope, the electron microscope can produce sharp images at higher magnifications. The electron beam in an electron microscope is focused by magnetic fields.

PARTICLE IN A BOX Why the energy of a trapped particle is quantized

The wave nature of a moving particle leads to some remarkable consequences when the particle is restricted to a certain region of space instead of being able to move freely.

The simplest case is that of a particle that bounces back and forth between the walls of a box, as in Fig. 3.9. We shall assume that the walls of the box are infinitely hard, so the particle does not lose energy each time it strikes a wall, and that its velocity is sufficiently small so that we can ignore relativistic considerations. Simple as it is, this model situation requires fairly elaborate mathematics in order to be properly analyzed, as we shall learn in Chap. 5. However, even a relatively crude treatment can reveal the essential results.

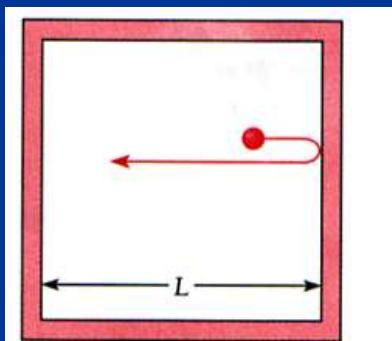


Figure 3.9 A particle confined to a box of width L .

From a wave point of view, a particle trapped in a box is like a standing wave in a string stretched between the box's walls. In both cases the wave variable (transverse displacement for the string, wave function Ψ for the moving particle) must be 0 at the walls, since the waves stop there. The possible de Broglie wavelengths of the particle in the box therefore are determined by the width L of the box, as in Fig. 3.10. The longest wavelength is specified by $\lambda = 2L$, the next by $\lambda = L$, then $\lambda = 2L/3$, and so forth. The general formula for the permitted wavelengths is

**De Broglie
wavelengths of
trapped particle**

$$\lambda_n = \frac{2L}{n} \quad n = 1, 2, 3, \dots \quad (3.17)$$

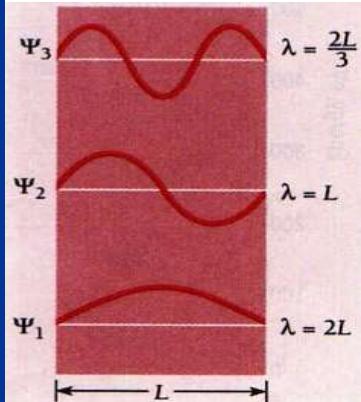


Figure 3.10 Wave functions of a particle trapped in a box L wide.

Because $mv = h/\lambda$, the restrictions on de Broglie wavelength λ imposed by the width of the box are equivalent to limits on the momentum of the particle and, in turn, to limits on its kinetic energy. The kinetic energy of a particle of momentum mv is

$$KE = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{h^2}{2m\lambda^2}$$

The permitted wavelengths are $\lambda_n = 2L/n$, and so, because the particle has no potential energy in this model, the only energies it can have are

Particle in a box $E_n = \frac{n^2h^2}{8mL^2} \quad n = 1, 2, 3, \dots \quad (3.18)$

Each permitted energy is called an **energy level**, and the integer n that specifies an energy level E_n is called its **quantum number**.

We can draw three general conclusions from Eq. (3.18). These conclusions apply to any particle confined to a certain region of space (even if the region does not have a well-defined boundary), for instance an atomic electron held captive by the attraction of the positively charged nucleus.

- 1 A trapped particle cannot have an arbitrary energy, as a free particle can. The fact of its confinement leads to restrictions on its wave function that allow the particle to have only certain specific energies and no others. Exactly what these energies are depends on the mass of the particle and on the details of how it is trapped.
- 2 A trapped particle cannot have zero energy. Since the de Broglie wavelength of the particle is $\lambda = h/mv$, a speed of $v = 0$ means an infinite wavelength. But there is no way to reconcile an infinite wavelength with a trapped particle, so such a particle must have at least some kinetic energy. The exclusion of $E = 0$ for a trapped particle, like the limitation of E to a set of discrete values, is a result with no counterpart in classical physics, where all non-negative energies, including zero, are allowed.
- 3 Because Planck's constant is so small—only $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ —quantization of energy is conspicuous only when m and L are also small. This is why we are not aware of energy quantization in our own experience. Two examples will make this clear.

Example 3.4

An electron is in a box 0.10 nm across, which is the order of magnitude of atomic dimensions. Find its permitted energies.

Solution

Here $m = 9.1 \times 10^{-31} \text{ kg}$ and $L = 0.10 \text{ nm} = 1.0 \times 10^{-10} \text{ m}$, so that the permitted electron energies are

$$E_n = \frac{(n^2)(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(8)(9.1 \times 10^{-31} \text{ kg})(1.0 \times 10^{-10} \text{ m})^2} = 6.0 \times 10^{-18} n^2 \text{ J}$$

$$= 38n^2 \text{ eV}$$

$n = 1$	$E_1 = 38 \text{ eV}$
$n = 2$	$E_2 = 152 \text{ eV}$
$n = 3$	$E_3 = 342 \text{ eV}$
$n = 4$	$E_4 = 608 \text{ eV}$

Energy quantization is prominent and it is indeed also the case for an atomic electron

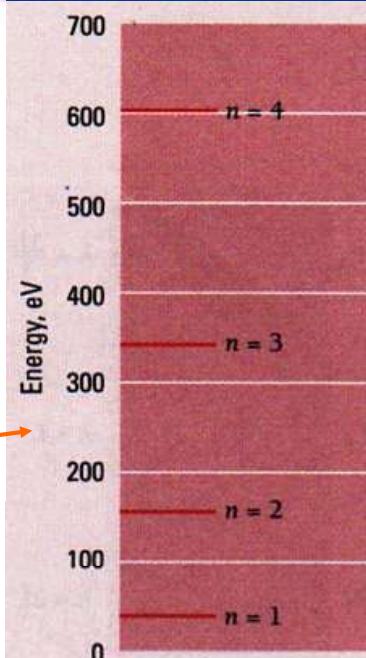


Figure 3.11 Energy levels of an electron confined to a box 0.1 nm wide.

Example 3.5

A 10-g marble is in a box 10 cm across. Find its permitted energies.

Solution

With $m = 10 \text{ g} = 1.0 \times 10^{-2} \text{ kg}$ and $L = 10 \text{ cm} = 1.0 \times 10^{-1} \text{ m}$,

$$E_n = \frac{(n^2)(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(8)(1.0 \times 10^{-2} \text{ kg})(1.0 \times 10^{-1} \text{ m})^2}$$
$$= 5.5 \times 10^{-64} n^2 \text{ J} = 3.4 \times 10^{-45} n^2 \text{ eV}$$

The minimum energy the marble can have is $5.5 \times 10^{-64} \text{ J}$, corresponding to $n = 1$. A marble with this kinetic energy has a speed of only $3.3 \times 10^{-31} \text{ m/s}$ and therefore cannot be experimentally distinguished from a stationary marble. A reasonable speed a marble might have is, say, $\frac{1}{2} \text{ m/s}$ —which corresponds to the energy level of quantum number $n = 10^{30}$! The permissible energy levels are so very close together, then, that there is no way to determine whether the marble can take on only those energies predicted by Eq. (3.18) or any energy whatever. Hence in the domain of everyday experience, quantum effects are imperceptible, which accounts for the success of newtonian mechanics in this domain.

$$E_{n+1}/E_n = (n+1)^2/n^2 = 1 + (2/n) + (1/n^2); \text{ if } n=1000, E_{n+1}/E_n = 1.002$$

UNCERTAINTY PRINCIPLE I

We cannot know the future because we cannot know the present

To regard a moving particle as a wave group implies that there are fundamental limits to the accuracy with which we can measure such “particle” properties as position and momentum.

To make clear what is involved, let us look at the wave group of Fig. 3.3. The particle that corresponds to this wave group may be located anywhere within the group at a given time. Of course, the probability density $|\Psi|^2$ is a maximum in the middle of the group, so it is most likely to be found there. Nevertheless, we may still find the particle anywhere that $|\Psi|^2$ is not actually 0.

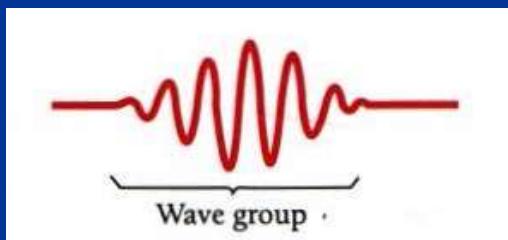


Figure 3.3 A wave group.

The narrower its wave group, the more precisely a particle's position can be specified (Fig. 3.12a). However, the wavelength of the waves in a narrow packet is not well defined; there are not enough waves to measure λ accurately. This means that since $\lambda = h/mv$, the particle's momentum mv is not a precise quantity. If we make a series of momentum measurements, we will find a broad range of values.

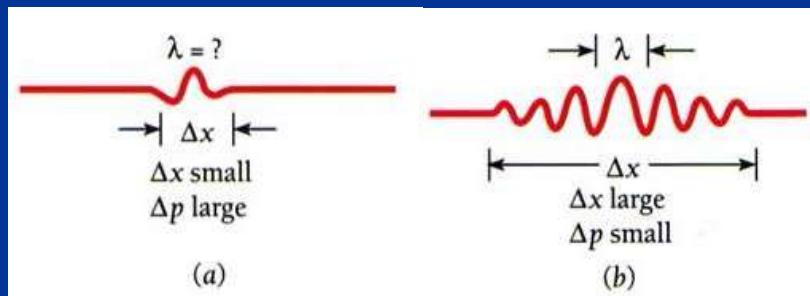
On the other hand, a wide wave group, such as that in Fig. 3.12b, has a clearly defined wavelength. The momentum that corresponds to this wavelength is therefore a precise quantity, and a series of measurements will give a narrow range of values. But where is the particle located? The width of the group is now too great for us to be able to say exactly where it is at a given time.

Thus we have the **uncertainty principle**:

It is impossible to know both the exact position and exact momentum of an object at the same time.

This principle, which was discovered by Werner Heisenberg in 1927, is one of the most significant of physical laws.

Figure 3.12



A formal analysis supports the above conclusion and enables us to put it on a quantitative basis. The simplest example of the formation of wave groups is that given in Sec. 3.4, where two wave trains slightly different in angular frequency ω and wave number k were superposed to yield the series of groups shown in Fig. 3.4. A moving body corresponds to a single wave group, not a series of them, but a single wave group can also be thought of in terms of the superposition of trains of harmonic waves. However, an infinite number of wave trains with different frequencies, wave numbers, and amplitudes is required for an isolated group of arbitrary shape, as in Fig. 3.13.

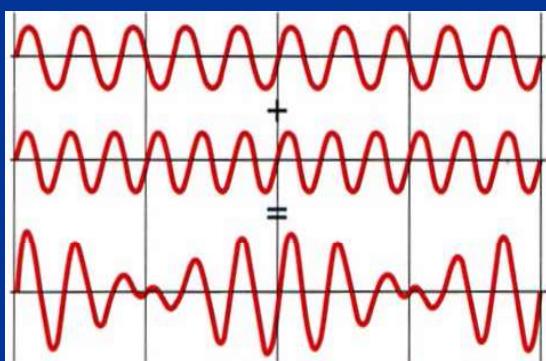


Figure 3.4

Beats are produced by the superposition of two waves with different frequencies.

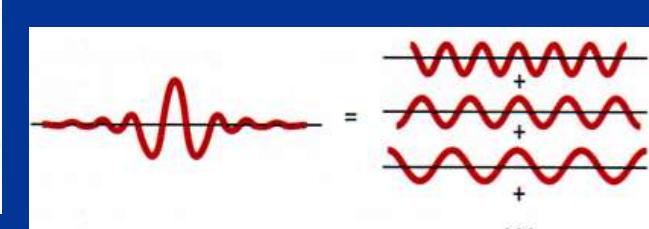


Figure 3.13 An isolated wave group is the result of superposing an infinite number of waves with different wavelengths. The narrower the wave group, the greater the range of wavelengths involved. A narrow de Broglie wave group thus means a well-defined position (Δx smaller) but a poorly defined wavelength and a large uncertainty Δp in the momentum of the particle the group represents. A wide wave group means a more precise momentum but a less precise position.

At a certain time t , the wave group $\Psi(x)$ can be represented by the **Fourier integral**

$$\Psi(x) = \int_0^\infty g(k) \cos kx dk \quad (3.19)$$

where the function $g(k)$ describes how the amplitudes of the waves that contribute to $\Psi(x)$ vary with wave number k . This function is called the **Fourier transform** of $\Psi(x)$, and it specifies the wave group just as completely as $\Psi(x)$ does. Figure 3.14 contains graphs of the Fourier transforms of a pulse and of a wave group. For comparison, the Fourier transform of an infinite train of harmonic waves is also included. There is only a single wave number in this case, of course.

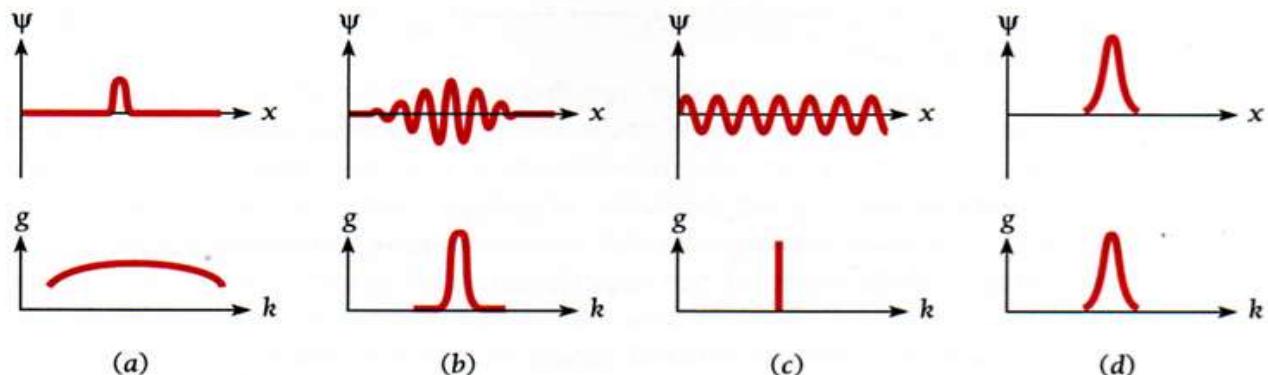


Figure 3.14 The wave functions and Fourier transforms for (a) a pulse, (b) a wave group, (c) an wave train, and (d) a gaussian distribution. A brief disturbance needs a broader range of frequencies to describe it than a disturbance of greater duration. The Fourier transform of a gaussian function is also a gaussian function.

Strictly speaking, the wave numbers needed to represent a wave group extend from $k = 0$ to $k = \infty$, but for a group whose length Δx is finite, the waves whose amplitudes $g(k)$ are appreciable have wave numbers that lie within a finite interval Δk . As Fig. 3.14 indicates, the shorter the group, the broader the range of wave numbers needed to describe it, and vice versa.

The relationship between the distance Δx and the wave-number spread Δk depends upon the shape of the wave group and upon how Δx and Δk are defined. The minimum value of the product $\Delta x \Delta k$ occurs when the envelope of the group has the familiar bell shape of a gaussian function. In this case the Fourier transform happens to be a gaussian function also. If Δx and Δk are taken as the standard deviations of the respective functions $\Psi(x)$ and $g(k)$, then this minimum value is $\Delta x \Delta k = \frac{1}{2}$. Because wave groups in general do not have gaussian forms, it is more realistic to express the relationship between Δx and Δk as

$$\Delta x \Delta k \geq \frac{1}{2} \quad (3.20)$$

The de Broglie wavelength of a particle of momentum p is $\lambda = h/p$ and the corresponding wave number is

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$$

In terms of wave number the particle's momentum is therefore

$$p = \frac{hk}{2\pi}$$

Hence an uncertainty Δk in the wave number of the de Broglie waves associated with the particle results in an uncertainty Δp in the particle's momentum according to the formula

$$\Delta p = \frac{h \Delta k}{2\pi}$$

Since $\Delta x \Delta k \geq \frac{1}{2}$, $\Delta k \geq 1/(2\Delta x)$ and

Uncertainty principle

$$\boxed{\Delta x \Delta p \geq \frac{h}{4\pi}} \quad (3.21)$$

This equation states that the product of the uncertainty Δx in the position of an object at some instant and the uncertainty Δp in its momentum component in the x direction at the same instant is equal to or greater than $h/4\pi$.

Uncertainty principle

$$\Delta x \Delta p \geq \frac{h}{4\pi} \quad (3.21)$$

If we arrange matters so that Δx is small, corresponding to a narrow wave group, then Δp will be large. If we reduce Δp in some way, a broad wave group is inevitable and Δx will be large.

These uncertainties are due not to inadequate apparatus but to the imprecise character in nature of the quantities involved. Any instrumental or statistical uncertainties that arise during a measurement only increase the product $\Delta x \Delta p$. Since we cannot know exactly both where a particle is right now and what its momentum is, we cannot say anything definite about where it will be in the future or how fast it will be moving then. **We cannot know the future for sure because we cannot know the present for sure.** But our ignorance is not total: we can still say that the particle is more likely to be in one place than another and that its momentum is more likely to have a certain value than another.

H-Bar

The quantity $h/2\pi$ appears often in modern physics because it turns out to be the basic unit of angular momentum. It is therefore customary to abbreviate $h/2\pi$ by the symbol \hbar ("h-bar"):

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{ J} \cdot \text{s}$$

In the remainder of this book \hbar is used in place of $h/2\pi$. In terms of \hbar , the uncertainty principle becomes

Uncertainty
principle

$$\Delta x \Delta p \geq \frac{\hbar}{2} \quad (3.22)$$

3.8 UNCERTAINTY PRINCIPLE II

A particle approach gives the same result

The uncertainty principle can be arrived at from the point of view of the particle properties of waves as well as from the point of view of the wave properties of particles.

We might want to measure the position and momentum of an object at a certain moment. To do so, we must touch it with something that will carry the required information back to us. That is, we must poke it with a stick, shine light on it, or perform some similar act. The measurement process itself thus requires that the object be interfered with in some way. If we consider such interferences in detail, we are led to the same uncertainty principle as before even without taking into account the wave nature of moving bodies.

Suppose we look at an electron using light of wavelength λ , as in Fig. 3.16. Each photon of this light has the momentum h/λ . When one of these photons bounces off the electron (which must happen if we are to “see” the electron), the electron’s original momentum will be changed.

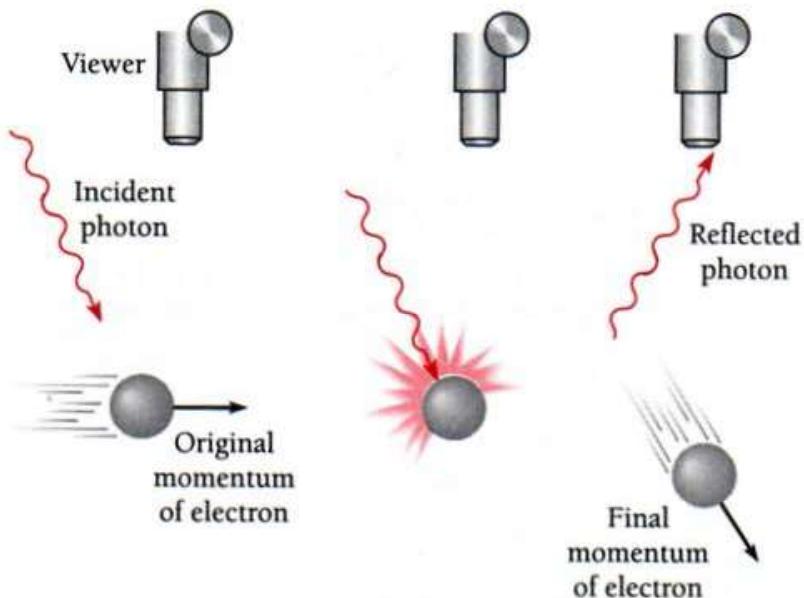


Figure 3.16 An electron cannot be observed without changing its momentum.

The exact amount of the change Δp cannot be predicted, but it will be of the same order of magnitude as the photon momentum h/λ . Hence

$$\Delta p \approx \frac{h}{\lambda} \quad (3.23)$$

The longer the wavelength of the observing photon, the smaller the uncertainty in the electron’s momentum.

Because light is a wave phenomenon as well as a particle phenomenon, we cannot expect to determine the electron’s location with perfect accuracy regardless of the instrument used. A reasonable estimate of the minimum uncertainty in the measurement might be one photon wavelength, so that

$$\Delta x \geq \lambda \quad (3.24)$$

The shorter the wavelength, the smaller the uncertainty in location. If we use light of short wavelength to increase the accuracy of the position measurement, there will be a corresponding decrease in the accuracy of the momentum measurement because the higher photon momentum will disturb the electron’s motion to a greater extent. Light of long wavelength will give a more accurate momentum but a less accurate position.

Combining Eqs. (3.23) and (3.24) gives

$$\Delta x \Delta p \geq h \quad (3.25)$$

This result is consistent with Eq. (3.22), $\Delta x \Delta p \geq \hbar/2$.

Arguments like the preceding one, although superficially attractive, must be approached with caution. The argument above implies that the electron can possess a definite position and momentum at any instant and that it is the measurement process that introduces the indeterminacy in $\Delta x \Delta p$. On the contrary, this *indeterminacy is inherent in the nature of a moving body*. The justification for the many “derivations” of this kind is first, they show it is impossible to imagine a way around the uncertainty principle; and second, they present a view of the principle that can be appreciated in a more familiar context than that of wave groups.

APPLYING THE UNCERTAINTY PRINCIPLE

A useful tool, not just a negative statement

Planck's constant h is so small that the limitations imposed by the uncertainty principle are significant only in the realm of the atom. On such a scale, however, this principle is of great help in understanding many phenomena. It is worth keeping in mind that the lower limit of $\hbar/2$ for $\Delta x \Delta p$ is rarely attained. More usually $\Delta x \Delta p \geq \hbar$, or even (as we just saw) $\Delta x \Delta p \geq h$.

Example 3.7

A typical atomic nucleus is about 5.0×10^{-15} m in radius. Use the uncertainty principle to place a lower limit on the energy an electron must have if it is to be part of a nucleus.

Solution

Letting $\Delta x = 5.0 \times 10^{-15}$ m we have

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq \frac{1.054 \times 10^{-34} \text{ J} \cdot \text{s}}{(2)(5.0 \times 10^{-15} \text{ m})} \geq 1.1 \times 10^{-20} \text{ kg} \cdot \text{m/s}$$

If this is the uncertainty in a nuclear electron's momentum, the momentum p itself must be at least comparable in magnitude. An electron with such a momentum has a kinetic energy KE many times greater than its rest energy $m_0 c^2$. From Eq. (1.24) we see that we can let KE = pc here to a sufficient degree of accuracy. Therefore

$$KE = pc \geq (1.1 \times 10^{-20} \text{ kg} \cdot \text{m/s})(3.0 \times 10^8 \text{ m/s}) \geq 3.3 \times 10^{-12} \text{ J} \quad (= 20.6 \text{ MeV})$$

Since $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$, the kinetic energy of an electron must exceed 20 MeV if it is to be inside a nucleus. Experiments show that even the electrons associated with unstable atoms never have more than a fraction of this energy, and we conclude that nuclei do not contain electrons.

Example 3.8

A hydrogen atom is 5.3×10^{-11} m in radius. Use the uncertainty principle to estimate the minimum energy an electron can have in this atom.

Solution

Here we find that with $\Delta x = 5.3 \times 10^{-11}$ m,

$$\Delta p \geq \frac{\hbar}{2\Delta x} \geq 9.9 \times 10^{-25} \text{ kg} \cdot \text{m/s}$$

An electron whose momentum is of this order of magnitude behaves like a classical particle, and its kinetic energy is

$$KE = \frac{p^2}{2m} \geq \frac{(9.9 \times 10^{-25} \text{ kg} \cdot \text{m/s})^2}{(2)(9.1 \times 10^{-31} \text{ kg})} \geq 5.4 \times 10^{-19} \text{ J}$$

which is 3.4 eV. The kinetic energy of an electron in the lowest energy level of a hydrogen atom is actually 13.6 eV.

Energy and Time

Another form of the uncertainty principle concerns energy and time. We might wish to measure the energy E emitted during the time interval Δt in an atomic process. If the energy is in the form of em waves, the limited time available restricts the accuracy with which we can determine the frequency ν of the waves. Let us assume that the minimum uncertainty in the number of waves we count in a wave group is one wave. Since the frequency of the waves under study is equal to the number of them we count divided by the time interval, the uncertainty $\Delta\nu$ in our frequency measurement is

$$\Delta\nu \geq \frac{1}{\Delta t}$$

The corresponding energy uncertainty is

$$\Delta E = h \Delta\nu$$

and so

$$\Delta E \geq \frac{h}{\Delta t} \quad \text{or} \quad \Delta E \Delta t \geq h$$

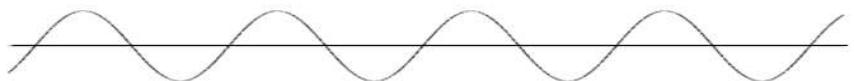
A more precise calculation based on the nature of wave groups changes this result to

Uncertainties in energy and time

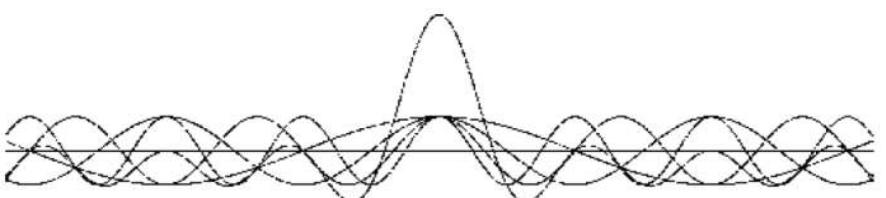
$$\boxed{\Delta E \Delta t \geq \frac{\hbar}{2}} \quad (3.26)$$

Equation (3.26) states that the product of the uncertainty ΔE in an energy measurement and the uncertainty Δt in the time at which the measurement is made is equal to or greater than $\hbar/2$. This result can be derived in other ways as well and is a general one not limited to em waves.

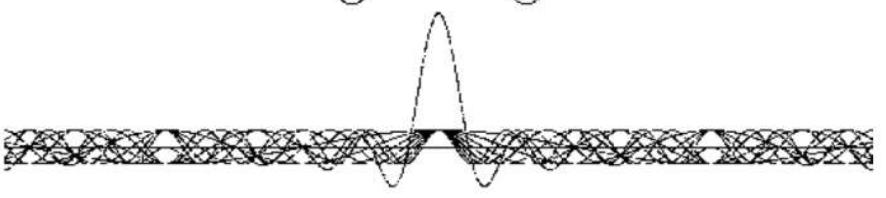
A pure cosine wave extends infinitely in both directions with no change in the size of the peaks or valleys.



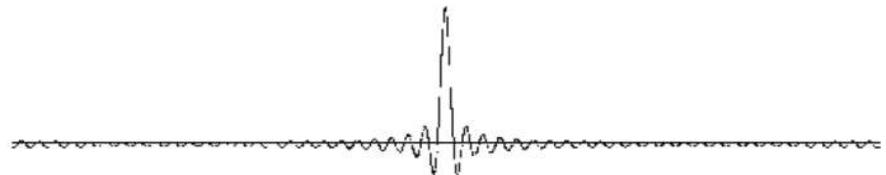
4 cosine waves and their sum



8 cosine waves and their sum



The sum of 32 cosine waves



An impulse has all frequencies

Gaussian Function

When a set of measurements is made of some quantity x in which the experimental errors are random, the result is often a **gaussian distribution** whose form is the bell-shaped curve shown in Fig. 3.15. The **standard deviation** σ of the measurements is a measure of the spread of x values about the mean of x_0 , where σ equals the square root of the average of the squared deviations from x_0 . If N measurements were made,

Standard deviation
$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - x_0)^2}$$

The width of a gaussian curve at half its maximum value is 2.35σ .

The **gaussian function** $f(x)$ that describes the above curve is given by

Gaussian function
$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-x_0)^2/2\sigma^2}$$

where $f(x)$ is the probability that the value x be found in a particular measurement. Gaussian functions occur elsewhere in physics and mathematics as well.

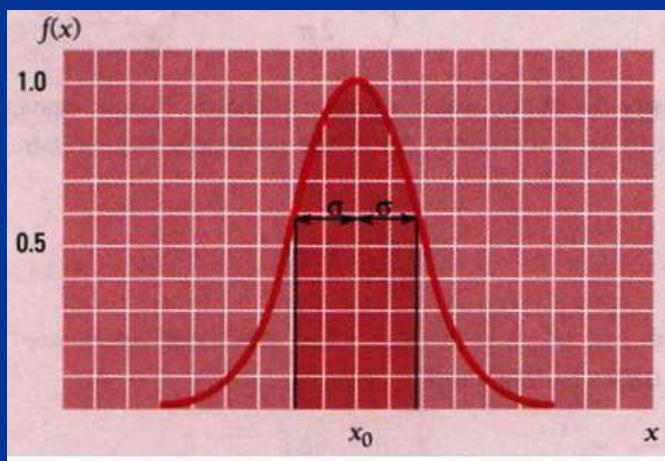


Figure 3.15 A gaussian distribution.

The probability that a measurement lie inside a certain range of x values, say between x_1 and x_2 , is given by the area of the $f(x)$ curve between these limits. This area is the integral

$$P_{x_1 x_2} = \int_{x_1}^{x_2} f(x) dx$$

An interesting question is what fraction of a series of measurements has values within a standard deviation of the mean value x_0 . In this case $x_1 = x_0 - \sigma$ and $x_2 = x_0 + \sigma$, and

$$P_{x_0 \pm \sigma} = \int_{x_0 - \sigma}^{x_0 + \sigma} f(x) dx = 0.683$$

Hence 68.3 percent of the measurements fall in this interval, which is shaded in Fig. 3.15. A similar calculation shows that 95.4 percent of the measurements fall within two standard deviations of the mean value.

Atomic Structure

4.1 THE NUCLEAR ATOM

An atom is largely empty space

Most scientists of the late nineteenth century accepted the idea that the chemical elements consist of atoms, but they knew almost nothing about the atoms themselves. One clue was the discovery that all atoms contain electrons. Since electrons carry negative charges whereas atoms are neutral, positively charged matter of some kind must be present in atoms. But what kind? And arranged in what way?

Old atomic models

- Substances are made up of chemical elements — 1789, Lavoisier
- Chemical elements are made up of atoms — 1803, Dalton
- Discovery of electron — 1897, Thomson
- The charge and mass of electron — 1909, Millikan (oil drop experiment)

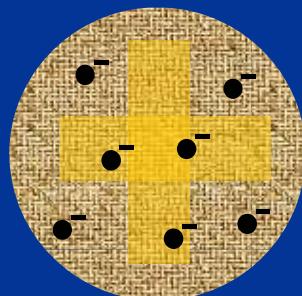


By 1910 most physicists had come to believe that atoms are made of some combination of positive and negative electric charges, and that the attractions and repulsions of these charges are the basis for all the chemical and physical properties observed in matters.

The Thomson Model of the Atom

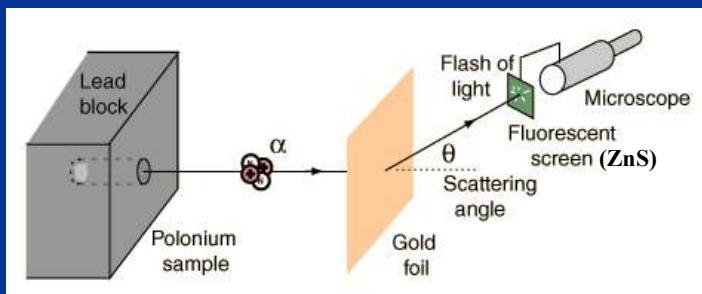
- electrons are embedded in a positively charged sphere
- configuration of electrons determines the spectra

i.e. the atom was a positively charged blob with sprinkled negatively charged electrons in it — "raisin pudding model"



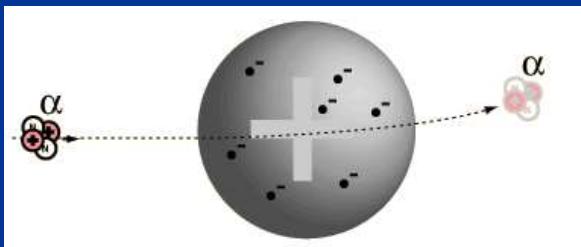
Rutherford Scattering

Microscopes at that time were not powerful enough to reveal the inside of atoms. Rutherford's technique (bombard atoms with a particle beam) was used to "feel" the interior of atom.

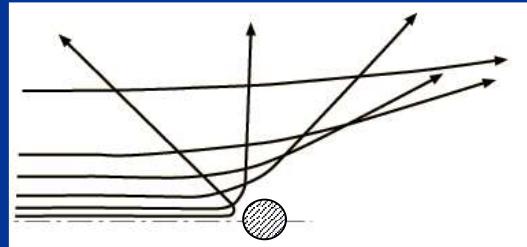


Ernest Rutherford

"raisin pudding model" expected a very small θ ($<0.02^\circ$)



Actual experimental results: most of alpha particles indeed passed through, but some scattered with $\theta > 90^\circ$!



To get a scattering angle greater than 90° , the target must be more massive than the projectile !

The result raised a serious doubt about "raisin pudding model".

Rutherford Scattering Formula

The formula that Rutherford obtained for alpha particle scattering by a thin foil on the basis of the nuclear model of the atom is

Rutherford scattering formula
$$N(\theta) = \frac{N_i n t Z^2 e^4}{(8\pi\epsilon_0)^2 r^2 KE^2 \sin^4(\theta/2)} \quad (4.1)$$

This formula is derived in the Appendix to this chapter. The symbols in Eq. (4.1) have the following meanings:

$N(\theta)$ = number of alpha particles per unit area that reach the screen at a scattering angle of θ

N_i = total number of alpha particles that reach the screen

n = number of atoms per unit volume in the foil

Z = atomic number of the foil atoms

r = distance of the screen from the foil

KE = kinetic energy of the alpha particles

t = foil thickness

The predictions of Eq. (4.1) agreed with the measurements of Geiger and Marsden, which supported the hypothesis of the nuclear atom. This is why Rutherford is credited with the "discovery" of the nucleus. Because $N(\theta)$ is inversely proportional to $\sin^4(\theta/2)$ the variation of $N(\theta)$ with θ is very pronounced (Fig. 4.4): only 0.14 percent of the incident alpha particles are scattered by more than 1° .

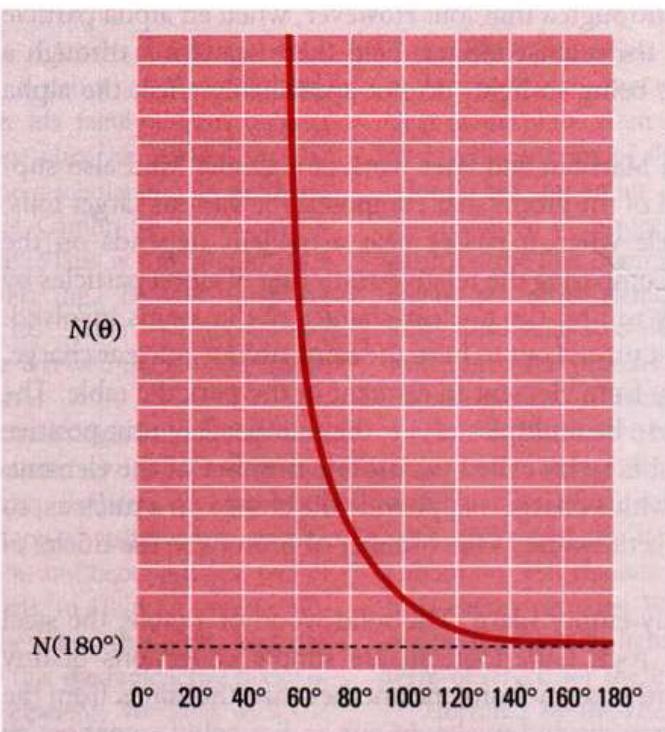


Figure 4.4 Rutherford scattering. $N(\theta)$ is the number of alpha particles per unit area that reach the screen at a scattering angle of θ ; $N(180^\circ)$ is this number for backward scattering. The experimental findings follow this curve, which is based on the nuclear model of the atom.

Nuclear Dimensions

In his derivation of Eq. (4.1) Rutherford assumed that the size of a target nucleus is small compared with the minimum distance R to which incident alpha particles approach the nucleus before being deflected away. Rutherford scattering therefore gives us a way to find an upper limit to nuclear dimensions.

Let us see what the distance of closest approach R was for the most energetic alpha particles employed in the early experiments. An alpha particle will have its smallest R when it approaches a nucleus head on, which will be followed by a 180° scattering. At the instant of closest approach the initial kinetic energy KE of the particle is entirely converted to electric potential energy, and so at that instant

$$KE = PE = \frac{1}{4\pi\epsilon_0} \frac{2Ze^2}{R}$$

since the charge of the alpha particle is $2e$ and that of the nucleus is Ze . Hence

Distance of closest approach

$$R = \frac{2Ze^2}{4\pi\epsilon_0 KE} \quad (4.2)$$

Distance of closest approach

$$R = \frac{2Ze^2}{4\pi\epsilon_0 KE} \quad (4.2)$$

The maximum KE found in alpha particles of natural origin is 7.7 MeV, which is 1.2×10^{-12} J. Since $1/4\pi\epsilon_0 = 9.0 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2$,

$$\begin{aligned} R &= \frac{(2)(9.0 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2 Z}{1.2 \times 10^{-12} \text{ J}} \\ &= 3.8 \times 10^{-16} Z \text{ m} \end{aligned}$$

The atomic number of gold, a typical foil material, is $Z = 79$, so that

$$R (\text{Au}) = 3.0 \times 10^{-14} \text{ m}$$

The radius of the gold nucleus is therefore less than 3.0×10^{-14} m, well under 10^{-4} the radius of the atom as a whole.

In more recent years particles of much higher energies than 7.7 MeV have been artificially accelerated, and it has been found that the Rutherford scattering formula does indeed eventually fail to agree with experiment. These experiments and the information they provide on actual nuclear dimensions are discussed in Chap. 11. The radius of the gold nucleus turns out to be about $\frac{1}{3}$ of the value of $R (\text{Au})$ found above.

4.2 ELECTRON ORBITS

The planetary model of the atom and why it fails

The Rutherford model of the atom, so convincingly confirmed by experiment, pictures a tiny, massive, positively charged nucleus surrounded at a relatively great distance by enough electrons to render the atom electrically neutral as a whole. The electrons cannot be stationary in this model, because there is nothing that can keep them in place against the electric force pulling them to the nucleus. If the electrons are in motion, however, dynamically stable orbits like those of the planets around the sun are possible (Fig. 4.5).

Let us look at the classical dynamics of the hydrogen atom, whose single electron makes it the simplest of all atoms. We assume a circular electron orbit for convenience, though it might as reasonably be assumed to be elliptical in shape. The centripetal force

$$F_c = \frac{mv^2}{r}$$

holding the electron in an orbit r from the nucleus is provided by the electric force

$$F_e = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}$$

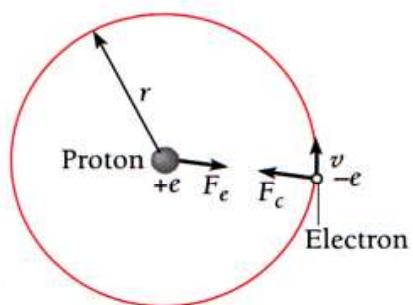


Figure 4.5 Force balance in the hydrogen atom.

between them. The condition for a dynamically stable orbit is

$$\begin{aligned}F_c &= F_e \\ \frac{mv^2}{r} &= \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2}\end{aligned}\quad (4.3)$$

The electron velocity v is therefore related to its orbit radius r by the formula

Electron velocity $v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}}$ (4.4)

The total energy E of the electron in a hydrogen atom is the sum of its kinetic and potential energies, which are

$$\text{KE} = \frac{1}{2}mv^2 \quad \text{PE} = -\frac{e^2}{4\pi\epsilon_0 r}$$

(The minus sign signifies that the force on the electron is in the $-r$ direction.) Hence

$$E = \text{KE} + \text{PE} = \frac{mv^2}{2} - \frac{e^2}{4\pi\epsilon_0 r}$$

Substituting for v from Eq. (4.4) gives

$$E = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r}$$

Total energy of hydrogen atom

$$E = -\frac{e^2}{8\pi\epsilon_0 r} \quad (4.5)$$

Total energy of hydrogen atom

$$E = -\frac{e^2}{8\pi\epsilon_0 r} \quad (4.5)$$

The total energy of the electron is negative. This holds for every atomic electron and reflects the fact that it is bound to the nucleus. If E were greater than zero, an electron would not follow a closed orbit around the nucleus.

Actually, of course, the energy E is not a property of the electron alone but is a property of the system of electron + nucleus. The effect of the sharing of E between the electron and the nucleus is considered in Sec. 4.8.

Example 4.1

Experiments indicate that 13.6 eV is required to separate a hydrogen atom into a proton and an electron; that is, its total energy is $E = -13.6$ eV. Find the orbital radius and velocity of the electron in a hydrogen atom.

Solution

Since $13.6 \text{ eV} = 2.2 \times 10^{-18} \text{ J}$, from Eq. (4.5)

$$\begin{aligned}r &= -\frac{e^2}{8\pi\epsilon_0 E} = -\frac{(1.6 \times 10^{-19} \text{ C})^2}{(8\pi)(8.85 \times 10^{-12} \text{ F/m})(-2.2 \times 10^{-18} \text{ J})} \\ &= 5.3 \times 10^{-11} \text{ m}\end{aligned}$$

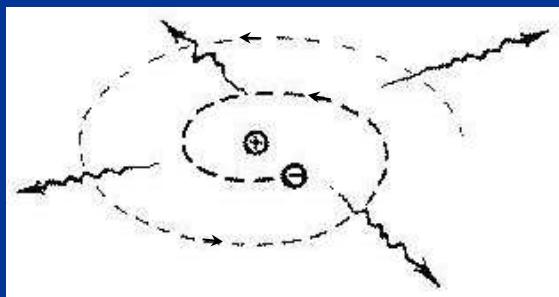
An atomic radius of this magnitude agrees with estimates made in other ways. The electron's velocity can be found from Eq. (4.4):

$$\begin{aligned}v &= \frac{e}{\sqrt{4\pi\epsilon_0 mr}} = \frac{1.6 \times 10^{-19} \text{ C}}{\sqrt{(4\pi)(8.85 \times 10^{-12} \text{ F/m})(9.1 \times 10^{-31} \text{ kg})(5.3 \times 10^{-11} \text{ m})}} \\ &= 2.2 \times 10^6 \text{ m/s}\end{aligned}$$

Since $v \ll c$, we can ignore special relativity when considering the hydrogen atom.

Problems of Rutherford's atom

When the electrons circle round the nucleus, they are constantly changing their direction. According to classical electrodynamics (which deals with the motion of electrons), such electrons which either constantly change their direction or their velocity or both should continuously emit radiation. While doing so, they should lose energy, and thus spiral into the nucleus. This means **every atom is unstable**, quite contrary to our observation!



Inherent instability of Rutherford's atom

If electrons are free to orbit at any distance, then the light emitted from them will be spread evenly across the electromagnetic spectrum, not discrete lines!

$$V = \frac{e}{\sqrt{4\pi\varepsilon_0 mr}} \quad T = \frac{1}{\nu} = \frac{2\pi r}{V} = \frac{2\pi}{e} \sqrt{4\pi\varepsilon_0 m} \cdot r^{\frac{3}{2}} \quad \lambda = \frac{c}{\nu} \propto r^{\frac{3}{2}}$$

Is Rutherford's Analysis Valid?

An interesting question comes up at this point. When he derived his scattering formula, Rutherford used the same laws of physics that prove such dismal failures when applied to atomic stability. Might it not be that this formula is not correct and that in reality the atom does not resemble Rutherford's model of a small central nucleus surrounded by distant electrons? This is not a trivial point. It is a curious coincidence that the quantum-mechanical analysis of alpha particle scattering by thin foils yields precisely the same formula that Rutherford found.

To verify that a classical calculation ought to be at least approximately correct, we note that the de Broglie wavelength of an alpha particle whose speed is 2.0×10^7 m/s is

$$\begin{aligned}\lambda &= \frac{h}{mv} = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{(6.6 \times 10^{-27} \text{ kg})(2.0 \times 10^7 \text{ m/s})} \\ &= 5.0 \times 10^{-15} \text{ m}\end{aligned}$$

As we saw in Sec. 4.1, the closest an alpha particle with this wavelength ever gets to a gold nucleus is 3.0×10^{-14} m, which is six de Broglie wavelengths. It is therefore just reasonable to regard the alpha particle as a classical particle in the interaction. We are correct in thinking of the atom in terms of Rutherford's model, though the dynamics of the atomic electrons—which is another matter—requires a nonclassical approach.

4.3 ATOMIC SPECTRA

Each element has a characteristic line spectrum

Atomic stability is not the only thing that a successful theory of the atom must account for. The existence of spectral lines is another important aspect of the atom that finds no explanation in classical physics.

Light emitted by a hot solid or liquid exhibits a continuous spectrum (backbody radiation). However, light emitted by a gas/vapour shows only a few isolated sharp lines

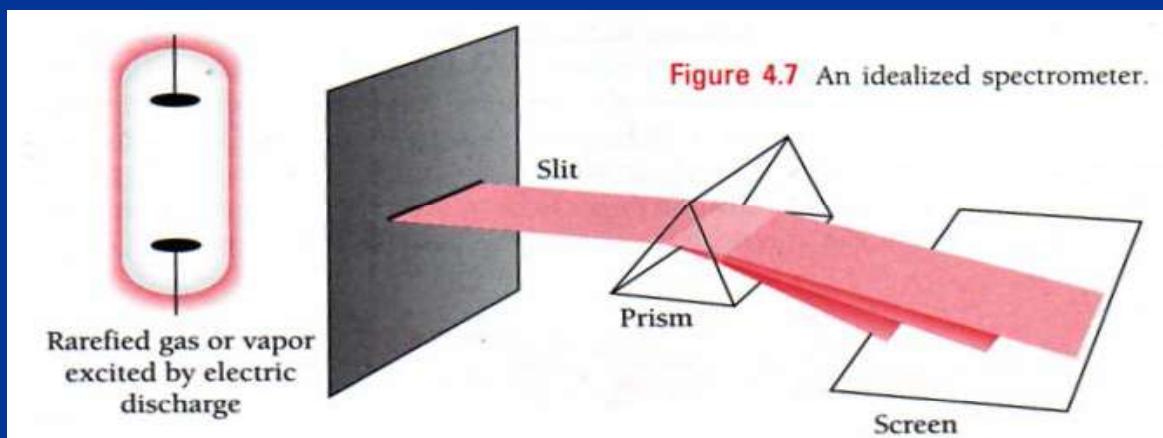
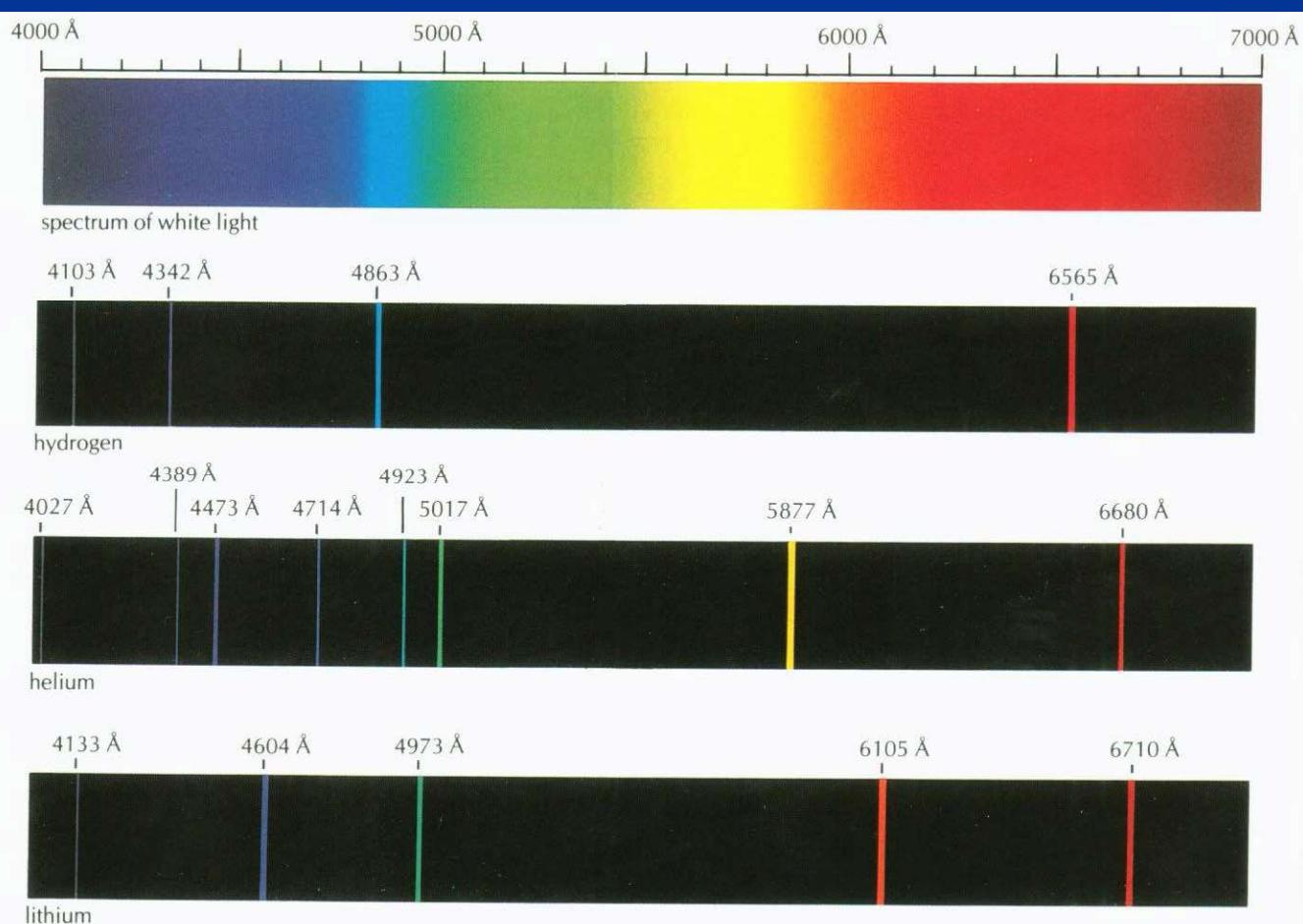
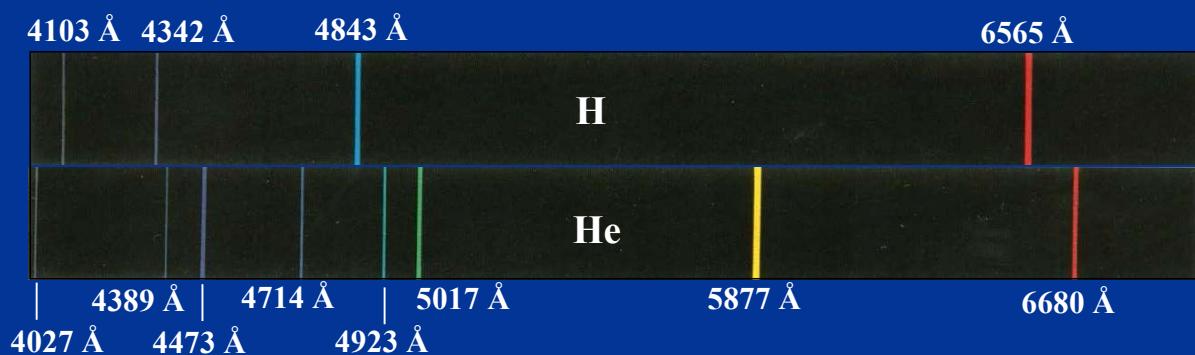
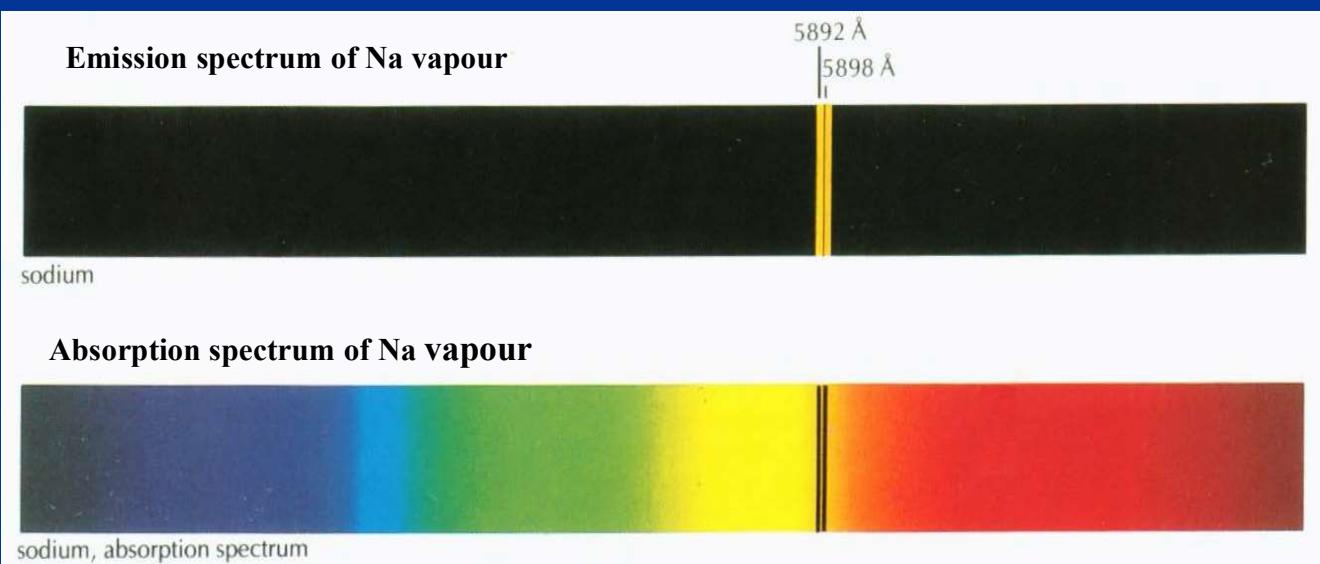


Figure 4.7 An idealized spectrometer.





- Each line corresponds to a different frequency.
- Different gases produce different set of lines.
- When the temperature of the gas increases, more lines at higher frequencies are emitted.

Once again, classical wave theory of light is having problem: evidently, the spectra shows that the energy is proportional to frequency, not to the amplitude of the emitted light. Moreover, this shows that the structure of atoms is not continuous.

So, what is an atom composed of? How does the discrete spectrum relate to the internal structure of the atom?

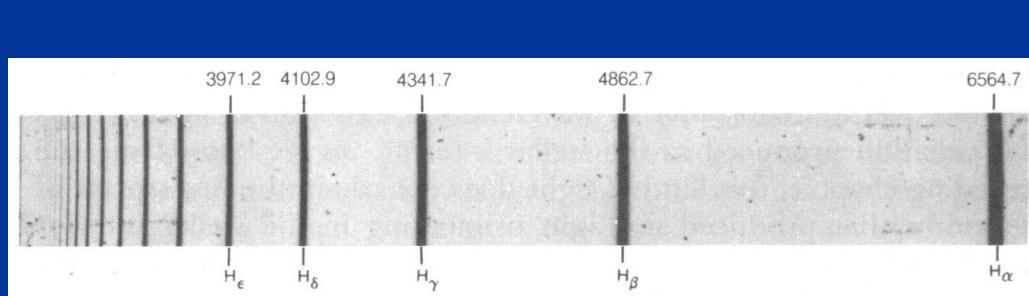
The Balmer Series — Regularities in Spectral Lines

Careful examination of spectral lines reveals certain systematic regularities in the spacing of lines. In 1885, **Johann Balmer** discovered the hydrogen spectral lines fit the formula

$$\lambda = 911.76 \times \text{\AA} \frac{4n^2}{n^2 - 4}, \text{ where } n = 3, 4, 6, \text{ etc}$$

If written in terms of frequency, $\nu = \frac{c}{\lambda} = \frac{c}{911.76} \left(\frac{1}{4} - \frac{1}{n^2} \right)$

or $\nu = cR_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$, where $R_H = \frac{1}{911.76 \text{\AA}} = 109678 \text{ cm}^{-1}$ is the **Rydberg constant**.



Hydrogen spectrum

Wavelength (Å)
6564.7
4862.7
4341.7
4102.9
3971.2
3890.2
3836.5
3799.0
etc.

$$\nu = cR_H \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad \text{—— Balmer series}$$

Balmer also proposed there might be other series in the hydrogen spectrum, with the 2 in the formula replaced by 1, or 3, or 4, or 5, etc

that is:

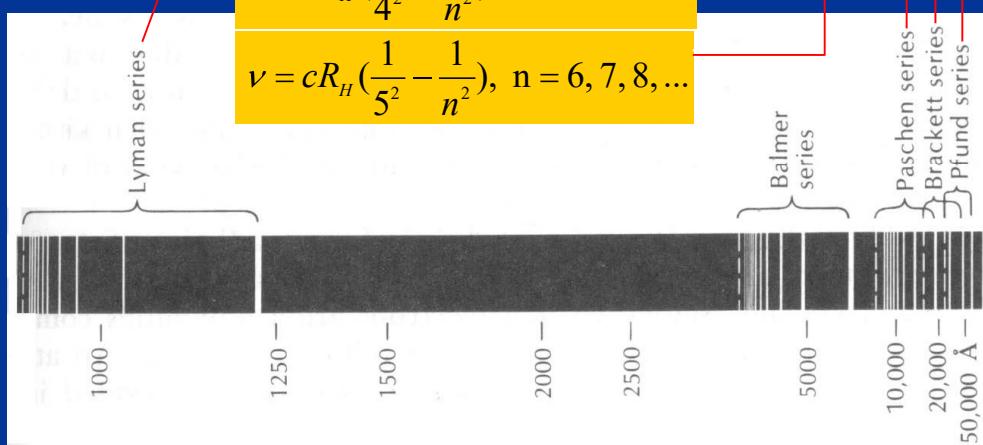
$$\nu = cR_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right), \quad n = 2, 3, 4, \dots$$

$$\nu = cR_H \left(\frac{1}{3^2} - \frac{1}{n^2} \right), \quad n = 4, 5, 6, \dots$$

$$\nu = cR_H \left(\frac{1}{4^2} - \frac{1}{n^2} \right), \quad n = 5, 6, 7, \dots$$

$$\nu = cR_H \left(\frac{1}{5^2} - \frac{1}{n^2} \right), \quad n = 6, 7, 8, \dots$$

These four series of spectral lines were actually discovered many years after Balmer proposed them. They are called the **Lyman**, the **Paschen**, the **Brackett**, and the **Pfund** series.



Rydberg-Ritz formula, 1890

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{for any hydrogen-like element, e.g. He}^+, \text{Li}^{2+}, \text{Be}^{3+} \text{ etc}$$

n_1 and n_2 are integers, with $n_1 < n_2$

Z is the atomic number of the element

R is the Rydberg constant for this particular element

(For hydrogen, Rydberg constant $R_H = 109,678 \text{ cm}^{-1}$)

Bohr's atom (1)

(the de Broglie's approach)

We start by examining the wave behavior of an electron in orbit around a hydrogen nucleus. The de Broglie wavelength of this electron is

$$\lambda = \frac{h}{mv}$$

where the electron velocity v is that given by Eq. (4.4):

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

Hence

Orbital electron wavelength

$$\lambda = \frac{h}{e} \sqrt{\frac{4\pi\epsilon_0 r}{m}} \quad (4.11)$$

By substituting 5.3×10^{-11} m for the radius r of the electron orbit (see Example 4.1), we find the electron wavelength to be

$$\lambda = \frac{6.63 \times 10^{-34} \text{ J} \cdot \text{s}}{1.6 \times 10^{-19} \text{ C}} \sqrt{\frac{(4\pi)(8.85 \times 10^{-12} \text{ F/m})(5.3 \times 10^{-11} \text{ m})}{9.1 \times 10^{-31} \text{ kg}}} \\ = 33 \times 10^{-11} \text{ m}$$

This wavelength is exactly the same as the circumference of the electron orbit,

$$2\pi r = 33 \times 10^{-11} \text{ m}$$

The orbit of the electron in a hydrogen atom corresponds to one complete electron wave joined on itself (Fig. 4.12)!

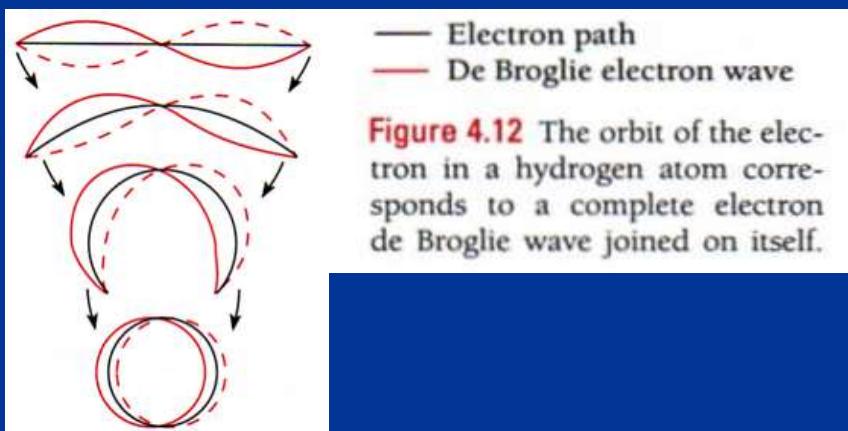


Figure 4.12 The orbit of the electron in a hydrogen atom corresponds to one complete electron de Broglie wave joined on itself.

The fact that the electron orbit in a hydrogen atom is one electron wavelength in circumference provides the clue we need to construct a theory of the atom. If we consider the vibrations of a wire loop (Fig. 4.13), we find that their wavelengths always fit an integral number of times into the loop's circumference so that each wave joins smoothly with the next. If the wire were perfectly elastic, these vibrations would continue indefinitely. Why are these the only vibrations possible in a wire loop? If a fractional number of wavelengths is placed around the loop, as in Fig. 4.14, destructive interference will occur as the waves travel around the loop, and the vibrations will die out rapidly.

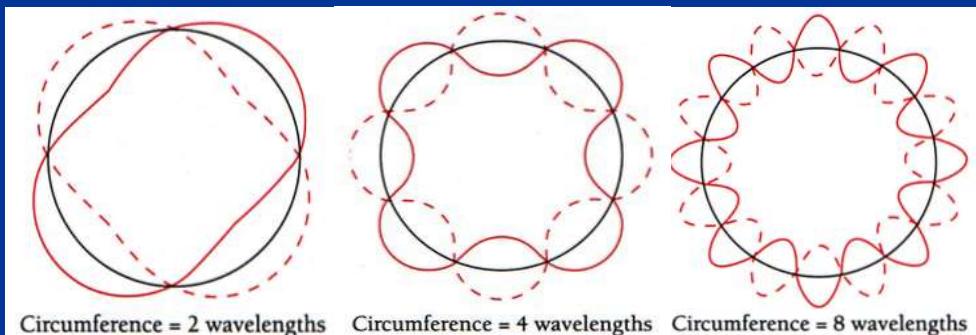


Figure 4.13 Some modes of vibration of a wire loop. In each case a whole number of wavelengths fit into the circumference of the loop.

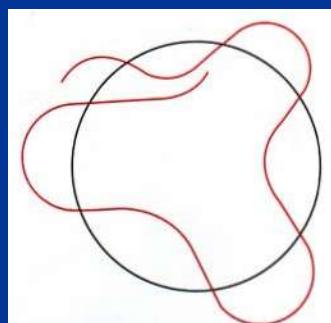


Figure 4.14 A fractional number of wavelengths cannot persist because destructive interference will occur.

By considering the behavior of electron waves in the hydrogen atom as analogous to the vibrations of a wire loop, then, we can say that

An electron can circle a nucleus only if its orbit contains an integral number of de Broglie wavelengths.

This statement combines both the particle and wave characters of the electron since the electron wavelength depends upon the orbital velocity needed to balance the pull of the nucleus. To be sure, the analogy between an atomic electron and the standing waves of Fig. 4.13 is hardly the last word on the subject, but it represents an illuminating step along the path to the more profound and comprehensive, but also more abstract, quantum-mechanical theory of the atom.

It is easy to express the condition that an electron orbit contain an integral number of de Broglie wavelengths. The circumference of a circular orbit of radius r is $2\pi r$, and so the condition for orbit stability is

Condition for orbit stability $n\lambda = 2\pi r_n \quad n = 1, 2, 3, \dots$ (4.12)

where r_n designates the radius of the orbit that contain n wavelengths. The integer n is called the **quantum number** of the orbit. Substituting for λ , the electron wavelength given by Eq. (4.11), yields

$$\frac{nh}{e} \sqrt{\frac{4\pi\epsilon_0 r_n}{m}} = 2\pi r_n$$

and so the possible electron orbits are those whose radii are given by

Orbital radii in Bohr atom $r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2} \quad n = 1, 2, 3, \dots$ (4.13)

The radius of the innermost orbit is customarily called the **Bohr radius** of the hydrogen atom and is denoted by the symbol a_0 :

Bohr radius $a_0 = r_1 = 5.292 \times 10^{-11} \text{ m}$

The other radii are given in terms of a_0 by the formula:

$$r_n = n^2 a_0 \quad (4.14)$$

4.5 ENERGY LEVELS AND SPECTRA

A photon is emitted when an electron jumps from one energy level to a lower level

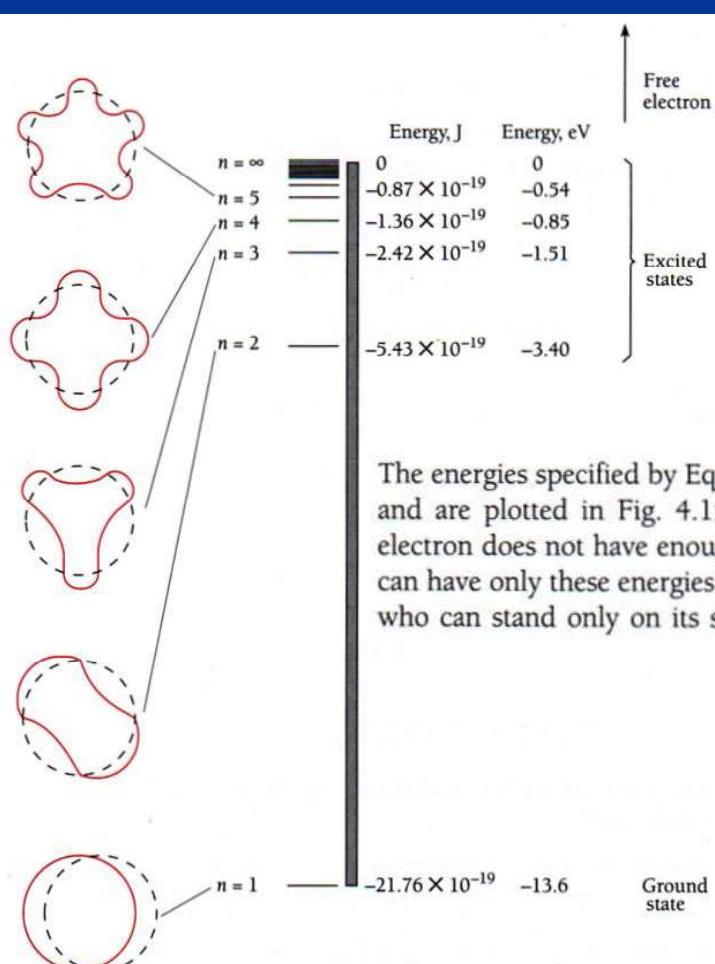
The various permitted orbits involve different electron energies. The electron energy E_n is given in terms of the orbit radius r_n by Eq. (4.5) as

$$E_n = \frac{e^2}{8\pi\epsilon_0 r_n}$$

Substituting for r_n from Eq (4.13), we see that

Energy levels $E_n = -\frac{me^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2} \right) = \frac{E_1}{n^2} \quad n = 1, 2, 3, \dots$ (4.15)

$$E_1 = -2.18 \times 10^{-18} \text{ J} = -13.6 \text{ eV}$$



The energies specified by Eq. (4.15) are called the **energy levels** of the hydrogen atom and are plotted in Fig. 4.15. These levels are all negative, which signifies that the electron does not have enough energy to escape from the nucleus. An atomic electron can have only these energies and no others. An analogy might be a person on a ladder, who can stand only on its steps and not in between.

Figure 4.15 Energy levels of the hydrogen atom.

The lowest energy level E_1 is called the **ground state** of the atom, and the higher levels E_2, E_3, E_4, \dots are called **excited states**. As the quantum number n increases, the corresponding energy E_n approaches closer to 0. In the limit of $n = \infty$, $E_\infty = 0$ and the electron is no longer bound to the nucleus to form an atom. A positive energy for a nucleus-electron combination means that the electron is free and has no quantum conditions to fulfill; such a combination does not constitute an atom, of course.

The work needed to remove an electron from an atom in its ground state is called its **ionization energy**. The ionization energy is accordingly equal to $-E_1$, the energy that must be provided to raise an electron from its ground state to an energy of $E = 0$, when it is free. In the case of hydrogen, the ionization energy is 13.6 eV since the ground-state energy of the hydrogen atom is -13.6 eV. Figure 7.10 shows the ionization energies of the elements.

Quantization in the Atomic World

Sequences of energy levels are characteristic of all atoms, not just those of hydrogen. As in the case of a particle in a box, the confinement of an electron to a region of space leads to restrictions on its possible wave functions that in turn limit the possible energies to well-defined values only. The existence of atomic energy levels is a further example of the quantization, or graininess, of physical quantities on a microscopic scale.

In the world of our daily lives, matter, electric charge, energy, and so forth appear to be continuous. In the world of the atom, in contrast, matter is composed of elementary particles that have definite rest masses; charge always comes in multiples of $+e$ or $-e$; electromagnetic waves of frequency ν appear as streams of photons each with the energy $h\nu$, and stable systems of particles, such as atoms, can possess only certain energies. As we shall find, other quantities in nature are also quantized, and this quantization enters into every aspect of how electrons, protons, and neutrons interact to endow the matter around us (and of which we consist) with its familiar properties.

Origin of Line Spectra

We must now confront the equations developed above with experiment. An especially striking observation is that atoms exhibit line spectra in both emission and absorption. Do such spectra follow from our model?

The presence of discrete energy levels in the hydrogen atom suggests the connection. Let us suppose that when an electron in an excited state drops to a lower state, the lost energy is emitted as a single photon of light. According to our model, electrons cannot exist in an atom except in certain specific energy levels. The jump of an electron from one level to another, with the difference in energy between the levels being given off all at once in a photon rather than in some more gradual manner, fits in well with this model.

If the quantum number of the initial (higher-energy) state is n_i and the quantum number of the final (lower-energy) state is n_f , we are asserting that

Initial energy - final energy = photon energy

$$E_i - E_f = h\nu \quad (4.16)$$

where ν is the frequency of the emitted photon. From Eq. (4.15) we have

$$E_i - E_f = E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = -E_1 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

We recall that E_1 is a negative quantity (-13.6 eV, in fact), so $-E_1$ is a positive quantity. The frequency of the photon released in this transition is therefore

$$\nu = \frac{E_i - E_f}{h} = -\frac{E_1}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4.17)$$

Since $\lambda = c/\nu$, $1/\lambda = \nu/c$ and

Hydrogen spectrum

$$\frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4.18)$$

Hydrogen spectrum

$$\frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4.18)$$

Equation (4.18) states that the radiation emitted by excited hydrogen atoms should contain certain wavelengths only. These wavelengths, furthermore, fall into definite sequences that depend upon the quantum number n_f of the final energy level of the electron (Fig. 4.16). Since $n_i > n_f$ in each case, in order that there be an excess of energy to be given off as a photon, the calculated formulas for the first five series are

Lyman $n_f = 1: \frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad n = 2, 3, 4, \dots$

Balmer $n_f = 2: \frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad n = 3, 4, 5, \dots$

Link

Paschen $n_f = 3: \frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad n = 4, 5, 6, \dots$

Brackett $n_f = 4: \frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{4^2} - \frac{1}{n^2} \right) \quad n = 5, 6, 7, \dots$

Pfund $n_f = 5: \frac{1}{\lambda} = -\frac{E_1}{ch} \left(\frac{1}{5^2} - \frac{1}{n^2} \right) \quad n = 6, 7, 8, \dots$

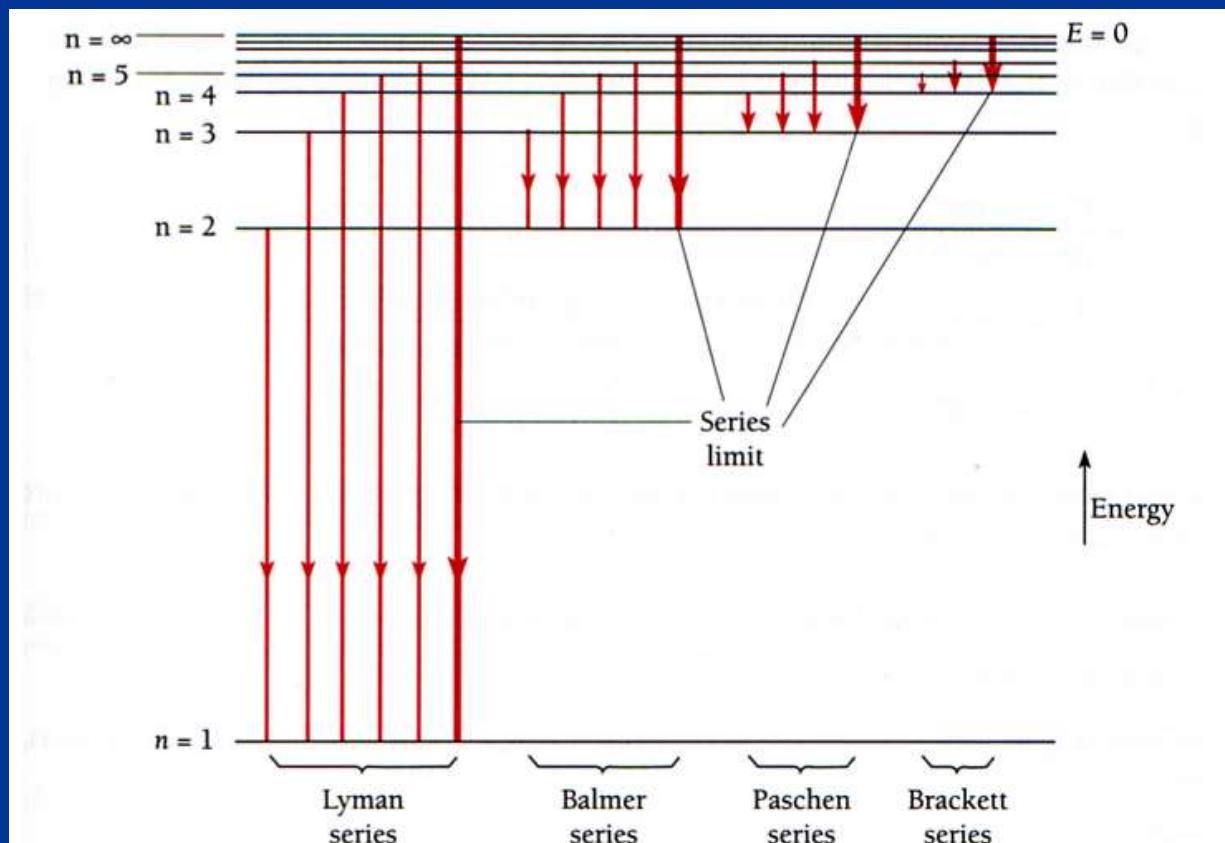


Figure 4.16 Spectral lines originate in transitions between energy levels. Shown are the spectral series of hydrogen. When $n = \infty$, the electron is free.

4.6 CORRESPONDENCE PRINCIPLE

The greater the quantum number, the closer quantum physics approaches classical physics

Quantum physics, so different from classical physics in the microworld beyond reach of our senses, must nevertheless give the same results as classical physics in the macro-world where experiments show that the latter is valid. We have already seen that this basic requirement is true for the wave theory of moving bodies. We shall now find that it is also true for Bohr's model of the hydrogen atom.

According to electromagnetic theory, an electron moving in a circular orbit radiates em waves whose frequencies are equal to its frequency of revolution and to harmonics (that is, integral multiples) of that frequency. In a hydrogen atom the electron's speed is

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

according to Eq. (4.4), where r is the radius of its orbit. Hence the frequency of revolution f of the electron is

$$f = \frac{\text{electron speed}}{\text{orbit circumference}} = \frac{v}{2\pi r} = \frac{e}{2\pi\sqrt{4\pi\epsilon_0 mr^3}}$$

The radius r_n of a stable orbit is given in terms of its quantum number n by Eq. (4.13) as

$$r_n = \frac{n^2 h^2 \epsilon_0}{\pi m e^2}$$

and so the frequency of revolution is

Frequency of revolution
$$f = \frac{me^4}{8\epsilon_0^2 h^3} \left(\frac{2}{n^3} \right) = \frac{-E_1}{h} \left(\frac{2}{n^3} \right) \quad (4.19)$$

Under what circumstances should the Bohr atom behave classically? If the electron orbit is so large that we might be able to measure it directly, quantum effects ought to be negligible. An orbit 0.01 mm across, for instance, meets this specification. As we found earlier, its quantum number is $n = 435$, and, while hydrogen atoms in such a state never occur in nature because their energies would be only infinitesimally below the ionization energy, they are possible in theory.

What does the Bohr theory predict such an atom will radiate? According to Eq. (4.17), a hydrogen atom dropping from the n_i th energy level to the n_f th energy level emits a photon whose frequency is

$$\nu = \frac{-E_1}{h} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (4.19a)$$

Let us write n for the initial quantum number n_i and $n - p$ (where $p = 1, 2, 3, \dots$) for the final quantum number n_f . With this substitution,

$$\nu = \frac{-E_1}{h} \left[\frac{1}{(n-p)^2} - \frac{1}{n^2} \right] = \frac{-E_1}{h} \left[\frac{2np - p^2}{n^2(n-p)^2} \right]$$

When n_i and n_f are both very large, n is much greater than p , and

$$2np - p^2 \approx 2np \\ (n-p)^2 \approx n^2$$

so that

Frequency of photon

$$\nu = \frac{-E_1}{h} \left(\frac{2p}{n^3} \right) \quad (4.20)$$

Frequency of photon

$$\nu = \frac{-E_1}{h} \left(\frac{2p}{n^3} \right) \quad (4.20)$$

When $p = 1$, the frequency ν of the radiation is exactly the same as the frequency of rotation f of the orbital electron given in Eq. (4.19). Multiples of this frequency are radiated when $p = 2, 3, 4, \dots$. Hence both quantum and classical pictures of the hydrogen atom make the same predictions in the limit of very large quantum numbers. When $n = 2$, Eq. (4.19) predicts a radiation frequency that differs from that given by Eq. (4.19a) by almost 300 percent. When $n = 10,000$, the discrepancy is only about 0.01 percent.

The requirement that quantum physics give the same results as classical physics in the limit of large quantum numbers was called by Bohr the **correspondence principle**. It has played an important role in the development of the quantum theory of matter.

Bohr himself used the correspondence principle in reverse, so to speak, to look for the condition for orbit stability. Starting from Eq. (4.19) he was able to show that stable orbits must have electron orbital angular momenta of

Condition for orbital stability

$$mv r = \frac{n\hbar}{2\pi} \quad n = 1, 2, 3, \dots \quad (4.21)$$

Since the de Broglie electron wavelength is $\lambda = h/mv$, Eq. (4.21) is the same as Eq. (4.12), $n\lambda = 2\pi r$, which states that an electron orbit must contain an integral number of wavelengths.

4.7 NUCLEAR MOTION

The nuclear mass affects the wavelengths of spectral lines

Thus far we have been assuming that the hydrogen nucleus (a proton) remains stationary while the orbital electron revolves around it. What must actually happen, of course, is that both nucleus and electron revolve around their common center of mass, which is very close to the nucleus because the nuclear mass is much greater than that of the electron (Fig. 4.17). A system of this kind is equivalent to a single particle of mass m' that revolves around the position of the heavier particle. (This equivalence is demonstrated in Sec. 8.6.) If m is the electron mass and M the nuclear mass, then m' is given by

Reduced mass

$$m' = \frac{mM}{m + M} \quad (4.22)$$

The quantity m' is called the **reduced mass** of the electron because its value is less than m .

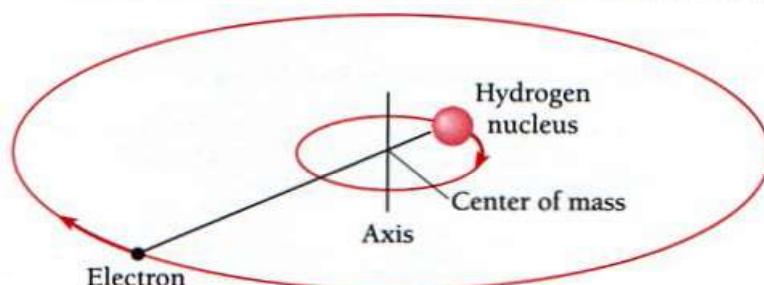


Figure 4.17 Both the electron and nucleus of a hydrogen atom revolve around a common center of mass

Energy levels corrected for nuclear motion

$$E'_n = -\frac{m'e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2}\right) = \left(\frac{m'}{m}\right) \left(\frac{E_1}{n^2}\right) \quad (4.23)$$

Owing to motion of the nucleus, all the energy levels of hydrogen are changed by the fraction

$$\frac{m'}{m} = \frac{M}{M + m} = 0.99945$$

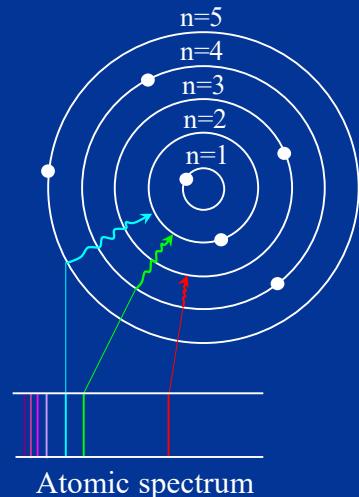
This represents an increase of 0.055 percent because the energies E_n , being smaller in absolute value, are therefore less negative.

Bohr's atom (2)

— Bohr's own approach

- First postulate – Non-radiating orbits

Electron can move only in certain stable, circular orbits – stationary states



Atomic spectrum

- Second postulate – Photon emission frequency

$$E_{ph} = E_j - E_i = h\nu$$

Photons emitted or absorbed must match the energy difference of the orbits

$$\nu = \frac{E_j - E_i}{h}$$

- Third postulate – Quantized angular momentum

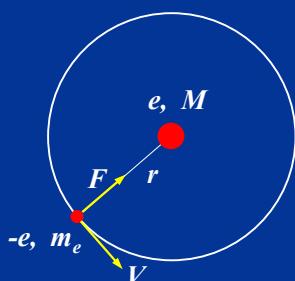
$$L \equiv mVr = n \frac{\hbar}{2\pi} = n\hbar, \quad n = 1, 2, 3, \dots$$



$$m \frac{V^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \quad (m = \frac{Mm_e}{M+m_e} \text{ the "effective" mass in two-body problem})$$

H

It works out: $r = \frac{e^2}{4\pi\epsilon_0 m} \frac{1}{V^2}$. It follows from Bohr's third postulate: $V = \frac{n\hbar}{mr}$



$$\text{So, } r = \frac{e^2}{4\pi\epsilon_0 m} \frac{m^2 r^2}{n^2 \hbar^2} \Rightarrow r = \frac{4\pi\epsilon_0 \hbar^2}{me^2} n^2 \quad \text{and} \quad V = \frac{e^2}{4\pi\epsilon_0 \hbar} \frac{1}{n}$$

Energy of H atom ant its spectral lines

$$E = K_{kinetic} + U_{potential} = \frac{1}{2} m V^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

Substitute with $r = \frac{4\pi\epsilon_0 h^2}{me^2} n^2$ and $V = \frac{e^2}{4\pi\epsilon_0 h} \frac{1}{n}$

$$E = \frac{1}{2} m \left(\frac{e^2}{4\pi\epsilon_0 h} \frac{1}{n} \right)^2 - \frac{e^2}{4\pi\epsilon_0} \frac{m e^2}{4\pi\epsilon_0 h^2} \frac{1}{n^2} = -\frac{m}{2} \left(\frac{e^2}{4\pi\epsilon_0 h} \right)^2 \frac{1}{n^2}$$

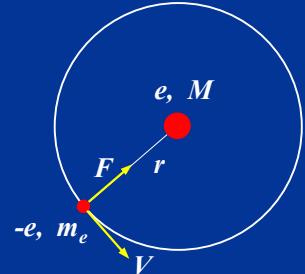
According to Bohr's second postulate: $E_{ph} = E_j - E_i = h\nu$

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{E_j - E_i}{hc} = \frac{E_j - E_i}{2\pi\hbar c} = \frac{1}{2\pi\hbar c} \frac{m}{2} \left(\frac{e^2}{4\pi\epsilon_0 h} \right)^2 \left(\frac{1}{n_i^2} - \frac{1}{n_j^2} \right)$$

$$\frac{1}{\lambda} = \frac{m e^4}{(4\pi\epsilon_0)^2 h^3 4\pi c} \left(\frac{1}{n_i^2} - \frac{1}{n_j^2} \right) = R Z^2 \left(\frac{1}{n_i^2} - \frac{1}{n_j^2} \right)$$

Rydberg-Ritz formula !

$$Z=1, R = \frac{m e^4}{(4\pi\epsilon_0)^2 h^3 4\pi c}, \text{ the Rydberg constant}$$



$$R = \frac{m e^4}{(4\pi\epsilon_0)^2 h^3 4\pi c} = \frac{M}{M + m_e} \frac{m_e e^4}{(4\pi\epsilon_0)^2 h^3 4\pi c} = \frac{M}{M + m_e} R_\infty,$$

$$R_\infty = \frac{m_e e^4}{(4\pi\epsilon_0)^2 h^3 4\pi c} = 109737.3 \text{ (1/cm)}, \text{ the "infinity" Rydberg constant}$$

For H there is only one proton, so $M = 1.672623 \times 10^{-27} \text{ Kg}$; $m_e = 9.109390 \times 10^{-31} \text{ Kg}$

$$R = \frac{M}{M + m_e} R_\infty = \frac{1.672623 \times 10^{-27}}{1.672623 \times 10^{-27} + 9.109390 \times 10^{-31}} \times 109737.3 \text{ (1/cm)}$$

$$= 109677.6 \text{ (cm}^{-1}\text{)}$$

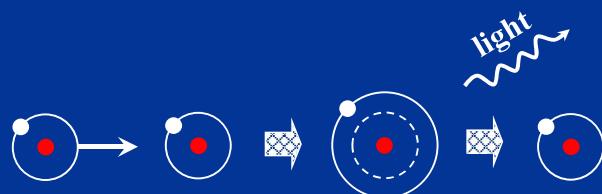
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In perfect agreement with Balmer's experimental result: $R_H = 109678 \text{ cm}^{-1}$!

Atomic Excitation

Two ways

1. Collision between particles → kinetic energy absorbed by atom elevates electrons to the excited states. On returning to ground states, an electron is emitted.



Achieved by discharging rarefied gas and then accelerating electrons and ions through a high electric field.

Example: Neon — reddish light, Mercury — bluish light

2. Absorption of a photon of light whose energy is just the right amount to raise the atom to a higher energy level.

For example,

a photon of wavelength 121.7 nm is emitted when a hydrogen atom in the $n = 2$ state drops to the $n = 1$ state. Absorbing a photon of wavelength 121.7 nm by a hydrogen atom initially in the $n = 1$ state will therefore bring it up to the $n = 2$ state (Fig. 4.19). This process explains the origin of absorption spectra.

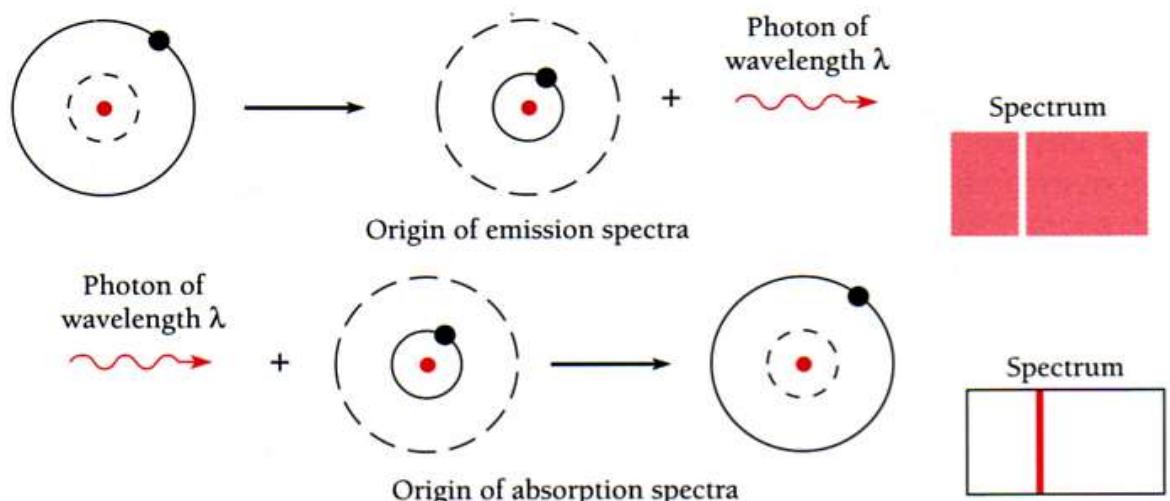


Figure 4.19 How emission and absorption spectral lines originate.

When white light, which contains all wavelengths, is passed through hydrogen gas, photons of those wavelengths that correspond to transitions between energy levels are absorbed. The resulting excited hydrogen atoms reradiate their excitation energy almost at once, but these photons come off in random directions with only a few in the same direction as the original beam of white light (Fig. 4.20). The dark lines in an absorption spectrum are therefore never completely black, but only appear so by contrast with the bright background. We expect the lines in the absorption spectrum of any element to coincide with those in its emission spectrum that represent transitions to the ground state, which agrees with observation (see Fig. 4.9).

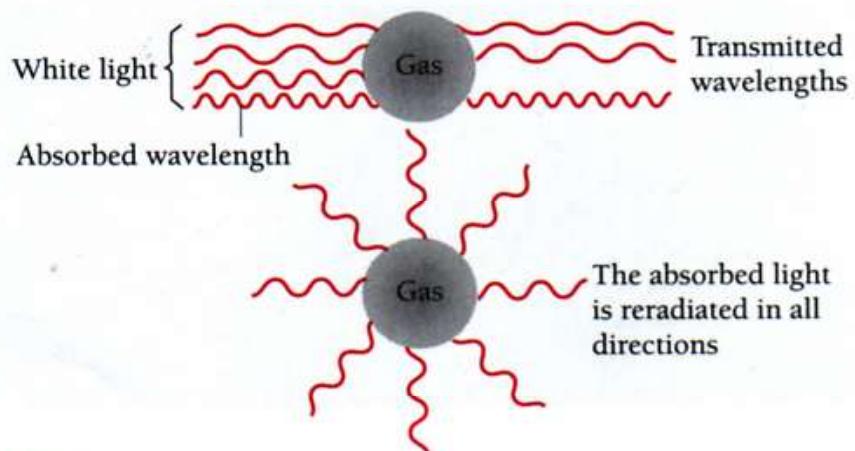


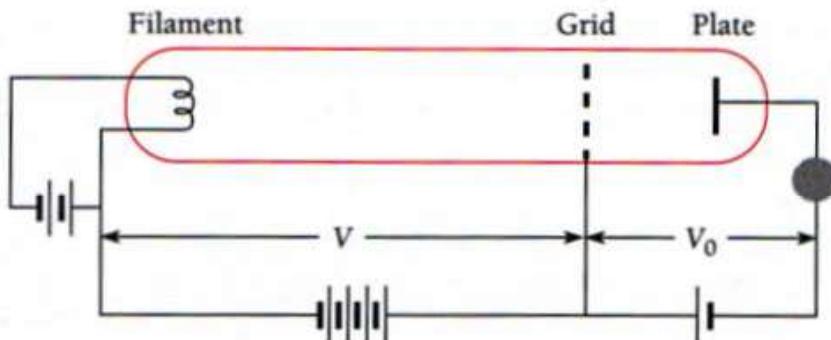
Figure 4.20 The dark lines in an absorption spectrum are never totally dark.

Franck-Hertz Experiment

Atomic spectra are not the only way to investigate energy levels inside atoms. A series of experiments based on excitation by collision was performed by James Franck and Gustav Hertz (a nephew of Heinrich Hertz) starting in 1914. These experiments demonstrated that atomic energy levels indeed exist and, furthermore, that the ones found in this way are the same as those suggested by line spectra.

Franck and Hertz bombarded the vapors of various elements with electrons of known energy, using an apparatus like that shown in Fig. 4.21. A small potential difference V_0 between the grid and collecting plate prevents electrons having energies less than a certain minimum from contributing to the current I through the ammeter. As the accelerating potential V is increased, more and more electrons arrive at the plate and I rises (Fig. 4.22).

Figure 4.21 Apparatus for the Franck-Hertz experiment.



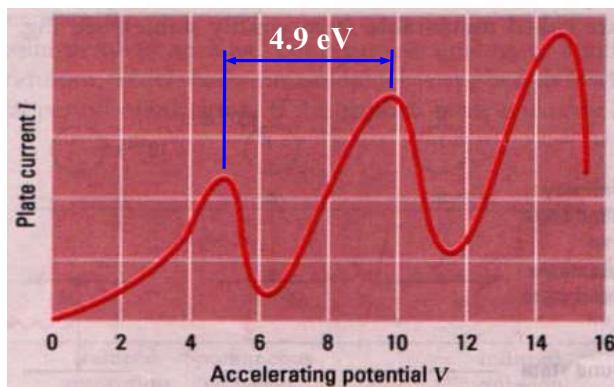
If KE is conserved when an electron collides with one of the atoms in the vapor, the electron merely bounces off in a new direction. Because an atom is much heavier than an electron, the electron loses almost no KE in the process. After a certain critical energy is reached, however, the plate current drops abruptly. This suggests that an electron colliding with one of the atoms gives up some or all of its KE to excite the atom to an energy level above its ground state. Such a collision is called inelastic, in contrast to an elastic collision in which KE is conserved. The critical electron energy equals the energy needed to raise the atom to its lowest excited state.

Then, as the accelerating potential V is raised further, the plate current again increases, since the electrons now have enough energy left to reach the plate after undergoing an inelastic collision on the way. Eventually another sharp drop in plate current occurs, which arises from the excitation of the same energy level in other atoms by the electrons. As Fig. 4.22 shows, a series of critical potentials for a given atomic vapor is obtained. Thus the higher potentials result from two or more inelastic collisions and are multiples of the lowest one.

Figure 4.22 Results of the Franck-Hertz experiment, showing critical potentials in mercury vapor.

In experiment, minimum electron energy of 4.9 eV was required to excite 253.6 nm light of mercury.

$$E = h\nu = hc/\lambda = hc/253.6 \text{ (nm)} = 4.89 \text{ eV}$$



4.9 THE LASER

How to produce light waves all in step

The **laser** is a device that produces a light beam with some remarkable properties:

- 1 The light is coherent, with the waves all exactly in phase with one another (Fig. 4.23). An interference pattern can be obtained not only by placing two slits in a laser beam but also by using beams from two separate lasers.
- 2 The light is very nearly monochromatic.
- 3 A laser beam diverges hardly at all. Such a beam sent from the earth to a mirror left on the moon by the Apollo 11 expedition remained narrow enough to be detected on its return to the earth, a total distance of over three-quarters of a million kilometers. A light beam produced by any other means would have spread out too much for this to be done.
- 4 The beam is extremely intense, more intense by far than the light from any other source. To achieve an energy density equal to that in some laser beams, a hot object would have to be at a temperature of 10^{30} K .

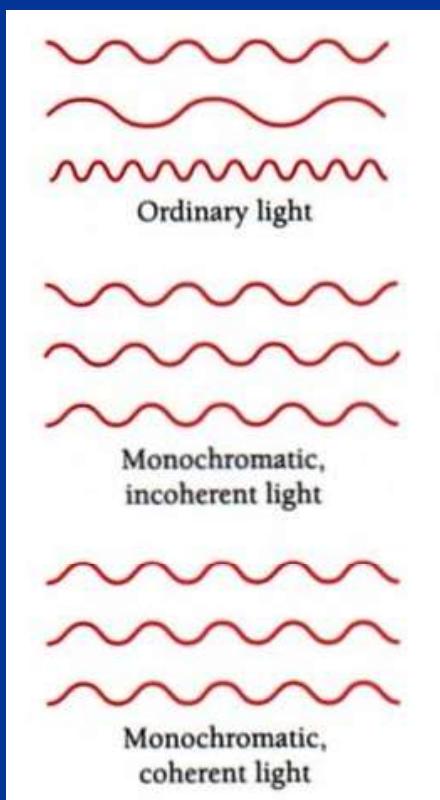


Figure 4.23 A laser produces a beam of light whose waves all have the same frequency (monochromatic) and are in phase with one another (coherent). The beam is also well collimated and so spreads out very little, even over long distances.

The term *laser* stands for **light amplification by stimulated emission of radiation**. The key to the laser is the presence in many atoms of one or more excited energy levels whose lifetimes may be 10^{-3} s or more instead of the usual 10^{-8} s. Such relatively long-lived states are called **metastable** (temporarily stable); see Fig. 4.24.

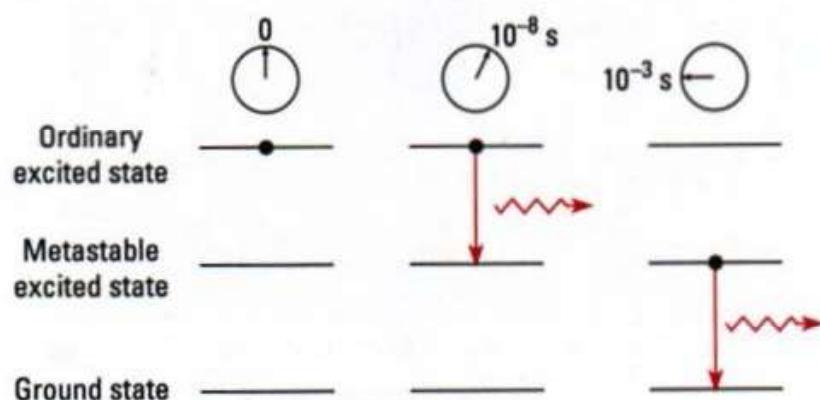


Figure 4.24 An atom can exist in a metastable energy level for a longer time before radiating than it can in an ordinary energy level.

Three kinds of transition involving electromagnetic radiation are possible between two energy levels, E_0 and E_1 , in an atom (Fig. 4.25). If the atom is initially in the lower state E_0 , it can be raised to E_1 by absorbing a photon of energy $E_1 - E_0 = h\nu$. This process is called **induced absorption**. If the atom is initially in the upper state E_1 , it can drop to E_0 by emitting a photon of energy $h\nu$. This is **spontaneous emission**.

Einstein, in 1917, was the first to point out a third possibility, **induced emission**, in which an incident photon of energy $h\nu$ causes a transition from E_1 to E_0 . In induced emission, the radiated light waves are exactly in phase with the incident ones, so the result is an enhanced beam of coherent light. Einstein showed that **induced emission has the same probability as induced absorption**. That is, a photon of energy $h\nu$ incident on an atom in the upper state E_1 has the same likelihood of causing the emission of another photon of energy $h\nu$ as its likelihood of being absorbed if it is incident on an atom in the lower state E_0 .

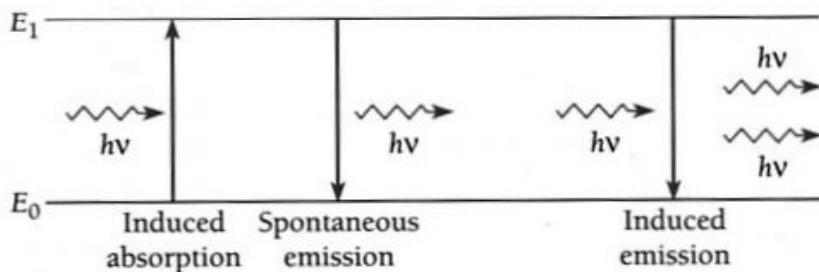


Figure 4.25 Transitions between two energy levels in an atom can occur by induced absorption, spontaneous emission, and induced emission.

A **three-level laser**, the simplest kind, uses an assembly of atoms (or molecules) that have a metastable state $h\nu$ in energy above the ground state and a still higher excited state that decays to the metastable state (Fig. 4.26). What we want is more atoms in the metastable state than in the ground state. If we can arrange this and then shine light of frequency ν on the assembly, there will be more induced emissions from atoms in the metastable state than induced absorptions by atoms in the ground state. The result will be an amplification of the original light. This is the concept that underlies the operation of the laser.

The term **population inversion** describes an assembly of atoms in which the majority are in energy levels above the ground state; normally the ground state is occupied to the greatest extent.

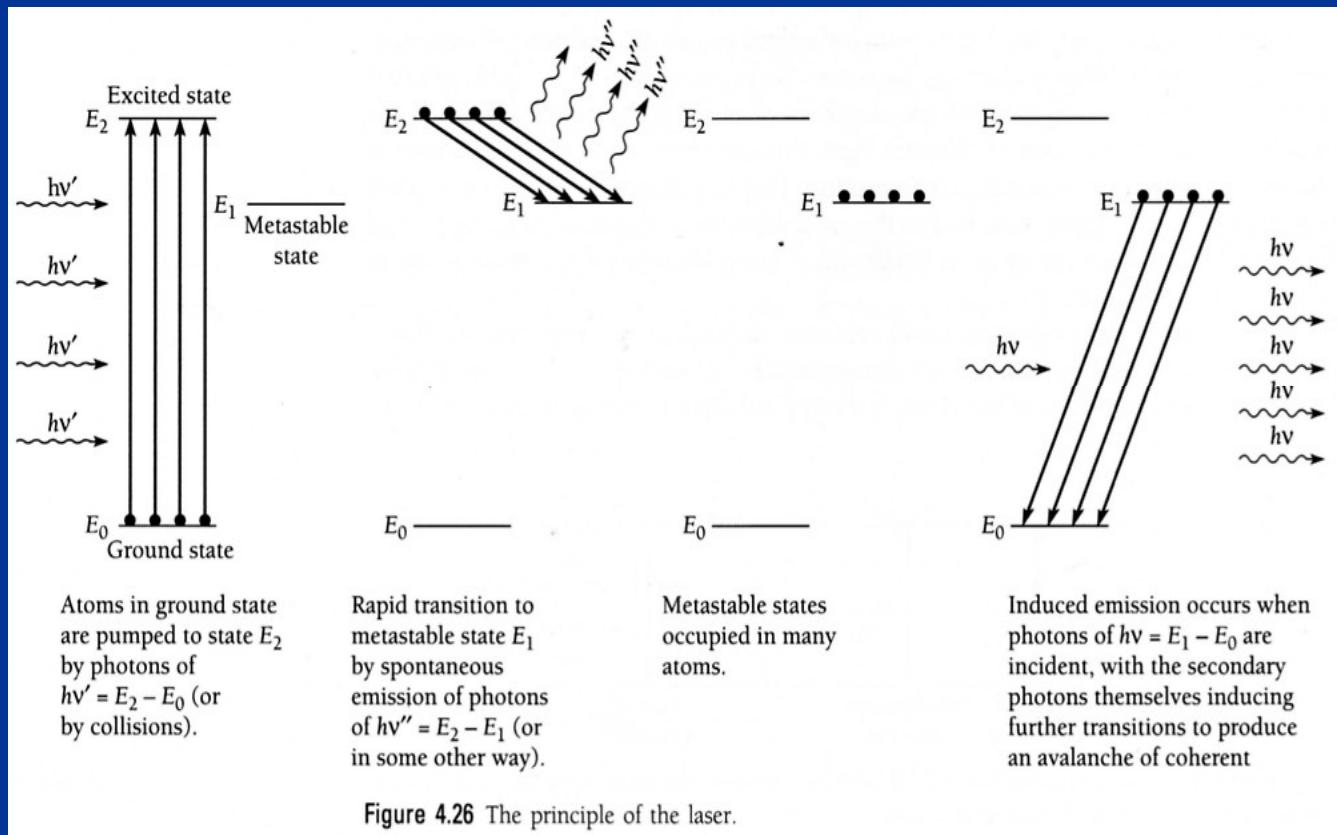


Figure 4.26 The principle of the laser.

A number of ways exist to produce a population inversion. One of them, called **optical pumping**, is illustrated in Fig. 4.27. Here an external light source is used some of whose photons have the right frequency to raise ground-state atoms to the excited state that decays spontaneously to the desired metastable state.

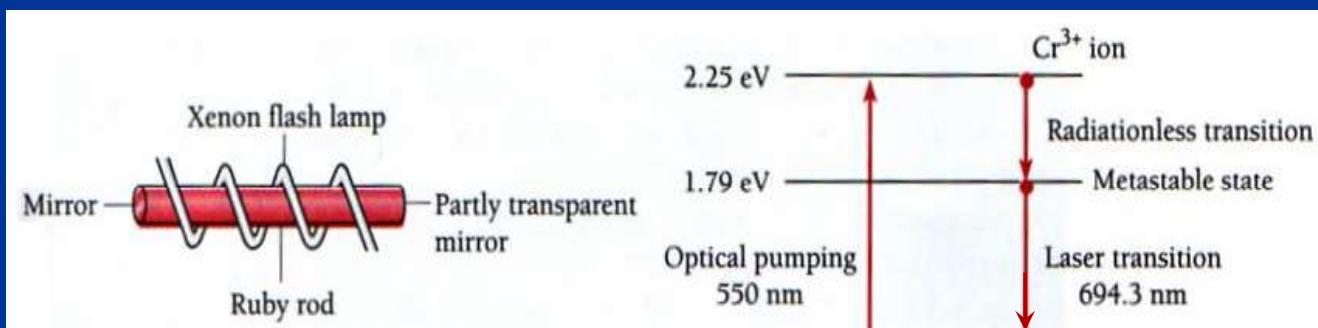
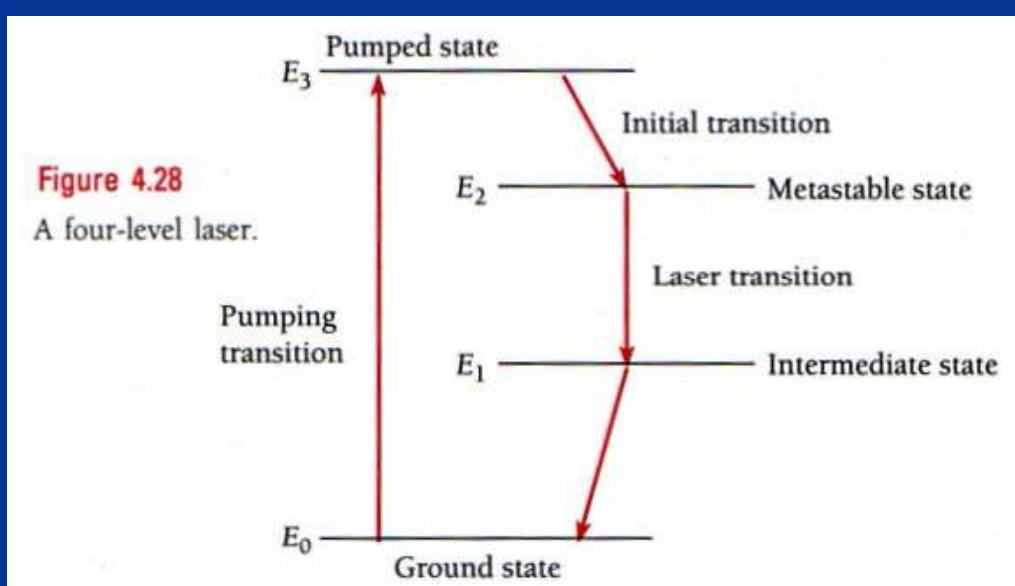


Figure 4.27 The ruby laser. In order for induced emission to exceed induced absorption, more than half the Cr^{3+} ions in the ruby rod must be in the metastable state. This laser produces a pulse of red light after each flash of the lamp.

Why are three levels needed? Suppose there are only two levels, a metastable state $h\nu$ above the ground state. The more photons of frequency ν we pump into the assembly of atoms, the more upward transitions there will be from the ground state to the metastable state. However, at the same time the pumping will induce downward transitions from the metastable state to the ground state. When half the atoms are in each state, the rate of induced emissions will equal the rate of induced absorptions, so the assembly cannot ever have more than half its atoms in the metastable state. In this situation laser amplification cannot occur. A population inversion is only possible when the induced absorptions are to a higher energy level than the metastable one from which the induced emission takes place, which prevents the pumping from depopulating the metastable state.

In a three-level laser, more than half the atoms must be in the metastable state for induced emission to predominate. This is not the case for a four-level laser. As in Fig. 4.28, the laser transition from the metastable state ends at an unstable intermediate state rather than at the ground state. Because the intermediate state decays rapidly to the ground state, very few atoms are in the intermediate state. Hence even a modest amount of pumping is enough to populate the metastable state to a greater extent than the intermediate state, as required for laser amplification.



Practical Lasers

The first successful laser, the **ruby laser**, is based on the three energy levels in the chromium ion Cr^{3+} shown in Fig. 4.27. A ruby is a crystal of aluminum oxide, Al_2O_3 , in which some of the Al^{3+} ions are replaced by Cr^{3+} ions, which are responsible for the red color. A Cr^{3+} ion has a metastable level whose lifetime is about 0.003 s. In the ruby laser, a xenon flash lamp excites the Cr^{3+} ions to a level of higher energy from which they fall to the metastable level by losing energy to other ions in the crystal. Photons from the spontaneous decay of some Cr^{3+} ions are reflected back and forth between the mirrored ends of the ruby rod, stimulating other excited Cr^{3+} ions to radiate. After a few microseconds the result is a large pulse of monochromatic, coherent red light from the partly transparent end of the rod.

The rod's length is made precisely an integral number of half-wavelengths long, so the radiation trapped in it forms an optical standing wave. Since the induced emissions are stimulated by the standing wave, their waves are all in step with it.

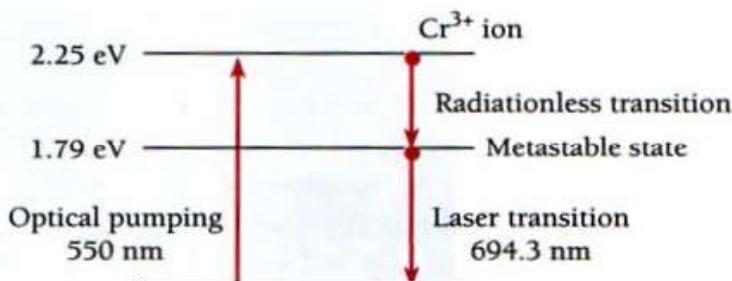


Figure 4.27

The common **helium-neon gas laser** achieves a population inversion in a different way. A mixture of about 10 parts of helium and 1 part of neon at a low pressure (~ 1 torr) is placed in a glass tube that has parallel mirrors, one of them partly transparent, at both ends. The spacing of the mirrors is again (as in all lasers) equal to an integral number of half-wavelengths of the laser light. An electric discharge is produced in the gas by means of electrodes outside the tube connected to a source of high-frequency alternating current, and collisions with electrons from the discharge excite He and Ne atoms to metastable states respectively 20.61 and 20.66 eV above their ground states.

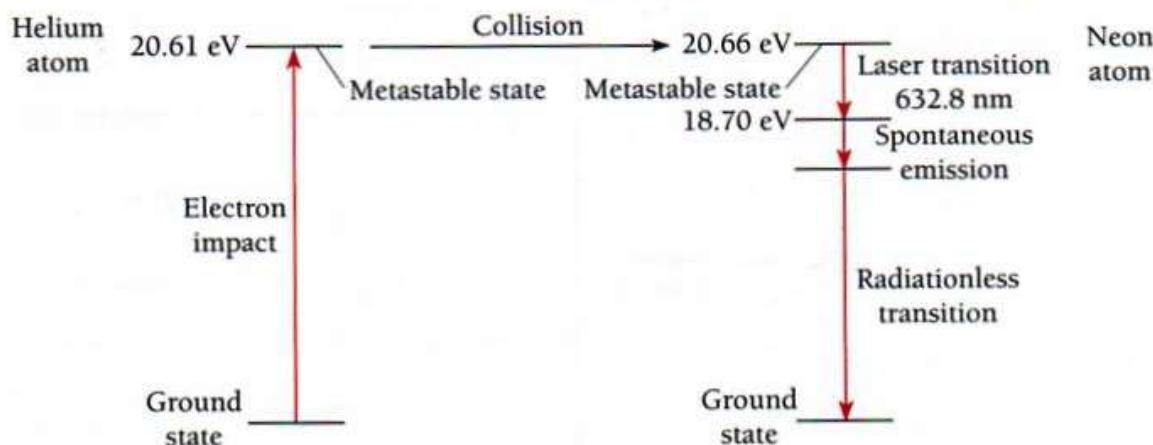


Figure 4.29 The helium-neon laser. In a four-level laser such as this, continuous operation is possible. Helium-neon lasers are commonly used to read bar codes.

There are many other types of lasers

Some of them use molecules instead of atoms

Chemical lasers work on the metastable excited states of molecules produced by chemical reactions, e.g. KrF, HF lasers. Very fast and powerful.

Dye lasers use dye molecules, whose energy levels are so close together that they can “laser” over a virtually continuous range of wavelength by adjusting the spacing of the resonance mirrors.

CO₂ lasers are continuous and very powerful (>100 W), used in surgery as well as cutting tools in industry.

Semiconductor lasers, used in CD/DVD players, and fibre-optic communications.

5.1 QUANTUM MECHANICS

Classical mechanics is an approximation of quantum mechanics

The fundamental difference between classical (or newtonian) mechanics and quantum mechanics lies in what they describe. In classical mechanics, the future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it. In the everyday world these quantities can all be determined well enough for the predictions of newtonian mechanics to agree with what we find.

Quantum mechanics also arrives at relationships between observable quantities, but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic realm. Cause and effect are still related in quantum mechanics, but what they concern needs careful interpretation. In quantum mechanics the kind of certainty about the future characteristic of classical mechanics is impossible because the initial state of a particle cannot be established with sufficient accuracy. As we saw in Sec. 3.7, the more we know about the position of a particle now, the less we know about its momentum and hence about its position later.

The quantities whose relationships quantum mechanics explores are *probabilities*. Instead of asserting, for example, that the radius of the electron's orbit in a ground-state hydrogen atom is always exactly 5.3×10^{-11} m, as the Bohr theory does, quantum mechanics states that this is the *most probable* radius. In a suitable experiment most trials will yield a different value, either larger or smaller, but the value most likely to be found will be 5.3×10^{-11} m.

Quantum mechanics might seem a poor substitute for classical mechanics. However, classical mechanics turns out to be just an approximate version of quantum mechanics. The certainties of classical mechanics are illusory, and their apparent agreement with experiment occurs because ordinary objects consist of so many individual atoms that departures from average behavior are unnoticeable. Instead of two sets of physical principles, one for the macroworld and one for the microworld, there is only the single set included in quantum mechanics.

Wave Function

As mentioned in Chap. 3, the quantity with which quantum mechanics is concerned is the **wave function** Ψ of a body. While Ψ itself has no physical interpretation, the square of its absolute magnitude $|\Psi|^2$ evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time. The linear momentum, angular momentum, and energy of the body are other quantities that can be established from Ψ . The problem of quantum mechanics is to determine Ψ for a body when its freedom of motion is limited by the action of external forces.

Wave functions are usually complex with both real and imaginary parts. A probability, however, must be a positive real quantity. The probability density $|\Psi|^2$ for a complex Ψ is therefore taken as the product $\Psi^*\Psi$ of Ψ and its **complex conjugate** Ψ^* . The complex conjugate of any function is obtained by replacing $i (= \sqrt{-1})$ by $-i$ wherever it appears in the function. Every complex function Ψ can be written in the form

Wave function

$$\Psi = A + iB$$

where A and B are real functions. The complex conjugate Ψ^* of Ψ is

Complex conjugate

$$\Psi^* = A - iB$$

and so

$$\Psi^*\Psi = A^2 - i^2B^2 = A^2 + B^2$$

since $i^2 = -1$. Hence $\Psi^*\Psi$ is always a positive real quantity, as required.

Even before we consider the actual calculation of Ψ , we can establish certain requirements it must always fulfill. For one thing, since $|\Psi|^2$ is proportional to the probability density P of finding the body described by Ψ , the integral of $|\Psi|^2$ over all space must be finite—the body is *somewhere*, after all. If

$$\int_{-\infty}^{\infty} |\Psi|^2 dV = 0$$

the particle does not exist, and the integral obviously cannot be ∞ and still mean anything. Furthermore, $|\Psi|^2$ cannot be negative or complex because of the way it is defined. The only possibility left is that the integral be a finite quantity if Ψ is to describe properly a real body.

It is usually convenient to have $|\Psi|^2$ be *equal* to the probability density P of finding the particle described by Ψ , rather than merely be proportional to P . If $|\Psi|^2$ is to equal P , then it must be true that

Normalization

$$\int_{-\infty}^{\infty} |\Psi|^2 dV = 1 \quad (5.1)$$

since if the particle exists somewhere at all times,

$$\int_{-\infty}^{\infty} P dV = 1$$

A wave function that obeys Eq. (5.1) is said to be **normalized**. Every acceptable wave function can be normalized by multiplying it by an appropriate constant; we shall shortly see how this is done.

Besides being normalizable, Ψ must be single-valued, since P can have only one value at a particular place and time, and continuous. Momentum considerations (see the Appendix to this chapter) require that the partial derivatives $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ be finite, continuous, and single-valued. Only wave functions with all these properties can yield physically meaningful results when used in calculations, so only such “well-behaved” wave functions are admissible as mathematical representations of real bodies. To summarize:

1. Ψ must be continuous and single-valued everywhere.
2. $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ must be continuous and single-valued everywhere.
3. Ψ must be normalizable, which means that Ψ must go to 0 as $x \rightarrow \pm\infty$, $y \rightarrow \pm\infty$, $z \rightarrow \pm\infty$ in order that $\int |\Psi|^2 dV$ over all space be a finite constant.

The above rules are not always obeyed by the wave functions of particles in model situations that only approximate actual ones. For instance, the wave functions of a particle in a box with infinitely hard walls do not have continuous derivatives at the walls, since $\Psi = 0$ outside the box (see Fig. 5.4). But in the real world, where walls are never infinitely hard, there is no sharp change in Ψ at the walls (see Fig. 5.7) and the derivatives are continuous. Exercise 7 gives another example of a wave function that is not well-behaved.

Partial Derivatives

Suppose we have a function $f(x, y)$ of two variables, x and y , and we want to know how f varies with only one of them, say x . To find out, we differentiate f with respect to x while treating the other variable y as a constant. The result is the **partial derivative** of f with respect to x , which is written $\partial f / \partial x$:

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx} \right)_{y=\text{constant}}$$

The rules for ordinary differentiation hold for partial differentiation as well. For instance, if $f = cx^2$,

$$\frac{df}{dx} = 2cx$$

and so, if $f = yx^2$,

$$\frac{\partial f}{\partial x} = \left(\frac{df}{dx} \right)_{y=\text{constant}} = 2yx$$

The partial derivative of $f = yx^2$ with respect to the other variable, y , is

$$\frac{\partial f}{\partial y} = \left(\frac{df}{dy} \right)_{x=\text{constant}} = x^2$$

Second order partial derivatives occur often in physics, as in the wave equation. To find $\partial^2 f / \partial x^2$, we first calculate $\partial f / \partial x$ and then differentiate again, still keeping y constant:

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x} \right). \text{ For } f = yx^2, \frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial x} (2yx) = 2y. \text{ Similarly } \frac{\partial^2 f}{\partial x^2} = \frac{\partial}{\partial y} (x^2) = 0$$

Given a normalized and otherwise acceptable wave function Ψ , the probability that the particle it describes will be found in a certain region is simply the integral of the probability density $|\Psi|^2$ over that region. Thus for a particle restricted to motion in the x direction, the probability of finding it between x_1 and x_2 is given by

Probability $P_{x_1 x_2} = \int_{x_1}^{x_2} |\Psi|^2 dx \quad (5.2)$

We will see examples of such calculations later in this chapter and in the next chapter.

5.2 THE WAVE EQUATION

It can have a variety of solutions, including complex ones

Schrödinger's equation, which is the fundamental equation of quantum mechanics in the same sense that the second law of motion is the fundamental equation of newtonian mechanics, is a wave equation in the variable Ψ .

Before we tackle Schrödinger's equation, let us review the wave equation

Wave equation

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2} \quad (5.3)$$

which governs a wave whose variable quantity is y that propagates in the x direction with the speed v . In the case of a wave in a stretched string, y is the displacement of the string from the x axis; in the case of a sound wave, y is the pressure difference; in the case of a light wave, y is either the electric or the magnetic field magnitude. Equation (5.3) can be derived from the second law of motion for mechanical waves and from Maxwell's equations for electromagnetic waves.

Solutions of the wave equation may be of many kinds, reflecting the variety of waves that can occur—a single traveling pulse, a train of waves of constant amplitude and wavelength, a train of superposed waves of the same amplitudes and wavelengths, a train of superposed waves of different amplitudes and wavelengths, a standing wave in a string fastened at both ends, and so on. All solutions must be of the form

$$y = F\left(t \pm \frac{x}{v}\right) \quad (5.4)$$

where F is any function that can be differentiated. The solutions $F(t - x/v)$ represent waves traveling in the $+x$ direction, and the solutions $F(t + x/v)$ represent waves traveling in the $-x$ direction.

Let us consider the wave equivalent of a “free particle,” which is a particle that is not under the influence of any forces and therefore pursues a straight path at constant speed. This wave is described by the general solution of Eq. (5.3) for undamped (that is, constant amplitude A), monochromatic (constant angular frequency ω) harmonic waves in the $+x$ direction, namely

$$y = Ae^{-i\omega(t-x/v)} \quad (5.5)$$

In this formula y is a complex quantity, with both real and imaginary parts.

Because $e^{-i\theta} = \cos \theta - i \sin \theta$, Eq. (5.5) can be written in the form

$$y = A \cos \omega \left(t - \frac{x}{v} \right) - iA \sin \omega \left(t - \frac{x}{v} \right) \quad (5.6)$$

Only the real part of Eq. (5.6) [which is the same as Eq. (3.5)] has significance in the case of waves in a stretched string. There y represents the displacement of the string from its normal position (Fig. 5.1), and the imaginary part of Eq. (5.6) is discarded as irrelevant.

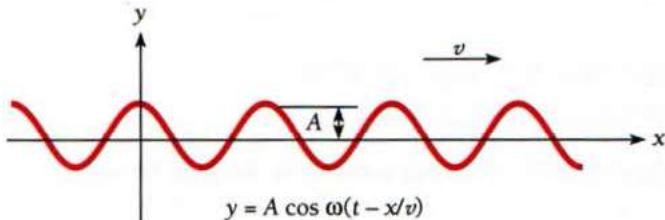


Figure 5.1 Waves in the xy plane traveling in the $+x$ direction along a stretched string lying on the x axis.

5.3 SCHRÖDINGER'S EQUATION: TIME-DEPENDENT FORM

A basic physical principle that cannot be derived from anything else

In quantum mechanics the wave function Ψ corresponds to the wave variable y of wave motion in general. However, Ψ , unlike y , is not itself a measurable quantity and may therefore be complex. For this reason we assume that Ψ for a particle moving freely in the $+x$ direction is specified by

$$\Psi = Ae^{-i\omega(t-x/v)} \quad (5.7)$$

Replacing ω in the above formula by $2\pi\nu$ and v by $\lambda\nu$ gives

$$\Psi = Ae^{-2\pi i(\nu t - x/\lambda)} \quad (5.8)$$

This is convenient since we already know what ν and λ are in terms of the total energy E and momentum p of the particle being described by Ψ . Because

$$E = h\nu = 2\pi\hbar\nu \quad \text{and} \quad \lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

we have

Free particle

$$\Psi = Ae^{-(i\hbar/Et - px)} \quad (5.9)$$

Free particle

$$\Psi = Ae^{-(i/\hbar)(Et - px)} \quad (5.9)$$

Equation (5.9) describes the wave equivalent of an unrestricted particle of total energy E and momentum p moving in the $+x$ direction, just as Eq. (5.5) describes, for example, a harmonic displacement wave moving freely along a stretched string.

The expression for the wave function Ψ given by Eq. (5.9) is correct only for freely moving particles. However, we are most interested in situations where the motion of a particle is subject to various restrictions. An important concern, for example, is an electron bound to an atom by the electric field of its nucleus. What we must now do is obtain the fundamental differential equation for Ψ , which we can then solve for Ψ in a specific situation. This equation, which is Schrödinger's equation, can be arrived at in various ways, but it *cannot* be rigorously derived from existing physical principles: the equation represents something new. What will be done here is to show one route to the wave equation for Ψ and then to discuss the significance of the result.

Free particle

$$\Psi = Ae^{-(i/\hbar)(Et - px)} \quad (5.9)$$

We begin by differentiating Eq. (5.9) for Ψ twice with respect to x , which gives

$$\frac{\partial^2 \Psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \Psi$$

$p^2 \Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2}$

(5.10)

Differentiating Eq. (5.9) once with respect to t gives

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \Psi$$

$E \Psi = -\frac{\hbar}{i} \frac{\partial \Psi}{\partial t}$

(5.11)

At speeds small compared with that of light, the total energy E of a particle is the sum of its kinetic energy $p^2/2m$ and its potential energy U , where U is in general a function of position x and time t :

$$E = \frac{p^2}{2m} + U(x, t) \quad (5.12)$$

$$E = \frac{p^2}{2m} + U(x, t) \quad (5.12)$$

The function U represents the influence of the rest of the universe on the particle. Of course, only a small part of the universe interacts with the particle to any extent; for instance, in the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account.

Multiplying both sides of Eq. (5.12) by the wave function Ψ gives

$$E\Psi = \frac{p^2\Psi}{2m} + U\Psi \quad (5.13)$$

Now we substitute for $E\Psi$ and $p^2\Psi$ from Eqs. (5.10) and (5.11) to obtain the **time-dependent form of Schrödinger's equation**:

**Time-dependent
Schrödinger
equation in one
dimension**

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi \quad (5.14)$$

**Time-dependent
Schrödinger
equation in one
dimension**

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + U\Psi \quad (5.14)$$

In three dimensions the time-dependent form of Schrödinger's equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right) + U\Psi \quad (5.15)$$

where the particle's potential energy U is some function of x, y, z , and t .

Any restrictions that may be present on the particle's motion will affect the potential-energy function U . Once U is known, Schrödinger's equation may be solved for the wave function Ψ of the particle, from which its probability density $|\Psi|^2$ may be determined for a specified x, y, z, t .

Schrödinger's equation was obtained here using the wave function of a freely moving particle (potential energy $U = \text{constant}$). How can we be sure it applies to the general case of a particle subject to arbitrary forces that vary in space and time [$U = U(x, y, z, t)$]? Substituting Eqs. (5.10) and (5.11) into Eq. (5.13) is really a wild leap with no formal justification; this is true for all other ways in which Schrödinger's equation can be arrived at, including Schrödinger's own approach.

What we must do is postulate Schrödinger's equation, solve it for a variety of physical situations, and compare the results of the calculations with the results of experiments. If both sets of results agree, the postulate embodied in Schrödinger's equation is valid. If they disagree, the postulate must be discarded and some other approach would then have to be explored. In other words,

Schrödinger's equation cannot be derived from other basic principles of physics; it is a basic principle in itself.

What has happened is that Schrödinger's equation has turned out to be remarkably accurate in predicting the results of experiments. To be sure, Eq. (5.15) can be used only for nonrelativistic problems, and a more elaborate formulation is needed when particle speeds near that of light are involved. But because it is in accord with experience within its range of applicability, we must consider Schrödinger's equation as a valid statement concerning certain aspects of the physical world.

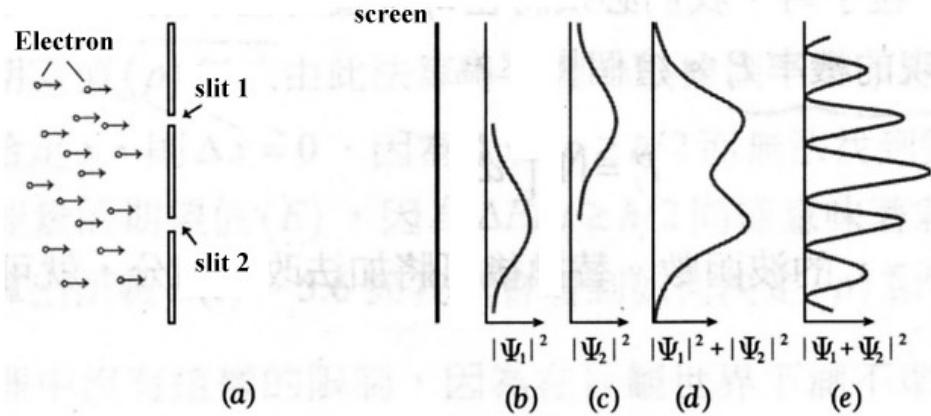
It is worth noting that Schrödinger's equation does not increase the number of principles needed to describe the workings of the physical world. Newton's second law of motion $F = ma$, the basic principle of classical mechanics, can be derived from Schrödinger's equation provided the quantities it relates are understood to be averages rather than precise values.

Linearity and Superposition

An important property of Schrödinger's equation is that it is linear in the wave function Ψ . By this is meant that the equation has terms that contain Ψ and its derivatives but no terms independent of Ψ or that involve higher powers of Ψ or its derivatives. As a result, a linear combination of solutions of Schrödinger's equation for a given system is also itself a solution. If Ψ_1 and Ψ_2 are two solutions (that is, two wave functions that satisfy the equation), then

$$\Psi = a_1\Psi_1 + a_2\Psi_2$$

is also a solution, where a_1 and a_2 are constants (see Exercise 8). Thus the wavefunctions Ψ_1 and Ψ_2 obey the superposition principle that other waves do (see Sec. 2.1) and we conclude that interference effects can occur for wave functions just as they can for light, sound, water, and electromagnetic waves. In fact, the discussions of Secs. 3.4 and 3.7 assumed that de Broglie waves are subject to the superposition principle.



- (a) Double slits experiment, (b) only slit 1 open, (c) only slit 2 open
 (d) sum of (b) and (c), (e) both slits 1 and 2 open

$$(b) P_1 = |\Psi_1|^2 = \Psi_1^* \Psi_1 \quad (c) P_2 = |\Psi_2|^2 = \Psi_2^* \Psi_2 \quad (d) |\Psi_1|^2 + |\Psi_2|^2$$

$$(e) \Psi = \Psi_1 + \Psi_2$$

$$\begin{aligned} P &= |\Psi|^2 = |\Psi_1 + \Psi_2|^2 = (\Psi_1^* + \Psi_2^*)(\Psi_1 + \Psi_2) \\ &= \Psi_1^* \Psi_1 + \Psi_2^* \Psi_2 + \Psi_1^* \Psi_2 + \Psi_2^* \Psi_1 \\ &= P_1 + P_2 + \underline{\Psi_1^* \Psi_2 + \Psi_2^* \Psi_1} \end{aligned}$$

5.4 EXPECTATION VALUES

How to extract information from a wave function

Once Schrödinger's equation has been solved for a particle in a given physical situation, the resulting wave function $\Psi(x, y, z, t)$ contains all the information about the particle that is permitted by the uncertainty principle. Except for those variables that are quantized this information is in the form of probabilities and not specific numbers.

As an example, let us calculate the **expectation value** $\langle x \rangle$ of the position of a particle confined to the x axis that is described by the wave function $\Psi(x, t)$. This is the value of x we would obtain if we measured the positions of a great many particles described by the same wave function at some instant t and then averaged the results.

To make the procedure clear, we first answer a slightly different question: What is the average position \bar{x} of a number of identical particles distributed along the x axis in such a way that there are N_1 particles at x_1 , N_2 particles at x_2 , and so on? The average position in this case is the same as the center of mass of the distribution, and so

$$\bar{x} = \frac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \dots}{N_1 + N_2 + N_3 + \dots} = \frac{\sum N_i x_i}{\sum N_i} \quad (5.16)$$

When we are dealing with a single particle, we must replace the number N_i of particles at x_i by the probability P_i that the particle be found in an interval dx at x_i . This probability is

$$P_i = |\Psi_i|^2 dx \quad (5.17)$$

where Ψ_i is the particle wave function evaluated at $x = x_i$. Making this substitution and changing the summations to integrals, we see that the expectation value of the position of the single particle is

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x|\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx} \quad (5.18)$$

If Ψ is a normalized wave function, the denominator of Eq. (5.18) equals the probability that the particle exists somewhere between $x = -\infty$ and $x = \infty$ and therefore has the value 1. In this case

Expectation value for position $\langle x \rangle = \int_{-\infty}^{\infty} x|\Psi|^2 dx \quad (5.19)$

This formula states that $\langle x \rangle$ is located at the center of mass (so to speak) of $|\Psi|^2$. If $|\Psi|^2$ is plotted versus x on a graph and the area enclosed by the curve and the x axis is cut out, the balance point will be at $\langle x \rangle$.

Example 5.2

A particle limited to the x axis has the wave function $\Psi = ax$ between $x = 0$ and $x = 1$; $\Psi = 0$ elsewhere. (a) Find the probability that the particle can be found between $x = 0.45$ and $x = 0.55$. (b) Find the expectation value $\langle x \rangle$ of the particle's position.

Solution

(a) The probability is

$$\int_{x_1}^{x_2} |\Psi|^2 dx = a^2 \int_{0.45}^{0.55} x^2 dx = a^2 \left[\frac{x^3}{3} \right]_{0.45}^{0.55} = 0.0251a^2$$

(b) The expectation value is

$$\langle x \rangle = \int_0^1 x|\Psi|^2 dx = a^2 \int_0^1 x^3 dx = a^2 \left[\frac{x^4}{4} \right]_0^1 = \frac{a^2}{4}$$

The same procedure as that followed above can be used to obtain the expectation value $\langle G(x) \rangle$ of any quantity—for instance, potential energy $U(x)$ —that is a function of the position x of a particle described by a wave function Ψ . The result is

Expectation value
$$\langle G(x) \rangle = \int_{-\infty}^{\infty} G(x) |\Psi|^2 dx \quad (5.20)$$

The expectation value $\langle p \rangle$ for momentum cannot be calculated this way because, according to the uncertainty principles, no such function as $p(x)$ can exist. If we specify x , so that $\Delta x = 0$, we cannot specify a corresponding p since $\Delta x \Delta p \geq \hbar/2$. The same problem occurs for the expectation value $\langle E \rangle$ for energy. The Appendix to this chapter discusses how $\langle p \rangle$ and $\langle E \rangle$ can be found without violating the uncertainty principle.

Link to p. 71

5.5 SCHRÖDINGER'S EQUATION: STEADY-STATE FORM

Eigenvalues and eigenfunctions

In a great many situations the potential energy of a particle does not depend on time explicitly; the forces that act on it, and hence U , vary with the position of the particle only. When this is true, Schrödinger's equation may be simplified by removing all reference to t .

We begin by noting that the one-dimensional wave function Ψ of an unrestricted particle may be written

$$\Psi = Ae^{-(i/\hbar)(Et - px)} = Ae^{-(iE/\hbar)t}e^{+(ip/\hbar)x} = \psi e^{-(iE/\hbar)t} \quad (5.21)$$

Evidently Ψ is the product of a time-dependent function $e^{-(iE/\hbar)t}$ and a position-dependent function ψ . As it happens, the time variations of *all* wave functions of particles acted on by stationary forces have the same form as that of an unrestricted particle.

An important property of Schrödinger's steady-state equation is that, if it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy E . Thus energy quantization appears in wave mechanics as a natural element of the theory, and energy quantization in the physical world is revealed as a universal phenomenon characteristic of *all* stable systems.

Substituting the Ψ of Eq. (5.21) into the time-dependent form of Schrödinger's equation, we find that

$$E\psi e^{-(iE/\hbar)t} = -\frac{\hbar^2}{2m}e^{-(iE/\hbar)t}\frac{\partial^2\psi}{\partial x^2} + U\psi e^{-(iE/\hbar)t}$$

Dividing through by the common exponential factor gives

**Steady-state
Schrödinger
equation in one
dimension**

$$\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \quad (5.22)$$

Equation (5.22) is the **steady-state form of Schrödinger's equation**. In three dimensions it is

**Steady-state
Schrödinger
equation in three
dimensions**

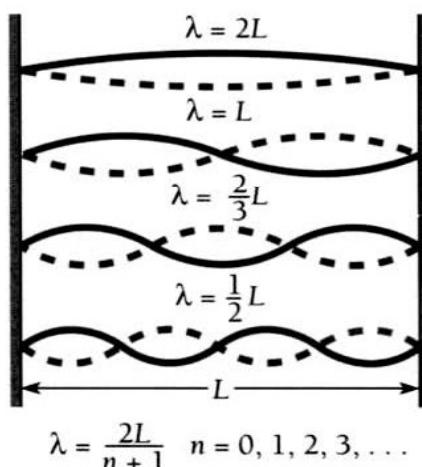
$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0 \quad (5.23)$$

A familiar and quite close analogy to the manner in which energy quantization occurs in solutions of Schrödinger's equation is with standing waves in a stretched string of length L that is fixed at both ends. Here, instead of a single wave propagating indefinitely in one direction, waves are traveling in both the $+x$ and $-x$ directions simultaneously. These waves are subject to the condition (called a **boundary condition**) that the displacement y always be zero at both ends of the string. An acceptable function $y(x, t)$ for the displacement must, with its derivatives (except at the ends), be as well-behaved as ψ and its derivatives—that is, be continuous, finite, and single-valued. In this case y must be real, not complex, as it represents a directly measurable quantity. The only solutions of the wave equation, Eq. (5.3), that are in accord with these various limitations are those in which the wavelengths are given by

$$\lambda_n = \frac{2L}{n+1} \quad n = 0, 1, 2, 3, \dots$$

as shown in Fig. 5.2. It is the *combination* of the wave equation and the restrictions placed on the nature of its solution that leads us to conclude that $y(x, t)$ can exist only for certain wavelengths λ_n .

Figure 5.2 Standing waves in a stretched string fastened at both ends.



$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

Eigenvalues and Eigenfunctions

The values of energy E_n for which Schrödinger's steady-state equation can be solved are called **eigenvalues** and the corresponding wave functions ψ_n are called **eigenfunctions**. (These terms come from the German *Eigenwert*, meaning "proper or characteristic value," and *Eigenfunktion*, "proper or characteristic function.") The discrete energy levels of the hydrogen atom

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\left(\frac{1}{n^2}\right) \quad n = 1, 2, 3, \dots$$

are an example of a set of eigenvalues. We shall see in Chap. 6 why these particular values of E are the only ones that yield acceptable wave functions for the electron in the hydrogen atom.

An important example of a dynamical variable other than total energy that is found to be quantized in stable systems is angular momentum \mathbf{L} . In the case of the hydrogen atom, we shall find that the eigenvalues of the magnitude of the total angular momentum are specified by

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

Of course, a dynamical variable G may not be quantized. In this case measurements of G made on a number of identical systems will not yield a unique result but instead a spread of values whose average is the expectation value

$$\langle G \rangle = \int_{-\infty}^{\infty} G|\psi|^2 dx$$

In the hydrogen atom, the electron's position is not quantized, for instance, so that we must think of the electron as being present in the vicinity of the nucleus with a certain probability $|\psi|^2$ per unit volume but with no predictable position or even orbit in the classical sense. This probabilistic statement does not conflict with the fact that experiments performed on hydrogen atoms always show that each one contains a whole electron, not 27 percent of an electron in a certain region and 73 percent elsewhere. The probability is one of *finding* the electron, and although this probability is smeared out in space, the electron itself is not.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

5.6 PARTICLE IN A BOX

How boundary conditions and normalization determine wave functions

To solve Schrödinger's equation, even in its simpler steady-state form, usually requires elaborate mathematical techniques. For this reason the study of quantum mechanics has traditionally been reserved for advanced students who have the required proficiency in mathematics. However, since quantum mechanics is the theoretical structure whose results are closest to experimental reality, we must explore its methods and applications to understand modern physics. As we shall see, even a modest mathematical background is enough for us to follow the trains of thought that have led quantum mechanics to its greatest achievements.

The simplest quantum-mechanical problem is that of a particle trapped in a box with infinitely hard walls. In Sec. 3.6 we saw how a quite simple argument yields the energy levels of the system. Let us now tackle the same problem in a more formal way, which will give us the wave function ψ_n that corresponds to each energy level.

We may specify the particle's motion by saying that it is restricted to traveling along the x axis between $x = 0$ and $x = L$ by infinitely hard walls. A particle does not lose energy when it collides with such walls, so that its total energy stays constant. From a formal point of view the potential energy U of the particle is infinite on both sides of the box, while U is a constant—say 0 for convenience—on the inside (Fig. 5.3). Because the particle cannot have an infinite amount of energy, it cannot exist outside the box, and so its wave function ψ is 0 for $x \leq 0$ and $x \geq L$. Our task is to find what ψ is within the box, namely, between $x = 0$ and $x = L$.

Within the box Schrödinger's equation becomes

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0 \quad (5.24)$$

since $U = 0$ there. (The total derivative $d^2 \psi / dx^2$ is the same as the partial derivative $\partial^2 \psi / \partial x^2$ because ψ is a function only of x in this problem.)

Equation (5.24) has the solution

$$\psi = A \sin \frac{\sqrt{2mE}}{\hbar} x + B \cos \frac{\sqrt{2mE}}{\hbar} x \quad (5.25)$$

which we can verify by substitution back into Eq. (5.24). A and B are constants to be evaluated.

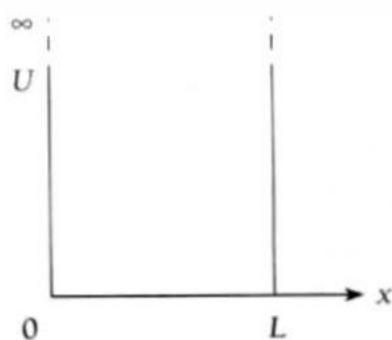


Figure 5.3 A square potential well with infinitely high barriers at each end corresponds to a box with infinitely hard walls.

This solution is subject to the boundary conditions that $\psi = 0$ for $x = 0$ and for $x = L$. Since $\cos 0 = 1$, the second term cannot describe the particle because it does not vanish at $x = 0$. Hence we conclude that $B = 0$. Since $\sin 0 = 0$, the sine term always yields $\psi = 0$ at $x = 0$, as required, but ψ will be 0 at $x = L$ only when

$$\frac{\sqrt{2mE}}{\hbar} L = n\pi \quad n = 1, 2, 3, \dots \quad (5.26)$$

This result comes about because the sines of the angles $\pi, 2\pi, 3\pi, \dots$ are all 0.

From Eq. (5.26) it is clear that the energy of the particle can have only certain values, which are the eigenvalues mentioned in the previous section. These eigenvalues, constituting the **energy levels** of the system, are found by solving Eq. (5.26) for E_n , which gives

$$\text{Particle in a box} \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \quad n = 1, 2, 3, \dots \quad (5.27)$$

Equation (5.27) is the same as Eq. (3.18) and has the same interpretation [see the discussion that follows Eq. (3.18) in Sec. 3.6].

Wave Functions of a Particle in a Box

The wave functions of a particle in a box whose energies are E_n are, from Eq. (5.25) with $B = 0$,

$$\psi_n = A \sin \frac{\sqrt{2mE_n}}{\hbar} x \quad (5.28)$$

Substituting Eq. (5.27) for E_n gives

$$\psi_n = A \sin \frac{n\pi x}{L} \quad (5.29)$$

for the eigenfunctions corresponding to the energy eigenvalues E_n .

It is easy to verify that these eigenfunctions meet all the requirements discussed in Sec. 5.1: for each quantum number n , ψ_n is a finite, single-valued function of x , and ψ_n and $\partial\psi_n/\partial x$ are continuous (except at the ends of the box). Furthermore, the integral of $|\psi_n|^2$ over all space is finite, as we can see by integrating $|\psi_n|^2 dx$ from $x = 0$ to $x = L$ (since the particle is confined within these limits). With the help of the trigonometric identity $\sin^2 \theta = \frac{1}{2}(1 - \cos 2\theta)$ we find that

$$\begin{aligned} \int_{-\infty}^{\infty} |\psi_n|^2 dx &= \int_0^L |\psi_n|^2 dx = A^2 \int_0^L \sin^2 \left(\frac{n\pi x}{L} \right) dx \\ &= \frac{A^2}{2} \left[\int_0^L dx - \int_0^L \cos \left(\frac{2n\pi x}{L} \right) dx \right] \\ &= \frac{A^2}{2} \left[x - \left(\frac{L}{2n\pi} \right) \sin \frac{2n\pi x}{L} \right]_0^L = A^2 \left(\frac{L}{2} \right) \end{aligned} \quad (5.30)$$

To normalize ψ we must assign a value to A such that $|\psi_n|^2 dx$ is *equal* to the probability $P dx$ of finding the particle between x and $x + dx$, rather than merely proportional to $P dx$. If $|\psi_n|^2 dx$ is to equal $P dx$, then it must be true that

$$\int_{-\infty}^{\infty} |\psi_n|^2 dx = 1 \quad (5.31)$$

Comparing Eqs. (5.30) and (5.31), we see that the wave functions of a particle in a box are normalized if

$$A = \sqrt{\frac{2}{L}} \quad (5.32)$$

The normalized wave functions of the particle are therefore

$$\text{Particle in a box} \quad \psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, \dots \quad (5.33)$$

Particle in a box $\psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad n = 1, 2, 3, \dots \quad (5.33)$

The normalized wave functions ψ_1 , ψ_2 , and ψ_3 together with the probability densities $|\psi_1|^2$, $|\psi_2|^2$, and $|\psi_3|^2$ are plotted in Fig. 5.4. Although ψ_n may be negative as well as positive, $|\psi_n|^2$ is always positive and, since ψ_n is normalized, its value at a given x is equal to the probability density of finding the particle there. In every case $|\psi_n|^2 = 0$ at $x = 0$ and $x = L$, the boundaries of the box.

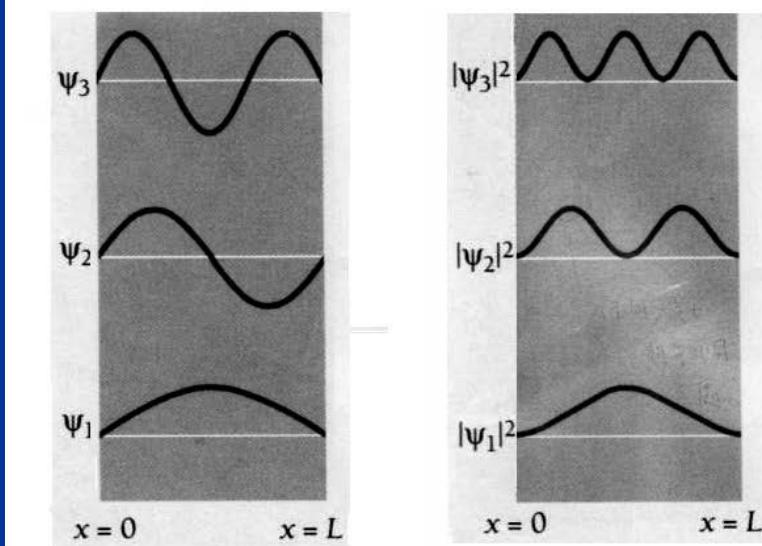


Figure 5.4 Wave functions and probability densities of a particle confined to a box with rigid walls.

At a particular place in the box the probability of the particle being present may be very different for different quantum numbers. For instance, $|\psi_1|^2$ has its maximum value of $2/L$ in the middle of the box, while $|\psi_2|^2 = 0$ there. A particle in the lowest energy level of $n = 1$ is most likely to be in the middle of the box, while a particle in the next higher state of $n = 2$ is *never* there! Classical physics, of course, suggests the same probability for the particle being anywhere in the box.

The wave functions shown in Fig. 5.4 resemble the possible vibrations of a string fixed at both ends, such as those of the stretched string of Fig. 5.2. This follows from the fact that waves in a stretched string and the wave representing a moving particle are described by equations of the same form, so that when identical restrictions are placed upon each kind of wave, the formal results are identical.

Example 5.3

Find the probability that a particle trapped in a box L wide can be found between $0.45L$ and $0.55L$ for the ground and first excited states.

Solution

This part of the box is one-tenth of the box's width and is centered on the middle of the box (Fig. 5.5). Classically we would expect the particle to be in this region 10 percent of the time. Quantum mechanics gives quite different predictions that depend on the quantum number of the particle's state. From Eqs. (5.2) and (5.33) the probability of finding the particle between x_1 and x_2 when it is in the n th state is

$$P_{x_1 x_2} = \int_{x_1}^{x_2} |\psi_n|^2 dx = \frac{2}{L} \int_{x_1}^{x_2} \sin^2 \frac{n\pi x}{L} dx \\ = \left[\frac{x}{L} - \frac{1}{2n\pi} \sin \frac{2n\pi x}{L} \right]_{x_1}^{x_2}$$

Here $x_1 = 0.45L$ and $x_2 = 0.55L$. For the ground state, which corresponds to $n = 1$, we have

$$P_{x_1 x_2} = 0.198 = 19.8 \text{ percent}$$

This is about twice the classical probability. For the first excited state, which corresponds to $n = 2$, we have $P_{x_1 x_2} = 0.0065 = 0.65 \text{ percent}$

This low figure is consistent with the probability density of $|\psi_n|^2 = 0$ at $x = 0.5L$.

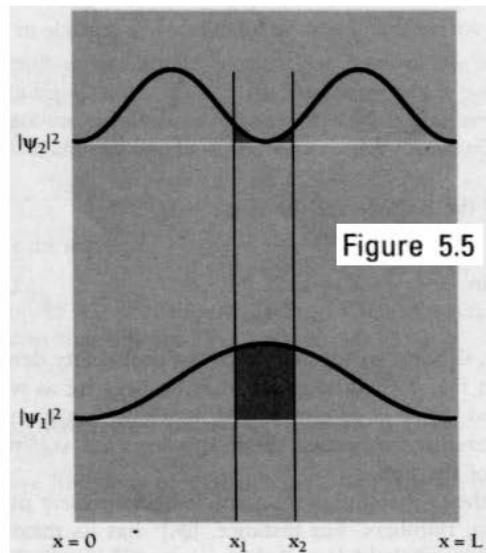


Figure 5.5

Example 5.4

Find the expectation value $\langle x \rangle$ of the position of a particle trapped in a box L wide.

Solution

From Eqs. (5.19) and (5.33) we have

$$\langle x \rangle = \int_{-\infty}^{\infty} x |\psi|^2 dx = \frac{2}{L} \int_0^L x \sin^2 \frac{n\pi x}{L} dx \\ = \frac{2}{L} \left[\frac{x^2}{4} - \frac{x \sin(2n\pi x/L)}{4n\pi/L} - \frac{\cos(2n\pi x/L)}{8(n\pi/L)^2} \right]_0^L$$

Since $\sin n\pi = 0$, $\cos 2n\pi = 1$, and $\cos 0 = 1$, for all the values of n the expectation value of x is

$$\langle x \rangle = \frac{2}{L} \left(\frac{L^2}{4} \right) = \frac{L}{2}$$

This result means that the average position of the particle is the middle of the box in all quantum states. There is no conflict with the fact that $|\psi|^2 = 0$ at $L/2$ in the $n = 2, 4, 6, \dots$ states because $\langle x \rangle$ is an *average*, not a probability, and it reflects the symmetry of $|\psi|^2$ about the middle of the box. (See the Appendix to this chapter for a calculation of the expectation value $\langle p \rangle$ of the particle's momentum.)

5.7 FINITE POTENTIAL WELL

The wave function penetrates the walls, which lowers the energy levels

Potential energies are never infinite in the real world, and the box with infinitely hard walls of the previous section has no physical counterpart. However, potential wells with barriers of finite height certainly do exist. Let us see what the wave functions and energy levels of a particle in such a well are.

Figure 5.6 shows a potential well with square corners that is U high and L wide and contains a particle whose energy E is less than U . According to classical mechanics, when the particle strikes the sides of the well, it bounces off without entering regions I and III. In quantum mechanics, the particle also bounces back and forth, but now it has a certain probability of penetrating into regions I and III even though $E < U$. In regions I and III Schrödinger's steady-state equation is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

which we can rewrite in the more convenient form

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \quad \begin{cases} x < 0 \\ x > L \end{cases} \quad (5.34)$$

$$\text{where } a = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.35)$$

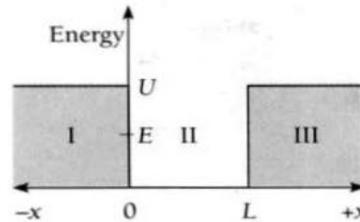


Figure 5.6 A square potential well with finite barriers. The energy E of the trapped particle is less than the height U of the barriers.

Return

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \quad \begin{cases} x < 0 \\ x > L \end{cases} \quad (5.34)$$

The solutions to Eq. (5.34) are real exponentials:

$$\psi_I = Ae^{ax} + Be^{-ax} \quad (5.36)$$

$$\psi_{III} = Ce^{ax} + De^{-ax} \quad (5.37)$$

Both ψ_I and ψ_{III} must be finite everywhere. Since $e^{-ax} \rightarrow \infty$ as $x \rightarrow -\infty$ and $e^{ax} \rightarrow \infty$ as $x \rightarrow \infty$, the coefficients B and C must therefore be 0. Hence we have

$$\psi_I = Ae^{ax} \quad (5.38)$$

$$\psi_{III} = De^{-ax} \quad (5.39)$$

These wave functions decrease exponentially inside the barriers at the sides of the well.

Within the well Schrödinger's equation is the same as Eq. (5.24) and its solution is again

$$\psi_{II} = E \sin \frac{\sqrt{2mE}}{\hbar} x + F \cos \frac{\sqrt{2mE}}{\hbar} x \quad (5.40)$$

In the case of a well with infinitely high barriers, we found that $F = 0$ in order that $\psi = 0$ at $x = 0$ and $x = L$. Here, however, $\psi_{II} = A$ at $x = 0$ and $\psi_{II} = D$ at $x = L$, so both the sine and cosine solutions of Eq. (5.40) are possible.

For either solution, both ψ and $d\psi/dx$ must be continuous at $x = 0$ and $x = L$: the wave functions inside and outside each side of the well must not only have the same value where they join but also the same slopes, so they match up perfectly. When these boundary conditions are taken into account, the result is that exact matching only occurs for certain specific values E_n of the particle energy. The complete wave functions and their probability densities are shown in Fig. 5.7.

Because the wavelengths that fit into the well are longer than for an infinite well of the same width (see Fig. 5.4), the corresponding particle momenta are lower (we recall that $\lambda = h/p$). Hence the energy levels E_n are lower for each n than they are for a particle in an infinite well.

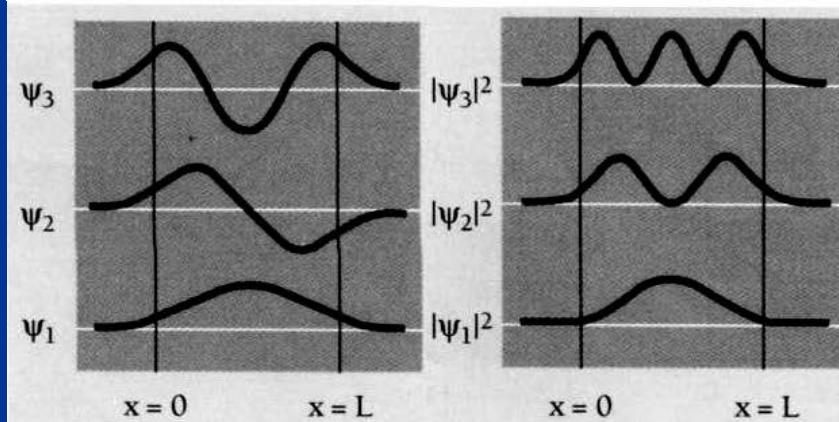


Figure 5.7 Wave functions and probability densities of a particle in a finite potential well. The particle has a certain probability of being found outside the wall.

[Link to Fig.5.4](#)

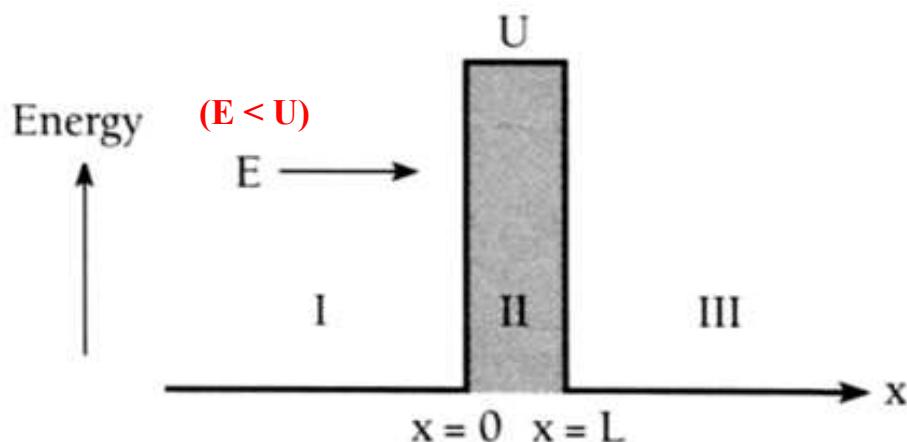
5.8 TUNNEL EFFECT

A particle without the energy to pass over a potential barrier may still tunnel through it

Although the walls of the potential well of Fig. 5.6 were of finite height, they were assumed to be infinitely thick. As a result the particle was trapped forever even though it could penetrate the walls. We next look at the situation of a particle that strikes a potential barrier of height U , again with $E < U$, but here the barrier has a finite width (Fig. 5.8). What we will find is that the particle has a certain probability—not necessarily great, but not zero either—of passing through the barrier and emerging on the other side. The particle lacks the energy to go over the top of the barrier, but it can nevertheless tunnel through it, so to speak. Not surprisingly, the higher the barrier and the wider it is, the less the chance that the particle can get through.

The **tunnel effect** actually occurs, notably in the case of the alpha particles emitted by certain radioactive nuclei. As we shall learn in Chap. 12, an alpha particle whose kinetic energy is only a few MeV is able to escape from a nucleus whose potential wall is perhaps 25 MeV high. The probability of escape is so small that the alpha particle might have to strike the wall 10^{38} or more times before it emerges, but sooner or later it does get out. Tunneling also occurs in the operation of certain semiconductor diodes (Sec. 10.7) in which electrons pass through potential barriers even though their kinetic energies are smaller than the barrier heights.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$



$$U(x) = \begin{cases} 0 & x \leq 0, x \geq L \\ U & 0 < x < L \end{cases}$$

Link

Let us consider a beam of identical particles all of which have the kinetic energy E . The beam is incident from the left on a potential barrier of height U and width L , as in Fig. 5.8. On both sides of the barrier $U = 0$, which means that no forces act on the particles there. In these regions Schrödinger's equation for the particles (all of which are described by the same wave function ψ) takes the forms

$$\frac{d^2 \psi_I}{dx^2} + \frac{2m}{\hbar^2} E \psi_I = 0 \quad (5.41)$$

$$\frac{d^2 \psi_{III}}{dx^2} + \frac{2m}{\hbar^2} E \psi_{III} = 0 \quad (5.42)$$

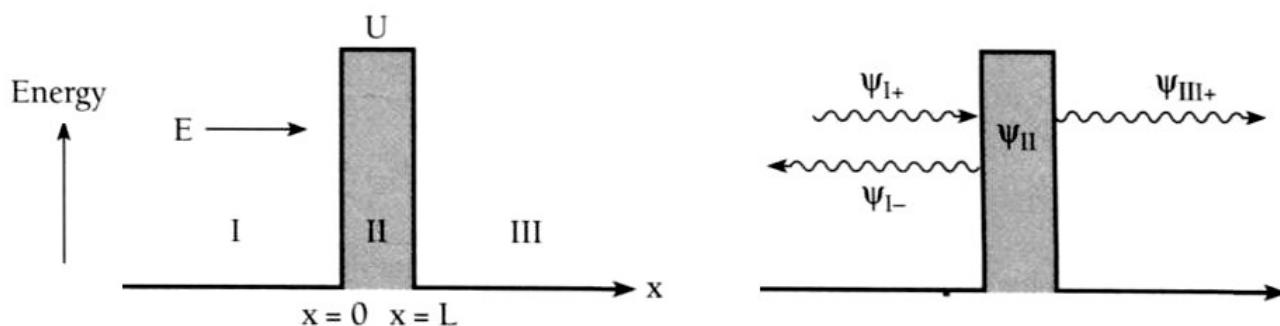
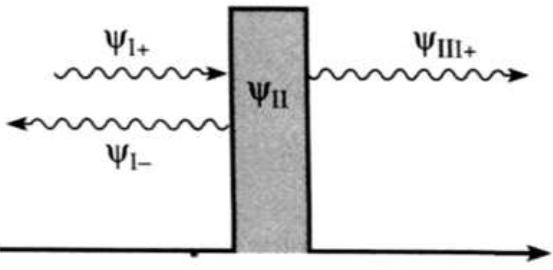


Figure 5.8 When a particle of energy $E < U$ approaches a potential barrier, according to classical mechanics the particle must be reflected. In quantum mechanics, the de Broglie waves that correspond to the particle are partly reflected and partly transmitted, which means that the particle has a finite chance of penetrating the barrier.



$$\frac{d^2\psi_I}{dx^2} + \frac{2m}{\hbar^2} E \psi_I = 0 \quad (5.41)$$

$$\frac{d^2\psi_{III}}{dx^2} + \frac{2m}{\hbar^2} E \psi_{III} = 0 \quad (5.42)$$

The solutions to these equations that are appropriate here are

$$\psi_I = A e^{ik_I x} + B e^{-ik_I x} \quad (5.43)$$

$$\psi_{III} = F e^{ik_{III} x} + G e^{-ik_{III} x} \quad (5.44) \quad \text{where}$$

Wave number outside barrier $k_I = \frac{\sqrt{2mE}}{\hbar} = \frac{p}{\hbar} = \frac{2\pi}{\lambda} \quad (5.45)$

is the wave number of the de Broglie waves that represent the particles outside the barrier. Because

$$e^{i\theta} = \cos \theta + i \sin \theta$$

$$e^{-i\theta} = \cos \theta - i \sin \theta$$

these solutions are equivalent to Eq. (5.25)—the values of the coefficients are different in each case, of course—but are in a more suitable form to describe particles that are not trapped.

The various terms in Eqs. (5.43) and (5.44) are not hard to interpret. As shown schematically in Fig. 5.8, $A e^{ik_I x}$ is a wave of amplitude A incident from the left on the barrier. Hence we can write

Incoming wave $\psi_{I+} = A e^{ik_I x} \quad (5.46)$

This wave corresponds to the incident beam of particles in the sense that $|\psi_{I+}|^2$ is their probability density. If v_{I+} is the group velocity of the incoming wave, which equals the velocity of the particles, then

$$S = |\psi_{I+}|^2 v_{I+}$$

[Link](#)

is the flux of particles that arrive at the barrier. That is, S is the number of particles per square meter per second that arrive there.

At $x = 0$ the incident wave strikes the barrier and is partially reflected, with

Reflected wave $\psi_{I-} = B e^{-ik_I x} \quad (5.47)$

representing the reflected wave. Hence

$$\psi_I = \psi_{I+} + \psi_{I-} \quad (5.48)$$

On the far side of the barrier ($x > L$) there can only be a wave

Transmitted wave $\psi_{III+} = F e^{ik_{III} x} \quad (5.49)$

traveling in the $+x$ direction at the velocity v_{III+} since region III contains nothing that could reflect the wave. Hence $G = 0$ and

$$\psi_{III} = \psi_{III+} = F e^{ik_{III} x} \quad (5.50)$$

The transmission probability T for a particle to pass through the barrier is the ratio

Transmission probability

$$T = \frac{|\psi_{III+}|^2 v_{III+}}{|\psi_{I+}|^2 v_{I+}} = \frac{FF^* v_{III+}}{AA^* v_{I+}} \quad (5.51)$$

between the flux of particles that emerges from the barrier and the flux that arrives at it. In other words, T is the fraction of incident particles that succeed in tunneling through the barrier. Classically $T = 0$ because a particle with $E < U$ cannot exist inside the barrier; let us see what the quantum-mechanical result is.

In region II Schrödinger's equation for the particles is

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2}(E - U)\psi_{II} = 0 \quad (5.52)$$

Since $U > E$ the solution is

Wave function inside barrier

$$\psi_{II} = Ce^{-k_2 x} + De^{k_2 x} \quad k_2^2 = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.53)$$

where the wave number inside the barrier is

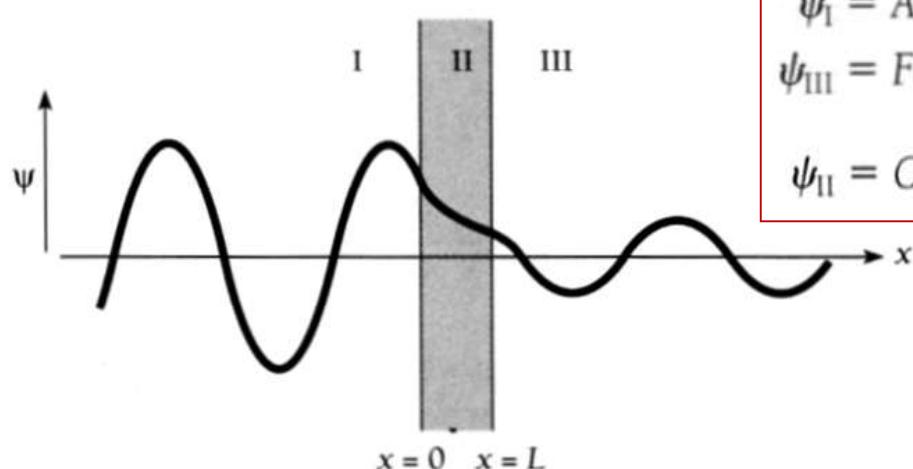
Wave number inside barrier

$$k_2 = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (5.54)$$

Since the exponents are real quantities, ψ_{II} does not oscillate and therefore does not represent a moving particle. However, the probability density $|\psi_{II}|^2$ is not zero, so there is a finite probability of finding a particle within the barrier. Such a particle may emerge into region III or it may return to region I.

Applying the Boundary Conditions

In order to calculate the transmission probability T we have to apply the appropriate boundary conditions to ψ_I , ψ_{II} , and ψ_{III} . Figure 5.9 shows the wave functions in regions I, II, and III. As discussed earlier, both ψ and its derivative $\partial\psi/\partial x$ must be continuous everywhere. With reference to Fig. 5.9, these conditions mean that for a perfect fit at each side of the barrier, the wave functions inside and outside must have the same value and the same slope.



$$\psi_I = Ae^{ik_1 x} + Be^{-ik_1 x} \quad (5.43)$$

$$\psi_{III} = Fe^{ik_1 x} + Ge^{-ik_1 x} \quad (5.44)$$

$$\psi_{II} = Ce^{-k_2 x} + De^{k_2 x} \quad (5.53)$$

Figure 5.9 At each wall of the barrier, the wave functions inside and outside it must match up perfectly, which means that they must have the same values and slopes there.

$$\psi_I = Ae^{ik_1x} + Be^{-ik_1x} \quad (5.43)$$

$$\psi_{III} = Fe^{ik_1x} + Ge^{-ik_1x} \quad (5.44)$$

$$\psi_{II} = Ce^{-k_2x} + De^{k_2x} \quad (5.53)$$

Hence at the left-hand side of the barrier

Boundary conditions at $x = 0$

$$\left. \begin{aligned} \psi_I &= \psi_{II} \\ \frac{d\psi_I}{dx} &= \frac{d\psi_{II}}{dx} \end{aligned} \right\} x = 0 \quad (5.56)$$

and at the right-hand side

Boundary conditions at $x = L$

$$\left. \begin{aligned} \psi_{II} &= \psi_{III} \\ \frac{d\psi_{II}}{dx} &= \frac{d\psi_{III}}{dx} \end{aligned} \right\} x = L \quad (5.58)$$

Now we substitute ψ_I , ψ_{II} , and ψ_{III} from Eqs. (5.43), (5.49), and (5.53) into the above equations. This yields in the same order

$$A + B = C + D \quad (5.59)$$

$$ik_1A - ik_1B = -k_2C + k_2D \quad (5.60)$$

Link

$$Ce^{-k_2L} + De^{k_2L} = Fe^{ik_1L} \quad (5.61)$$

$$-k_2Ce^{-k_2L} + k_2De^{k_2L} = ik_1Fe^{ik_1L} \quad (5.62)$$

Equations (5.59) to (5.62) may be solved for (A/F) to give

$$\left(\frac{A}{F} \right) = \left[\frac{1}{2} + \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1+k_2)L} + \left[\frac{1}{2} - \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1-k_2)L} \quad (5.63)$$

$$\left(\frac{A}{F} \right) = \left[\frac{1}{2} + \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1+k_2)L} + \left[\frac{1}{2} - \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2} \right) \right] e^{(ik_1-k_2)L} \quad (5.63)$$

Let us assume that the potential barrier U is high relative to the energy E of the incident particles. If this is the case, then $k_2/k_1 > k_1/k_2$ and

$$\frac{k_2}{k_1} - \frac{k_1}{k_2} \approx \frac{k_2}{k_1} \quad (5.64)$$

Let us also assume that the barrier is wide enough for ψ_{II} to be severely weakened between $x = 0$ and $x = L$. This means that $k_2L \gg 1$ and

$$e^{k_2L} \gg e^{-k_2L}$$

Hence Eq. (5.63) can be approximated by

$$\left(\frac{A}{F} \right) = \left(\frac{1}{2} + \frac{ik_2}{4k_1} \right) e^{(ik_1+k_2)L} = \left(\frac{1}{2} + \frac{ik_2}{4k_1} \right) e^{ik_1L} e^{k_2L} \quad (5.65)$$

The complex conjugate of (A/F) , which we need to compute the transmission probability T , is found by replacing i by $-i$ wherever it occurs in (A/F) :

$$\left(\frac{A}{F} \right)^* = \left(\frac{1}{2} - \frac{ik_2}{4k_1} \right) e^{(-ik_1+k_2)L} = \left(\frac{1}{2} - \frac{ik_2}{4k_1} \right) e^{-ik_1L} e^{k_2L} \quad (5.66)$$

Now we multiply (A/F) and $(A/F)^*$ to give $\frac{AA^*}{FF^*} = \left(\frac{1}{4} + \frac{k_2^2}{16k_1^2}\right)e^{2k_2 L}$

Here $v_{III+} = v_{I+}$ so $v_{III+}/v_{I+} = 1$ in Eq. (5.51), which means that the transmission probability is

Transmission probability $T = \frac{FF^*v_{III+}}{AA^*v_{I+}} = \left(\frac{AA^*}{FF^*}\right)^{-1} = \left[\frac{16}{4 + (k_2/k_1)^2}\right]e^{-2k_2 L}$ (5.67)

From the definitions of k_1 , Eq. (5.45), and of k_2 , Eq. (5.54), we see that

$$\left(\frac{k_2}{k_1}\right)^2 = \frac{2m(U - E)/\hbar^2}{2mE/\hbar^2} = \frac{U}{E} - 1 \quad (5.68)$$

This formula means that the quantity in brackets in Eq. (5.67) varies much less with E and U than does the exponential. The bracketed quantity, furthermore, always is of the order of magnitude of 1 in value. A reasonable approximation of the transmission probability is therefore

Approximate transmission probability

$$T = e^{-2k_2 L} \quad (5.69)$$

Example 5.5

Electrons with energies of 1.0 eV and 2.0 eV are incident on a barrier 10.0 eV high and 0.50 nm wide. (a) Find their respective transmission probabilities. (b) How are these affected if the barrier is doubled in width?

Solution

(a) For the 1.0-eV electrons $k_2 = \frac{\sqrt{2m(U - E)}}{\hbar}$

$$= \frac{\sqrt{(2)(9.1 \times 10^{-31} \text{ kg})[(10.0 - 1.0) \text{ eV}](1.6 \times 10^{-19} \text{ J/eV})}}{1.054 \times 10^{-34} \text{ J-s}}$$

$$= 1.6 \times 10^{10} \text{ m}^{-1}$$

Since $L = 0.50 \text{ nm} = 5.0 \times 10^{-10} \text{ m}$, $2k_2 L = (2)(1.6 \times 10^{10} \text{ m}^{-1})(5.0 \times 10^{-10} \text{ m}) = 16$, and the approximate transmission probability is

$$T_1 = e^{-2k_2 L} = e^{-16} = 1.1 \times 10^{-7}$$

One 1.0-eV electron out of 8.9 million can tunnel through the 10-eV barrier on the average. For the 2.0-eV electrons a similar calculation gives $T_2 = 2.4 \times 10^{-7}$. These electrons are over twice as likely to tunnel through the barrier.

(b) If the barrier is doubled in width to 1.0 nm, the transmission probabilities become

$$T'_1 = 1.3 \times 10^{-14} \quad T'_2 = 5.1 \times 10^{-14}$$

Evidently T is more sensitive to the width of the barrier than to the particle energy here.

Scanning Tunneling Microscope

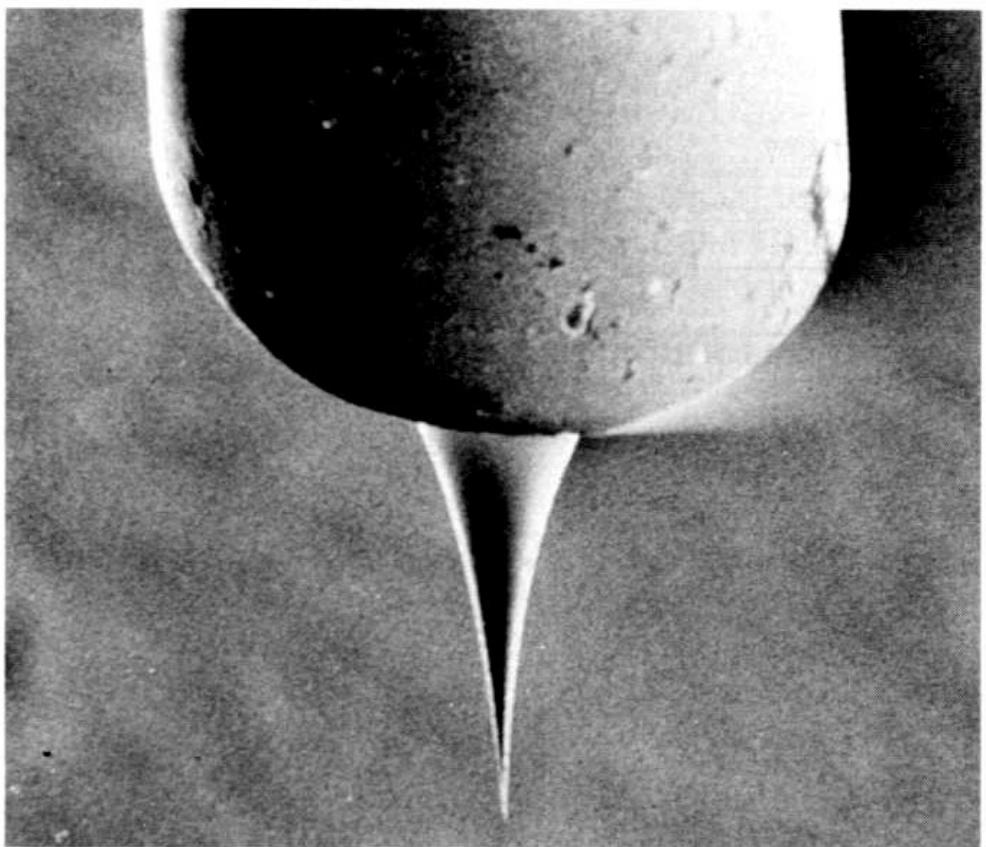
The ability of electrons to tunnel through a potential barrier is used in an ingenious way in the **scanning tunneling microscope** (STM) to study surfaces on an atomic scale of size. The STM was invented in 1981 by Gert Binning and Heinrich Rohrer, who shared the 1986 Nobel Prize in physics with Ernst Ruska, the inventor of the electron microscope. In an STM, a metal probe with a point so fine that its tip is a single atom is brought close to the surface of a conducting or semiconducting material. Normally even the most loosely bound electrons in an atom on a surface need several electron-volts of energy to escape—this is the work function discussed in Chap. 2 in connection with the photoelectric effect. However, when a voltage of only 10 mV or so is applied between the probe and the surface, electrons can tunnel across the gap between them if the gap is small enough, a nanometer or two.

Scanning Tunneling Microscope

According to Eq. (5.69) the electron transmission probability is proportional to e^{-L} , where L is the gap width, so even a small change in L (as little as 0.01 nm, less than a twentieth the diameter of most atoms) means a detectable change in the tunneling current. What is done is to move the probe across the surface in a series of closely spaced back-and-forth scans in about the same way an electron beam traces out an image on the screen of a television picture tube. The height of the probe is continually adjusted to give a constant tunneling current, and the adjustments are recorded so that a map of surface height versus position is built up. Such a map is able to resolve individual atoms on a surface.

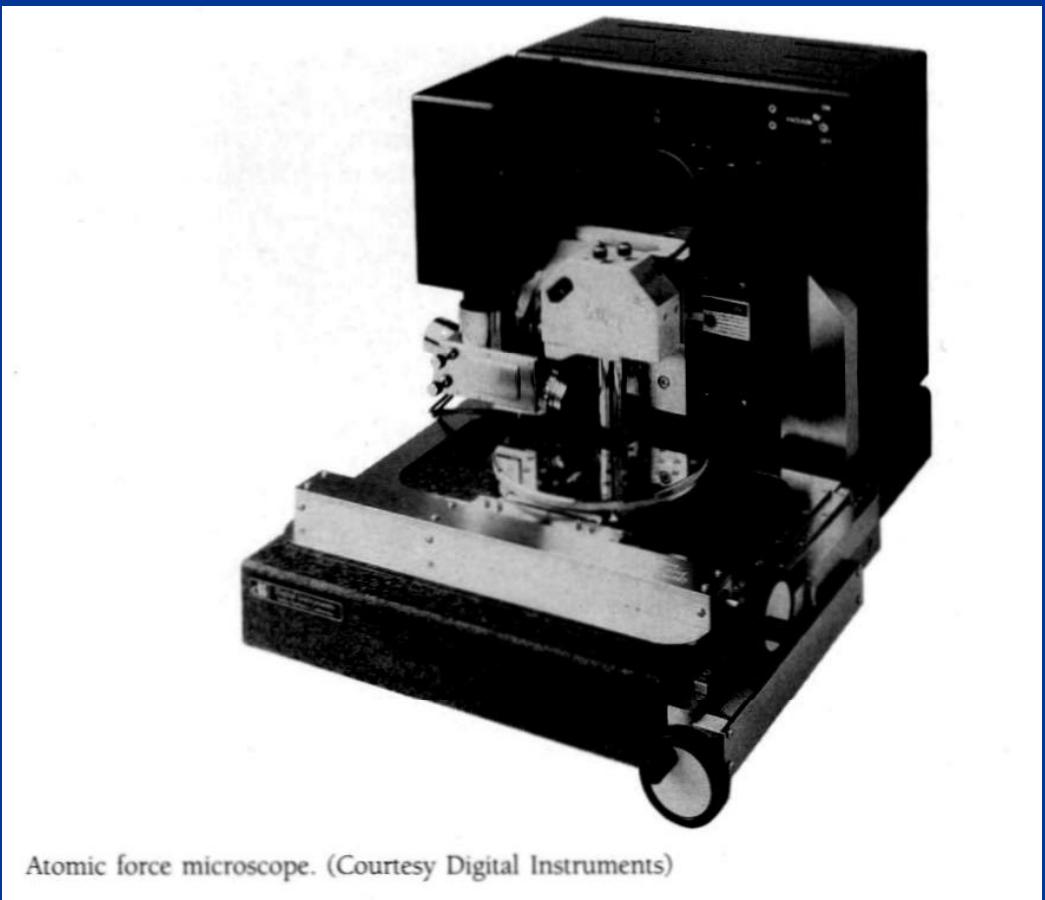
How can the position of the probe be controlled precisely enough to reveal the outlines of individual atoms? The thickness of certain ceramics changes when a voltage is applied across them, a property called **piezoelectricity**. The changes might be several tenths of a nanometer per volt. In an STM, piezoelectric controls move the probe in x and y directions across a surface and in the z direction perpendicular to the surface.

Actually, the result of an STM scan is not a true topographical map of surface height but a contour map of constant electron density on the surface. This means that atoms of different elements appear differently, which greatly increases the value of the STM as a research tool.



The tungsten probe of a scanning tunneling microscope. (IBM Research)

Although many biological materials conduct electricity, they do so by the flow of ions rather than of electrons and so cannot be studied with STMs. A more recent development, the **atomic force microscope** (AFM) can be used on any surface, although with somewhat less resolution than an STM. In an AFM, the sharp tip of a fractured diamond presses gently against the atoms on a surface. A spring keeps the pressure of the tip constant, and a record is made of the deflections of the tip as it moves across the surface. The result is a map showing contours of constant repulsive force between the electrons of the probe and the electrons of the surface atoms. Even relatively soft biological materials can be examined with an AFM and changes in them monitored. For example, the linking together of molecules of the blood protein fibrin, which occurs when blood clots, has been watched with an AFM.



Atomic force microscope. (Courtesy Digital Instruments)



Nerve cell growth cone imaged with an atomic force microscope. The width of the scan is 42 μm . (Courtesy Digital Instruments)

5.9 HARMONIC OSCILLATOR

Its energy levels are evenly spaced

Harmonic motion takes place when a system of some kind vibrates about an equilibrium configuration. The system may be an object supported by a spring or floating in a liquid, a diatomic molecule, an atom in a crystal lattice—there are countless examples on all scales of size. The condition for harmonic motion is the presence of a restoring force that acts to return the system to its equilibrium configuration when it is disturbed. The inertia of the masses involved causes them to overshoot equilibrium, and the system oscillates indefinitely if no energy is lost.

In the special case of simple harmonic motion, the restoring force F on a particle of mass m is linear; that is, F is proportional to the particle's displacement x from its equilibrium position and in the opposite direction. Thus

Hooke's law

$$F = -kx \quad (5.70)$$

Hooke's law

$$F = -kx \quad (5.70)$$

This relationship is customarily called Hooke's law. From the second law of motion, $F = ma$, we have

$$\begin{aligned} -kx &= m \frac{d^2x}{dt^2} \\ \text{Harmonic oscillator} \quad \frac{d^2x}{dt^2} + \frac{k}{m}x &= 0 \end{aligned} \quad (5.71)$$

There are various ways to write the solution to Eq. (5.71). A common one is

$$x = A \cos(2\pi\nu t + \phi) \quad (5.72)$$

where

$$\text{Frequency of harmonic oscillator} \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (5.73)$$

is the frequency of the oscillations and A is their amplitude. The value of ϕ , the phase angle, depends upon what x is at the time $t = 0$.

The importance of the simple harmonic oscillator in both classical and modern physics lies not in the strict adherence of actual restoring forces to Hooke's law, which is seldom true, but in the fact that these restoring forces reduce to Hooke's law for small displacements x . As a result, any system in which something executes small vibrations about an equilibrium position behaves very much like a simple harmonic oscillator.

To verify this important point, we note that any restoring force which is a function of x can be expressed in a Maclaurin's series about the equilibrium position $x = 0$ as

$$F(x) = F_{x=0} + \left(\frac{dF}{dx}\right)_{x=0} x + \frac{1}{2}\left(\frac{d^2F}{dx^2}\right)_{x=0} x^2 + \frac{1}{6}\left(\frac{d^3F}{dx^3}\right)_{x=0} x^3 + \dots$$

Since $x = 0$ is the equilibrium position, $F_{x=0} = 0$. For small x the values of x^2, x^3, \dots are very small compared with x , so the third and higher terms of the series can be neglected. The only term of significance when x is small is therefore the second one. Hence

$$F(x) = \left(\frac{dF}{dx}\right)_{x=0} x$$

which is Hooke's law when $(dF/dx)_{x=0}$ is negative, as of course it is for any restoring force. The conclusion, then, is that *all* oscillations are simple harmonic in character when their amplitudes are sufficiently small.

The potential-energy function $U(x)$ that corresponds to a Hooke's law force may be found by calculating the work needed to bring a particle from $x = 0$ to $x = x$ against such a force. The result is

$$U(x) = - \int_0^x F(x) dx = k \int_0^x x dx = \frac{1}{2}kx^2 \quad (5.74)$$

which is plotted in Fig. 5.10. The curve of $U(x)$ versus x is a parabola. If the energy of the oscillator is E , the particle vibrates back and forth between $x = -A$ and $x = +A$, where E and A are related by $E = \frac{1}{2}kA^2$. Figure 8.18 shows how a nonparabolic potential energy curve can be approximated by a parabola for small displacements.

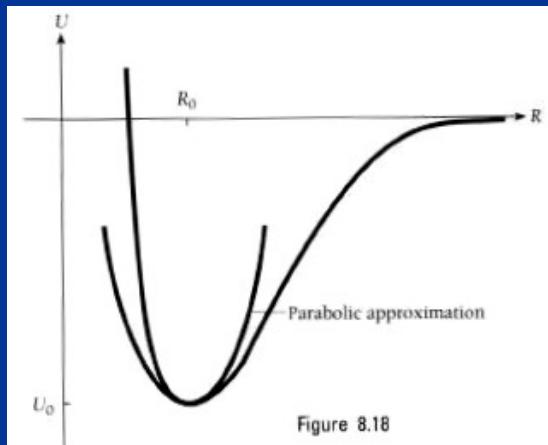
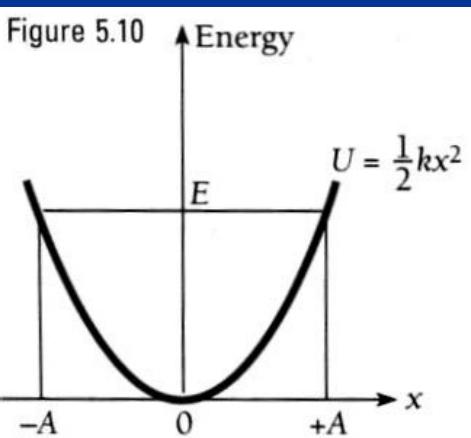


Figure 8.18

Even before we make a detailed calculation we can anticipate three quantum-mechanical modifications to this classical picture:

- 1 The allowed energies will not form a continuous spectrum but instead a discrete spectrum of certain specific values only.
- 2 The lowest allowed energy will not be $E = 0$ but will be some definite minimum $E = E_0$.
- 3 There will be a certain probability that the particle can penetrate the potential well it is in and go beyond the limits of $-A$ and $+A$.

Energy Levels

Schrödinger's equation for the harmonic oscillator is, with $U = \frac{1}{2}kx^2$,

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}kx^2 \right) \psi = 0 \quad (5.75)$$

It is convenient to simplify Eq. (5.75) by introducing the dimensionless quantities

$$y = \left(\frac{1}{\hbar} \sqrt{km} \right)^{1/2} x = \sqrt{\frac{2\pi m\nu}{\hbar}} x \quad (5.76)$$

and

$$\alpha = \frac{2E}{\hbar} \sqrt{\frac{m}{k}} = \frac{2E}{\hbar\nu} \quad (5.77)$$

where ν is the classical frequency of the oscillation given by Eq. (5.73). In making these substitutions, what we have done is change the units in which x and E are expressed from meters and joules, respectively, to dimensionless units.

In terms of y and α Schrödinger's equation becomes

$$\frac{d^2\psi}{dy^2} + (\alpha - y^2)\psi = 0 \quad (5.78)$$

The solutions to this equation that are acceptable here are limited by the condition that $\psi \rightarrow 0$ as $y \rightarrow \infty$ in order that

$$\int_{-\infty}^{\infty} |\psi|^2 dy = 1$$

Otherwise the wave function cannot represent an actual particle.

$$\frac{d^2\psi}{dy^2} + (\alpha - y^2)\psi = 0$$

The mathematical properties of Eq. (5.78) are such that this condition will be fulfilled only when

$$\alpha = 2n + 1 \quad n = 0, 1, 2, 3, \dots$$

Since $\alpha = 2E/h\nu$ according to Eq. (5.77), the energy levels of a harmonic oscillator whose classical frequency of oscillation is ν are given by the formula

Energy levels of harmonic oscillator $E_n = (n + \frac{1}{2})h\nu \quad n = 0, 1, 2, 3, \dots$ (5.79)

The energy of a harmonic oscillator is thus quantized in steps of $h\nu$.

We note that when $n = 0$,

Zero-point energy $E_0 = \frac{1}{2}h\nu$ (5.80)

which is the lowest value the energy of the oscillator can have. This value is called the **zero-point energy** because a harmonic oscillator in equilibrium with its surroundings would approach an energy of $E = E_0$ and not $E = 0$ as the temperature approaches 0 K.

Figure 5.11 is a comparison of the energy levels of a harmonic oscillator with those of a hydrogen atom and of a particle in a box with infinitely hard walls. The shapes of the respective potential-energy curves are also shown. The spacing of the energy levels is constant only for the harmonic oscillator.

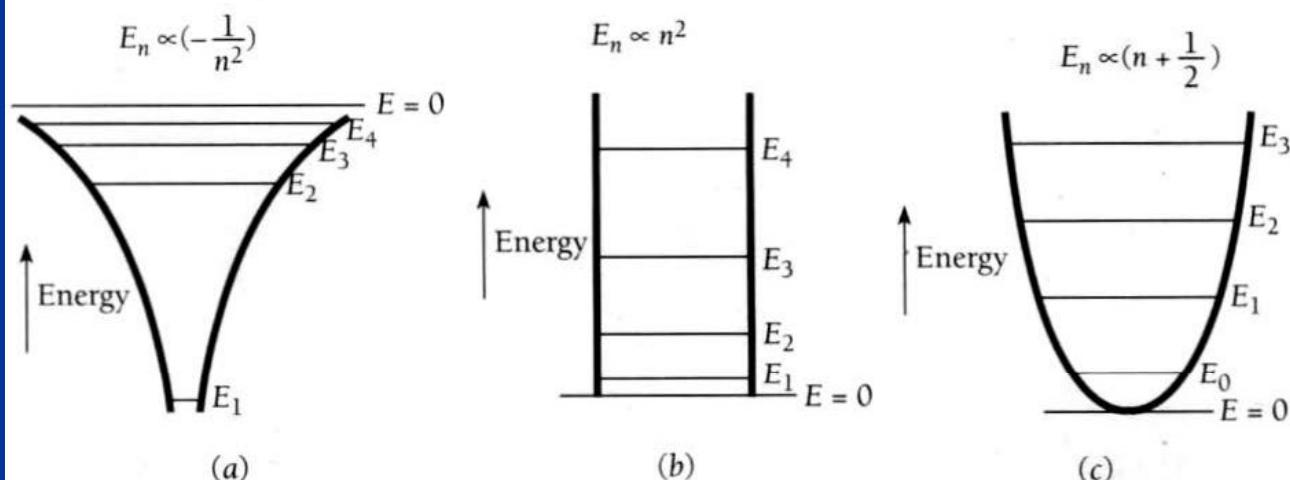


Figure 5.11 Potential wells and energy levels of (a) a hydrogen atom, (b) a particle in a box, and (c) a harmonic oscillator. In each case the energy levels depend in a different way on the quantum number n . Only for the harmonic oscillator are the levels equally spaced. The symbol \propto means "is proportional to."

Wave Functions

For each choice of the parameter α_n there is a different wave function ψ_n . Each function consists of a polynomial $H_n(y)$ (called a **Hermite polynomial**) in either odd or even powers of y , the exponential factor $e^{-y^2/2}$, and a numerical coefficient which is needed for ψ_n to meet the normalization condition

$$\int_{-\infty}^{\infty} |\psi_n|^2 dy = 1 \quad n = 0, 1, 2, \dots$$

The general formula for the n th wave function is

Harmonic oscillator	$\psi_n = \left(\frac{2m\nu}{\hbar} \right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2}$	(5.81)
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Harmonic oscillator	$\psi_n = \left(\frac{2m\nu}{\hbar} \right)^{1/4} (2^n n!)^{-1/2} H_n(y) e^{-y^2/2}$	(5.81)
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The first six Hermite polynomials $H_n(y)$ are listed in Table 5.1.

TABLE 5.1 Some Hermite Polynomials

n	$H_n(y)$	α_n	E_n
0	1	1	$\frac{1}{2}\hbar\nu$
1	$2y$	3	$\frac{3}{2}\hbar\nu$
2	$4y^2 - 2$	5	$\frac{5}{2}\hbar\nu$
3	$8y^3 - 12y$	7	$\frac{7}{2}\hbar\nu$
4	$16y^4 - 48y^2 + 12$	9	$\frac{9}{2}\hbar\nu$
5	$32y^5 - 160y^3 + 120y$	11	$\frac{11}{2}\hbar\nu$

The wave functions that correspond to the first six energy levels of a harmonic oscillator are shown in Fig. 5.12. In each case the range to which a particle oscillating classically with the same total energy E_n would be confined is indicated. Evidently the particle is able to penetrate into classically forbidden regions—in other words, to exceed the amplitude A determined by the energy—with an exponentially decreasing probability, just as in the case of a particle in a finite square potential well.

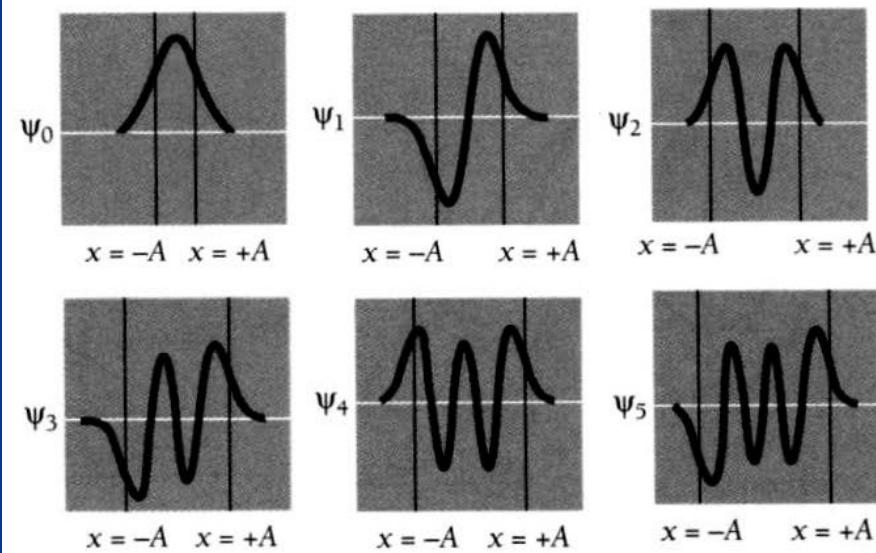


Figure 5.12 The first six harmonic-oscillator wave functions. The vertical lines show the limits $-A$ and $+A$ between which a classical oscillator with the same energy would vibrate.

It is interesting and instructive to compare the probability densities of a classical harmonic oscillator and a quantum-mechanical harmonic oscillator of the same energy. The upper curves in Fig. 5.13 show this density for the classical oscillator. The probability P of finding the particle at a given position is greatest at the endpoints of its motion, where it moves slowly, and least near the equilibrium position ($x = 0$), where it moves rapidly.

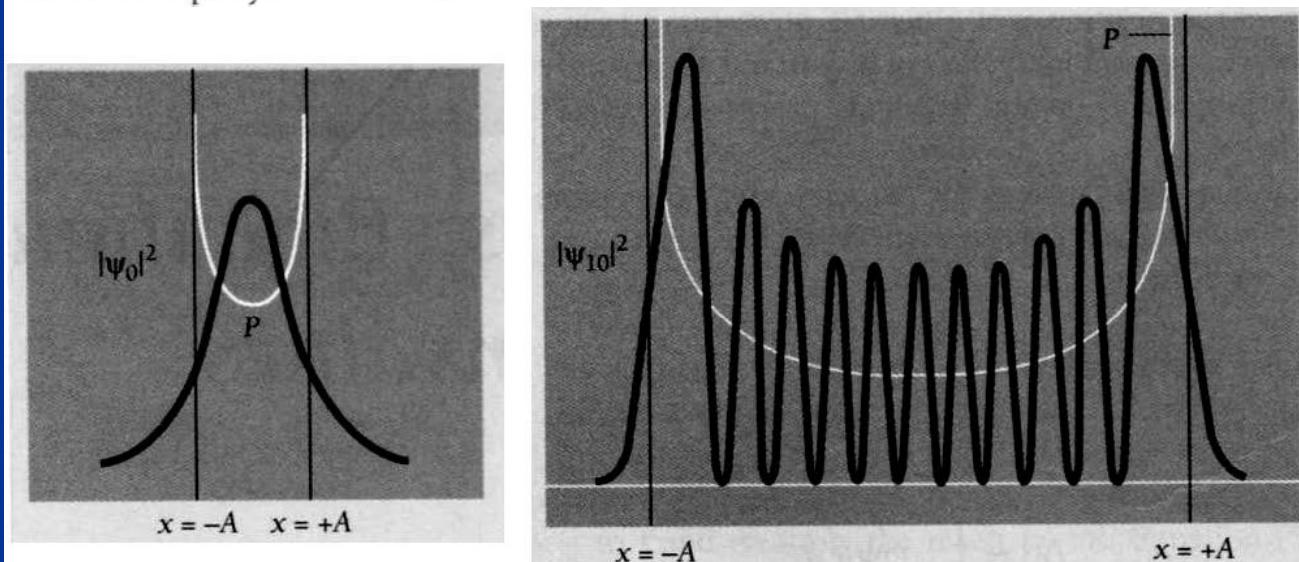


Figure 5.13 Probability densities for the $n = 0$ and $n = 10$ states of a quantum-mechanical harmonic oscillator. The probability densities for classical harmonic oscillators with the same energies are shown in white. In the $n = 10$ state, the wavelength is shortest at $x = 0$ and longest at $x = -A$.

Exactly the opposite behavior occurs when a quantum-mechanical oscillator is in its lowest energy state of $n = 0$. As shown, the probability density $|\psi_0|^2$ has its maximum value at $x = 0$ and drops off on either side of this position. However, this disagreement becomes less and less marked with increasing n . The lower graph of Fig. 5.13 corresponds to $n = 10$, and it is clear that $|\psi_{10}|^2$ when averaged over x has approximately the general character of the classical probability P . This is another example of the correspondence principle mentioned in Chap. 4: In the limit of large quantum numbers, quantum physics yields the same results as classical physics.

It might be objected that although $|\psi_{10}|^2$ does indeed approach P when smoothed out, nevertheless $|\psi_{10}|^2$ fluctuates rapidly with x whereas P does not. However, this objection has meaning only if the fluctuations are observable, and the smaller the spacing of the peaks and hollows, the more difficult it is to detect them experimentally. The exponential “tails” of $|\psi_{10}|^2$ beyond $x = \pm A$ also decrease in magnitude with increasing n . Thus the classical and quantum pictures begin to resemble each other more and more the larger the value of n , in agreement with the correspondence principle, although they are very different for small n .

In general, expectation value for any observable quantity is found by putting the quantum mechanical operator for that observable in the integral of the wavefunction over space:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \psi^* Q_{operator} \psi dV$$

integral over
all space

Operators in Quantum Mechanics

Associated with each measurable parameter in a physical system is a quantum mechanical operator.

Such operators arise because in quantum mechanics you are describing nature with waves (mathematically, the wavefunction) rather than with discrete particles whose motion and dynamics can be described with the deterministic equations of Newtonian physics.

Part of the development of quantum mechanics is the establishment of operators associated with the parameters needed to describe the system. Some of those operators are listed below.

$f(x)$	Any function of position, such as x , or potential $V(x)$	$f(x)$
p_x	x component of momentum (y and z same form)	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m} + V(x)$
E	Hamiltonian (time dependent)	$i\hbar \frac{\partial}{\partial t}$
KE	Kinetic energy	$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i\hbar \frac{\partial}{\partial \phi}$

Return to p.22

Return to p.27

$|\psi|^2$ \propto probability of finding an electron at a particular location
 \propto for many electrons, percentage of electrons at this location
i.e. the density of the electrons (numbers of electron/unit volume)

The volume of the cylinder:

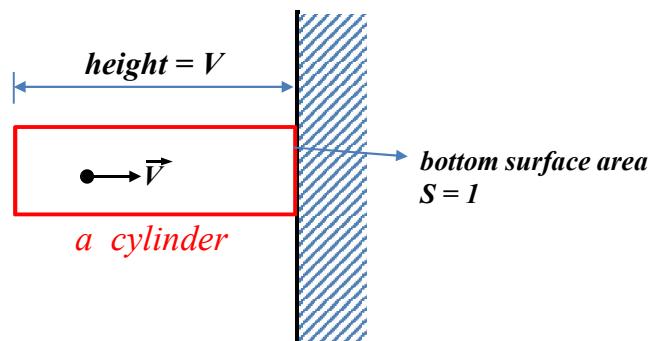
$V \cdot S$ (height \times area)

The numbers of electrons in the cylinder:

$|\psi|^2 V \cdot S$ (density \times volume)

For unit area, $S=1$

$|\psi|^2 V \cdot S = |\psi|^2 V$



In 1 second, all the electrons in the cylinder will pass through the bottom surface, because the cylinder height is V (i.e. the distance of electrons will go in 1 second).

So, $|\psi|^2 V =$ **the numbers of electrons passing unit area per second**

Return

$$A + B = C + D \quad \Rightarrow \quad 2A = \left[1 - \frac{k_2}{ik_1}\right]C + \left[1 + \frac{k_2}{ik_1}\right]D$$

$$ik_1A - ik_1B = -k_2C + k_2D \quad \Rightarrow \quad A = \frac{1}{2} \left[1 + \frac{ik_2}{k_1}\right]C + \frac{1}{2} \left[1 - \frac{ik_2}{k_1}\right]D \quad (1)$$

$$Ce^{-k_2L} + De^{k_2L} = Fe^{ik_1L}$$

$$-k_2Ce^{-k_2L} + k_2De^{k_2L} = ik_1Fe^{ik_1L}$$

$$\Rightarrow 2De^{k_2L} = \left[1 + \frac{ik_1}{k_2}\right]Fe^{ik_1L}$$

$$D = \frac{1}{2} \left[1 + \frac{ik_1}{k_2}\right]Fe^{(ik_1 - k_2)L} \quad (2)$$

$$2Ce^{-k_2L} = \left[1 - \frac{ik_1}{k_2}\right]Fe^{ik_1L} \quad \rightarrow C = \frac{1}{2} \left[1 - \frac{ik_1}{k_2}\right]Fe^{(ik_1 + k_2)L} \quad (3)$$

Substitute (2) & (3) into (1):

$$A = \frac{1}{4} \left[1 + \frac{ik_2}{k_1}\right] \left[1 - \frac{ik_1}{k_2}\right] Fe^{(ik_1 + k_2)L} + \frac{1}{4} \left[1 - \frac{ik_2}{k_1}\right] \left[1 + \frac{ik_1}{k_2}\right] Fe^{(ik_1 - k_2)L}$$

$$\frac{A}{F} = \frac{1}{4} \left[1 - \frac{ik_1}{k_2} + \frac{ik_2}{k_1} + 1\right] e^{(ik_1 + k_2)L} + \frac{1}{4} \left[1 + \frac{ik_1}{k_2} - \frac{ik_2}{k_1} + 1\right] e^{(ik_1 - k_2)L}$$

$$\frac{A}{F} = \frac{1}{4} \left[1 - \frac{ik_1}{k_2} + \frac{ik_2}{k_1} + 1\right] e^{(ik_1 + k_2)L} + \frac{1}{4} \left[1 + \frac{ik_1}{k_2} - \frac{ik_2}{k_1} + 1\right] e^{(ik_1 - k_2)L}$$

$$\frac{A}{F} = \left[\frac{1}{2} + \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right] e^{(ik_1 + k_2)L} + \left[\frac{1}{2} - \frac{i}{4} \left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\right] e^{(ik_1 - k_2)L} \quad (5.63)$$

Return

6.1 SCHRÖDINGER'S EQUATION FOR THE HYDROGEN ATOM

Symmetry suggests spherical polar coordinates

A hydrogen atom consists of a proton, a particle of electric charge $+e$, and an electron, a particle of charge $-e$ which is 1836 times lighter than the proton. For the sake of convenience we shall consider the proton to be stationary, with the electron moving about in its vicinity but prevented from escaping by the proton's electric field. As in the Bohr theory, the correction for proton motion is simply a matter of replacing the electron mass m by the reduced mass m' .

Schrödinger's equation for the electron in three dimensions, which is what we must use for the hydrogen atom, is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad (6.1)$$

The potential energy U here is the electric potential energy

Electric potential energy $U = -\frac{e^2}{4\pi\epsilon_0 r}$ (6.2)

of a charge $-e$ when it is the distance r from another charge $+e$.

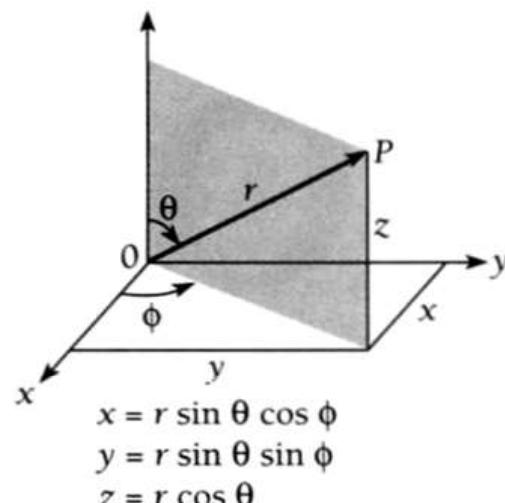
The spherical polar coordinates r, θ, ϕ of the point P shown in Fig. 6.1 have the following interpretations:

Spherical polar coordinates $r = \text{length of radius vector from origin } O \text{ to point } P$
 $= \sqrt{x^2 + y^2 + z^2}$

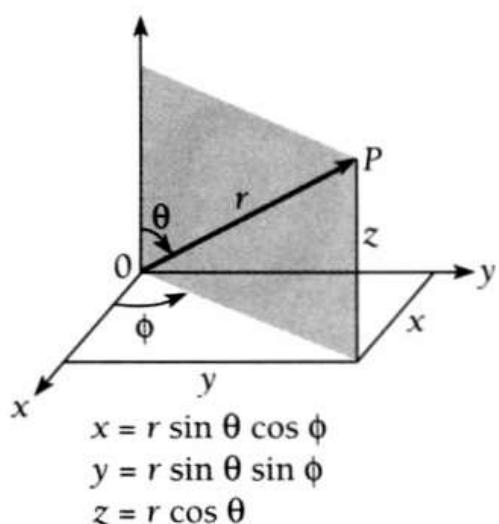
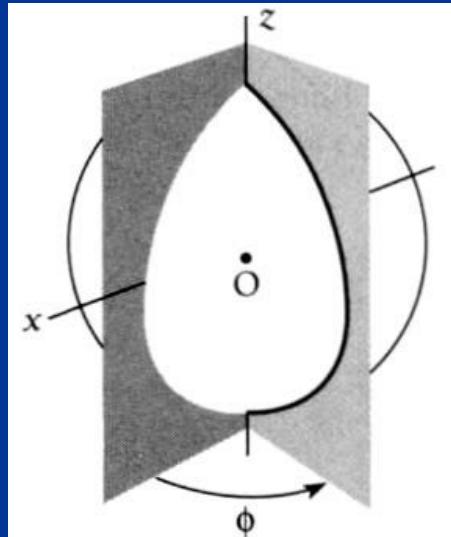
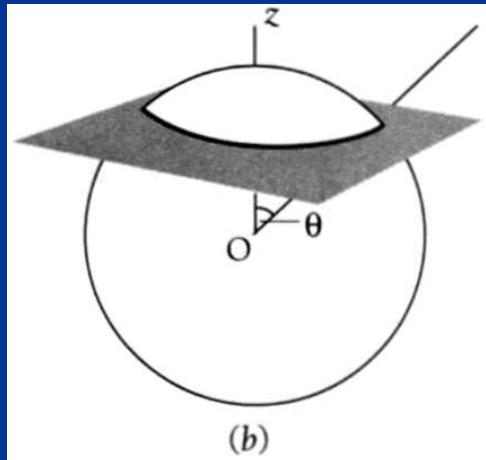
$\theta = \text{angle between radius vector and } +z \text{ axis}$
 $= \text{zenith angle} = \cos^{-1} \frac{z}{\sqrt{x^2 + y^2 + z^2}}$

$\phi = \text{angle between the projection of the radius vector}$
 $\text{in the } xy \text{ plane and the } +x \text{ axis, measured}$
 $\text{in the direction shown}$

$= \text{azimuth angle} = \tan^{-1} \frac{y}{x}$



On the surface of a sphere whose center is at O , lines of constant zenith angle θ are like parallels of latitude on a globe (but we note that the value of θ of a point is *not* the same as its latitude; $\theta = 90^\circ$ at the equator, for instance, but the latitude of the equator is 0°). Lines of constant azimuth angle ϕ are like meridians of longitude (here the definitions coincide if the axis of the globe is taken as the $+z$ axis and the $+x$ axis is at $\phi = 0^\circ$).



$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\cos \theta = \frac{z}{\sqrt{x^2 + y^2 + z^2}}$$

$$\tan \phi = \frac{y}{x}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad (6.1)$$

In spherical polar coordinates Schrödinger's equation is written

[Link](#)

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0 \quad (6.3)$$

Substituting Eq. (6.2) for the potential energy U and multiplying the entire equation by $r^2 \sin^2 \theta$, we obtain

Hydrogen atom

$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0 \quad (6.4)$$

Equation (6.4) is the partial differential equation for the wave function ψ of the electron in a hydrogen atom. Together with the various conditions ψ must obey, namely that ψ be normalizable and that ψ and its derivatives be continuous and single-valued at each point r, θ, ϕ , this equation completely specifies the behavior of the electron. In order to see exactly what this behavior is, we must solve Eq. (6.4) for ψ .

When Eq. (6.4) is solved, it turns out that three quantum numbers are required to describe the electron in a hydrogen atom, in place of the single quantum number of the Bohr theory. (In the next chapter we shall find that a fourth quantum number is needed to describe the spin of the electron.) In the Bohr model, the electron's motion is basically one-dimensional, since the only quantity that varies as it moves is its position in a definite orbit. One quantum number is enough to specify the state of such an electron, just as one quantum number is enough to specify the state of a particle in a one-dimensional box.

A particle in a three-dimensional box needs three quantum numbers for its description, since there are now three sets of boundary conditions that the particle's wave function ψ must obey: ψ must be 0 at the walls of the box in the x , y , and z directions independently. In a hydrogen atom the electron's motion is restricted by the inverse-square electric field of the nucleus instead of by the walls of a box, but the electron is nevertheless free to move in three dimensions, and it is accordingly not surprising that three quantum numbers govern its wave function also.

6.2 SEPARATION OF VARIABLES

A differential equation for each variable

The advantage of writing Schrödinger's equation in spherical polar coordinates for the problem of the hydrogen atom is that in this form it may be separated into three independent equations, each involving only a single coordinate. Such a separation is possible here because the wave function $\psi(r, \theta, \phi)$ has the form of a product of three different functions: $R(r)$, which depends on r alone; $\Theta(\theta)$ which depends on θ alone; and $\Phi(\phi)$, which depends on ϕ alone. Of course, we do not really know this yet, but we can proceed by assuming that

**Hydrogen-atom
wave function**

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (6.5)$$

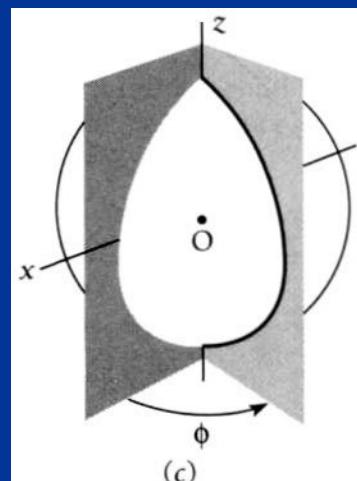
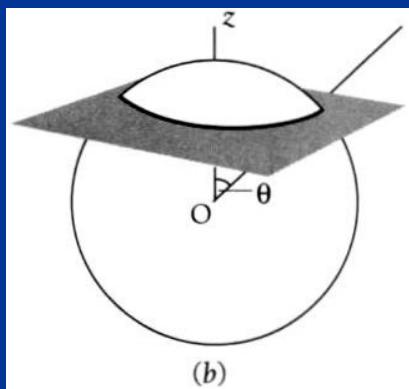
and then seeing if it leads to the desired separation.

The function $R(r)$ describes how the wave function ψ of the electron varies along a radius vector from the nucleus, with θ and ϕ constant.

The function $\Theta(\theta)$ describes how ψ varies with zenith angle θ along a meridian on a sphere centered at the nucleus, with r and ϕ constant (Fig. 6.1c).

The function $\Phi(\phi)$ describes how ψ varies with azimuth angle ϕ along a parallel on a sphere centered at the nucleus, with r and θ constant (Fig. 6.1b).

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$



$$\sin^2 \theta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) \psi = 0$$

$$\frac{\partial \psi}{\partial r} = \Theta \Phi \frac{\partial R}{\partial r} = \Theta \Phi \frac{dR}{dr}$$

$$\frac{\partial \psi}{\partial \theta} = R \Phi \frac{\partial \Theta}{\partial \theta} = R \Phi \frac{d\Theta}{d\theta}$$

$$\frac{\partial^2 \psi}{\partial \phi^2} = R \Theta \frac{\partial^2 \Phi}{\partial \phi^2} = R \Theta \frac{d^2 \Phi}{d\phi^2}$$

The change from partial derivatives to ordinary derivatives can be made because each of the functions R , Θ , and Φ depends only on the respective variables r , θ , and ϕ .

When we substitute $R\Theta\Phi$ for ψ in Schrödinger's equation for the hydrogen atom and divide the entire equation by $R\Theta\Phi$, we find that

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = 0 \quad (6.6)$$

The third term of Eq. (6.6) is a function of azimuth angle ϕ only, whereas the other terms are functions of r and θ only.

Let us rearrange Eq. (6.6) to read

$$\frac{\sin^2 \theta}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{\sin \theta}{\Theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \frac{2mr^2 \sin^2 \theta}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = m_l^2 \quad (6.7)$$

This equation can be correct only if both sides of it are equal to the same constant, since they are functions of different variables. As we shall see, it is convenient to call this constant m_l^2 . The differential equation for the function ϕ is therefore

$$-\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = m_l^2 \quad (6.8)$$

Next we substitute m_l^2 for the right-hand side of Eq. (6.7), divide the entire equation by $\sin^2 \theta$, and rearrange the various terms, which yields

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \quad (6.9)$$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = \frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) \quad (6.9)$$

Again we have an equation in which different variables appear on each side, requiring that both sides be equal to the same constant. This constant is called $l(l + 1)$, once more for reasons that will be apparent later. The equations for the functions Θ and R are therefore

$$\frac{m_l^2}{\sin^2 \theta} - \frac{1}{\Theta \sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) = l(l + 1) \quad (6.10)$$

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) = l(l + 1) \quad (6.11)$$

Equations (6.8), (6.10), and (6.11) are usually written

Equation for Φ $\frac{d^2\Phi}{d\phi^2} + m_l^2\Phi = 0 \quad (6.12)$

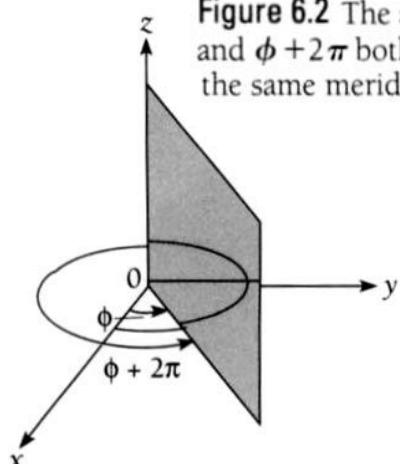
Equation for Θ $\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[l(l + 1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad (6.13)$

Equation for R $\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l + 1)}{r^2} \right] R = 0 \quad (6.14)$

Each of these is an ordinary differential equation for a single function of a single variable. Only the equation for R depends on the potential energy $U(r)$.

We have therefore accomplished our task of simplifying Schrödinger's equation for the hydrogen atom, which began as a partial differential equation for a function ψ of three variables. The assumption embodied in Eq. (6.5) is evidently valid.

Figure 6.2 The angles ϕ and $\phi + 2\pi$ both identify the same meridian plane.



6.3 QUANTUM NUMBERS

Three dimensions, three quantum numbers

The first of the above equations, Eq. (6.12), is readily solved. The result is

$$\Phi(\phi) = Ae^{im_l\phi} \quad (6.15)$$

As we know, one of the conditions that a wave function—and hence Φ , which is a component of the complete wave function ψ —must obey is that it have a single value at a given point in space. From Fig. 6.2 it is clear that ϕ and $\phi + 2\pi$ both identify the same meridian plane. Hence it must be true that $\Phi(\phi) = \Phi(\phi + 2\pi)$, or

$$Ae^{im_l\phi} = Ae^{im_l(\phi+2\pi)}$$

which can happen only when m_l is 0 or a positive or negative integer ($\pm 1, \pm 2, \pm 3, \dots$). The constant m_l is known as the **magnetic quantum number** of the hydrogen atom.

The differential equation for $\Theta(\theta)$, Eq. (6.13), has a solution provided that the constant l is an integer equal to or greater than $|m_l|$, the absolute value of m_l . This requirement can be expressed as a condition on m_l in the form

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

The constant l is known as the **orbital quantum number**.

The solution of the final equation, Eq. (6.14), for the radial part $R(r)$ of the hydrogen-atom wave function ψ also requires that a certain condition be fulfilled. This condition is that E be positive or have one of the negative values E_n (signifying that the electron is bound to the atom) specified by

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} \left(\frac{1}{n^2} \right) = \frac{E_1}{n^2} \quad n = 1, 2, 3, \dots \quad (6.16)$$

We recognize that this is precisely the same formula for the energy levels of the hydrogen atom that Bohr obtained.

Another condition that must be obeyed in order to solve Eq. (6.14) is that n , known as the **principal quantum number**, must be equal to or greater than $l + 1$. This requirement may be expressed as a condition on l in the form

$$l = 0, 1, 2, \dots, (n - 1)$$

Hence we may tabulate the three quantum numbers n , l , and m together with their permissible values as follows:

Principal quantum number $n = 1, 2, 3, \dots$

Orbital quantum number $l = 0, 1, 2, \dots, (n - 1)$ (6.17)

Magnetic quantum number $m_l = 0, \pm 1, \pm 2, \dots, \pm l$

It is worth noting again the natural way in which quantum numbers appear in quantum-mechanical theories of particles trapped in a particular region of space.

To exhibit the dependence of R , Θ , and Ψ upon the quantum numbers n , l , m , we may write for the electron wave functions of the hydrogen atom

$$\psi = R_{nl} \Theta_{lm_l} \Phi_{m_l} \quad (6.18)$$

The wave functions R , Θ , and Φ together with ψ are given in Table 6.1 for $n = 1, 2$, and 3 .

TABLE 6.1 Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2$, and 3^*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos \theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{1}{2\sqrt{6} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi} a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin \theta e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi} a_0^{3/2}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos \theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin \theta$	$\frac{4}{81\sqrt{6} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin \theta e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3 \cos^2 \theta - 1)$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3 \cos^2 \theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin \theta \cos \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \theta \cos \theta e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2 \theta$	$\frac{4}{81\sqrt{30} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2 \theta e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/m e^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

[<back>](#)

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.14)$$

Example 6.1

Find the ground-state electron energy E_1 by substituting the radial wave function R that corresponds to $n = 1, l = 0$ into Eq. (6.14).

Solution From Table 6.1 we see that $R = (2/a_0^{3/2})e^{-r/a_0}$. Hence

$$\frac{dR}{dr} = -\left(\frac{2}{a_0^{5/2}}\right)e^{-r/a_0} \quad \text{and} \quad \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = \left(\frac{2}{a_0^{7/2}} - \frac{4}{a_0^{5/2}r}\right)e^{-r/a_0}$$

Substituting in Eq. (6.14) with $E = E_1$ and $l = 0$ gives

$$\left[\left(\frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}}\right) + \left(\frac{me^2}{\pi\epsilon_0\hbar a_0^{3/2}} - \frac{4}{a_0^{5/2}}\right)\frac{1}{r} \right] e^{-r/a_0} = 0$$

Each parenthesis must equal 0 for the entire equation to equal 0.

$$\left[\left(\frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}}\right) + \left(\frac{me^2}{\pi\epsilon_0\hbar a_0^{3/2}} - \frac{4}{a_0^{5/2}}\right)\frac{1}{r} \right] e^{-r/a_0} = 0$$

For the second parenthesis this gives $\frac{me^2}{\pi\epsilon_0\hbar^2 a_0^{3/2}} - \frac{4}{a_0^{5/2}} = 0 \quad a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2}$

which is the Bohr radius $a_0 = r_1$ given by Eq. (4.13)—we recall that $\hbar = h/2\pi$. For the first parenthesis,

$$\frac{2}{a_0^{7/2}} + \frac{4mE_1}{\hbar^2 a_0^{3/2}} = 0 \quad E_1 = -\frac{\hbar^2}{2ma_0^2} = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}$$

which agrees with Eq. (6.16).

6.4 PRINCIPAL QUANTUM NUMBER

Quantization of energy

It is interesting to consider what the hydrogen-atom quantum numbers signify in terms of the classical model of the atom. This model, as we saw in Chap. 4, corresponds exactly to planetary motion in the solar system except that the inverse-square force holding the electron to the nucleus is electrical rather than gravitational. Two quantities are conserved—that is, maintain a constant value at all times—in planetary motion; the scalar total energy and the vector angular momentum of each planet.

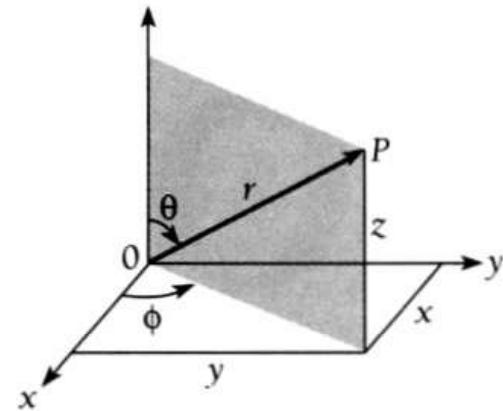
Classically the total energy can have any value whatever, but it must, of course, be negative if the planet is to be trapped permanently in the solar system. In the quantum theory of the hydrogen atom the electron energy is also a constant, but while it may have any positive value (corresponding to an ionized atom), the *only* negative values the electron can have are specified by the formula $E_n = E_1/n^2$. The quantization of electron energy in the hydrogen atom is therefore described by the principal quantum number n .

The theory of planetary motion can also be worked out from Schrödinger's equation, and it yields a similar energy restriction. However, the total quantum number n for any of the planets turns out to be so immense (see Exercise 11 of Chap. 4) that the separation of permitted levels is far too small to be observable. For this reason classical physics provides an adequate description of planetary motion but fails within the atom.

6.5 ORBITAL QUANTUM NUMBER

Quantization of angular momentum magnitude

The interpretation of the orbital quantum number l is



$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.14)$$

This equation is solely concerned with the radial aspect of the electron's motion, that is, its motion toward or away from the nucleus. However, we notice the presence of E , the total electron energy, in the equation. The total energy E includes the electron's kinetic energy of orbital motion, which should have nothing to do with its radial motion.

This contradiction may be removed by the following argument. The kinetic energy KE of the electron has two parts, KE_{radial} due to its motion toward or away from the nucleus, and KE_{orbital} due to its motion around the nucleus. The potential energy U of the electron is given by

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.14)$$

$$E = KE_{\text{radial}} + KE_{\text{orbital}} + U = KE_{\text{radial}} + KE_{\text{orbital}} - \frac{e^2}{4\pi\epsilon_0 r}$$

Inserting this expression for E in Eq. (6.14) we obtain, after a slight rearrangement,

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[KE_{\text{radial}} + KE_{\text{orbital}} - \frac{\hbar^2 l(l+1)}{2mr^2} \right] R = 0 \quad (6.19)$$

If the last two terms in the square brackets of this equation cancel each other out, we shall have what we want: a differential equation for $R(r)$ that involves functions of the radius vector r exclusively.

We therefore require that

$$KE_{\text{orbital}} = \frac{\hbar^2 l(l+1)}{2mr^2} \quad (6.20)$$

$$KE_{\text{orbital}} = \frac{\hbar^2 l(l+1)}{2mr^2} \quad (6.20)$$

Since the orbital kinetic energy of the electron and its angular momentum are respectively

$$KE_{\text{orbital}} = \frac{1}{2} mv_{\text{orbital}}^2 \quad L = rmv_{\text{orbital}}$$

we may write for the orbital kinetic energy

$$KE_{\text{orbital}} = \frac{L^2}{2mr^2}$$

$$\text{Hence, from Eq. (6.20), } \frac{L^2}{2mr^2} = \frac{\hbar^2 l(l+1)}{2mr^2}$$

Electron angular momentum

$$L = \sqrt{l(l+1)}\hbar$$

Electron angular momentum

$$L = \sqrt{l(l+1)}\hbar$$

Because the orbital quantum number l is restricted to the values

$$l = 0, 1, 2, \dots, (n-1) \quad (6.21)$$

the electron can have only those particular angular momenta L specified by Eq. (6.21). Like total energy E , angular momentum is both conserved and quantized. The quantity

$$\hbar = \frac{h}{2\pi} = 1.054 \times 10^{-34} \text{ J} \cdot \text{s}$$

is thus the natural unit of angular momentum.

In macroscopic planetary motion, as in the case of energy, the quantum number describing angular momentum is so large that the separation into discrete angular-momentum states cannot be experimentally observed. For example, an electron (or, for that matter, any other body) whose orbital quantum number is 2 has the angular momentum

$$\begin{aligned} L &= \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar \\ &= 2.6 \times 10^{-34} \text{ J} \cdot \text{s} \end{aligned}$$

By contrast the orbital angular momentum of the earth is $2.7 \times 10^{40} \text{ J} \cdot \text{s}$!

Designation of Angular Momentum States

It is customary to specify electron angular-momentum states by a letter, with s corresponding to $l = 0$, p to $l = 1$, and so on, according to the following scheme:

Angular-momentum states	$l = 0$	1	2	3	4	5	6	\dots
	s	p	d	f	g	h	i	\dots

This peculiar code originated in the empirical classification of spectra into series called sharp, principal, diffuse, and fundamental which occurred before the theory of the atom was developed. Thus an s state is one with no angular momentum, a p state has the angular moment $\sqrt{2}\hbar$, and so forth.

The combination of the total quantum number with the letter that represents orbital angular momentum provides a convenient and widely used notation for atomic electron states. In this notation a state in which $n = 2, l = 0$ is a $2s$ state, for example, and one in which $n = 4, l = 2$ is a $4d$ state. Table 6.2 gives the designations of electron states in an atom through $n = 6, l = 5$.

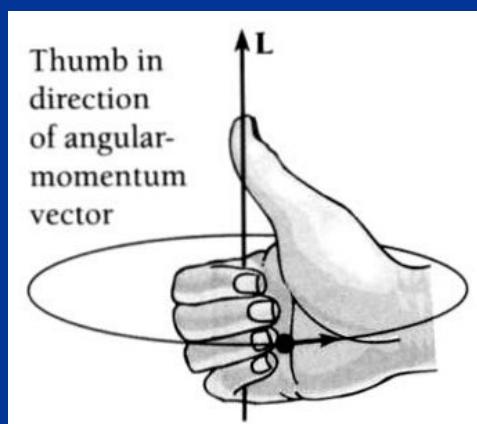
TABLE 6.2 Atomic Electron States

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

6.6 MAGNETIC QUANTUM NUMBER

Quantization of angular momentum direction

The orbital quantum number l determines the *magnitude L* of the electron's angular momentum \mathbf{L} . However, angular momentum, like linear momentum, is a vector quantity, and to describe it completely means that its *direction* be specified as well as its magnitude. (The vector \mathbf{L} , we recall, is perpendicular to the plane in which the rotational motion takes place, and its sense is given by the right-hand rule: When the fingers of the right hand point in the direction of the motion, the thumb is in the direction of \mathbf{L} . This rule is illustrated in Fig. 6.3.)



Fingers of right hand in direction of rotational motion

Figure 6.3 The right-hand rule for angular momentum.

What possible significance can a direction in space have for a hydrogen atom? The answer becomes clear when we reflect that an electron revolving about a nucleus is a minute current loop and has a magnetic field like that of a magnetic dipole. Hence an atomic electron that possesses angular momentum interacts with an external magnetic field **B**. The magnetic quantum number m_l specifies the direction of **L** by determining the component of **L** in the field direction. This phenomenon is often referred to as space quantization.

If we let the magnetic-field direction be parallel to the z axis, the component of **L** in this direction is

Space quantization $L_z = m_l \hbar$ $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ (6.22)

The possible values of m_l for a given value of l range from $+l$ through 0 to $-l$, so that the number of possible orientations of the angular-momentum vector **L** in a magnetic field is $2l + 1$. When $l = 0$, L_z can have only the single value of 0; when $l = 1$, L_z may be \hbar , 0, or $-\hbar$; when $l = 2$, L_z may be $2\hbar$, \hbar , 0, $-\hbar$, or $-2\hbar$; and so on.

Link

The space quantization of the orbital angular momentum of the hydrogen atom is shown in Fig. 6.4. An atom with a certain value of m_l will assume the corresponding orientation of its angular momentum **L** relative to an external magnetic field if it finds itself in such a field. We note that **L** can never be aligned exactly parallel or antiparallel to **B** because L_z is always smaller than the magnitude $\sqrt{l(l+1)}\hbar$ of the total angular momentum.

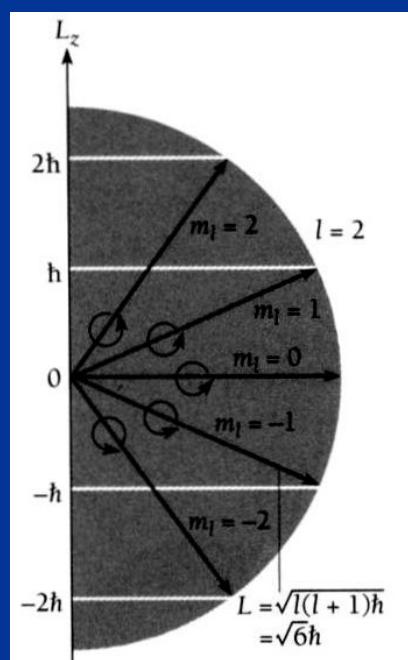


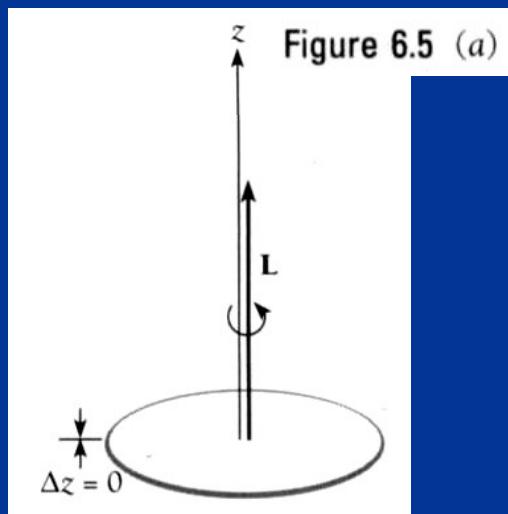
Figure 6.4 Space quantization of orbital angular momentum. Here the orbital quantum number is $l = 2$ and there are accordingly $2l + 1 = 5$ possible values of the magnetic quantum number m_l , with each value corresponding to a different orientation relative to the z axis.

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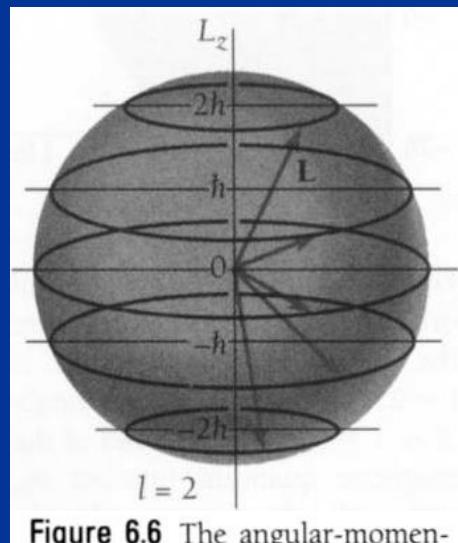
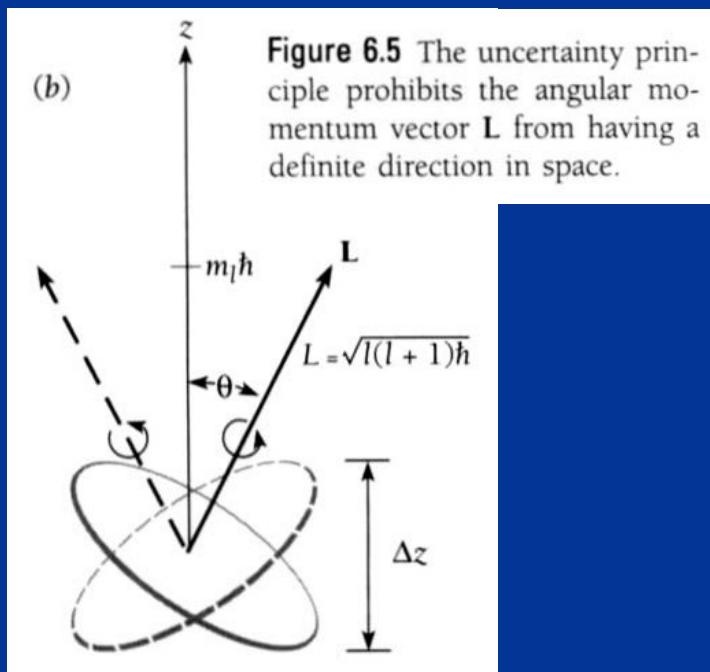
In the absence of an external magnetic field, the direction of the z axis is arbitrary. What must be true is that the component of \mathbf{L} in any direction we choose is $m_l\hbar$. What an external magnetic field does is to provide an experimentally meaningful reference direction. A magnetic field is not the only such reference direction possible. For example, the line between the two H atoms in the hydrogen molecule H_2 is just as experimentally meaningful as the direction of a magnetic field, and along this line the components of the angular momenta of the H atoms are determined by their m_l values.

The Uncertainty Principle and Space Quantization

Why is only one component of \mathbf{L} quantized? The answer is related to the fact that \mathbf{L} can never point in any specific direction but instead is somewhere on a cone in space such that its projection L_z is $m_l\hbar$. Were this not so, the uncertainty principle would be violated. If \mathbf{L} were fixed in space, so that L_x and L_y as well as L_z had definite values, the electron would be confined to a definite plane. For instance, if \mathbf{L} were in the z direction, the electron would have to be in the xy plane at all times (Fig. 6.5a). This can occur only if the electron's momentum component p_z in the z direction is infinitely uncertain, which of course is impossible if it is to be part of a hydrogen atom.



However, since in reality only *one* component L_z of \mathbf{L} together with its magnitude L have definite values and $|L| > |L_z|$, the electron is not limited to a single plane (Fig. 6.5b). Thus there is a built-in uncertainty in the electron's z coordinate. The direction of \mathbf{L} is not fixed, as in Fig. 6.6, and so the average values of L_x and L_y are 0, although L_z always has the specific value $m_l\hbar$.



6.7 ELECTRON PROBABILITY DENSITY

No definite orbits

In Bohr's model of the hydrogen atom the electron is visualized as revolving around the nucleus in a circular path. This model is pictured in a spherical polar coordinate system in Fig. 6.7. It implies that if a suitable experiment were performed, the electron would always be found a distance of $r = n^2 a_0$ (where n is the quantum number of the orbit and a_0 is the radius of the innermost orbit) from the nucleus and in the equatorial plane $\theta = 90^\circ$, while its azimuthal angle ϕ changes with time.

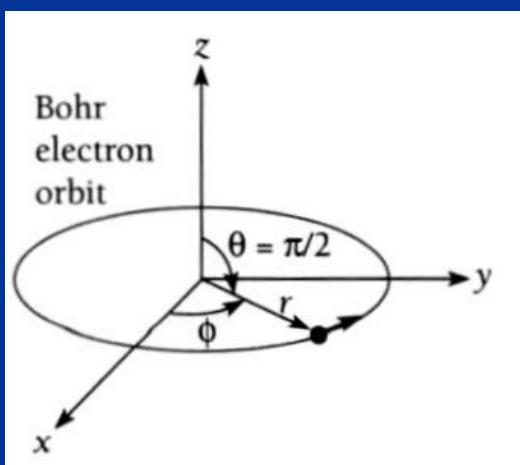


Figure 6.7 The Bohr model of the hydrogen atom in a spherical polar coordinate system.

The quantum theory of the hydrogen atom modifies the Bohr model in two ways:

- 1 No definite values for r , θ , or ϕ can be given, but only the relative probabilities for finding the electron at various locations. This imprecision is, of course, a consequence of the wave nature of the electron.
- 2 We cannot even think of the electron as moving around the nucleus in any conventional sense since the probability density $|\psi|^2$ is independent of time and varies from place to place.

The probability density $|\psi|^2$ that corresponds to the electron wave function $\psi = R\Theta\Phi$ in the hydrogen atom is

$$|\psi|^2 = |R|^2|\Theta|^2|\Phi|^2 \quad (6.23)$$

As usual the square of any function that is complex is to be replaced by the product of the function and its complex conjugate. (We recall that the complex conjugate of a function is formed by changing i to $-i$ whenever it appears.)

From Eq. (6.15) we see that the azimuthal wave function is given by

$$\Phi(\phi) = Ae^{im_l\phi}$$

The azimuthal probability density $|\Phi|^2$ is therefore

$$|\Phi|^2 = \Phi^* \Phi = A^2 e^{-im_l\phi} e^{im_l\phi} = A^2 e^0 = A^2$$

The likelihood of finding the electron at a particular azimuth angle ϕ is a constant that does not depend upon ϕ at all. The electron's probability density is symmetrical about the z axis regardless of the quantum state it is in, and the electron has the same chance of being found at one angle ϕ as at another.

The radial part R of the wave function, in contrast to Φ , not only varies with r but does so in a different way for each combination of quantum numbers n and l . Figure 6.8 contains graphs of R versus r for $1s$, $2s$, $2p$, $3s$, $3p$, and $3d$ states of the hydrogen atom. Evidently R is a maximum at $r = 0$ —that is, at the nucleus itself—for all s states, which correspond to $L = 0$ since $l = 0$ for such states. The value of R is zero at $r = 0$ for states that possess angular momentum.

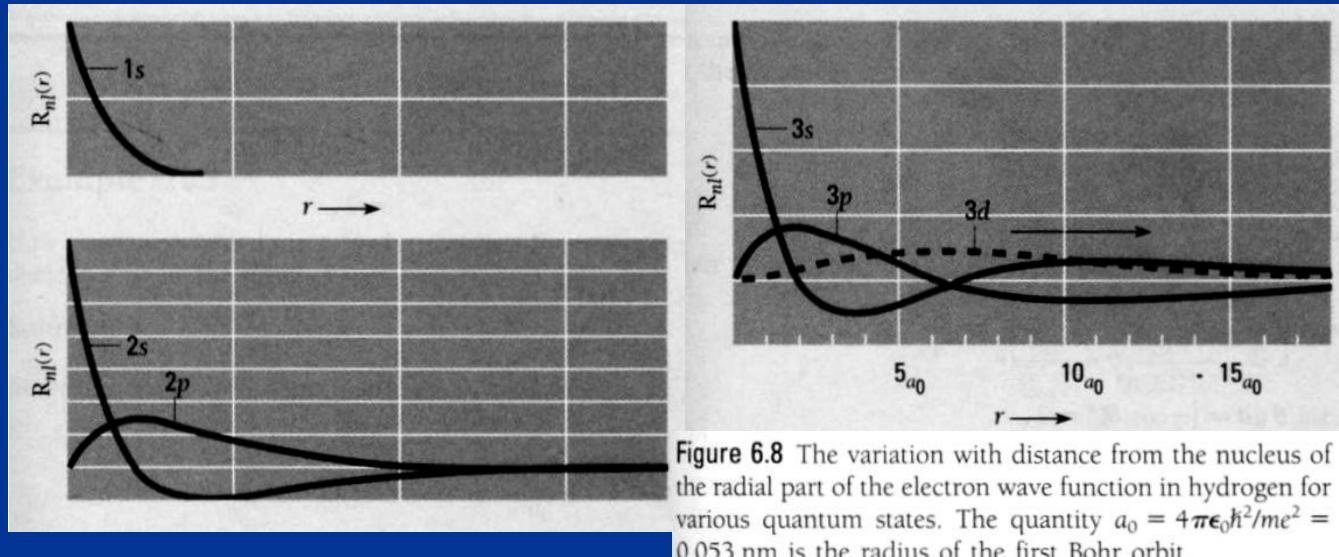


Figure 6.8 The variation with distance from the nucleus of the radial part of the electron wave function in hydrogen for various quantum states. The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 0.053 \text{ nm}$ is the radius of the first Bohr orbit.

Probability of Finding the Electron

The *probability density* of the electron at the point r, θ, ϕ is proportional to $|\psi|^2$, but the *actual probability* of finding it in the infinitesimal volume element dV there is $|\psi|^2 dV$. In spherical polar coordinates (Fig. 6.9),

$$\text{Volume element } dV = (dr)(r d\theta)(r \sin \theta d\phi) = r^2 \sin \theta dr d\theta d\phi \quad (6.24)$$

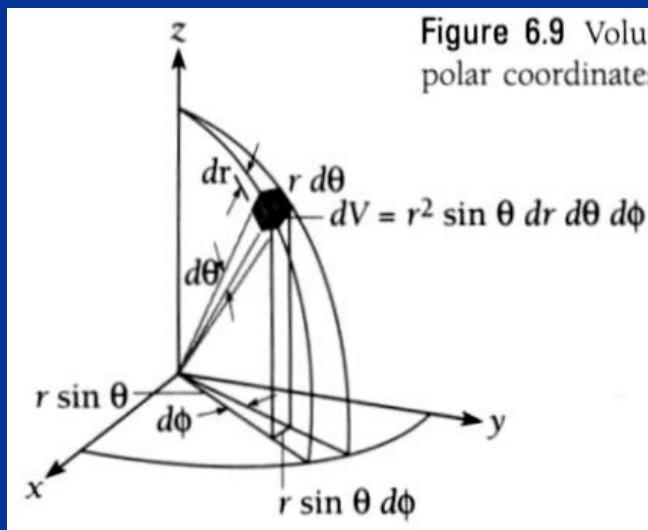


Figure 6.9 Volume element dV in spherical polar coordinates.

As Θ and Φ are normalized functions, the actual probability $P(r) dr$ of finding the electron in a hydrogen atom somewhere in the spherical shell between r and $r + dr$ from the nucleus (Fig. 6.10) is

$$P(r) dr = r^2|R|^2 dr \int_0^\pi |\Theta|^2 \sin \theta d\theta \int_0^{2\pi} |\Phi|^2 d\phi \\ = r^2|R|^2 dr \quad (6.25)$$

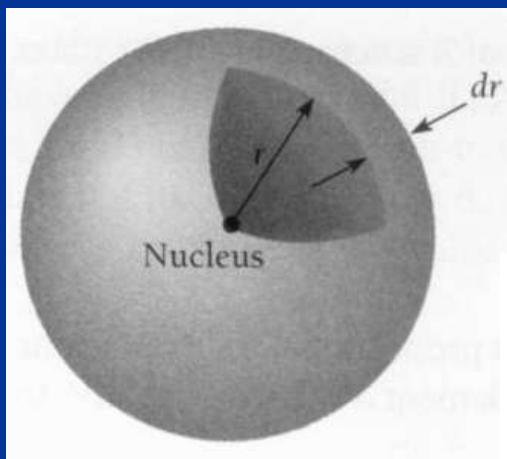


Figure 6.10 The probability of finding the electron in a hydrogen atom in the spherical shell between r and $r + dr$ from the nucleus is $P(r) dr$.

Equation (6.25) is plotted in Fig. 6.11 for the same states whose radial functions R were shown in Fig. 6.8. The curves are quite different as a rule. We note immediately that P is not a maximum at the nucleus for s states, as R itself is, but has its maximum a definite distance from it.

The most probable value of r for a 1s electron turns out to be exactly a_0 , the orbital radius of a ground-state electron in the Bohr model. However, the *average* value of r for a 1s electron is $1.5a_0$, which is puzzling at first sight because the energy levels are the same in both the quantum-mechanical and Bohr atomic models. This apparent discrepancy is removed when we recall that the electron energy depends upon $1/r$ rather than upon r directly, and the average value of $1/r$ for a 1s electron is exactly $1/a_0$.

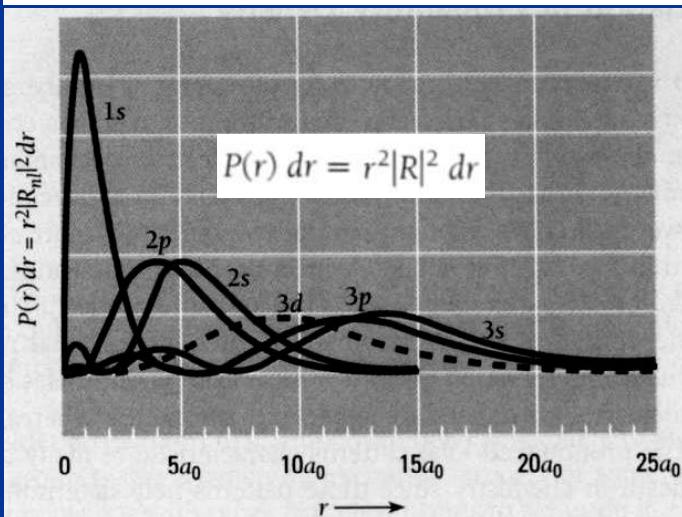


Figure 6.11 The probability of finding the electron in a hydrogen atom at a distance between r and $r + dr$ from the nucleus for the quantum states of Fig. 6.8.

$$dV = r^2 \sin \theta dr d\theta d\phi \quad (6.24)$$

Example 6.2

Verify that the average value of $1/r$ for a 1s electron in the hydrogen atom is $1/a_0$.

Solution

The wave function of a 1s electron is, from Table 6.1,

$$\psi = \frac{e^{-r/a_0}}{\sqrt{\pi} a_0^{3/2}}$$

Since $dV = r^2 \sin \theta dr d\theta d\phi$ we have for the expectation value of $1/r$

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \int_0^\infty \left(\frac{1}{r} \right) |\psi|^2 dV \\ &= \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0} dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi \end{aligned}$$

The integrals have the respective values

$$\begin{aligned} \int_0^\infty r e^{-2r/a_0} dr &= \left[\frac{a_0^2}{4} e^{-2r/a_0} - \frac{r a_0}{2} e^{-2r/a_0} \right]_0^\infty = \frac{a_0^2}{4} \\ \int_0^\pi \sin \theta d\theta &= [-\cos \theta]_0^\pi = 2 \\ \int_0^{2\pi} d\phi &= [\phi]_0^{2\pi} = 2\pi \end{aligned}$$

Hence $\left\langle \frac{1}{r} \right\rangle = \left(\frac{1}{\pi a_0^3} \right) \left(\frac{a_0^2}{4} \right) (2)(2\pi) = \frac{1}{a_0}$

Example 6.3

How much more likely is a 1s electron in a hydrogen atom to be at the distance a_0 from the nucleus than at the distance $a_0/2$?

Solution

According to Table 6.1 the radial wave function for a 1s electron is

$$R = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$

From Eq. (6.25) we have for the ratio of the probabilities that an electron in a hydrogen atom be at the distances r_1 and r_2 from the nucleus

$$\frac{P_1}{P_2} = \frac{r_1^2 |R_1|^2}{r_2^2 |R_2|^2} = \frac{r_1^2 e^{-2r_1/a_0}}{r_2^2 e^{-2r_2/a_0}}$$

Here $r_1 = a_0$ and $r_2 = a_0/2$, so

$$\frac{P_{a_0}}{P_{a_0/2}} = \frac{(a_0)^2 e^{-2}}{(a_0/2)^2 e^{-1}} = 4e^{-1} = 1.47$$

The electron is 47 percent more likely to be a_0 from the nucleus than half that distance (see Fig. 6.11).

$$|\psi|^2 = |R|^2 |\Theta|^2 |\Phi|^2$$

Angular Variation of Probability Density

[<Link>](#)

The function Θ varies with zenith angle θ for all quantum numbers l and m_l except $l = m_l = 0$, which are s states. The value of $|\Theta|^2$ for an s state is a constant; $\frac{1}{2}$, in fact. This means that since $|\Phi|^2$ is also a constant, the electron probability density $|\psi|^2$ is spherically symmetric: it has the same value at a given r in all directions. Electrons in other states, however, do have angular preferences, sometimes quite complicated ones. This can be seen in Fig. 6.12, in which electron probability densities as functions of r and θ are shown for several atomic states. (The quantity plotted is $|\psi|^2$, not $|\psi|^2 dV$.) Since $|\psi|^2$ is independent of ϕ , we can obtain a three-dimensional picture of $|\psi|^2$ by rotating a particular representation about a vertical axis. When this is done, we see that the probability densities for s states are spherically symmetric whereas those for other states are not. The pronounced lobe patterns characteristic of many of the states turn out to be significant in chemistry since these patterns help determine the manner in which adjacent atoms in a molecule interact.

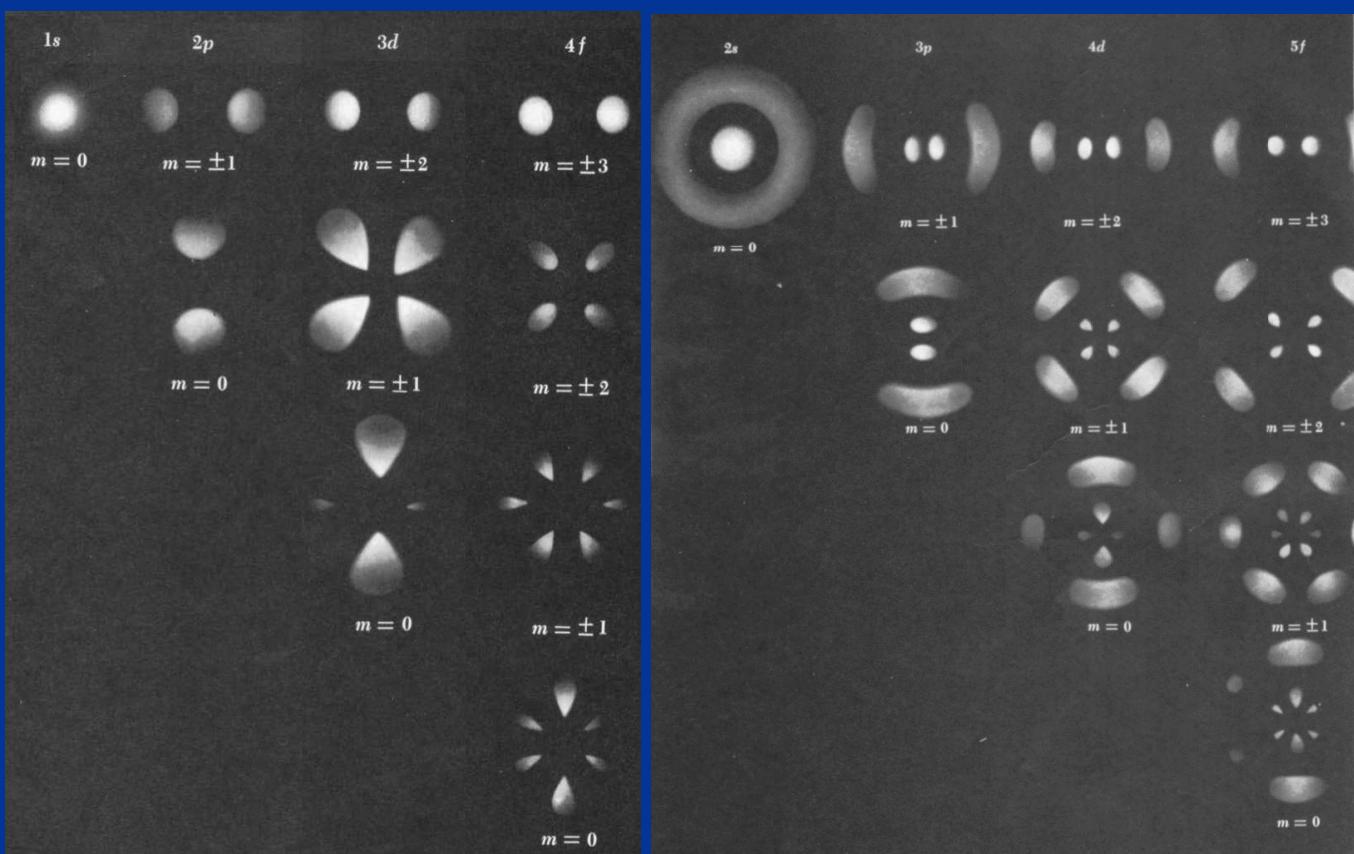


Figure 6.12 Photographic representation of the electron probability-density distribution $|\psi|^2$ for several energy states. These may be regarded as sectional views of the distribution in a plane containing the polar axis, which is vertical and in the plane of the paper. The scale varies from figure to figure.

A look at Figure 6.12 also reveals quantum-mechanical states that resemble those of the Bohr model. The electron probability-density distribution for a $2p$ state with $m_l = \pm 1$, for instance, is like a doughnut in the equatorial plane centered at the nucleus. Calculation shows the most probable distance of such an electron from the nucleus to be $4a_0$ —precisely the radius of the Bohr orbit for the same principal quantum number $n = 2$. Similar correspondences exist for $3d$ states with $m_l = \pm 2$, $4f$ states with $m_l = \pm 3$, and so on. In each of these cases the angular momentum is the highest possible for that energy level, and the angular-momentum vector is as near the z axis as possible so that the probability density is close to the equatorial plane. Thus the Bohr model predicts the most probable location of the electron in one of the several possible states in each energy level.

6.8 RADIATIVE TRANSITIONS

What happens when an electron goes from one state to another

In formulating his theory of the hydrogen atom, Bohr was obliged to postulate that the frequency ν of the radiation emitted by an atom dropping from an energy level E_m to a lower level E_n is

$$\nu = \frac{E_m - E_n}{h}$$

It is not hard to show that this relationship arises naturally in quantum mechanics. For simplicity we shall consider a system in which an electron moves only in the x direction.

From Sec. 5.5 we know that the time-dependent wave function Ψ_n of an electron in a state of quantum number n and energy E_n is the product of a time-independent wave function ψ_n and a time-varying function whose frequency is

$$\nu_n = \frac{E_n}{h}$$

Hence

$$\Psi_n = \psi_n e^{-(iE_n/\hbar)t} \quad \Psi_n^* = \psi_n^* e^{+(iE_n/\hbar)t} \quad (6.26)$$

The expectation value $\langle x \rangle$ of the position of such an electron is

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x \Psi_n^* \Psi_n dx = \int_{-\infty}^{\infty} x \psi_n^* \psi_n e^{[(iE_n/\hbar) - (iE_n/\hbar)]t} dx \\ &= \int_{-\infty}^{\infty} x \psi_n^* \psi_n dx \end{aligned} \quad (6.27)$$

The expectation value $\langle x \rangle$ is constant in time since ψ_n and ψ_n^* are, by definition, functions of position only. The electron does not oscillate, and no radiation occurs. Thus quantum mechanics predicts that a system in a specific quantum state does not radiate, as observed.

We next consider an electron that shifts from one energy state to another. A system might be in its ground state n when an excitation process of some kind (a beam of radiation, say, or collisions with other particles) begins to act upon it. Subsequently we find that the system emits radiation corresponding to a transition from an excited state of energy E_m to the ground state. We conclude that at some time during the intervening period the system existed in the state m . What is the frequency of the radiation?

The wave function Ψ of an electron that can exist in both states n and m is

$$\Psi = a\Psi_n + b\Psi_m \quad (6.28)$$

where a^*a is the probability that the electron is in state n and b^*b the probability that it is in state m . Of course, it must always be true that $a^*a + b^*b = 1$. Initially $a = 1$ and $b = 0$; when the electron is in the excited state, $a = 0$ and $b = 1$; and ultimately $a = 1$ and $b = 0$ once more. While the electron is in either state, there is no radiation, but when it is in the midst of the transition from m to n (that is, when both a and b have nonvanishing values), electromagnetic waves are produced.

The expectation value $\langle x \rangle$ that corresponds to the composite wave function of Eq. (6.28) is

$$\begin{aligned} \langle x \rangle &= \int_{-\infty}^{\infty} x(a^*\Psi_n^* + b^*\Psi_m^*)(a\Psi_n + b\Psi_m) dx \\ &= \int_{-\infty}^{\infty} x(a^2\Psi_n^*\Psi_n + b^*a\Psi_m^*\Psi_n + a^*b\Psi_n^*\Psi_m + b^2\Psi_m^*\Psi_m) dx \end{aligned} \quad (6.29)$$

Here, as before, we let $a^*a = a^2$ and $b^*b = b^2$. The first and last integrals do not vary with time, so the second and third integrals are the only ones able to contribute to a time variation in $\langle x \rangle$.

$$\Psi_n = \psi_n e^{-(iE_n/\hbar)t} \quad \Psi_n^* = \psi_n^* e^{+(iE_n/\hbar)t} \quad (6.26)$$

With the help of Eqs. (6.26) we expand Eq. (6.29) to give

$$\begin{aligned} \langle x \rangle &= a^2 \int_{-\infty}^{\infty} x\psi_n^*\psi_n dx + b^*a \int_{-\infty}^{\infty} x\psi_m^*e^{+(iE_m/\hbar)t}\psi_n e^{-(iE_n/\hbar)t} dx \rightarrow x\psi_m^*\psi_n e^{i\frac{E_m-E_n}{\hbar}t} \\ &\quad + a^*b \int_{-\infty}^{\infty} x\psi_n^*e^{+(iE_n/\hbar)t}\psi_m e^{-(iE_m/\hbar)t} dx + b^2 \int_{-\infty}^{\infty} x\psi_m^*\psi_m dx \end{aligned} \quad (6.30)$$

Because $e^{i\theta} = \cos \theta + i \sin \theta$ and $e^{-i\theta} = \cos \theta - i \sin \theta$

the two middle terms of Eq. (6.30), which are functions of time, become

$$\begin{aligned} \cos\left(\frac{E_m - E_n}{\hbar}\right)t \int_{-\infty}^{\infty} x[b^*a\psi_m^*\psi_n + a^*b\psi_n^*\psi_m] dx &\quad \text{*<Back>*} \\ &\quad + i \sin\left(\frac{E_m - E_n}{\hbar}\right)t \int_{-\infty}^{\infty} x[b^*a\psi_m^*\psi_n - a^*b\psi_n^*\psi_m] dx \end{aligned} \quad (6.31)$$

The real part of this result varies with time as

$$\cos\left(\frac{E_m - E_n}{\hbar}\right)t = \cos 2\pi\left(\frac{E_m - E_n}{h}\right)t = \cos 2\pi\nu t \quad (6.32)$$

The electron's position therefore oscillates sinusoidally at the frequency

$$\nu = \frac{E_m - E_n}{h} \quad (6.33)$$

$$\nu = \frac{E_m - E_n}{h} \quad (6.33)$$

When the electron is in state n or state m the expectation value of the electron's position is constant. When the electron is undergoing a transition between these states, its position oscillates with the frequency ν . Such an electron, of course, is like an electric dipole and radiates electromagnetic waves of the same frequency ν . This result is the same as that postulated by Bohr and verified by experiment. As we have seen, quantum mechanics gives Eq. (6.33) without the need for any special assumptions.

6.9 SELECTION RULES

Some transitions are more likely to occur than others

We did not have to know the values of the probabilities a and b as functions of time, nor the electron wave functions ψ_n and ψ_m , in order to find the frequency ν . We need these quantities, however, to calculate the chance a given transition will occur. The general condition necessary for an atom in an excited state to radiate is that the integral

$$\int_{-\infty}^{\infty} x\psi_n\psi_m^* dx \quad (6.34) \quad <\text{Link}>$$

not be zero, since the intensity of the radiation is proportional to it. Transitions for which this integral is finite are called **allowed transitions**, while those for which it is zero are called **forbidden transitions**.

In the case of the hydrogen atom, three quantum numbers are needed to specify the initial and final states involved in a radiative transition. If the principal, orbital, and magnetic quantum numbers of the initial state are n' , l' , m_l' , respectively, and those of the final state are n , l , m_l , and the coordinate u represents either the x , y , or z coordinate, the condition for an allowed transition is

Allowed transitions
$$\int_{-\infty}^{\infty} u \psi_{n,l,m_l} \psi_{n',l',m_l'}^* dV \neq 0 \quad (6.35)$$

where the integral is now over all space. When u is taken as x , for example, the radiation would be that produced by a dipole antenna lying on the x axis.

Since the wave functions ψ_{n,l,m_l} for the hydrogen atom are known, Eq. (6.35) can be evaluated for $u = x$, $u = y$, and $u = z$ for all pairs of states differing in one or more quantum numbers. When this is done, it is found that the only transitions between states of different n that can occur are those in which the orbital quantum number l changes by ± 1 or -1 and the magnetic quantum number m_l does not change or changes by ± 1 or -1 . That is, the condition for an allowed transition is that

$$\Delta l = \pm 1 \quad (6.36)$$

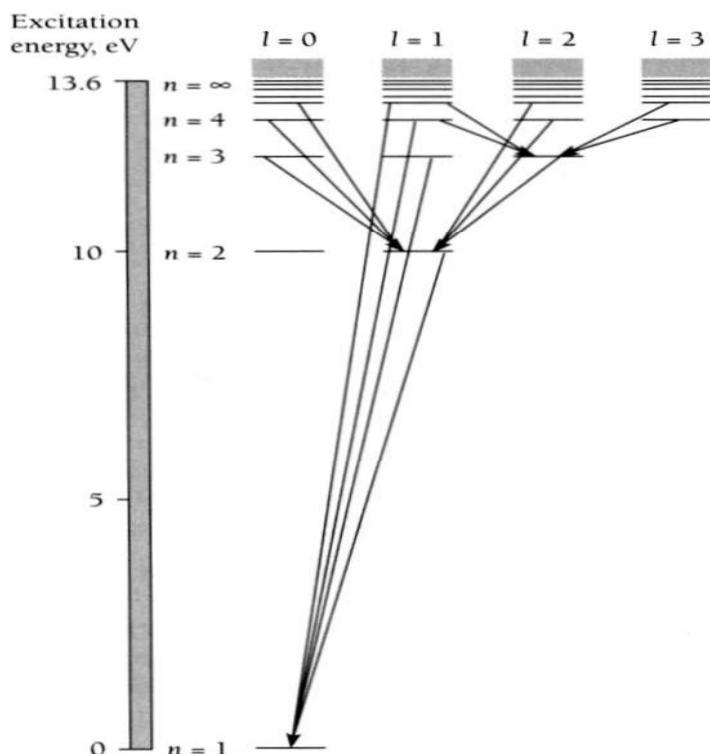
Selection rules

$$\Delta m_l = 0, \pm 1 \quad (6.37)$$

The change in total quantum number n is not restricted. Equations (6.36) and (6.37) are known as the **selection rules** for allowed transitions (Fig. 6.13).

The selection rule requiring that l change by ± 1 if an atom is to radiate means that an emitted photon carries off the angular momentum $\pm \hbar$ equal to the difference between the angular momenta of the atom's initial and final states. The classical analog of a photon with angular momentum $\pm \hbar$ is a left or right circularly polarized electromagnetic wave, so this notion is not unique with quantum theory.

Figure 6.13 Energy-level diagram for hydrogen showing transitions allowed by the selection rule $\Delta l = \pm 1$. In this diagram the vertical axis represents excitation energy above the ground state.



6.10 ZEEMAN EFFECT

What happens to an atom in a magnetic field

In an external magnetic field \mathbf{B} , a magnetic dipole has an amount of potential energy U_m that depends upon both the magnitude μ of its magnetic moment and the orientation of this moment with respect to the field (Fig. 6.15).

The torque τ on a magnetic dipole in a magnetic field of flux density \mathbf{B} is

$$\tau = \mu B \sin \theta$$

where θ is the angle between μ and \mathbf{B} . The torque is a maximum when the dipole is perpendicular to the field, and zero when it is parallel or antiparallel to it.

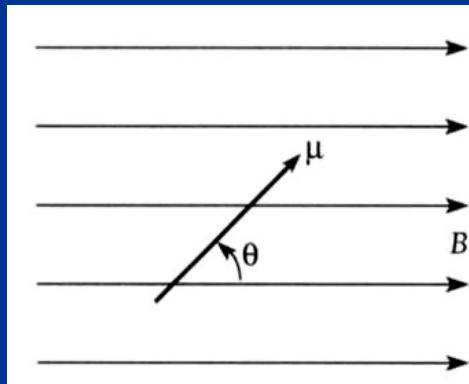


Figure 6.15 A magnetic dipole of moment μ at the angle θ relative to a magnetic field B .

Link

To calculate the potential energy U_m we must first establish a reference configuration in which U_m is zero by definition. (Since only *changes* in potential energy are ever experimentally observed, the choice of a reference configuration is arbitrary.) It is convenient to set $U_m = 0$ when $\theta = \pi/2 = 90^\circ$, that is, when μ is perpendicular to \mathbf{B} . The potential energy at any other orientation of μ is equal to the external work that must be done to rotate the dipole from $\theta_0 = \pi/2$ to the angle θ that corresponds to that orientation. Hence

$$\begin{aligned} U_m &= \int_{\pi/2}^{\theta} \tau d\theta = \mu B \int_{\pi/2}^{\theta} \sin \theta d\theta \\ &= -\mu B \cos \theta \end{aligned} \quad \text{<*Back*>} \quad (6.38)$$

When μ points in the same direction as \mathbf{B} , then $U_m = -\mu B$, its minimum value. This follows from the fact that a magnetic dipole tends to align itself with an external magnetic field.

The magnetic moment of the orbital electron in a hydrogen atom depends on its angular momentum \mathbf{L} . Hence both the magnitude of \mathbf{L} and its orientation with respect to the field determine the extent of the magnetic contribution to the total energy of the atom when it is in a magnetic field. The magnetic moment of a current loop is

$$\mu = IA$$

where I is the current and A the area it encloses. An electron that makes f rev/s in a circular orbit of radius r is equivalent to a current of $-ef$ (since the electronic charge is $-e$), and its magnetic moment is therefore

$$\mu = -ef\pi r^2$$

Because the linear speed v of the electron is $2\pi r f$ its angular momentum is

$$L = mvr = 2\pi mfr^2$$

Comparing the formulas for magnetic moment μ and angular momentum L shows that

Electron magnetic moment

$$\mu = -\left(\frac{e}{2m}\right)L \quad (6.39)$$

for an orbital electron (Fig. 6.16).

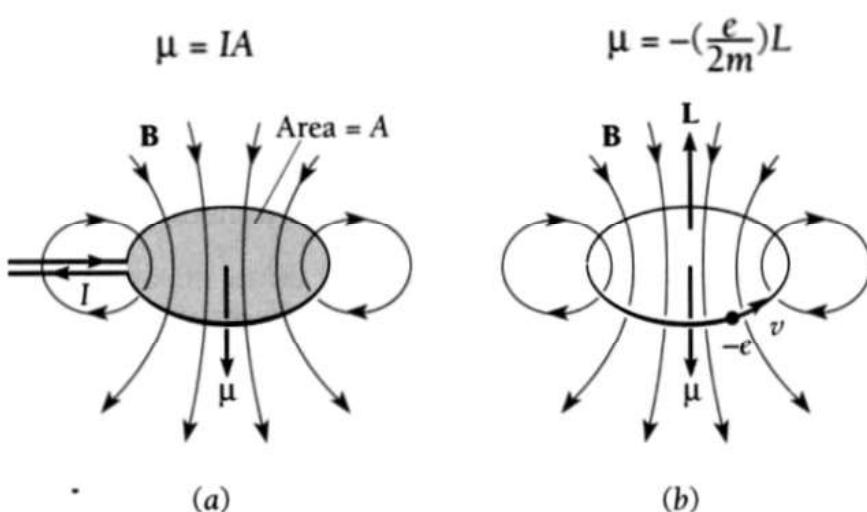


Figure 6.16 (a) Magnetic moment of a current loop enclosing area A . (b) Magnetic moment of an orbiting electron of angular momentum \mathbf{L} .

The quantity $(-e/2m)$, which involves only the charge and mass of the electron, is called its **gyromagnetic ratio**. The minus sign means that μ is in the opposite direction to \mathbf{L} and is a consequence of the negative charge of the electron. While the above expression for the magnetic moment of an orbital electron has been obtained by a classical calculation, quantum mechanics yields the same result. The magnetic potential energy of an atom in a magnetic field is therefore

$$U_m = \left(\frac{e}{2m} \right) LB \cos \theta \quad (6.40) \quad \text{<Link>}$$

which depends on both B and θ .

From Fig. 6.4 we see that the angle θ between \mathbf{L} and the z direction can have only the values specified by

$$\cos \theta = \frac{m_l}{\sqrt{l(l+1)}}$$

with the permitted values of L specified by

$$L = \sqrt{l(l+1)}\hbar$$

To find the magnetic energy that an atom of magnetic quantum number m_l has when it is in a magnetic field \mathbf{B} , we put the above expressions for $\cos \theta$ and L in Eq. (6.40) to give

Magnetic energy $U_m = m_l \left(\frac{e\hbar}{2m} \right) B \quad (6.41)$

The quantity $e\hbar/2m$ is called the **Bohr magneton**:

Bohr magneton $\mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-24} \text{ J/T} = 5.788 \times 10^{-5} \text{ eV/T} \quad (6.42)$

Magnetic energy $U_m = m_l \left(\frac{e\hbar}{2m} \right) B$ (6.41)

In a magnetic field, then, the energy of a particular atomic state depends on the value of m_l as well as on that of n . A state of total quantum number n breaks up into several substates when the atom is in a magnetic field, and their energies are slightly more or slightly less than the energy of the state in the absence of the field. This phenomenon leads to a “splitting” of individual spectral lines into separate lines when atoms radiate in a magnetic field. The spacing of the lines depends on the magnitude of the field.

The splitting of spectral lines by a magnetic field is called the **Zeeman effect** after the Dutch physicist Pieter Zeeman, who first observed it in 1896. The Zeeman effect is a vivid confirmation of space quantization.

Because m_l can have the $2l + 1$ values of $+l$ through 0 to $-l$, a state of given orbital quantum number l is split into $2l + 1$ substates that differ in energy by $\mu_B B$ when the atom is in a magnetic field. However, because changes in m_l are restricted to $\Delta m_l = 0, \pm 1$, we expect a spectral line from a transition between two states of different l to be split into only three components, as shown in Fig. 6.17. The **normal Zeeman effect** consists of the splitting of a spectral line of frequency ν_0 into three components whose frequencies are

$$\nu_1 = \nu_0 - \mu_B \frac{B}{h} = \nu_0 - \frac{e}{4\pi m} B$$

Normal Zeeman effect

$$\nu_2 = \nu_0 \quad (6.43)$$

$$\nu_3 = \nu_0 + \mu_B \frac{B}{h} = \nu_0 + \frac{e}{4\pi m} B$$

In Secs. 7.1 and 7.7 we will see that this is not the whole story of the Zeeman effect.

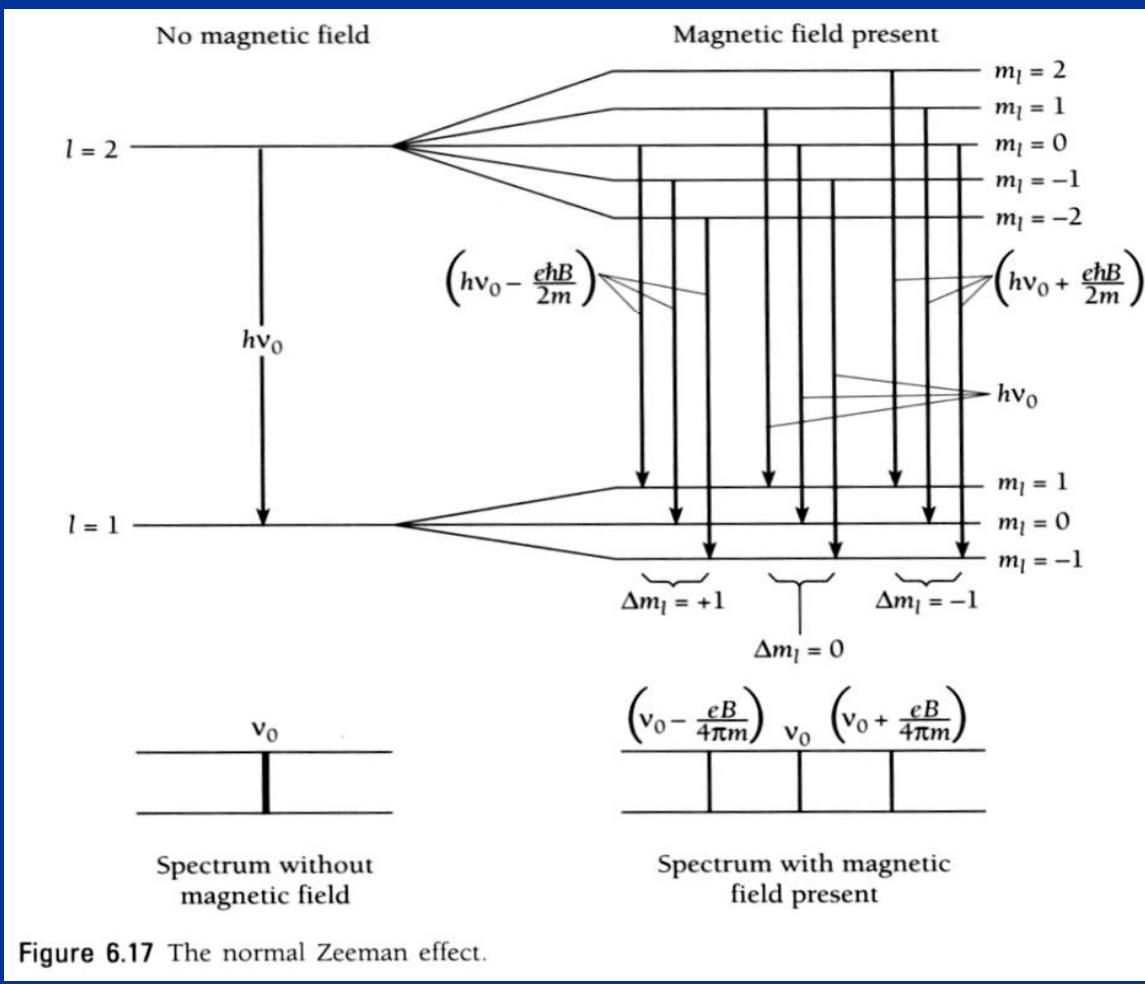


Figure 6.17 The normal Zeeman effect.

Example 6.4

A sample of a certain element is placed in a 0.300-T magnetic field and suitably excited. How far apart are the Zeeman components of the 450-nm spectral line of this element?

Solution

The separation of the Zeeman components is

$$\Delta\nu = \frac{eB}{4\pi m}$$

Since $\nu = c/\lambda$, $d\nu = -c d\lambda/\lambda^2$, and so, disregarding the minus sign,

$$\begin{aligned}
 \Delta\lambda &= \frac{\lambda^2 \Delta\nu}{c} = \frac{eB\lambda^2}{4\pi mc} \\
 &= \frac{(1.60 \times 10^{-19} \text{ C})(0.300 \text{ T})(4.50 \times 10^{-7} \text{ m})^2}{(4\pi)(9.11 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m/s})} \\
 &= 2.83 \times 10^{-12} \text{ m} = 0.00283 \text{ nm}
 \end{aligned}$$



$$r = (x^2 + y^2 + z^2)^{\frac{1}{2}} \quad \frac{\partial r}{\partial x} = \frac{1}{2} \frac{2x}{(x^2 + y^2 + z^2)^{\frac{1}{2}}} = \frac{x}{r}$$

$$\text{If } \psi = \psi(r) \quad \frac{\partial \psi}{\partial x} = \frac{\partial \psi}{\partial r} \frac{\partial r}{\partial x} = \frac{x}{r} \frac{\partial \psi}{\partial r}$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{1}{r} \frac{\partial \psi}{\partial r} - \frac{x^2}{r^3} \frac{\partial \psi}{\partial r} + \frac{x^2}{r^2} \frac{\partial^2 \psi}{\partial r^2}$$

$$\frac{\partial^2 \psi}{\partial y^2} = \frac{1}{r} \frac{\partial \psi}{\partial r} - \frac{y^2}{r^3} \frac{\partial \psi}{\partial r} + \frac{y^2}{r^2} \frac{\partial^2 \psi}{\partial r^2}$$

$$\frac{\partial^2 \psi}{\partial z^2} = \frac{1}{r} \frac{\partial \psi}{\partial r} - \frac{z^2}{r^3} \frac{\partial \psi}{\partial r} + \frac{z^2}{r^2} \frac{\partial^2 \psi}{\partial r^2}.$$

$$(x^2 + y^2 + z^2 = r^2)$$

$$\begin{aligned} \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} &= \left(\frac{3}{r} - \frac{r^2}{r^3} \right) \frac{\partial \psi}{\partial r} + \frac{r^2}{r^2} \frac{\partial^2 \psi}{\partial r^2} \\ &= \frac{\partial^2 \psi}{\partial r^2} + \frac{2}{r} \frac{\partial \psi}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) \end{aligned}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right)$$

Equations (6.8), (6.10), and (6.11) are usually written

Equation for Φ $\frac{d^2 \Phi}{d\phi^2} + m_l^2 \Phi = 0 \quad (6.12)$

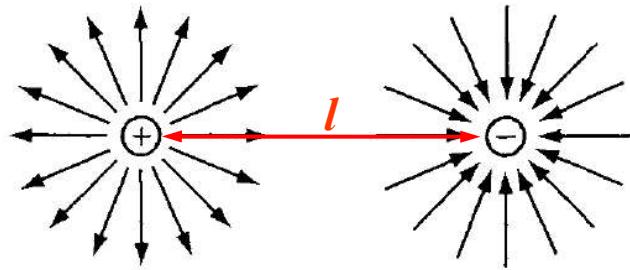
Equation for Θ $\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right] \Theta = 0 \quad (6.13)$

Equation for R $\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0 r} + E \right) - \frac{l(l+1)}{r^2} \right] R = 0 \quad (6.14)$

Each of these is an ordinary differential equation for a single function of a single variable. Only the equation for R depends on the potential energy $U(r)$.

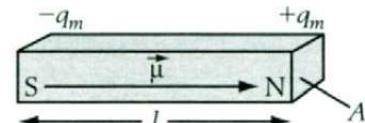
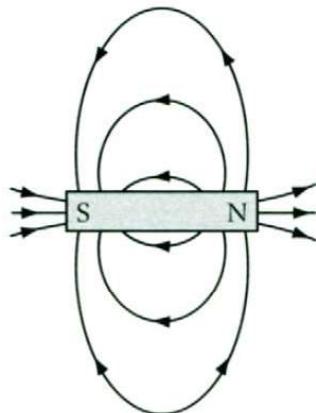
We have therefore accomplished our task of simplifying Schrödinger's equation for the hydrogen atom, which began as a partial differential equation for a function ψ of three variables. The assumption embodied in Eq. (6.5) is evidently valid.

Electrical charges



$$\text{Electric dipole moment: } \mathbf{p} = \mathbf{q} \cdot \mathbf{l}$$

Magnetic dipoles



Magnetic dipole moment

$$\mu = q_m \cdot l$$

Unlike electrical charge, there is no single magnetic pole discovered so far. If you cut a magnet into smaller pieces, each of them always has two poles! **Inside a magnet there really are no poles!**

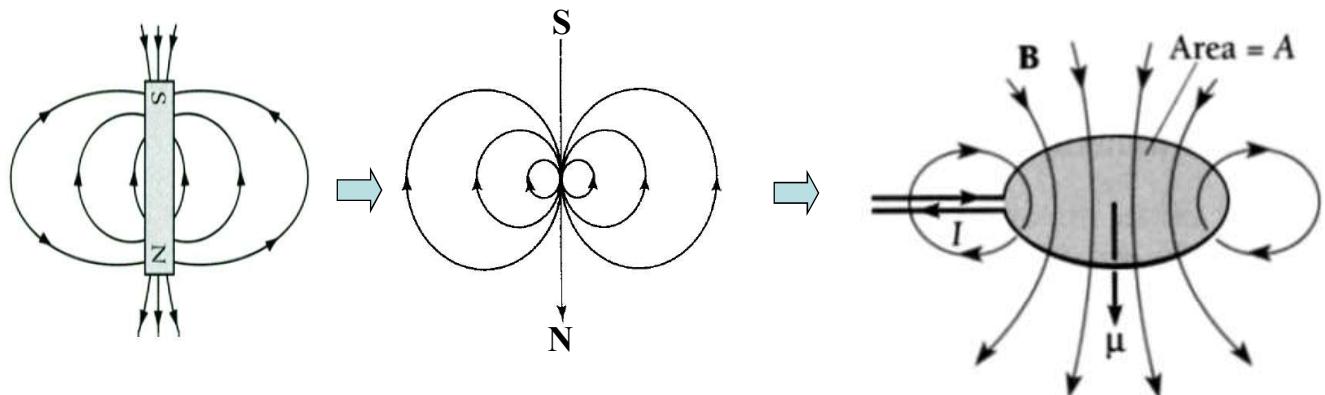
Equivalent magnetic dipole of an electric current loop

The field of a magnet of pole strength q_m and length l , at a distance r from the magnet, depends only on the moment $q_m \cdot l$ of the magnet and not on the separate values of q_m and l , provided r is large relative to l .

Thus the field is the same if we halve the length of the magnet and double its pole strength. Continuing this process, we obtain in the limit a **very short magnet of finite moment equal to that from a circular electrical loop**.

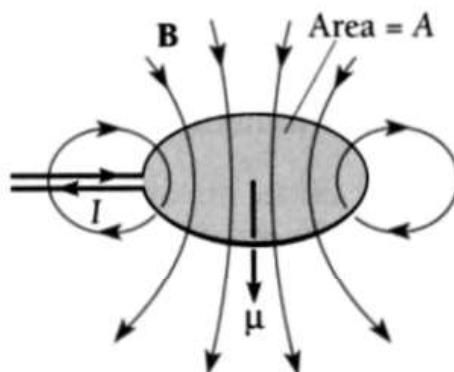
Any magnet, as far as its external field is concerned, may be thought as being made up of such dipoles.

$$\mu = IA$$



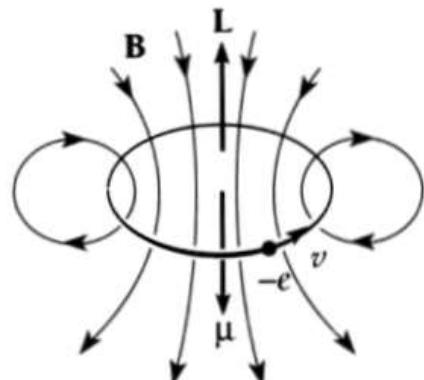
Magnetic moment of a current loop enclosing area A

$$\mu = IA$$



Magnetic moment of an orbiting electron of angular momentum L

$$\mu = -\left(\frac{e}{2m}\right)L$$



Puck

7.1 ELECTRON SPIN

Round and round it goes forever

The theory of the atom developed in the previous chapter cannot account for a number of well-known experimental observations. One is the fact that many spectral lines actually consist of two separate lines that are very close together. An example of this **fine structure** is the first line of the Balmer series of hydrogen, which arises from transitions between the $n = 3$ and $n = 2$ levels in hydrogen atoms. Here the theoretical prediction is for a single line of wavelength 656.3 nm while in reality there are two lines 0.14 nm apart—a small effect, but a conspicuous failure for the theory.

Another failure of the simple quantum-mechanical theory of the atom occurs in the Zeeman effect, which was discussed in Sec. 6.10. There we saw that the spectral lines of an atom in a magnetic field should each be split into the three components specified by Eq. (6.43). While the normal Zeeman effect is indeed observed in the spectra of a few elements under certain circumstances, more often it is not. Four, six, or even more components may appear, and even when three components are present their spacing may not agree with Eq. (6.43).

Several anomalous Zeeman patterns are shown in Fig. 7.1 together with the predictions of Eq. (6.43).

In order to account for both fine structure in spectral lines and the anomalous Zeeman effect, two Dutch graduate students, Samuel Goudsmit and George Uhlenbeck, proposed in 1925 that

Every electron has an intrinsic angular momentum, called spin, whose magnitude is the same for all electrons. Associated with this angular momentum is a magnetic moment.

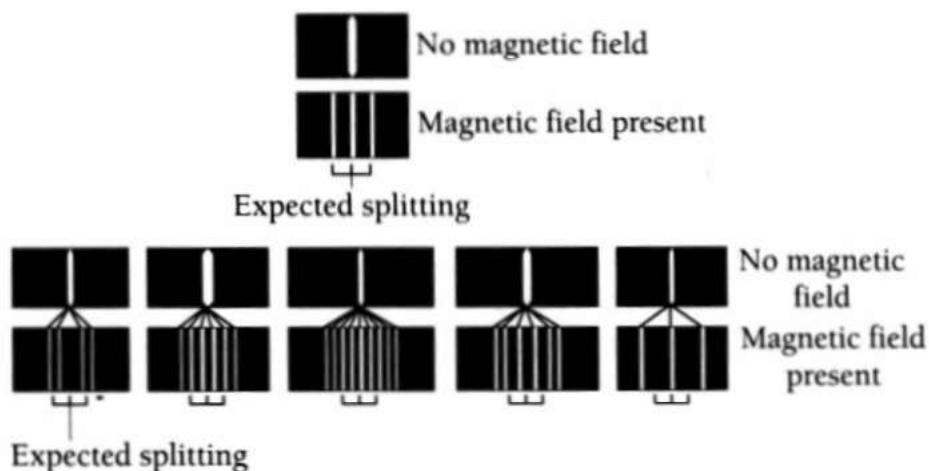


Figure 7.1 The normal and anomalous Zeeman effects in various spectral lines.

What Goudsmit and Uhlenbeck had in mind was a classical picture of an electron as a charged sphere spinning on its axis. The rotation involves angular momentum, and because the electron is negatively charged, it has a magnetic moment μ_s opposite in direction to its angular momentum vector \mathbf{S} . The notion of electron spin proved to be successful in explaining not only fine structure and the anomalous Zeeman effect but a wide variety of other atomic effects as well.

To be sure, the picture of an electron as a spinning charged sphere is open to serious objections. For one thing, observations of the scattering of electrons by other electrons at high energy indicate that the electron must be less than 10^{-16} m across, and quite possibly is a point particle. In order to have the observed angular momentum associated with electron spin, so small an object would have to rotate with an equatorial velocity many times greater than the velocity of light.

But the failure of a model taken from everyday life does not invalidate the idea of electron spin. We have already found plenty of ideas in relativity and quantum physics that are mandated by experiment although at odds with classical concepts. In 1929 the fundamental nature of electron spin was confirmed by Paul Dirac's development of relativistic quantum mechanics. He found that a particle with the mass and charge of the electron must have the intrinsic angular momentum and magnetic moment proposed for the electron by Goudsmit and Uhlenbeck.

The quantum number s describes the spin angular momentum of the electron. The only value s can have is $s = \frac{1}{2}$, which follows both from Dirac's theory and from spectral data. The magnitude S of the angular momentum due to electron spin is given in terms of the spin quantum number s by

Spin angular momentum

$$S = \sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar \quad (7.1)$$

This is the same formula as that giving the magnitude L of the orbital angular momentum in terms of the orbital quantum number l , $L = \sqrt{l(l+1)}\hbar$.

Example 7.1

Find the equatorial velocity v of an electron under the assumption that it is a uniform sphere of radius $r = 5.00 \times 10^{-17}$ m.

Solution

The angular momentum of a spinning sphere is $I\omega$, where $I = \frac{2}{5}mr^2$ is its moment of inertia and $\omega = v/r$ is its angular velocity. From Eq. (7.1) the spin angular momentum of an electron is $S = (\sqrt{3}/2)\hbar$, so

$$S = \frac{\sqrt{3}}{2}\hbar = I\omega = \left(\frac{2}{5}mr^2\right)\left(\frac{v}{r}\right) = \frac{2}{5}mv r$$
$$v = \left(\frac{5\sqrt{3}}{4}\right)\frac{\hbar}{mr} = \frac{(5\sqrt{3})(1.055 \times 10^{-34} \text{ J} \cdot \text{s})}{(4)(9.11 \times 10^{-31} \text{ kg})(5.00 \times 10^{-17} \text{ m})} = 5.01 \times 10^{12} \text{ m/s} = 1.67 \times 10^4 c$$

The equatorial velocity of an electron on the basis of this model must be over 10,000 times the velocity of light, which is impossible. No classical model of the electron can overcome this objection.

The space quantization of electron spin is described by the spin magnetic quantum number m_s . We recall that the orbital angular-momentum vector can have the $2l + 1$ orientations in a magnetic field from $+l$ to $-l$. Similarly the spin angular-momentum vector can have the $2s + 1 = 2$ orientations specified by $m_s = +\frac{1}{2}$ ("spin up") and $m_s = -\frac{1}{2}$ ("spin down"), as in Fig. 7.2. The component S_z of the spin angular momentum of an electron along a magnetic field in the z direction is determined by the spin magnetic quantum number, so that

**z component of
spin angular
momentum**

$$S_z = m_s \hbar = \pm \frac{1}{2} \hbar \quad (7.2)$$

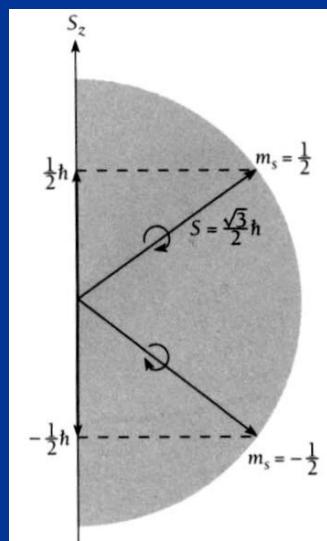


Figure 7.2 The two possible orientations of the spin angular-momentum vector are "spin up" ($m_s = +\frac{1}{2}$) and "spin down" ($m_s = -\frac{1}{2}$).

The gyromagnetic ratio characteristic of electron spin is almost exactly twice that characteristic of electron orbital motion. Taking this ratio as equal to 2, the spin magnetic moment μ_s of an electron is related to its spin angular momentum \mathbf{S} by

**Spin magnetic
moment**

$$\mu_s = -\frac{e}{m} \mathbf{S} \quad (7.3)$$

The possible components of μ_s along any axis, say the z axis, are therefore limited to

**z component of
spin magnetic
moment**

$$\mu_{sz} = \pm \frac{e\hbar}{2m} = \pm \mu_B \quad (7.4)$$

where μ_B is the Bohr magneton.

The Stern-Gerlach Experiment

Space quantization was first explicitly demonstrated in 1921 by Otto Stern and Walter Gerlach. They directed a beam of neutral silver atoms from an oven through a set of collimating slits into an inhomogeneous magnetic field, as in Fig. 7.3. A photographic plate recorded the shape of the beam after it had passed through the field.

In its normal state, the entire magnetic moment of a silver atom is due to the spin of only one of its electrons. In a uniform magnetic field, such a dipole would merely experience a torque tending to align it with the field. In an inhomogeneous field, however, each “pole” of the dipole is subject to a force of different magnitude, and therefore there is a resultant force on the dipole that varies with its orientation relative to the field.

Classically, all orientations should be present in a beam of atoms. The result would merely be a broad trace on the photographic plate instead of the thin line formed without any magnetic field. Stern and Gerlach found, however, that the initial beam split into two distinct parts that correspond to the two opposite spin orientations in the magnetic field permitted by space quantization.

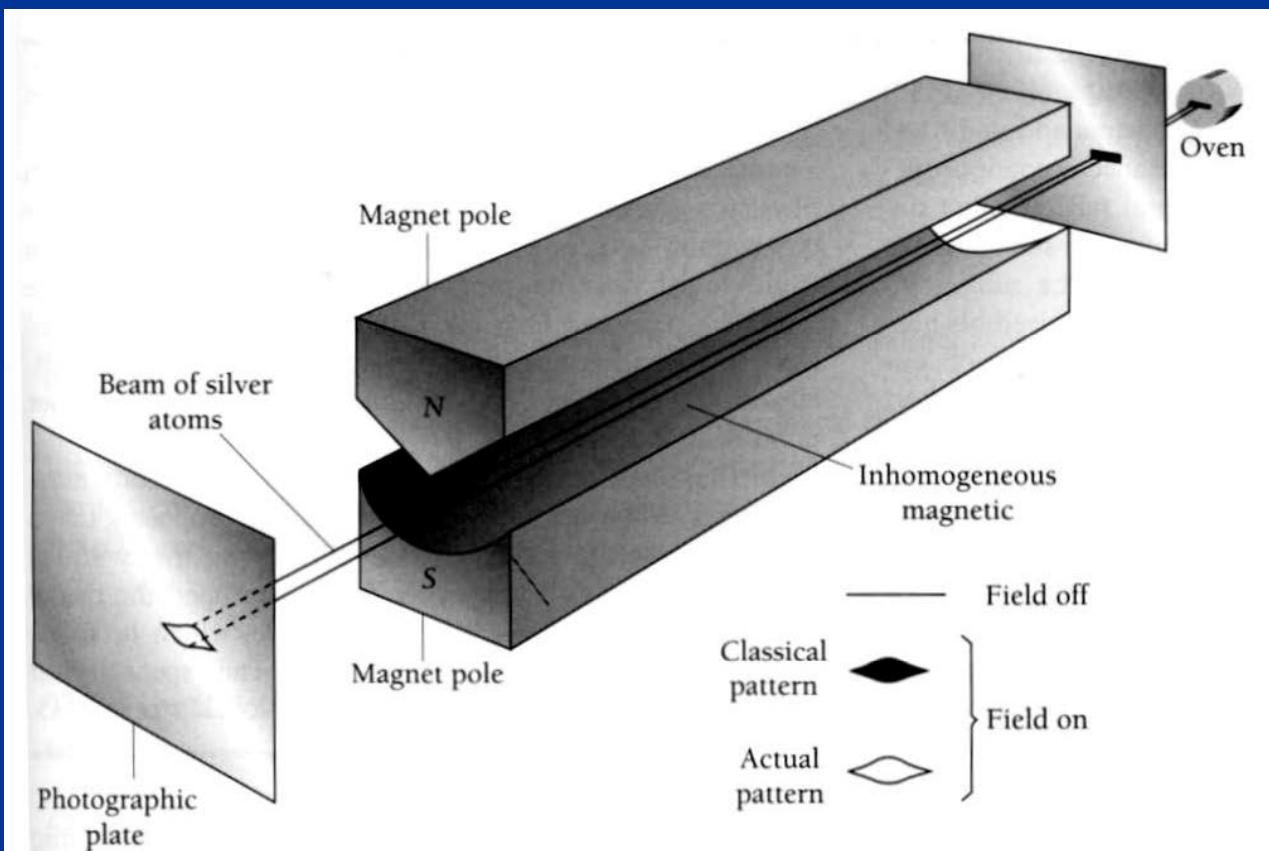


Figure 7.3 The Stern-Gerlach experiment.

The introduction of electron spin into the theory of the atom means that a total of four quantum numbers, n , l , m_l , and m_s , is needed to describe each possible state of an atomic electron. These are listed in Table 7.1.

TABLE 7.1 Quantum Numbers of an Atomic Electron

Name	Symbol	Possible Values	Quantity Determined
Principal	n	1, 2, 3, . . .	Electron energy
Orbital	l	0, 1, 2, . . . , $n - 1$	Orbital angular-momentum magnitude
Magnetic	m_l	$-l, \dots, 0, \dots, +l$	Orbital angular-momentum direction
Spin magnetic	m_s	$-\frac{1}{2}, +\frac{1}{2}$	Electron spin direction

<back>

7.2 EXCLUSION PRINCIPLE

A different set of quantum numbers for each electron in an atom

In a normal hydrogen atom, the electron is in its quantum state of lowest energy. What about more complex atoms? Are all 92 electrons of a uranium atom in the same quantum state, jammed into a single probability cloud? Many lines of evidence make this idea unlikely.

A example is the great difference in chemical behavior shown by certain elements whose atomic structures differ by only one electron. Thus the elements that have the atomic numbers 9, 10, and 11 are respectively the chemically active halogen gas fluorine, the inert gas neon, and the alkali metal sodium. Since the electron structure of an atom controls how it interacts with other atoms, it makes no sense that the chemical properties of the elements should change so sharply with a small change in atomic number if all the electrons in an atom were in the same quantum state.

In 1925 Wolfgang Pauli discovered the fundamental principle that governs the electronic configurations of atoms having more than one electron. His **exclusion principle** states that

No two electrons in an atom can exist in the same quantum state. Each electron must have a different set of quantum numbers n, l, m_l, m_s .

Pauli was led to the exclusion principle by a study of atomic spectra. The various states of an atom can be determined from its spectrum, and the quantum numbers of these states can be inferred. In the spectra of every element but hydrogen a number of lines are *missing* that correspond to transitions to and from states having certain combinations of quantum numbers. For instance, no transitions are observed in helium to or from the ground-state configuration in which the spins of both electrons are in the same direction. However, transitions *are* observed to and from the other ground-state configuration, in which the spins are in opposite directions.

In the absent state the quantum numbers of *both* electrons would be $n = 1, l = 0, m_l = 0, m_s = \frac{1}{2}$. On the other hand, in the state known to exist one of the electrons has $m_s = \frac{1}{2}$ and the other $m_s = -\frac{1}{2}$. Pauli showed that every unobserved atomic state involves two or more electrons with identical quantum numbers, and the exclusion principle is a statement of this finding.

7.3 SYMMETRIC AND ANTSYMMETRIC WAVE FUNCTIONS

Fermions and bosons

Before we explore the role of the exclusion principle in determining atomic structures, it is interesting to look into its quantum-mechanical implications.

We saw in the previous chapter that the complete wave function ψ of the electron in a hydrogen atom can be expressed as the product of three separate wave functions, each describing that part of ψ which is a function of one of the three coordinates r, θ, ϕ . In an analogous way the complete wave function $\psi(1, 2, 3, \dots, n)$ of a system of n noninteracting particles can be expressed as the product of the wave functions $\psi(1), \psi(2), \psi(3), \dots, \psi(n)$ of the individual particles. That is,

$$\psi(1, 2, 3, \dots, n) = \psi(1) \psi(2) \psi(3) \dots \psi(n) \quad (7.5)$$

Let us use this result to look into the kinds of wave functions that can be used to describe a system of two identical particles.

Suppose one of the particles is in quantum state a and the other in state b . Because the particles are identical, it should make no difference in the probability density $|\psi|^2$ of the system if the particles are exchanged, with the one in state a replacing the one in state b , and vice versa. Symbolically, we require that

$$|\psi|^2(1, 2) = |\psi|^2(2, 1) \quad (7.6)$$

The wave function $\psi(2, 1)$ that represents the exchanged particles can be given by either

Symmetric $\psi(2, 1) = \psi(1, 2)$ (7.7)

or

Antisymmetric $\psi(2, 1) = -\psi(1, 2)$ (7.8)

and still fulfill Eq. (7.6). The wave function of the system is not itself a measurable quantity, and so it can be altered in sign by the exchange of the particles. Wave functions that are unaffected by an exchange of particles are said to be **symmetric**, while those that reverse sign upon such an exchange are said to be **antisymmetric**.

If particle 1 is in state a and particle 2 is in state b , the wave function of the system is, according to Eq. (7.5),

$$\psi_I = \psi_a(1)\psi_b(2) \quad (7.9)$$

If particle 2 is in state a and particle 1 is in state b , the wave function is

$$\psi_{II} = \psi_a(2)\psi_b(1) \quad (7.10)$$

Because the two particles are indistinguishable, we have no way to know at any moment whether ψ_I or ψ_{II} describes the system. The likelihood that ψ_I is correct at any moment is the same as the likelihood that ψ_{II} is correct.

Equivalently, we can say that the system spends half the time in the configuration whose wave function is ψ_I and the other half in the configuration whose wave function is ψ_{II} . Therefore a linear combination of ψ_I and ψ_{II} is the proper description of the system. Two such combinations, symmetric and antisymmetric, are possible:

Symmetric $\psi_S = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) + \psi_a(2)\psi_b(1)]$ (7.11)

Antisymmetric $\psi_A = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_b(2) - \psi_a(2)\psi_b(1)]$ (7.12)

The factor $1/\sqrt{2}$ is needed to normalize ψ_S and ψ_A . Exchanging particles 1 and 2 leaves ψ_S unaffected, while it reverses the sign of ψ_A . Both ψ_S and ψ_A obey Eq. (7.6).

There are a number of important distinctions between the behavior of particles in systems whose wave functions are symmetric and that of particles in systems whose wave functions are antisymmetric. The most obvious is that in the symmetric case, both particles 1 and 2 can simultaneously exist in the same state, with $a = b$. In the antisymmetric case, if we set $a = b$, we find that

$$\psi_A = \frac{1}{\sqrt{2}} [\psi_a(1)\psi_a(2) - \psi_a(2)\psi_a(1)] = 0$$

Hence the two particles *cannot* be in the same quantum state. Pauli found that no two electrons in an atom can be in the same quantum state, so we conclude that systems of electrons are described by wave functions that reverse sign upon the exchange of any pair of them.

The results of various experiments show that all particles which have odd half-integral spins ($\frac{1}{2}, \frac{3}{2}, \dots$) have wave functions that are antisymmetric to an exchange of any pair of them. Such particles, which include protons and neutrons as well as electrons, obey the exclusion principle when they are in the same system. That is, when they move in a common force field, each member of the system must be in a different quantum state. Particles of odd half-integral spin are often referred to as fermions because, as we shall learn in Chap. 9, the behavior of systems of them (such as free electrons in a metal) is governed by a statistical distribution law discovered by Fermi and Dirac.

Particles whose spins are 0 or an integer have wave functions that are symmetric to an exchange of any pair of them. These particles, which include photons, alpha particles, and helium atoms, do not obey the exclusion principle. Particles of 0 or integral spin are often referred to as bosons because the behavior of systems of them (such as photons in a cavity) is governed by a statistical distribution law discovered by Bose and Einstein.

There are other consequences of the symmetry or antisymmetry of particle wave functions besides that expressed in the exclusion principle. It is these consequences that make it useful to classify particles according to the natures of their wave functions rather than merely according to whether or not they obey the exclusion principle.

7.4 PERIODIC TABLE

Organizing the elements

In 1869 the Russian chemist Dmitri Mendeleev formulated the **periodic law** whose modern statement is

When the elements are listed in order of atomic number, elements with similar chemical and physical properties recur at regular intervals.

Although the modern quantum theory of the atom was many years in the future, Mendeleev was fully aware of the significance his work would turn out to have. As he remarked, “The periodic law, together with the revelations of spectrum analysis, have contributed to again revive an old but remarkably long-lived hope—that of discovering, if not by experiment, at least by mental effort, the *primary matter*.”

A **periodic table** is an arrangement of the elements according to atomic number in a series of rows such that elements with similar properties form vertical columns. Table 7.2 is a simple form of periodic table.

TABLE 7.2 The Periodic Table of the Elements

Group	I	II					III	IV	V	VI	VII	VIII																	
Period 1	1.008 H 1		The number above the symbol of each element is its atomic mass, and the number below the symbol is its atomic number. The elements whose atomic masses are given in parentheses do not occur in nature, but have been prepared artificially in nuclear reactions. The atomic mass in such a case is the mass number of the most long-lived radioactive isotope of the element.									4.00 He 2																	
2	6.94 Li 9.01 Be 3 4						10.81 B 5	12.01 C 6	14.01 N 7	16.00 O 8	19.00 F 9	20.18 Ne 10																	
3	22.99 Na 24.31 Mg 11 12						26.98 Al 13	28.09 Si 14	30.97 P 15	32.06 S 16	35.45 Cl 17	39.95 Ar 18																	
4	39.10 K 40.08 Ca 19 20	44.96 Sc 21	47.90 Ti 22	50.94 V 23	52.00 Cr 24	54.94 Mn 25	55.85 Fe 26	58.93 Co 27	58.70 Ni 28	63.55 Cu 29	65.38 Zn 30	69.72 Ga 31	72.59 Ge 32	74.92 As 33	78.96 Se 34	79.90 Br 35	83.8 Kr 36												
5	85.47 Rb 87.62 Sr 37 38	88.91 Y 39	91.22 Zr 40	92.91 Nb 41	95.94 Mo 42	(97) Tc 43	101.1 Ru 44	102.9 Rh 45	106.4 Pd 46	107.9 Ag 47	112.4 Cd 48	114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54												
6	132.9 Cs 55	137.3 Ba 56	* 57–71	178.5 Hf 72	180.9 Ta 73	183.9 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77	195.1 Pt 78	197.0 Au 79	200.6 Hg 80	204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86											
7	(223) Fr 87	226.0 Ra 88	† 89–105											Halogens	Inert gases														
	Alkali metals																												
	*Rare earths (Lanthanides)												138.91 La 57	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.4 Sm 62	152.0 Eu 63	157.3 Gd 64	158.9 Tb 65	162.5 Dy 66	164.9 Ho 67	167.3 Er 68	168.9 Tm 69	173.0 Yb 70	175.0 Lu 71		
	†Actinides												(227) Ac 89	232.0 Th 90	231.0 Pa 91	238.0 U 92	(237) Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(254) Es 99	(257) Fm 100	(258) Md 101	(255) No 102	(260) Lr 103	(257) Rf 104	(260) Ha 105

Elements created in the laboratory

Elements with similar properties form the **groups** shown as vertical columns in Table 7.2 (Fig. 7.4). Thus group I consists of hydrogen plus the alkali metals, which are all soft, have low melting points, and are very active chemically. Lithium, sodium, and potassium are examples. Hydrogen, although physically a nonmetal, behaves chemically much like an active metal. Group VII consists of the halogens, volatile nonmetals that form diatomic molecules in the gaseous state. Like the alkali metals, the halogens are chemically active, but as oxidizing agents rather than as reducing agents. Fluorine, chlorine, bromine, and iodine are examples; fluorine is so active it can corrode platinum. Group VIII consists of the inert gases, of which helium, neon, and argon are examples. As their name suggests, they are inactive chemically: they form virtually no compounds with other elements, and their atoms do not join together into molecules.

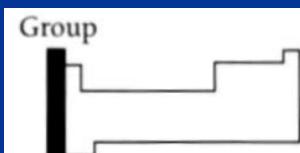


Figure 7.4 The elements in a group of the periodic table have similar properties

The horizontal rows in Table 7.2 are called **periods**. The first three periods are broken in order to keep their members aligned with the most closely related elements of the long periods below. Most of the elements are metals (Fig. 7.5). Across each period is a more or less steady transition from an active metal through less active metals and weakly active nonmetals to highly active nonmetals and finally to an inert gas (Fig. 7.6). Within each column there are also regular changes in properties, but they are far less conspicuous than those in each period. For example, increasing atomic number in the alkali metals is accompanied by greater chemical activity, while the reverse is true in the halogens.

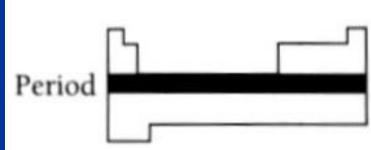


Figure 7.4 The elements in a period have different properties.

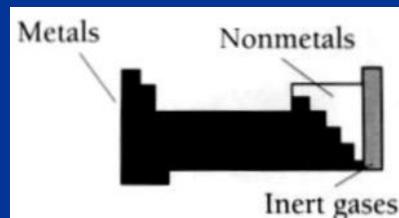


Figure 7.5 The majority of the elements are metals.

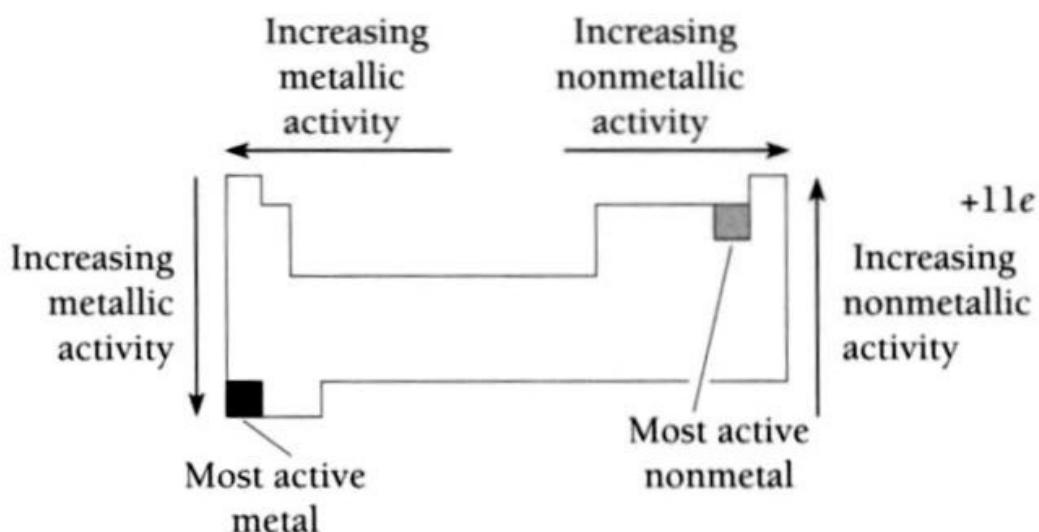


Figure 7.6 How chemical activity varies in the periodic table.

A series of **transition elements** appears in each period after the third between the group II and group III elements (Fig. 7.7). The transition elements are metals, in general hard and brittle with high melting points, that have similar chemical behavior. Fifteen of the transition elements in period 6 are virtually indistinguishable in their properties and are known as the **lanthanide** elements (or **rare earths**). Another group of closely related metals, the **actinide** elements, is found in period 7.

For over a century the periodic law has been indispensable to chemists because it provides a framework for organizing their knowledge of the elements. It is one of the triumphs of the quantum theory of the atom that it enables us to account in a natural way for the periodic law without invoking any new assumptions.

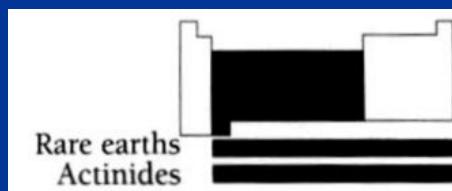


Figure 7.7 The transition elements are metals.

7.5 ATOMIC STRUCTURES

Shells and subshells of electrons

Two basic principles determine the structures of atoms with more than one electron:

- 1 A system of particles is stable when its total energy is a minimum.
- 2 Only one electron can exist in any particular quantum state in an atom.

Before we apply these rules to actual atoms, let us examine the variation of electron energy with quantum state.

While the various electrons in a complex atom certainly interact directly with one another, much about atomic structure can be understood by simply considering each electron as though it exists in a constant mean electric field. For a given electron this effective field is approximately that of the nuclear charge Ze decreased by the partial shielding of those other electrons that are closer to the nucleus (see Fig. 7.9).

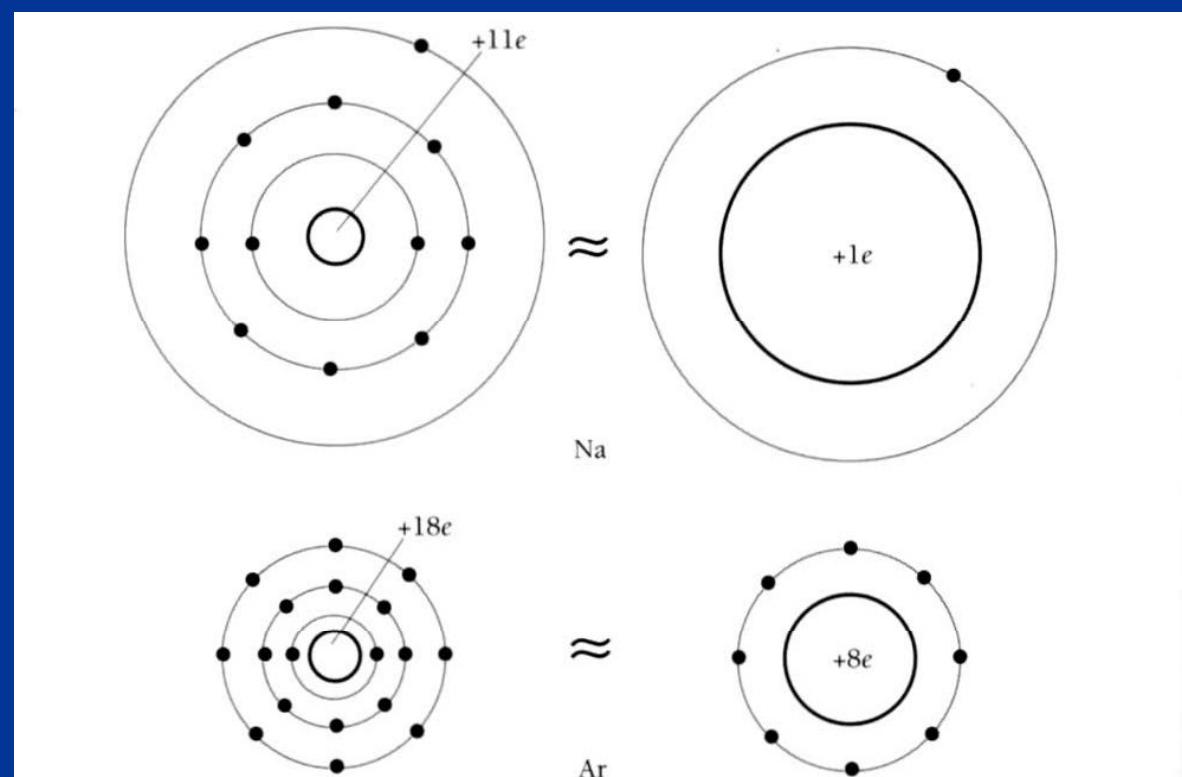


Figure 7.9 Schematic representation of electron shielding in the sodium and argon atoms. In this crude model, each outer electron in an Ar atom is acted upon by an effective nuclear charge 8 times greater than that acting upon the outer electron in a Na atom. The Ar atom is accordingly smaller in size and has a higher ionization energy. In the actual atoms, the probability-density distributions of the various electrons overlap in complex ways and thus alter the amount of shielding, but the basic effect remains the same.

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Self-Consistent Field Method (Hartree-Fock)

⇒ single-electron wave functions and energy levels for many-electron atoms

Electrons that have the same principal quantum number n usually (though not always) average roughly the same distance from the nucleus. These electrons therefore interact with roughly the same electric field and have similar energies. It is conventional to speak of such electrons as occupying the same atomic **shell**. Shells are denoted by capital letters according to the following scheme:

Atomic shells	$n = 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad \dots$	
	K L M N O ...	

(7.13)

The energy of an electron in a particular shell also depends to a certain extent on its orbital quantum number l , though not as much as on n . In a complex atom the degree to which the full nuclear charge is shielded from a given electron by intervening shells of other electrons varies with its probability-density distribution. An electron of small l is more likely to be found near the nucleus where it is poorly shielded by the other electrons than is one of higher l (see Fig. 6.11). The result is a lower total energy (that is, higher binding energy) for the electron. The electrons in each shell accordingly increase in energy with increasing l . This effect is illustrated in Fig. 7.8, which is a plot of the binding energies of various atomic electrons as a function of atomic number for the lighter elements.

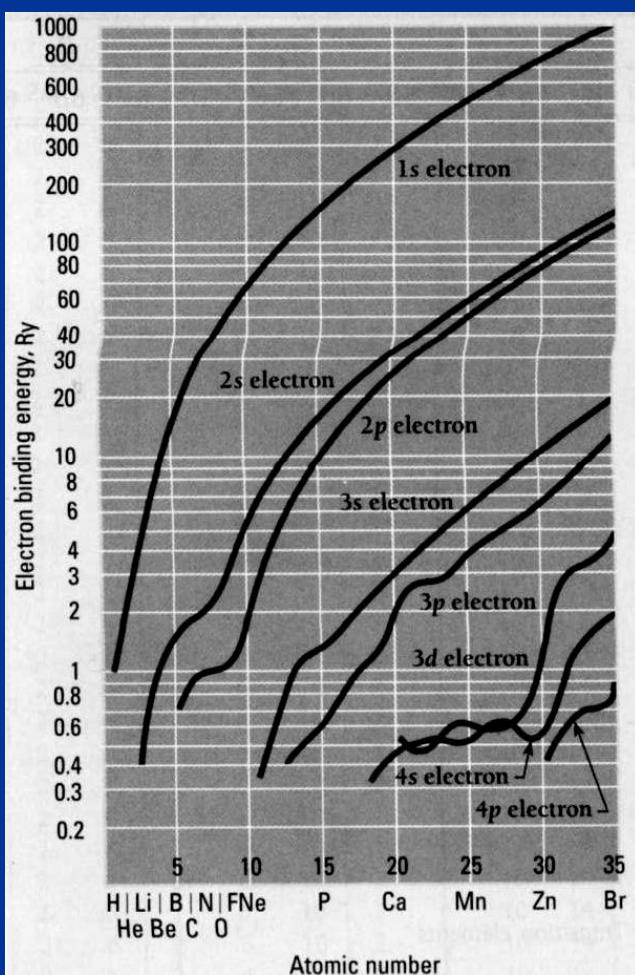
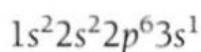


Figure 7.8 The binding energies of atomic electrons in rydbergs.
(1 Ry = 13.6 eV = ground-state energy of H atom.)

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Electrons that share a certain value of l in a shell are said to occupy the same **subshell**. All the electrons in a subshell have almost identical energies, since the dependence of electron energy upon m_l and m_s is comparatively minor.

The occupancy of the various subshells in an atom is usually expressed with the help of the notation introduced in the previous chapter for the various quantum states of the hydrogen atom. As indicated in Table 6.2, each subshell is identified by its principal quantum number n followed by the letter corresponding to its orbital quantum number l . A superscript after the letter indicates the number of electrons in that subshell. For example, the electron configuration of sodium is written



which means that the $1s$ ($n = 1, l = 0$) and $2s$ ($n = 2, l = 0$) subshells contain two electrons each, the $2p$ ($n = 2, l = 1$) subshell contains six electrons, and the $3s$ ($n = 3, l = 0$) subshell contains one electron.

Shell and Subshell Capacities

The exclusion principle limits the number of electrons that can occupy a given subshell. A subshell is characterized by a certain principal quantum number n and orbital quantum number l , where l can have the values $0, 1, 2, \dots, (n - 1)$. There are $2l + 1$ different values of the magnetic quantum number m_l for any l , since $m_l = 0, \pm 1, \pm 2, \dots, \pm l$. Finally, the spin magnetic quantum number m_s has the two possible values of $+\frac{1}{2}$ and $-\frac{1}{2}$ for any m_l . The result is that each subshell can contain a maximum of $2(2l + 1)$ electrons (Table 7.3).

TABLE 7.3 Subshell Capacities in the M ($n = 3$) Shell of an Atom

	$m_l = 0$	$m_l = -1$	$m_l = +1$	$m_l = -2$	$m_l = +2$	
$l = 0:$	↓					$\uparrow m_s = +\frac{1}{2}$
$l = 1:$	↓	↑	↑			$\downarrow m_s = -\frac{1}{2}$
$l = 2:$	↓	↓	↓	↓	↓	

The maximum number of electrons a shell can hold is the sum of the electrons in its filled subshells. This number is

$$N_{\max} = \sum_{l=0}^{l=n-1} 2(2l + 1) = 2[1 + 3 + 5 + \dots + 2(n - 1) + 1] \\ = 2[1 + 3 + 5 + \dots + 2n - 1]$$

The quantity in brackets has n terms whose average value is $\frac{1}{2}[1 + (2n - 1)]$. The number of electrons in a filled shell is therefore

$$N_{\max} = (n)(2)(\frac{1}{2})[1 + (2n - 1)] = 2n^2 \quad (7.14)$$

Thus a closed K shell holds 2 electrons, a closed L shell holds 8 electrons, a closed M shell holds 18 electrons, and so on.

7.6 EXPLAINING THE PERIODIC TABLE

How an atom's electron structure determines its chemical behavior

The notion of electron shells and subshells fits perfectly into the pattern of the periodic table, which mirrors the atomic structures of the elements. Let us see how this pattern arises.

An atomic shell or subshell that contains its full quota of electrons is said to be **closed**. A closed s subshell ($l = 0$) holds two electrons, a closed p subshell ($l = 1$) six electrons, a closed d subshell ($l = 2$) ten electrons, and so on.

Figure 7.12 The sequence of quantum states in an atom. Not to scale.

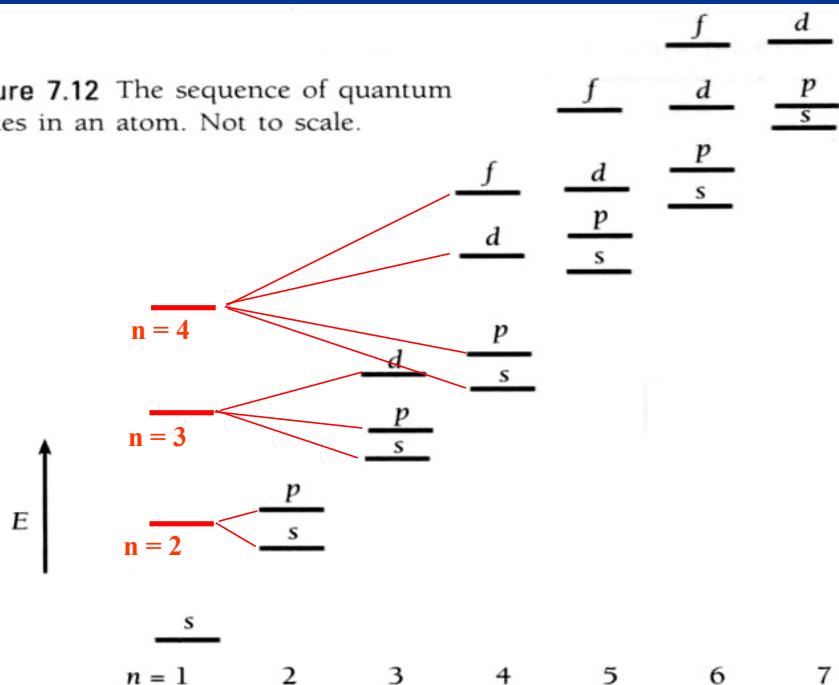


Figure 7.12 illustrates this sequence. The remarkable similarities in chemical behavior among the lanthanides and actinides are easy to understand on the basis of this sequence. All the lanthanides have the same $5s^25p^66s^2$ configurations but have incomplete $4f$ subshells. The addition of $4f$ electrons has almost no effect on the chemical properties of the lanthanide elements, which are determined by the outer electrons. Similarly, all the actinides have $6s^26p^67s^2$ configurations and differ only in the numbers of their $5f$ and $6d$ electrons.

The order in which electron subshells tend to be filled, together with the maximum occupancy of each subshell, is usually as follows:

$$\begin{array}{cccccccccc}
 1s^2 & 2s^2 & 2p^6 & 3s^2 & 3p^6 & 4s^2 & 3d^{10} & 4p^6 & 5s^2 \\
 4d^{10} & 5p^6 & 6s^2 & 4f^{14} & 5d^{10} & 6p^6 & 7s^2 & 6d^{10} & 5f^{14}
 \end{array}$$

TABLE 7.4 Electron Configurations of the Elements

	<i>K</i>	<i>L</i>		<i>M</i>			<i>N</i>				<i>O</i>			<i>P</i>			<i>Q</i>		
		<i>1s</i>	<i>2s</i>	<i>2p</i>	<i>3s</i>	<i>3p</i>	<i>3d</i>	<i>4s</i>	<i>4p</i>	<i>4d</i>	<i>4f</i>	<i>5s</i>	<i>5p</i>	<i>5d</i>	<i>5f</i>	<i>6s</i>	<i>6p</i>	<i>6d</i>	<i>7s</i>
1 H	1																		
2 He	2	Inert gas																	
3 Li	2		1	← Alkali metal															
4 Be	2	2																	
5 B	2	2	1																
6 C	2	2	2																
7 N	2	2	3																
8 O	2	2	4																
9 F	2	2	5	← Halogen															
10 Ne	2	2	6	Inert gas															
11 Na	2	2	6		1	← Alkali metal													
12 Mg	2	2	6	2															
13 Al	2	2	6	2	1														
14 Si	2	2	6	2	2														
15 P	2	2	6	2	3														
16 S	2	2	6	2	4														
17 Cl	2	2	6	2	5	← Halogen													
18 Ar	2	2	6	2	6	Inert gas													
19 K	2	2	6	2	6			1	← Alkali metal										
20 Ca	2	2	6	2	6				2										
21 Sc	2	2	6	2	6		1	2											
22 Ti	2	2	6	2	6		2	2											
23 V	2	2	6	2	6		3	2											
24 Cr	2	2	6	2	6		5	1											
25 Mn	2	2	6	2	6		5	2											
26 Fe	2	2	6	2	6		6	2											
27 Co	2	2	6	2	6		7	2											
28 Ni	2	2	6	2	6	8	2												
29 Cu	2	2	6	2	6	10	1												
30 Zn	2	2	6	2	6	10	2												

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TABLE 7.4 Electron Configurations of the Elements

	<i>K</i>	<i>L</i>		<i>M</i>			<i>N</i>				<i>O</i>			<i>P</i>			<i>Q</i>		
		<i>1s</i>	<i>2s</i>	<i>2p</i>	<i>3s</i>	<i>3p</i>	<i>3d</i>	<i>4s</i>	<i>4p</i>	<i>4d</i>	<i>4f</i>	<i>5s</i>	<i>5p</i>	<i>5d</i>	<i>5f</i>	<i>6s</i>	<i>6p</i>	<i>6d</i>	<i>7s</i>
31 Ga	2	2	6	2	6	10	2	1											
32 Ge	2	2	6	2	6	10	2	2											
33 As	2	2	6	2	6	10	2	3											
34 Se	2	2	6	2	6	10	2	4											
35 Br	2	2	6	2	6	10	2	5	← Halogen										
36 Kr	2	2	6	2	6	10	2	6	Inert gas										
37 Rb	2	2	6	2	6	10	2	6					1	← Alkali metal					
38 Sr	2	2	6	2	6	10	2	6					2						
39 Y	2	2	6	2	6	10	2	6	1				2						
40 Zr	2	2	6	2	6	10	2	6	2				2						
41 Nb	2	2	6	2	6	10	2	6	4				1						
42 Mo	2	2	6	2	6	10	2	6	5				1						
43 Tc	2	2	6	2	6	10	2	6	5				2	Transition	elements				
44 Ru	2	2	6	2	6	10	2	6	7				1						
45 Rh	2	2	6	2	6	10	2	6	8				1						
46 Pd	2	2	6	2	6	10	2	6	10										
47 Ag	2	2	6	2	6	10	2	6	10					1					
48 Cd	2	2	6	2	6	10	2	6	10				2						
49 In	2	2	6	2	6	10	2	6	10				2	1					
50 Sn	2	2	6	2	6	10	2	6	10				2	2					
51 Sb	2	2	6	2	6	10	2	6	10				2	3					
52 Te	2	2	6	2	6	10	2	6	10				2	4					

	<i>K</i>	<i>L</i>		<i>M</i>			<i>N</i>				<i>O</i>			<i>P</i>				
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	
53 I	2	2	6	2	6	10	2	6	10		2	5	← Halogen					
54 Xe	2	2	6	2	6	10	2	6	10		2	6	← Inert gas					
55 Cs	2	2	6	2	6	10	2	6	10		2	6		1 ← Alkali metal				
56 Ba	2	2	6	2	6	10	2	6	10		2	6		2				
57 La	2	2	6	2	6	10	2	6	10		2	6	1					
58 Ce	2	2	6	2	6	10	2	6	10	2	2	6		2				
59 Pr	2	2	6	2	6	10	2	6	10	3	2	6		2				
60 Nd	2	2	6	2	6	10	2	6	10	4	2	6		2				
61 Pm	2	2	6	2	6	10	2	6	10	5	2	6		2				
62 Sm	2	2	6	2	6	10	2	6	10	6	2	6		2				
63 Eu	2	2	6	2	6	10	2	6	10	7	2	6		2				
64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1	2				
65 Tb	2	2	6	2	6	10	2	6	10	9	2	6		2				
66 Dy	2	2	6	2	6	10	2	6	10	10	2	6		2				
67 Ho	2	2	6	2	6	10	2	6	10	11	2	6		2				
68 Er	2	2	6	2	6	10	2	6	10	12	2	6		2				
69 Tm	2	2	6	2	6	10	2	6	10	13	2	6		2				
70 Yb	2	2	6	2	6	10	2	6	10	14	2	6		2				
71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1	2				
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	2				
73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	2				
74 W	2	2	6	2	6	10	2	6	10	14	2	6	4	2				
75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5	2				
76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6	2				
77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7	2				
78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9	1				
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1				
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10	2				

81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1			
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2			
83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3			
84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4			
85 At	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5	← Halogen		
86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	← Inert gas		
87 Fr	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1 ← Alkali metal		
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	6	
89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2	
90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2	2	
91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	1	2	
92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93 Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94 Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2
95 Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2
96 Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97 Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98 Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6		2
99 Es	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6		2
100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6		2
101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6		2
102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6		2
103 Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2

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The total orbital and spin angular momenta of the electrons in a closed subshell are zero, and their effective charge distributions are perfectly symmetrical (see Exercise 23 of Chap. 6). The electrons in a closed shell are all very tightly bound, since the positive nuclear charge is large relative to the negative charge of the inner shielding electrons (Fig. 7.9). Because an atom with only closed shells has no dipole moment, it does not attract other electrons, and its electrons cannot be easily detached. We expect such atoms to be passive chemically, like the inert gases—and the inert gases all turn out to have closed-shell electron configurations or their equivalents. This is evident from Table 7.4, which shows the electron configurations of the elements.

An atom of any of the alkali metals of group I has a single s electron in its outer shell. Such an electron is relatively far from the nucleus. It is also shielded by the inner electrons from all but an effective nuclear charge of approximately $+e$ rather than $+Ze$. Relatively little work is needed to detach an electron from such an atom, and the alkali metals accordingly form positive ions of charge $+e$ readily.

At the other extreme from alkali metal atoms, which tend to lose their outermost electrons, are halogen atoms, whose imperfectly shielded nuclear charges tend to complete their outer subshells by picking up an additional electron each. Halogen atoms accordingly form negative ions of charge $-e$ readily. Reasoning of this kind accounts for the similarities of the members of the various groups of the periodic table.

Example 7.2

The ionization energy of lithium is 5.39 eV. Use this figure to find the effective charge that acts on the outer (2s) electron of the lithium atom.

Solution

If the effective nuclear charge is Ze instead of e , Eq. (4.15) becomes

$$E_n = \frac{Z^2 E_1}{n^2}$$

Here $n = 2$ for the 2s electron, its ionization energy is $E_2 = 5.39$ eV, and $E_1 = 13.6$ eV is the ionization energy of the hydrogen atom. Hence

$$Z = n \sqrt{\frac{E_2}{E_1}} = 2 \sqrt{\frac{5.39 \text{ eV}}{13.6 \text{ eV}}} = 1.26$$

The effective charge is $1.26e$ and not e because the shielding of $2e$ of the nuclear charge of $3e$ by the two 1s electrons is not complete: as we can see in Fig. 6.11, the 2s electron has a certain probability of being found inside the 1s electrons.

Figure 7.10 shows how the ionization energies of the elements vary with atomic number. As we expect, the inert gases have the highest ionization energies and the alkali metals the lowest. The larger an atom, the farther the outer electron is from the nucleus and the weaker the force is that holds it to the atom. This is why the ionization energy generally decreases as we go down a group in the periodic table. The increase in ionization energy from left to right across any period is accounted for by the increase in nuclear charge while the number of inner shielding electrons stays constant. In period 2, for instance, the outer electron in a lithium atom is held by an effective charge of about $+e$, while each outer electron in beryllium, boron, carbon, and so on, is held by effective charges of about $+2e$, $+3e$, $+4e$, and so on. The ionization energy of lithium is 5.4 eV whereas that of neon, which ends the period, is 21.6 eV.

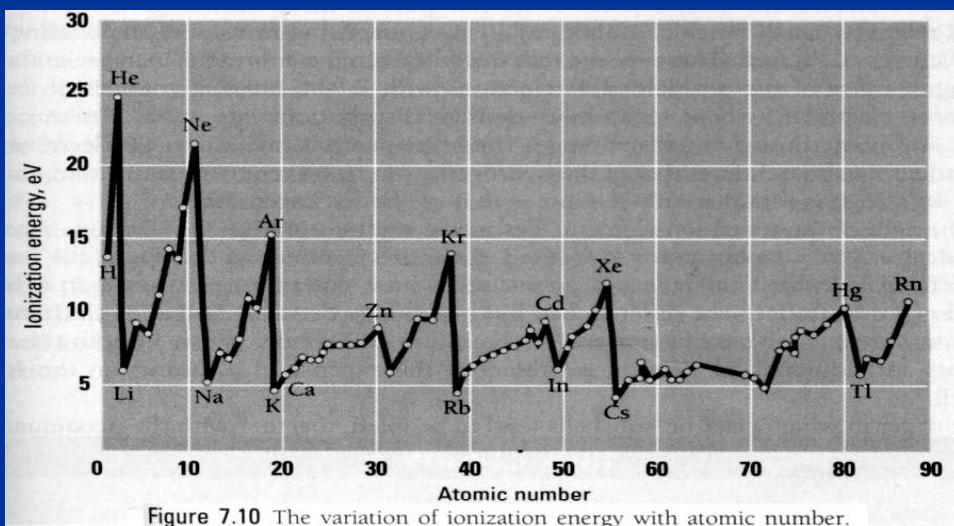


Figure 7.10 The variation of ionization energy with atomic number.

Although, strictly speaking, an atom of a certain kind cannot be said to have a definite size, from a practical point of view a fairly definite size can usually be attributed to it on the basis of the observed interatomic spacings in closely packed crystal lattices. Figure 7.11 shows how the resulting radii vary with atomic number. The periodicity here is as conspicuous as in the case of ionization energy and has a similar origin in the partial shielding by inner electrons of the full nuclear charge. The greater the shielding, the lower the binding energy of an outer electron and the farther it is on the average from the nucleus.

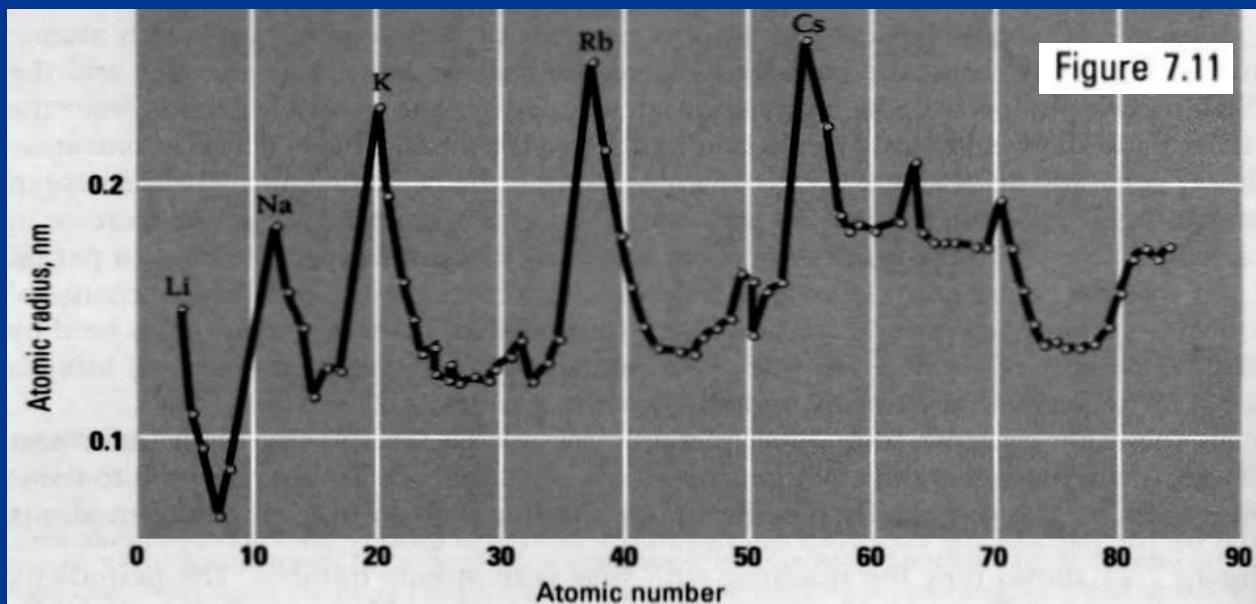


Figure 7.11

The relatively small range of atomic radii is not surprising in view of the binding-energy curves of Fig. 7.8. There we see that in contrast to the enormous increase in the binding energies of the unshielded 1s electrons with Z , the binding energies of the outermost electrons (whose probability-density distributions are what determine atomic size) vary through a narrow range. The heaviest atoms, with over 90 electrons, have radii only about 3 times that of the hydrogen atom, and even the cesium atom, the largest in size, has a radius only 4.4 times that of the hydrogen atom.

The origin of the transition elements lies in the tighter binding of s electrons than d or f electrons in complex atoms, discussed in the previous section (see Fig. 7.8). The first element to exhibit this effect is potassium, whose outermost electron is in a 4s instead of a 3d substate. The difference in binding energy between 3d and 4s electrons is not very great, as the configurations of chromium and copper show. In both these elements an additional 3d electron is present at the expense of a vacancy in the 4s subshell.

<Table 7.4>

These irregularities in the binding energies of atomic electrons are also responsible for the lack of completely full outer shells in the heavier inert gases. Helium ($Z = 2$) and neon ($Z = 10$) contain closed K and L shells, respectively, but argon ($Z = 18$) has only 8 electrons in its M shell, corresponding to closed 3s and 3p subshells. The reason the 3d subshell is not filled next is that 4s electrons have higher binding energies than do 3d electrons. Hence the 4s subshell is filled first in potassium and calcium. As the 3d subshell is filled in successively heavier transition elements, there are still one or two outer 4s electrons that make possible chemical activity. Not until krypton ($Z = 36$) is another inert gas reached, and here a similarly incomplete outer shell occurs with only the 4s and 4p subshells filled. Following krypton is rubidium ($Z = 37$), which skips both the 4d and 4f subshells to have a 5s electron. The next inert gas is xenon ($Z = 54$), which has filled 4d, 5s, and 5p subshells, but now even the inner 4f subshell is empty as well as the 5d and 5f subshells. The same pattern recurs with the remainder of the inert gases.

<Table 7.4>

Hund's Rule

In general, the electrons in a subshell remain unpaired—that is, have parallel spins—whenever possible (Table 7.5). This principle is called **Hund's rule**. The ferromagnetism of iron, cobalt, and nickel ($Z = 26, 27, 28$) is in part a consequence of Hund's rule. The $3d$ subshells of their atoms are only partially occupied, and the electrons in these subshells do not pair off to permit their spin magnetic moments to cancel out. In iron, for instance, five of the six $3d$ electrons have parallel spins, so that each iron atom has a large resultant magnetic moment.

The origin of Hund's rule lies in the mutual repulsion of atomic electrons. Because of this repulsion, the farther apart the electrons in an atom are, the lower the energy of the atom. Electrons in the same subshell with the same spin must have different m_l values and accordingly are described by wave functions whose spatial distributions are different. Electrons with parallel spins are therefore more separated in space than they would be if they paired off. This arrangement, having less energy, is the more stable one.

TABLE 7.5 Electron configurations of elements from $Z = 5$ to $Z = 10$. The p electrons have parallel spins whenever possible, in accord with Hund's rule.

Element	Atomic number	Configuration	Spins of p electrons
Boron	5	$1s^2 2s^2 2p^1$	↑
Carbon	6	$1s^2 2s^2 2p^2$	↑ ↑
Nitrogen	7	$1s^2 2s^2 2p^3$	↑ ↑ ↑
Oxygen	8	$1s^2 2s^2 2p^4$	↓ ↑ ↑
Fluorine	9	$1s^2 2s^2 2p^5$	↓ ↓ ↑
Neon	10	$1s^2 2s^2 2p^6$	↓ ↓ ↓

7.7 SPIN-ORBIT COUPLING

Angular momenta linked magnetically

The fine-structure doubling of spectral lines arises from a magnetic interaction between the spin and orbital angular momenta of an atomic electron called **spin-orbit coupling**.

Spin-orbit coupling can be understood in terms of a straightforward classical model. An electron revolving about a nucleus finds itself in a magnetic field because in its own frame of reference, the nucleus is circling about it (Fig. 7.13). This magnetic field then acts upon the electron's own spin magnetic moment to produce a kind of internal Zeeman effect.

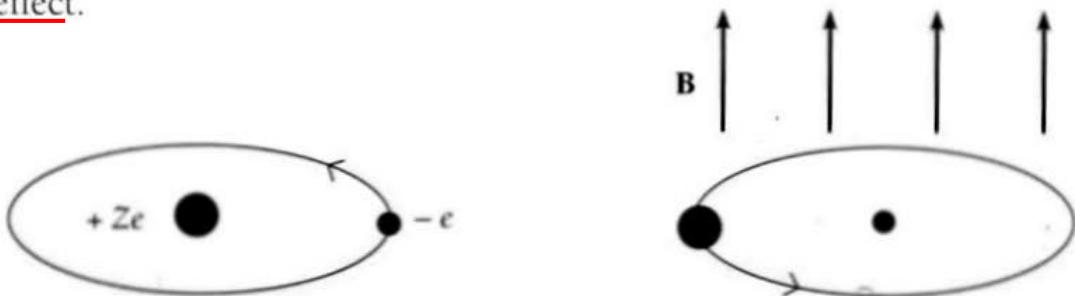


Figure 7.13 (a) An electron circles an atomic nucleus, as viewed from the frame of reference of the nucleus. (b) From the electron's frame of reference, the nucleus is circling it. The magnetic field the electron experiences as a result is directed upward from the plane of the orbit. The interaction between the electron's spin magnetic moment and this magnetic field leads to the phenomenon of spin-orbit coupling.

The potential energy U_m of a magnetic dipole of moment μ in a magnetic field \mathbf{B} is, as we know,

$$U_m = -\mu B \cos \theta \quad (6.38)$$

where θ is the angle between μ and \mathbf{B} . The quantity $\mu \cos \theta$ is the component of μ parallel to \mathbf{B} . In the case of the spin magnetic moment of the electron this component is $\mu_{sz} = \pm \mu_B$. Hence

$$\mu \cos \theta = \pm \mu_B$$

and so

Spin-orbit coupling $U_m = \pm \mu_B B \quad (7.15)$

Depending on the orientation of its spin vector \mathbf{S} , the energy of an atomic electron will be higher or lower by $\mu_B B$ than its energy without spin-orbit coupling. The result is that every quantum state (except s states in which there is no orbital angular momentum) is split into two substates.

The assignment of $s = \frac{1}{2}$ is the only one that agrees with the observed fine-structure doubling. Because what would be single states without spin are in fact twin states, the $2s + 1$ possible orientations of the spin vector \mathbf{S} must total 2. With $2s + 1 = 2$, the result is $s = \frac{1}{2}$.

Example 7.3

Estimate the magnetic energy U_m for an electron in the $2p$ state of a hydrogen atom using the Bohr model, whose $n = 2$ state corresponds to the $2p$ state.

Solution

A circular wire loop of radius r that carries the current I has a magnetic field at its center of magnitude

$$B = \frac{\mu_0 I}{2r}$$

The orbiting electron “sees” itself circled f times per second by the proton of charge $+e$ that is the nucleus, for a resulting magnetic field of

$$B = \frac{\mu_0 f e}{2r}$$

The frequency of revolution and orbital radius for $n = 2$ are, from Eqs. (4.4) and (4.14),

$$f = \frac{v}{2\pi r} = 8.4 \times 10^{14} \text{ s}^{-1}$$

$$r = n^2 a_0 = 4a_0 = 2.1 \times 10^{-10} \text{ m}$$

Hence the magnetic field experienced by the electron is

$$B = \frac{(4\pi \times 10^{-7} \text{ T} \cdot \text{m/A})(8.4 \times 10^{14} \text{ s}^{-1})(1.6 \times 10^{-19} \text{ C})}{(2)(2.1 \times 10^{-10} \text{ m})} = 0.40 \text{ T}$$

which is a fairly strong field. Since the value of the Bohr magneton is $\mu_B = e\hbar/2m = 9.27 \times 10^{-24} \text{ J/T}$, the magnetic energy of the electron is

$$U_m = \mu_B B = 3.7 \times 10^{-24} \text{ J} = 2.3 \times 10^{-5} \text{ eV}$$

The energy difference between the upper and lower substates is twice this, $4.6 \times 10^{-5} \text{ eV}$, which is not far from what is observed (Fig. 7.14).

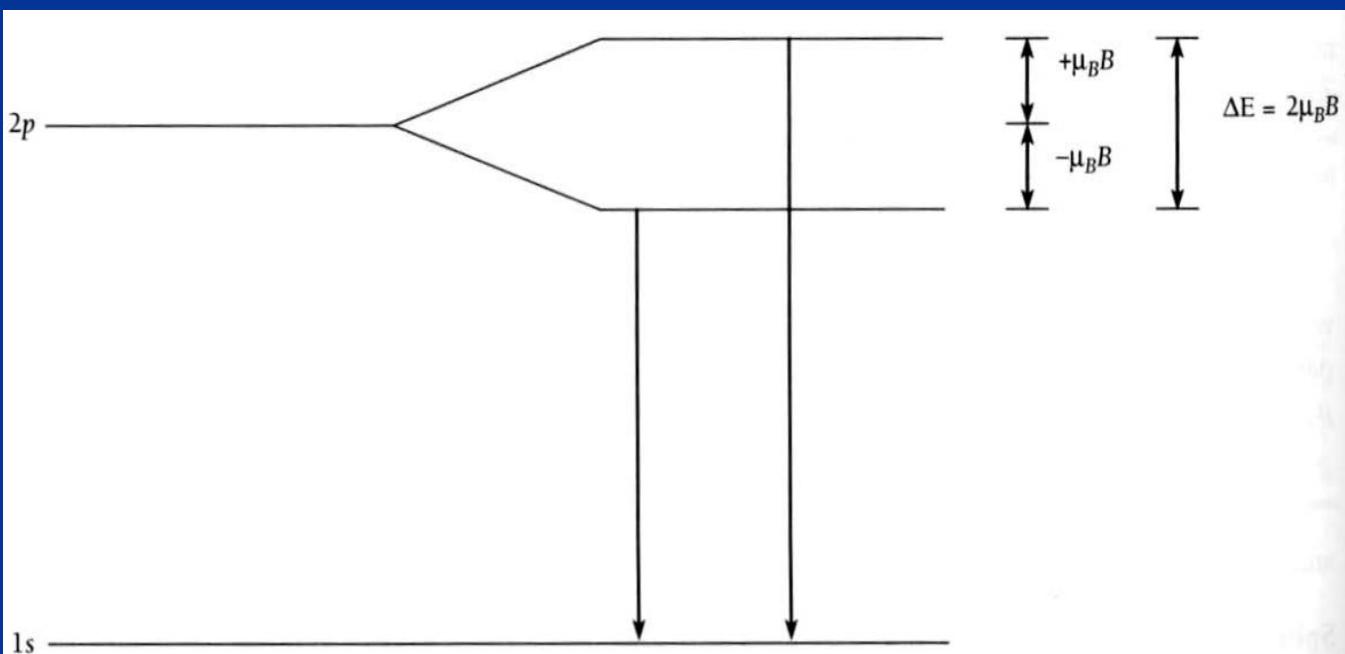


Figure 7.14 Spin-orbit coupling splits the $2p$ state in the hydrogen atom into two substates ΔE apart. The result is a doublet (two closely spaced lines) instead of a single spectral line for the $2p \rightarrow 1s$ transition.

7.8 TOTAL ANGULAR MOMENTUM

Both magnitude and direction are quantized

Each electron in an atom has a certain orbital angular momentum \mathbf{L} and a certain spin angular momentum \mathbf{S} , both of which contribute to the total angular momentum \mathbf{J} of the atom. Let us first consider an atom whose total angular momentum is provided by a single electron. Atoms of the elements in group I of the periodic table—hydrogen, lithium, sodium, and so on—are of this kind. They have single electrons outside closed inner shells (except for hydrogen, which has no inner electrons) and the exclusion principle ensures that the total angular momentum and magnetic moment of a closed shell are zero. Also in this category are the ions He^+ , Be^+ , Mg^+ , B^{2+} , Al^{2+} , and so on.

In these atoms and ions, the outer electron's total angular momentum \mathbf{J} is the vector sum of \mathbf{L} and \mathbf{S} :

Total atomic angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (7.16)$$

Like all angular momenta, \mathbf{J} is quantized in both magnitude and direction. The magnitude of \mathbf{J} is given by

$$J = \sqrt{j(j+1)}\hbar \quad j = l+s = l \pm \frac{1}{2} \quad (7.17)$$

If $l = 0$, j has the single value $j = \frac{1}{2}$. The component J_z of \mathbf{J} in the z direction is given by

$$J_z = m_j\hbar \quad m_j = -j, -j+1, \dots, j-1, j \quad (7.18)$$

Because of the simultaneous quantization of \mathbf{J} , \mathbf{L} , and \mathbf{S} they can have only certain specific relative orientations. This is a general conclusion; in the case of a one-electron atom, there are only two relative orientations possible. One relative orientation corresponds to $j = l + s$, so that $J > L$, and the other to $j = l - s$, so that $J < L$. Figure 7.15 shows the two ways in which \mathbf{L} and \mathbf{S} can combine to form \mathbf{J} when $l = 1$. Evidently the orbital and spin angular-momentum vectors can never be exactly parallel or antiparallel to each other or to the total angular-momentum vector.

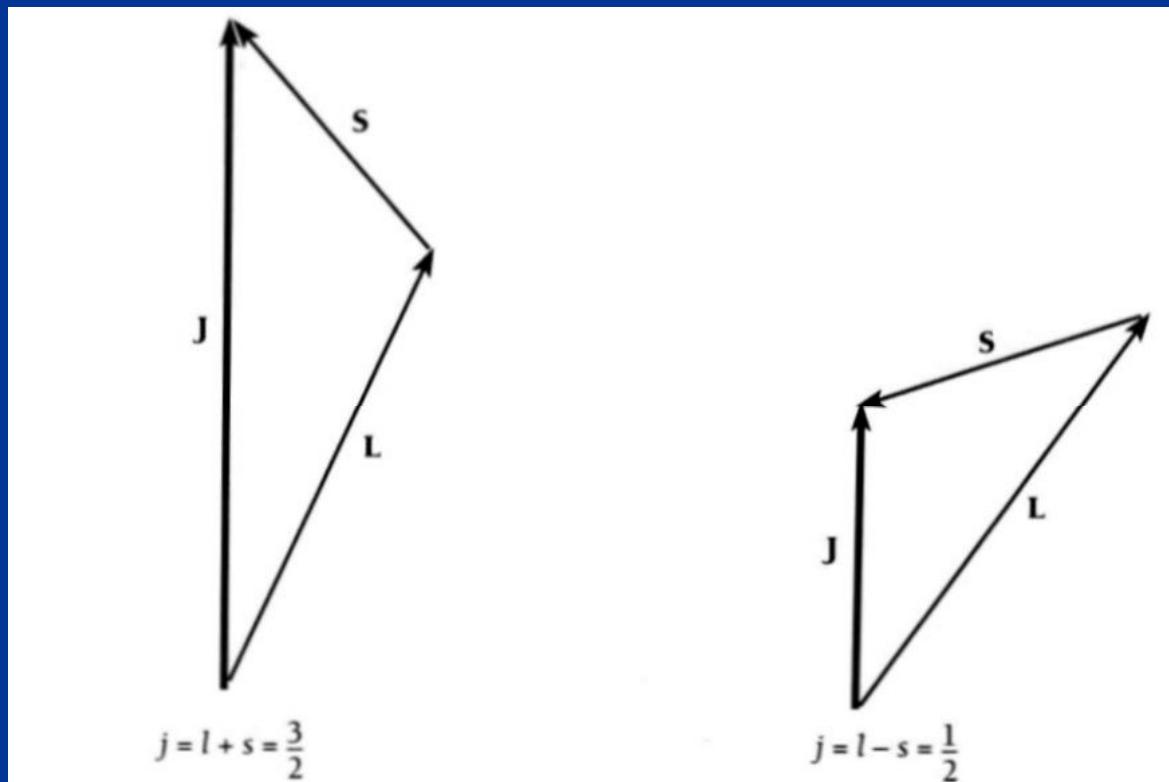


Figure 7.15 The two ways in which \mathbf{L} and \mathbf{S} can be added to form \mathbf{J} when $l = 1, s = \frac{1}{2}$.

LS Coupling

When more than one electron contributes orbital and spin angular momenta to the total angular momentum \mathbf{J} of an atom, \mathbf{J} is still the vector sum of these individual momenta. The usual pattern for all but the heaviest atoms is that the orbital angular momenta \mathbf{L}_i of the various electrons are coupled together into a single resultant \mathbf{L} . The spin angular momenta \mathbf{S}_i are also coupled together into another single resultant \mathbf{S} . The momenta \mathbf{L} and \mathbf{S} then interact via the spin-orbit effect to form a total angular momentum \mathbf{J} . This scheme, called **LS coupling**, can be summarized as follows:

$$\begin{aligned} \mathbf{L} &= \sum \mathbf{L}_i \\ \mathbf{S} &= \sum \mathbf{S}_i \\ \mathbf{J} &= \mathbf{L} + \mathbf{S} \end{aligned} \tag{7.19}$$

LS coupling

The angular momentum magnitudes L, S, J and their z components L_z, S_z , and J_z are all quantized in the usual ways, with the respective quantum numbers $\mathbf{L}, \mathbf{S}, \mathbf{J}, \mathbf{M_L}, \mathbf{M_S}$, and $\mathbf{M_J}$. Hence

$$\begin{aligned} L &= \sqrt{\mathbf{L}(\mathbf{L} + 1)} \hbar \\ L_z &= \mathbf{M_L} \hbar \\ S &= \sqrt{\mathbf{S}(\mathbf{S} + 1)} \hbar \\ S_z &= \mathbf{M_S} \hbar \\ J &= \sqrt{\mathbf{J}(\mathbf{J} + 1)} \hbar \\ J_z &= \mathbf{M_J} \hbar \end{aligned} \tag{7.20}$$

Both \mathbf{L} and $\mathbf{M_L}$ are always integers or 0, while the other quantum numbers are half-integral if an odd number of electrons is involved and integral or 0 if an even number of electrons is involved. When $\mathbf{L} > \mathbf{S}$, \mathbf{J} can have $2\mathbf{S} + 1$ values; when $\mathbf{L} < \mathbf{S}$, \mathbf{J} can have $2\mathbf{L} + 1$ values.

Example 7.4

What are the possible orientations of \mathbf{J} for the $j = \frac{3}{2}$ and $j = \frac{1}{2}$ states that correspond to $l = 1$?

Solution

For the $j = \frac{3}{2}$ state, Eq. (7.18) gives $m_j = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$. For the $j = \frac{1}{2}$ state, $m_j = -\frac{1}{2}, \frac{1}{2}$. Figure 7.16 shows the orientations of \mathbf{J} relative to the z axis for these values of j .

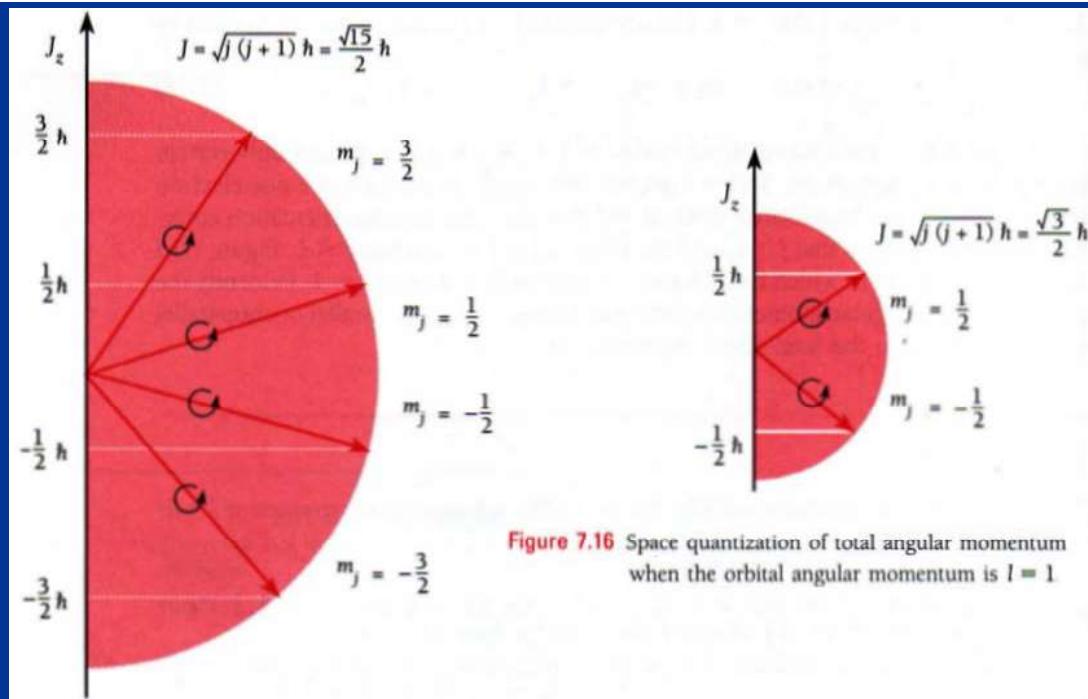


Figure 7.16 Space quantization of total angular momentum when the orbital angular momentum is $l = 1$

The angular momenta \mathbf{L} and \mathbf{S} interact magnetically, as we saw in Sec. 7.7. If there is no external magnetic field, the total angular momentum \mathbf{J} is conserved in magnitude and direction, and the effect of the internal torques is the precession of \mathbf{L} and \mathbf{S} around the direction of their resultant \mathbf{J} (Fig. 7.17). However, if there is an external magnetic field \mathbf{B} present, then \mathbf{J} precesses about the direction of \mathbf{B} while \mathbf{L} and \mathbf{S} continue precessing about \mathbf{J} , as in Fig. 7.18. The precession of \mathbf{J} about \mathbf{B} is what gives rise to the anomalous Zeeman effect, since different orientations of \mathbf{J} involve slightly different energies in the presence of \mathbf{B} .

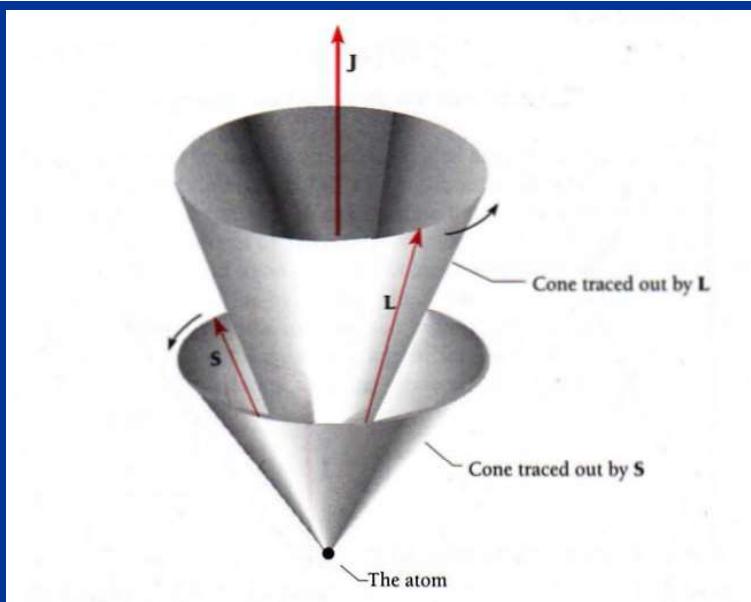


Figure 7.17 The orbital and spin angular-momentum vectors \mathbf{L} and \mathbf{S} precess about \mathbf{J} .

Link

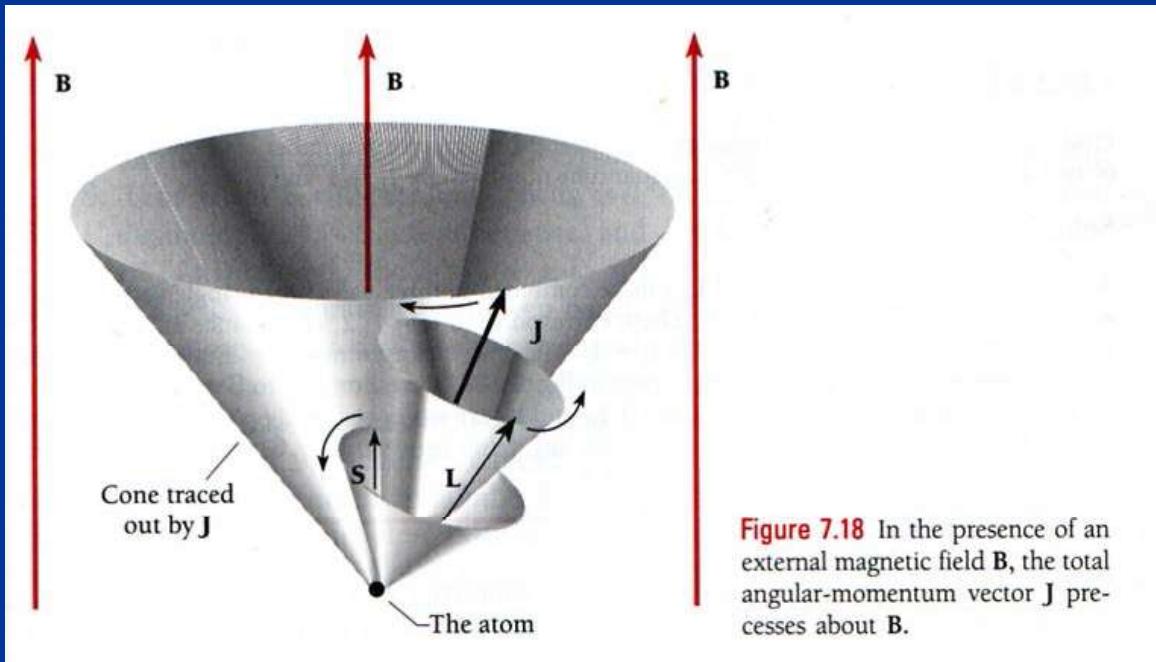


Figure 7.18 In the presence of an external magnetic field \mathbf{B} , the total angular-momentum vector \mathbf{J} precesses about \mathbf{B} .

Example 7.5

Find the possible values of the total angular-momentum quantum number \mathbf{J} under LS coupling of two atomic electrons whose orbital quantum numbers are $l_1 = 1$ and $l_2 = 2$.

Solution

As in Fig. 7.19a, the vectors \mathbf{L}_1 and \mathbf{L}_2 can be combined in three ways into a single vector \mathbf{L} that is quantized according to Eq. (7.20). These correspond to $\mathbf{L} = 1, 2$, and 3 since all values of \mathbf{L} are possible from $|l_1 - l_2|$ ($= 1$ here) to $l_1 + l_2$. The spin quantum number s is always $\frac{1}{2}$, which gives the two possibilities for $\mathbf{S}_1 + \mathbf{S}_2$ shown in Fig. 7.19b, corresponding to $\mathbf{S} = 0$ and $\mathbf{S} = 1$.

We note that if the vector sums are not 0 , \mathbf{L}_1 and \mathbf{L}_2 can never be exactly parallel to \mathbf{L} , nor can \mathbf{S}_1 and \mathbf{S}_2 be parallel to \mathbf{S} . Because \mathbf{J} can have any value between $|\mathbf{L} - \mathbf{S}|$ and $\mathbf{L} + \mathbf{S}$, the five possible values here are $\mathbf{J} = 0, 1, 2, 3$, and 4 .

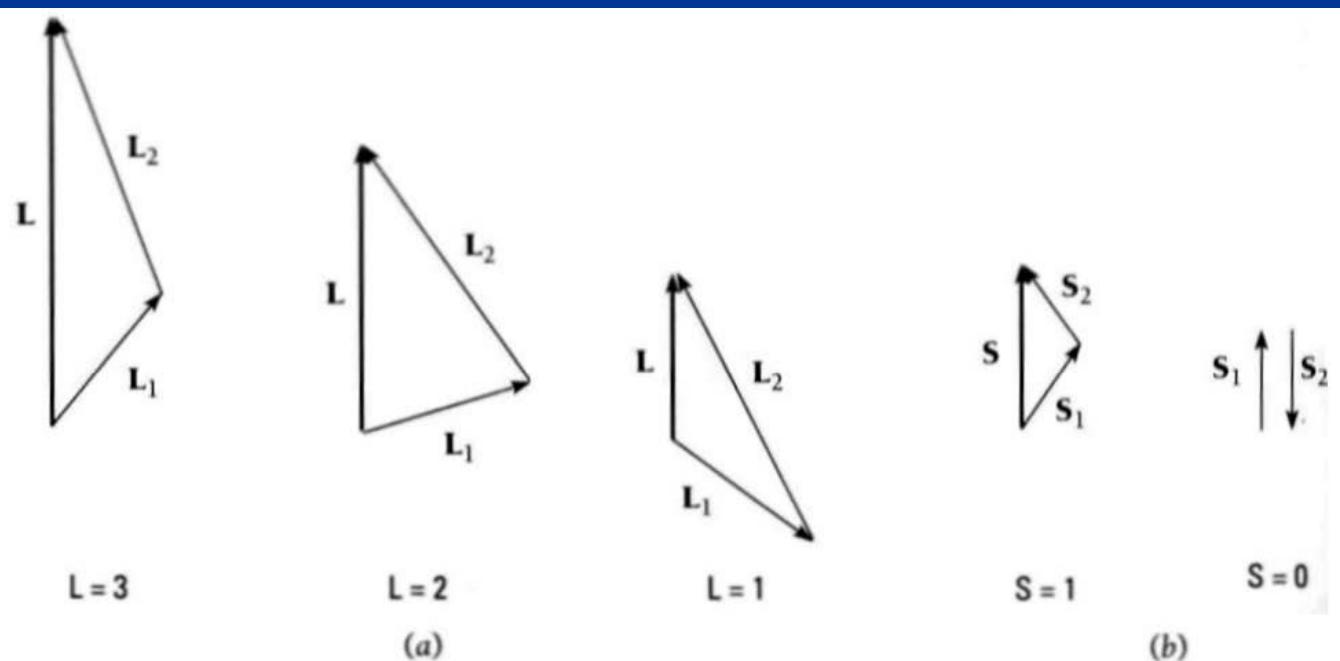


Figure 7.19 When $l_1 = 1$, $s_1 = \frac{1}{2}$, and $l_2 = 2$, $s_2 = \frac{1}{2}$, there are three ways in which \mathbf{L}_1 and \mathbf{L}_2 can combine to form \mathbf{L} and two ways in which \mathbf{S}_1 and \mathbf{S}_2 can combine to form \mathbf{S} .

Atomic nuclei also have intrinsic angular momenta and magnetic moments, and these contribute to the total atomic angular momenta and magnetic moments. Such contributions are small because nuclear magnetic moments are $\sim 10^{-3}$ the magnitude of electronic moments. They lead to the **hyperfine structure** of spectral lines with typical spacings between components of $\sim 10^{-3}$ nm as compared with typical fine-structure spacings a hundred times greater.

Term Symbols

In Sec. 6.5 we saw that individual orbital angular-momentum states are customarily described by a lowercase letter, with s corresponding to $l = 0$, p to $l = 1$, d to $l = 2$, and so on. A similar scheme using capital letters is used to designate the entire electronic state of an atom according to its total orbital angular-momentum quantum number \mathbf{L} as follows:

$$\begin{array}{cccccccc} \mathbf{L} = 0 & 1 & 2 & 3 & 4 & 5 & 6 \dots \\ S & P & D & F & G & H & I \dots \end{array}$$

A superscript number before the letter (2P , for instance) is used to indicate the **multiplicity** of the state, which is the number of different possible orientations of \mathbf{L} and \mathbf{S} and hence the number of different possible values of J . The multiplicity is equal to $2\mathbf{S} + 1$ in the usual situation where $\mathbf{L} > \mathbf{S}$, since J ranges from $\mathbf{L} + \mathbf{S}$ through 0 to $\mathbf{L} - \mathbf{S}$. Thus when $\mathbf{S} = 0$, the multiplicity is 1 (a **singlet** state) and $J = \mathbf{L}$; when $\mathbf{S} = \frac{1}{2}$, the multiplicity is 2 (a **doublet** state) and $J = \mathbf{L} \pm \frac{1}{2}$; when $\mathbf{S} = 1$, the multiplicity is 3 (a **triplet** state) and $J = \mathbf{L} + 1, \mathbf{L}$, or $\mathbf{L} - 1$; and so on. (In a configuration in which $\mathbf{S} > \mathbf{L}$, the multiplicity is given by $2\mathbf{L} + 1$.) The total angular-momentum quantum number J is used as a subscript after the letter, so that a $^2P_{3/2}$ state (read as “doublet P three-halves”) refers to an electronic configuration in which $\mathbf{S} = \frac{1}{2}$, $\mathbf{L} = 1$, and $J = \frac{3}{2}$. For historical reasons, these designations are called **term symbols**.

In the event that the angular momentum of the atom arises from a single outer electron, the principal quantum number n of this electron is used as a prefix. Thus the ground state of the sodium atom is described by $3^2S_{1/2}$, since its electronic configuration has an electron with $n = 3$, $l = 0$, and $s = \frac{1}{2}$ (and hence $j = \frac{1}{2}$) outside closed $n = 1$ and $n = 2$ shells. For consistency it is conventional to denote the above state by $3^2S_{1/2}$ with the superscript 2 indicating a doublet, even though there is only a single possibility for J since $\mathbf{L} = 0$.

Example 7.6

The term symbol of the ground state of sodium is $3^2S_{1/2}$ and that of its first excited state is $3^2P_{1/2}$. List the possible quantum numbers n , l , j , and m_j of the outer electron in each case.

Solution

$$3^2S_{1/2}: n = 3, l = 0, j = \frac{1}{2}, m_j = \pm \frac{1}{2}$$

$$3^2P_{1/2}: n = 3, l = 1, j = \frac{1}{2}, m_j = \pm \frac{1}{2}, \pm \frac{3}{2}$$

$$n = 3, l = 1, j = \frac{1}{2}, m_j = \pm \frac{1}{2}$$

Example 7.7

Why is it impossible for a $2^2P_{5/2}$ state to exist?

Solution

A P state has $\mathbf{L} = 1$ and $J = \mathbf{L} \pm \frac{1}{2}$, so $J = \frac{5}{2}$ is impossible.

7.9 X-RAY SPECTRA

They arise from transitions to inner shells

In Chap. 2 we learned that the x-ray spectra of targets bombarded by fast electrons show narrow spikes at wavelengths characteristic of the target material. These are besides a continuous distribution of wavelengths down to a minimum wavelength inversely proportional to the electron energy (see Fig. 2.17). The continuous x-ray spectrum is the result of the inverse photoelectric effect, with electron kinetic energy being transformed into photon energy $h\nu$. The line spectrum, on the other hand, comes from electronic transitions within atoms that have been disturbed by the incident electrons.

The transitions of the outer electrons of an atom usually involve only a few electron-volts of energy, and even removing an outer electron requires at most 24.6 eV (for helium). Such transitions accordingly are associated with photons whose wavelengths lie in or near the visible part of the electromagnetic spectrum. The inner electrons of heavier elements are a quite different matter, because these electrons are not well shielded from the full nuclear charge by intervening electron shells and so are very tightly bound.

In sodium, for example, only 5.13 eV is needed to remove the outermost 3s electron, whereas the corresponding figures for the inner ones are 31 eV for each 2p electron, 63 eV for each 2s electron, and 1041 eV for each 1s electron. Transitions that involve the inner electrons in an atom are what give rise to x-ray line spectra because of the high photon energies involved.

Figure 7.20 shows the energy levels (not to scale) of a heavy atom. The energy differences between angular momentum states within a shell are minor compared with the energy differences between shells. Let us look at what happens when an energetic electron strikes the atom and knocks out one of the K-shell electrons. The K electron could also be raised to one of the unfilled upper states of the atom, but the difference between the energy needed to do this and that needed to remove the electron completely is insignificant, only 0.2 percent in sodium and still less in heavier atoms.

An atom with a missing K electron gives up most of its considerable excitation energy in the form of an x-ray photon when an electron from an outer shell drops into the “hole” in the K shell. As indicated in Fig. 7.20, the **K series** of lines in the x-ray spectrum of an element consists of wavelengths arising in transitions from the L, M, N, . . . levels to the K level. Similarly the longer-wavelength **L series** originates when an L electron is knocked out of the atom, the **M series** when an M electron is knocked out, and so on. The two spikes in the x-ray spectrum of molybdenum in Fig. 2.17 are the K_{α} and K_{β} lines of its K series.

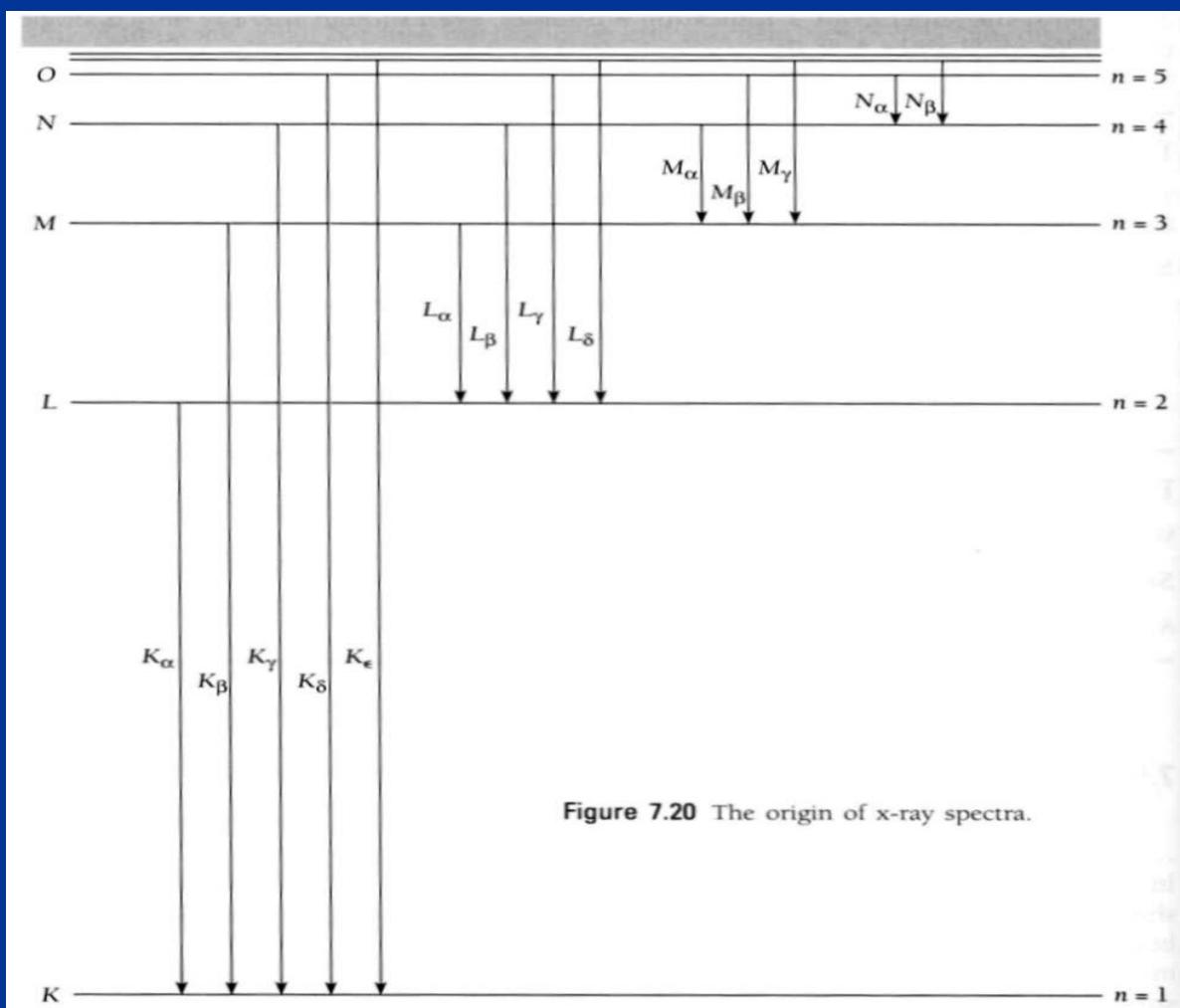


Figure 7.20 The origin of x-ray spectra.

It is easy to find an approximate relationship between the frequency of the K_{α} x-ray line of an element and its atomic number Z . A K_{α} photon is emitted when an L ($n = 2$) electron undergoes a transition to a vacant K ($n = 1$) state. The L electron experiences a nuclear charge of Ze that is reduced to an effective charge in the neighborhood of $(Z - 1)e$ by the shielding effect of the remaining K electron. Thus we can use Eqs. (4.15) and (4.16) to find the K_{α} photon frequency by letting $n_i = 2$ and $n_f = 1$, and replacing e^4 by $(Z - 1)^2 e^4$. This gives

$$\nu = \frac{m(Z - 1)^2 e^4}{8\epsilon_0^2 h^3} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = cR(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

K_{α} x-rays $\nu = \frac{3cR(Z - 1)^2}{4}$ (7.21)

where $R = me^4/8\epsilon_0^2 ch^3 = 1.097 \times 10^7 \text{ m}^{-1}$ is the Rydberg constant. The energy of a K_{α} x-ray photon is given in electronvolts in terms of $(Z - 1)$ by the formula

$$E(K_{\alpha}) = (10.2 \text{ eV})(Z - 1)^2 \quad (7.22)$$

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In 1913–1914 the young British physicist H. G. J. Moseley confirmed Eq. (7.21) by measuring the K_{α} frequencies of most of the then-known elements using the diffraction method described in Sec. 2.6. Besides supporting Bohr's newly formulated atomic model, Moseley's work provided for the first time a way to determine experimentally the atomic number Z of an element. As a result, the correct sequence of elements in the periodic table could be established. The ordering of the elements by atomic number (which is what matters) is not always the same as their ordering by atomic mass, which until then was the method used. Atomic number was originally just the number of an element in the list of atomic masses. For instance, $Z = 27$ for cobalt and $Z = 28$ for nickel, but their respective atomic masses are 58.93 and 58.71. The order dictated by atomic mass could not be understood on the basis of the chemical properties of cobalt and nickel.

In addition, Moseley found gaps in his data that corresponded to $Z = 43, 61, 72$, and 75 , which suggested the existence of hitherto unknown elements that were later discovered. The first two, technetium and promethium, have no stable isotopes and were first produced in the laboratory many years later. The last two, hafnium and rhenium, were isolated in the 1920s.

Example 7.8

Which element has a K_{α} x-ray line whose wavelength is 0.180 nm?

Solution

The frequency corresponding to a wavelength of 0.180 nm = 1.80×10^{-10} m is

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{1.80 \times 10^{-10} \text{ m}} = 1.67 \times 10^{18} \text{ Hz}$$

From Eq. (7.21) we have

$$Z - 1 = \sqrt{\frac{4}{3cR}} = \sqrt{\frac{(4)(1.67 \times 10^{18} \text{ Hz})}{(3)(3.00 \times 10^8 \text{ m/s})(1.097 \times 10^7 \text{ m}^{-1})}} = 26$$
$$Z = 27$$

The element with atomic number 27 is cobalt.

Auger Effect

An atom with a missing inner electron can also lose excitation energy by the **Auger effect** without emitting an x-ray photon. In this effect, which was discovered by the French physicist Pierre Auger, an outer-shell electron is ejected from the atom at the same time that another outer-shell electron drops to the incomplete inner shell. Thus the ejected electron carries off the atom's excitation energy instead of a photon doing this. In a sense the Auger effect represents an internal photoelectric effect, although the photon never actually comes into being within the atom. The Auger process is competitive with x-ray emission in most atoms, but the resulting electrons are usually absorbed in the target material while the x-rays emerge to be detected.

Summary for this Chapter (things you need to know)

Spin

- Why do we have to introduce Spin? What is the spin quantum number? What is the spin angular momentum? What is the z-component of spin angular momentum? (What is the z-component of spin magnetic moment?)
- What did the Stern-Gerlach experiment confirm?
- How many quantum numbers we need to determine a quantum state of an electron? What the quantity does each of the quantum numbers determine?

Many Electron Atoms

- What is Pauli Exclusion Principle?
- What is the origin of the periodic table?
- What are the shell and subshell capacities?
- What is the Hund's Rule?
- What is the Spin-Orbit coupling?
- What is the LS coupling?
- How does X-ray arise from? What do the K-series, L-series, etc mean?

TABLE 6.2 Atomic Electron States

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1s					
$n = 2$	2s	2p				
$n = 3$	3s	3p	3d			
$n = 4$	4s	4p	4d	4f		
$n = 5$	5s	5p	5d	5f	5g	
$n = 6$	6s	6p	6d	6f	6g	6h

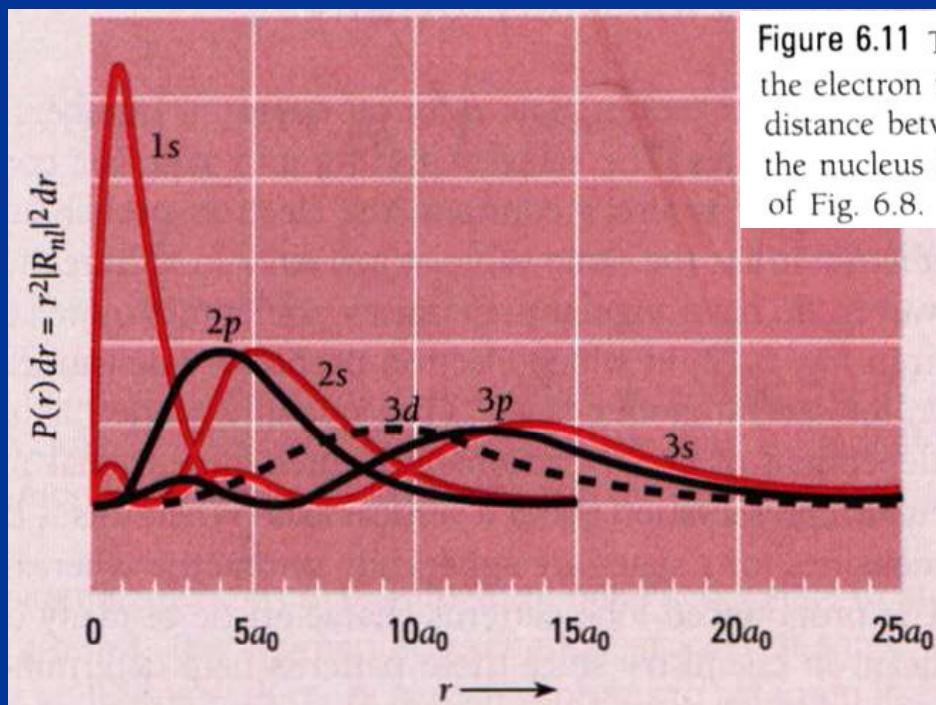
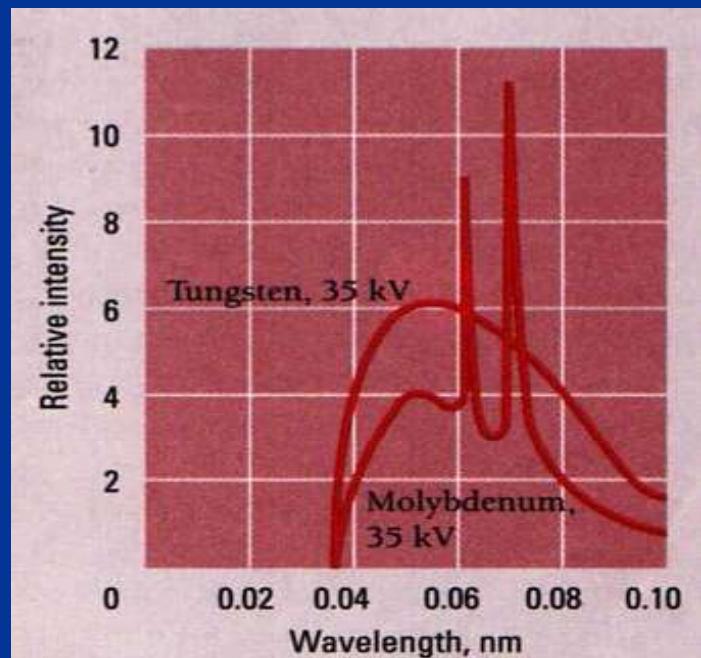


Figure 6.11 The probability of finding the electron in a hydrogen atom at a distance between r and $r + dr$ from the nucleus for the quantum states of Fig. 6.8.



X-ray spectra of tungsten and molybdenum at 35 kV accelerating potential.

Figure 6.5 (a)

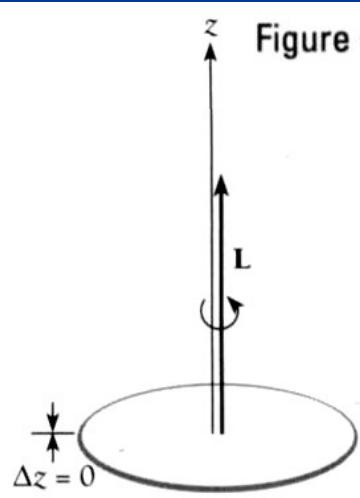
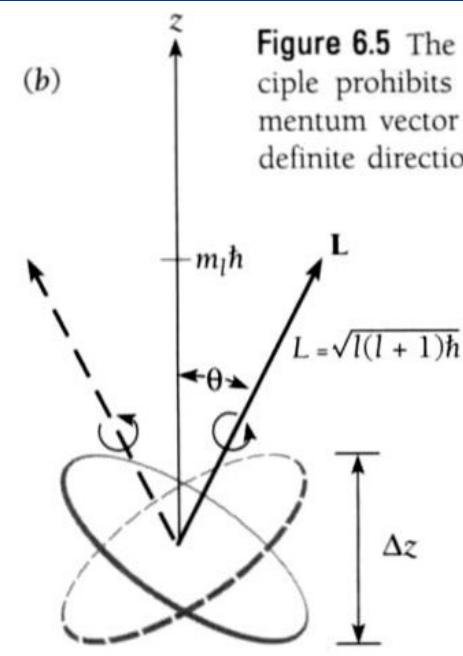


Figure 6.5 The uncertainty principle prohibits the angular momentum vector \mathbf{L} from having a definite direction in space.



Back

Molecules

Individual atoms are rare on the earth and in the lower part of its atmosphere. Only inert gas atoms occur by themselves. All other atoms are found joined together in small groups called molecules and in large groups as liquids and solids. Some molecules, liquids, and solids are composed entirely of atoms of the same element; others are composed of atoms of different elements.

What holds atoms together? This question, of fundamental importance to the chemist, is no less important to the physicist, whose quantum theory of the atom cannot be correct unless it provides a satisfactory answer. The ability of the quantum theory to explain chemical bonding with no special assumptions is further testimony to the power of this approach.

8.1 THE MOLECULAR BOND

Electric forces hold atoms together to form molecules

A molecule is an electrically neutral group of atoms held together strongly enough to behave as a single particle.

A molecule of a given kind always has a certain definite composition and structure. Hydrogen molecules, for instance, always consist of two hydrogen atoms each, and water molecules always consist of one oxygen atom and two hydrogen atoms each. If one of the atoms of a molecule is somehow removed or another atom becomes attached, the result is a molecule of a different kind with different properties.

A molecule exists because its energy is less than that of the system of separate noninteracting atoms. If the interactions among a certain group of atoms reduce their total energy, a molecule can be formed. If the interactions increase their total energy, the atoms repel one another.

Let us see what happens when two atoms are brought closer and closer together. Three extreme situations can occur:

1 A covalent bond is formed. One or more pairs of electrons are shared by the two atoms. As these electrons circulate between the atoms, they spend more time between the atoms than elsewhere, which produces an attractive force. An example is H_2 , the hydrogen molecule, whose electrons belong to both protons (Fig. 8.1). The attractive force the electrons exert on the protons is more than enough to counterbalance the direct repulsion between them. If the protons are too close together, however, their repulsion becomes dominant and the molecule is not stable.

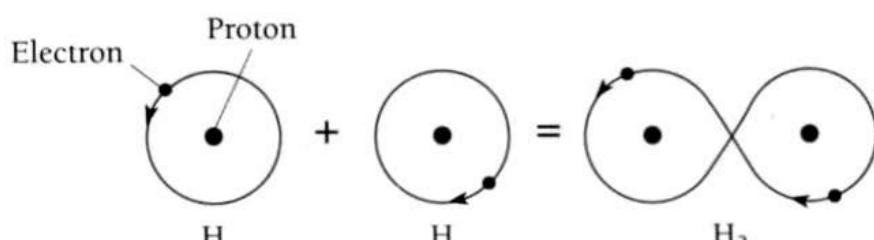
The balance between attractive and repulsive forces occurs at a separation of $7.42 \times 10^{-11} \text{ m}$, where the total energy of the H_2 molecule is -4.5 eV . Hence 4.5 eV of work must be done to break a H_2 molecule into two H atoms:



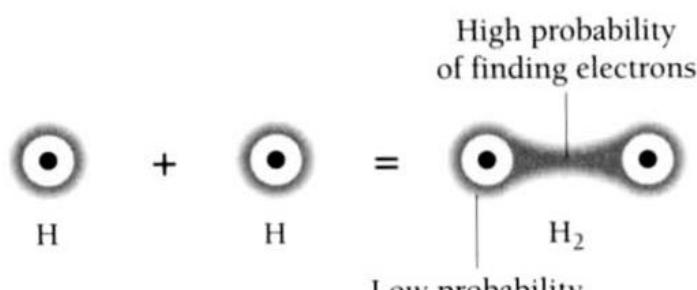
By comparison, the binding energy of the hydrogen atom is 13.6 eV :



This is an example of the general rule that it is easier to break up a molecule than to break up an atom.



(a)



(b)

Figure 8.1 (a) Orbit model of the hydrogen molecule. (b) Quantum-mechanical model of the hydrogen molecule. In both models the shared electrons spend more time on the average between the nuclei, which leads to an attractive force. Such a bond is said to be covalent.

2 An ionic bond is formed. One or more electrons from one atom may transfer to the other and the resulting positive and negative ions attract each other. An example is rock salt, NaCl, where the bond exists between Na^+ and Cl^- ions and not between Na and Cl atoms (Fig. 8.2). Ionic bonds usually do not result in the formation of molecules. The crystals of rock salt are aggregates of sodium and chlorine ions which, although always arranged in a certain definite structure (Fig. 8.3), do not pair off into molecules consisting of one Na^+ ion and one Cl^- ion. Rock salt crystals may have any size and shape. There are always equal numbers of Na^+ and Cl^- ions in rock salt, so that the formula NaCl correctly represents its composition. Molten NaCl also consists of Na^+ and Cl^- ions. However, these ions form molecules rather than crystals only in the gaseous state. Ionic bonding is further discussed in Chap. 10.

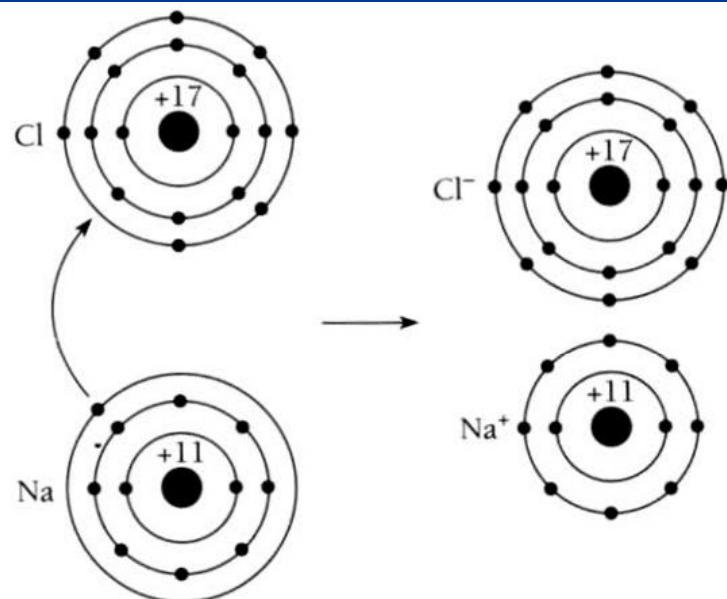


Figure 8.2 An example of ionic bonding. Sodium and chloride combine chemically by the transfer of electrons from sodium atoms to chlorine atoms; the resulting ions attract each other electrically.

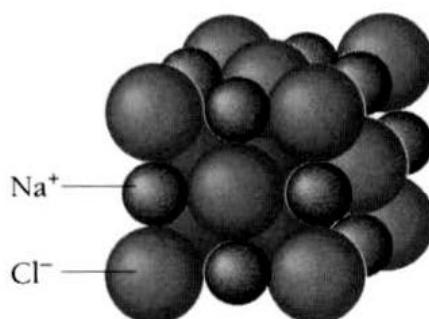


Figure 8.3 Scale model of an NaCl crystal.

In H_2 the bond is purely covalent and in NaCl it is purely ionic. In many molecules an intermediate type of bond occurs in which the atoms share electrons to an unequal extent. An example is the HCl molecule, where the Cl atom attracts the shared electrons more strongly than the H atom. We can think of the ionic bond as an extreme case of the covalent bond.

3 No bond is formed. When the electron structures of two atoms overlap, they constitute a single system. According to the exclusion principle, no two electrons in such a system can exist in the same quantum state. If some of the interacting electrons are forced into higher energy states than they occupied in the separate atoms, the system may have more energy than before and be unstable. Even when the exclusion principle can be obeyed with no increase in energy, there will be an electric repulsive force between the various electrons. This is a much less significant factor than the exclusion principle in influencing bond formation, however.

8.2 ELECTRON SHARING

The mechanism of the covalent bond

The simplest possible molecular system is H_2^+ , the hydrogen molecular ion, in which a single electron bonds two protons. Before we consider the bond in H_2^+ in detail, let us look in a general way into how it is possible for two protons to share an electron and why such sharing should lead to a lower total energy and hence to a stable system.

In Chap. 5 the phenomenon of quantum-mechanical barrier penetration was examined. There we saw that a particle can “leak” out of a box even without enough energy to break through the wall because the particle’s wave function extends beyond it. Only if the wall is infinitely strong is the wave function wholly inside the box.

The electric field around a proton is in effect a box for an electron, and two nearby protons correspond to a pair of boxes with a wall between them (Fig. 8.4). No mechanism in classical physics permits the electron in a hydrogen atom to jump spontaneously to a neighboring proton more distant than its parent proton. In quantum physics, however, such a mechanism does exist. There is a certain probability that an electron trapped in one box will tunnel through the wall and get into the other box, and once there it has the same probability for tunneling back. This situation can be described by saying the electron is shared by the protons.

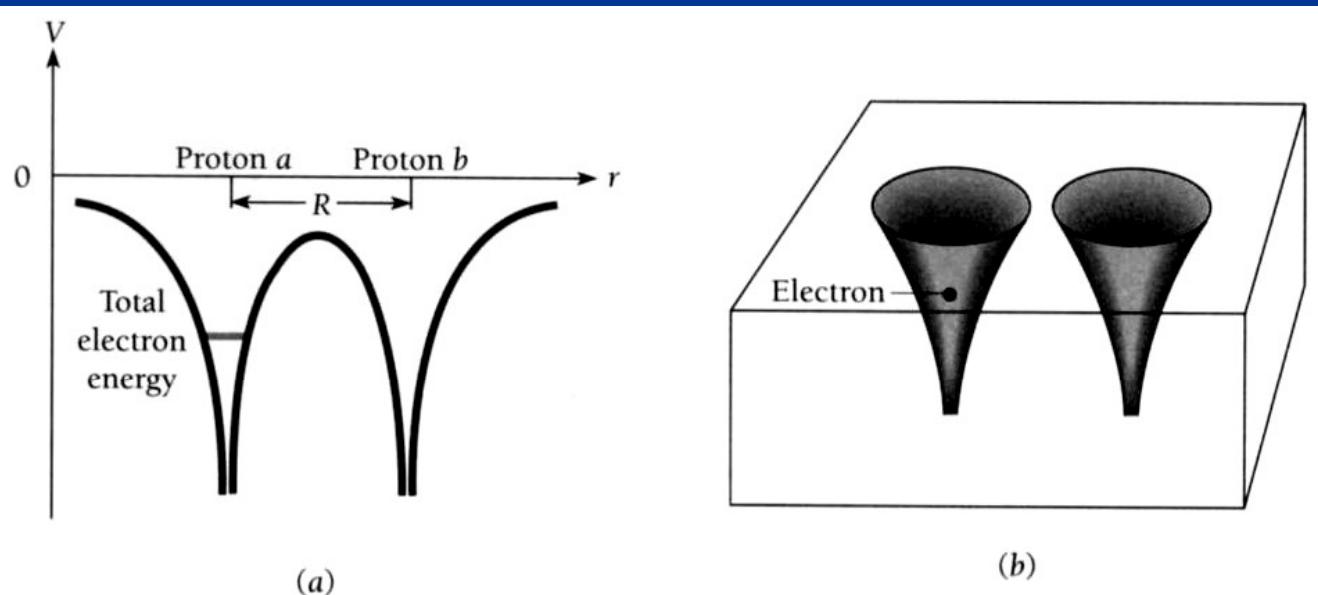


Figure 8.4 (a) Potential energy of an electron in the electric field of two nearby protons. The total energy of a ground-state electron in the hydrogen atom is indicated. (b) Two nearby protons correspond quantum-mechanically to a pair of boxes separated by a barrier.

To be sure, the likelihood that an electron will pass through the region of high potential energy—the “wall”—between two protons depends strongly on how far apart the protons are. If the proton-proton distance is 0.1 nm, the electron may be regarded as going from one proton to the other about every 10^{-15} s. We can legitimately consider such an electron as being shared by both. If the proton-proton distance is 1 nm, however, the electron shifts across an average of only about once per second, which is practically an infinite time on an atomic scale. Since the effective radius of the 1s wave function in hydrogen is 0.053 nm, we conclude that electron sharing can take place only between atoms whose wave functions overlap appreciably.

Granting that two protons can share an electron, a simple argument shows why the energy of such a system could be less than that of a separate hydrogen atom and proton. According to the uncertainty principle, the smaller the region to which we restrict a particle, the greater must be its momentum and hence kinetic energy. An electron shared by two protons is less confined than one belonging to a single proton, which means that it has less kinetic energy. The total energy of the electron in H_2^+ is therefore less than that of the electron in $\text{H} + \text{H}^+$. Provided the magnitude of the proton-proton repulsion in H_2^+ is not too great, then, H_2^+ ought to be stable.

8.3 THE H_2^+ MOLECULAR ION

Bonding requires a symmetric wave function

What we would like to know is the wave function ψ of the electron in H_2^+ , since from ψ we can calculate the energy of the system as a function of the separation R of the protons. If $E(R)$ has a minimum, we will know that a bond can exist, and we can also determine the bond energy and the equilibrium spacing of the protons.

Solving Schrödinger's equation for ψ is a long and complicated procedure. An intuitive approach that brings out the physics of the situation is more appropriate here. Let us begin by trying to predict what ψ is when R , the distance between the protons, is large compared with a_0 , the radius of the smallest Bohr orbit in the hydrogen atom. In this event ψ near each proton must closely resemble the 1s wave function of the hydrogen atom, as pictured in Fig. 8.5. The 1s wave function around proton a is called ψ_a and that around proton b is called ψ_b .

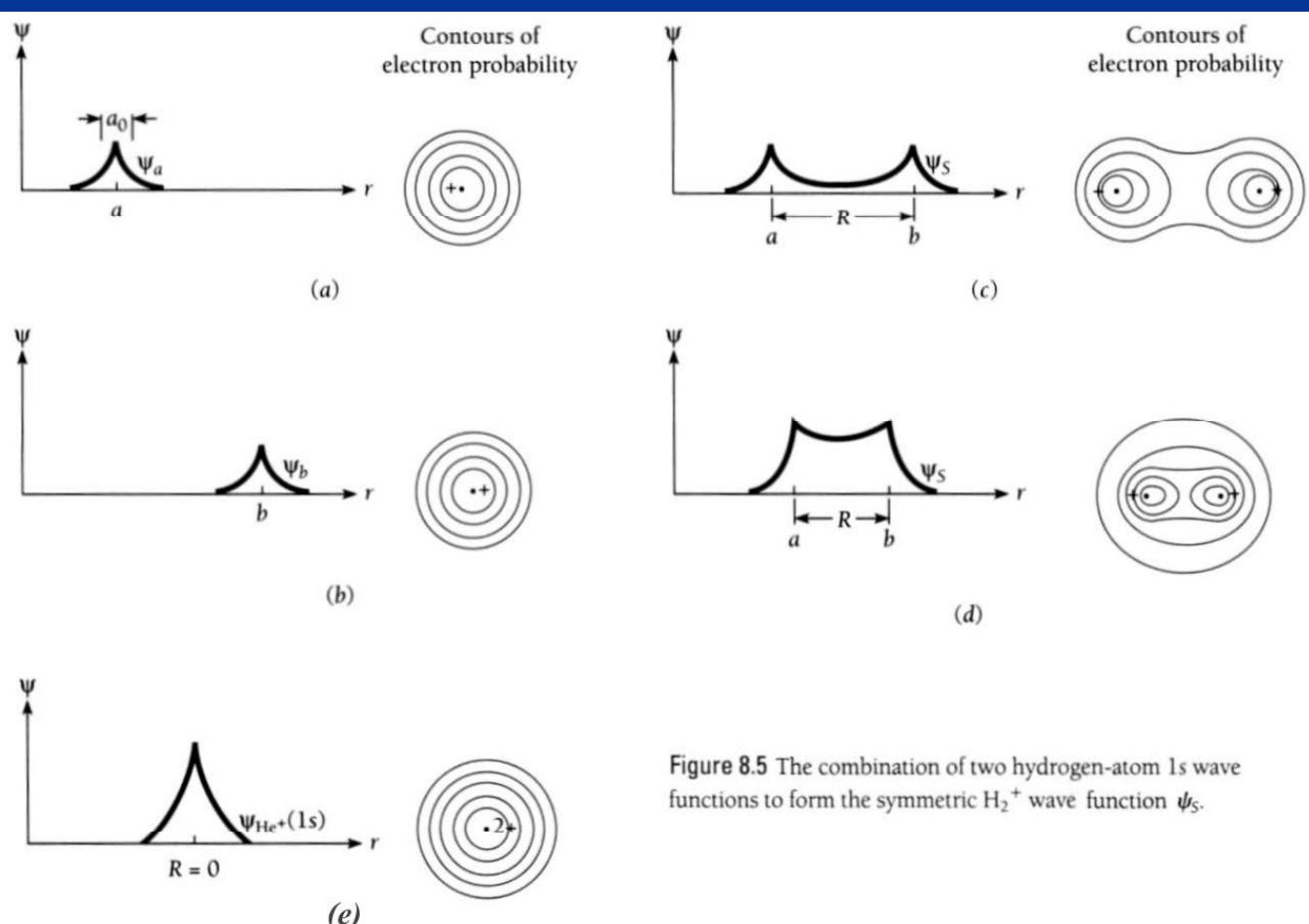


Figure 8.5 The combination of two hydrogen-atom 1s wave functions to form the symmetric H_2^+ wave function ψ_s .

We also know what ψ looks like when R is 0, that is, when the protons are imagined to be fused together. Here the situation is that of the He^+ ion, since the electron is now near a single nucleus whose charge is $+2e$. The 1s wave function of He^+ has the same form as that of H but with a greater amplitude at the origin, as in Fig. 8.5e. Evidently ψ is going to be something like the wave function sketched in Fig. 8.5d when R is comparable with a_0 . There is an enhanced likelihood of finding the electron in the region between the protons, which corresponds to the sharing of the electron by the protons. Thus there is on the average an excess of negative charge between the protons, and this attracts the protons together. We have still to establish whether this attraction is strong enough to overcome the mutual repulsion of the protons.

The combination of ψ_a and ψ_b in Fig. 8.5 is symmetric, since exchanging a and b does not affect ψ (see Sec. 7.3). However, it is also conceivable that we could have an antisymmetric combination of ψ_a and ψ_b , as in Fig. 8.6. Here there is a node between a and b where $\psi = 0$, which implies a reduced likelihood of finding the electron between the protons. Now there is on the average a deficiency of negative charge between the protons and in consequence a repulsive force. With only repulsive forces acting, bonding cannot occur.

An interesting question concerns the behavior of the antisymmetric H_2^+ wave function ψ_A as $R \rightarrow 0$. Obviously ψ_A does not become the 1s wave function of He^+ when $R = 0$. However, ψ_A does approach the 2p wave function of He^+ (Fig. 8.6e), which has a node at the origin. But the 2p state of He^+ is an excited state whereas the 1s state is the ground state. Hence H_2^+ in the antisymmetric state ought to have more energy than when it is in the symmetric state, which agrees with our inference from the shapes of the wave functions ψ_A and ψ_S that in the former case there is a repulsive force and in the latter, an attractive one.

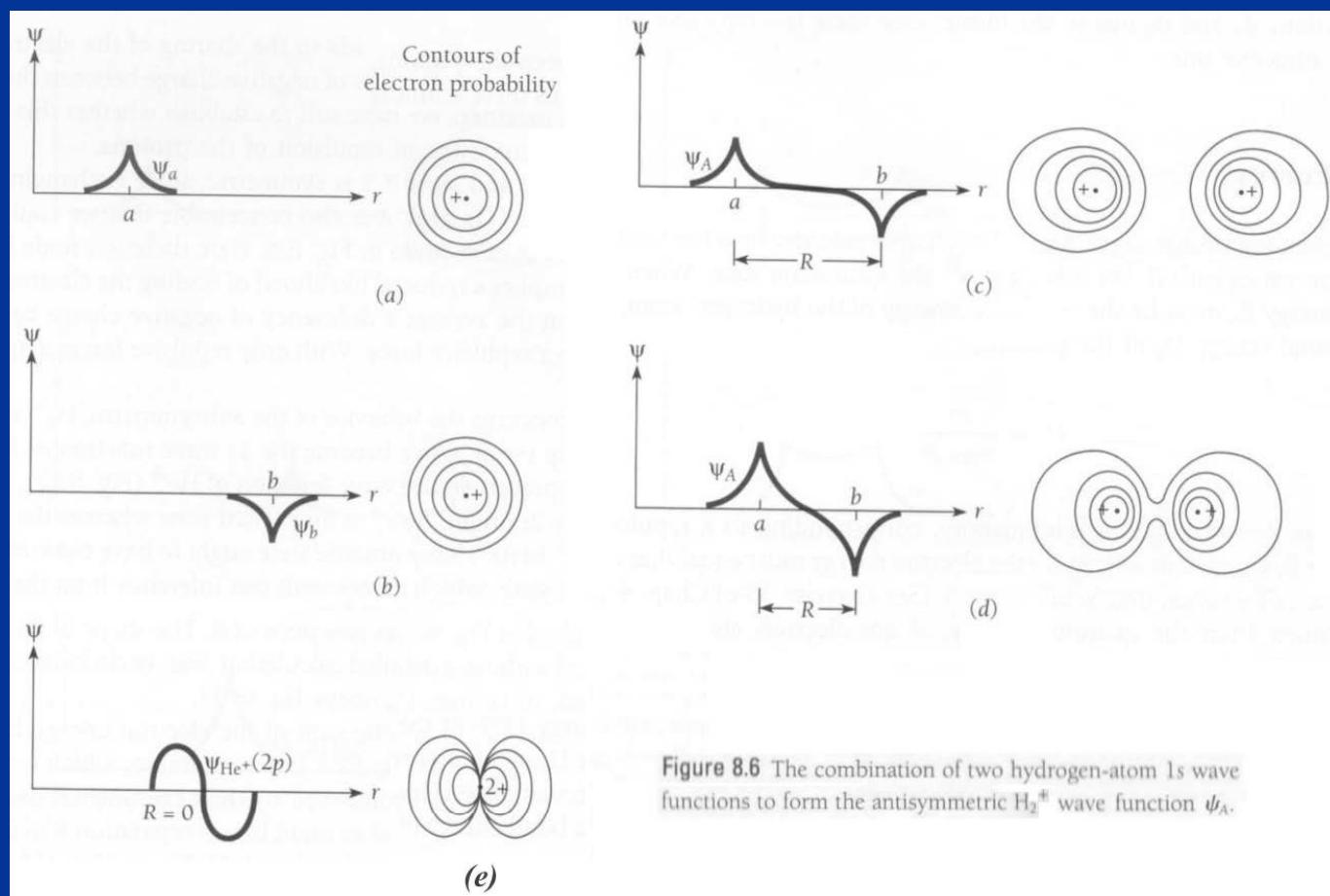


Figure 8.6 The combination of two hydrogen-atom 1s wave functions to form the antisymmetric H_2^+ wave function ψ_A .

System Energy

A line of reasoning similar to the preceding one lets us estimate how the total energy of the H_2^+ system varies with R . We first consider the symmetric state. When R is large, the electron energy E_S must be the -13.6-eV energy of the hydrogen atom, while the electron potential energy U_p of the protons,

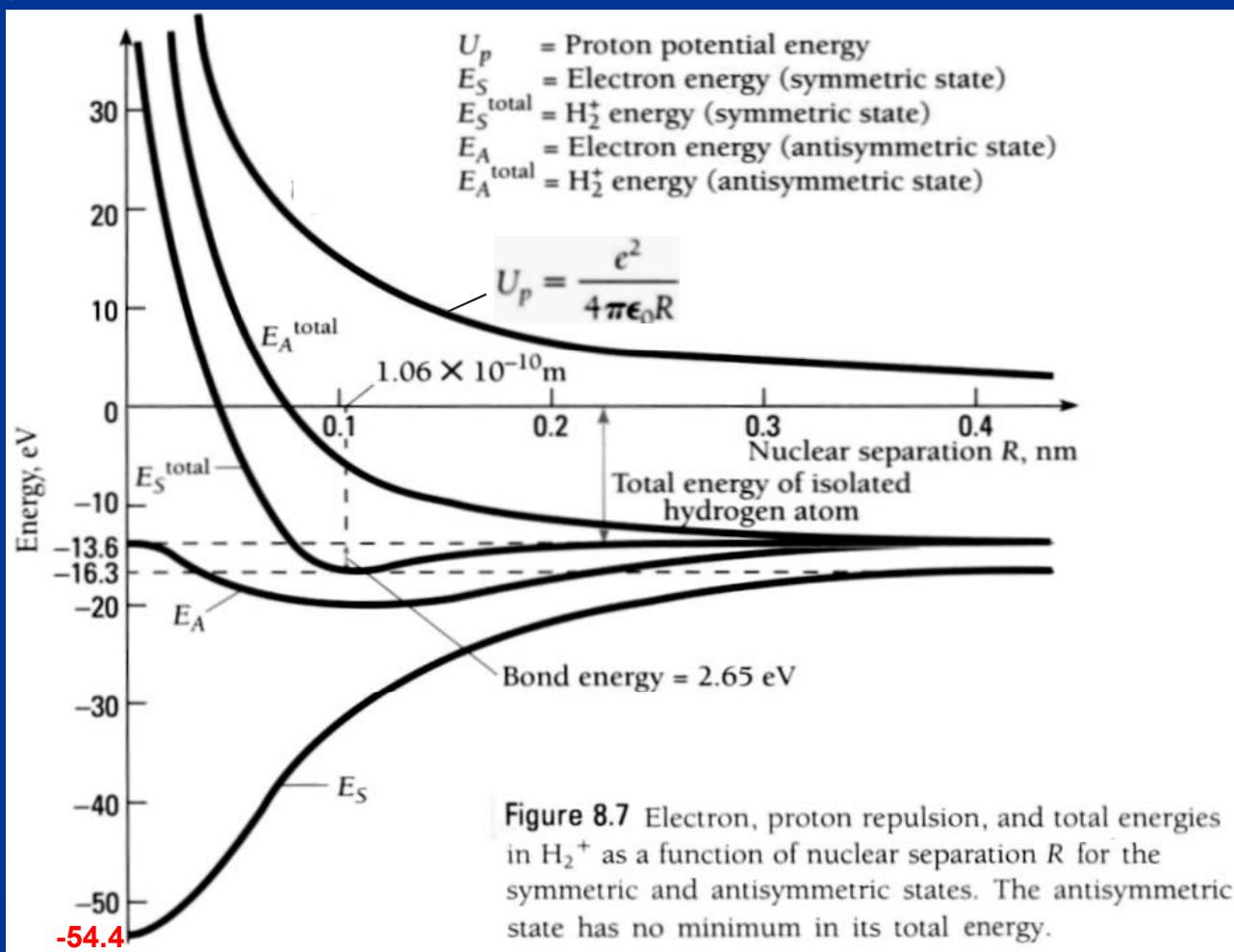
$$U_p = \frac{e^2}{4\pi\epsilon_0 R} \quad (8.1)$$

falls to 0 as $R \rightarrow \infty$. (U_p is a positive quantity, corresponding to a repulsive force.) When $R \rightarrow 0$, $U_p \rightarrow \infty$ as $1/R$. At $R = 0$, the electron energy must equal that of the He^+ ion, which is Z^2 , or 4 times, that of the H atom. (See Exercise 35 of Chap. 4; the same result is obtained from the quantum theory of one-electron atoms.) Hence $E_S = -54.4\text{ eV}$ when $R = 0$.

Both E_S and U_p are sketched in Fig. 8.7 as functions of R . The shape of the curve for E_S can only be approximated without a detailed calculation, but we do have its value for both $R = 0$ and $R = \infty$ and, of course, U_p obeys Eq. (8.1).

The total energy E_S^{total} of the system is the sum of the electron energy E_S and the potential energy U_p of the protons. Evidently E_S^{total} has a minimum, which corresponds to a stable molecular state. This result is confirmed by the experimental data on H_2^+ which indicate a bond energy of 2.65 eV and an equilibrium separation R of 0.106 nm. By "bond energy" is meant the energy needed to break H_2^+ into $\text{H} + \text{H}^+$. The total energy of H_2^+ is the -13.6 eV of the hydrogen atom plus the -2.65-eV bond energy, or -16.3 eV in all.

In the case of the antisymmetric state, the analysis proceeds in the same way except that the electron energy E_A when $R = 0$ is that of the $2p$ state of He^+ . This energy is proportional to Z^2/n^2 . With $Z = 2$ and $n = 2$, E_A is just equal to the -13.6 eV of the ground-state hydrogen atom. Since $E_A \rightarrow 13.6$ eV also as $R \rightarrow \infty$, we might think that the electron energy is constant, but actually there is a small dip at intermediate distances. However, the dip is not nearly enough to yield a minimum in the total energy curve for the antisymmetric state, as shown in Fig. 8.7, and so in this state no bond is formed.



8.4 THE HYDROGEN MOLECULE

The spins of the electrons must be antiparallel

The H_2 molecule has two electrons instead of the single electron of H_2^+ . According to the exclusion principle, both electrons can share the same **orbital** (that is, be described by the same wave function ψ_{nlm_l}) provided their spins are antiparallel.

With two electrons to contribute to the bond, H_2 ought to be more stable than H_2^+ —at first glance, twice as stable, with a bond energy of 5.3 eV compared with 2.65 eV for H_2^+ . However, the H_2 orbitals are not quite the same as those of H_2^+ because of the electric repulsion between the two electrons in H_2 , a factor absent in the case of H_2^+ . This repulsion weakens the bond in H_2 , so that the actual energy is 4.5 eV instead of 5.3 eV. For the same reason, the bond length in H_2 is 0.074 nm, which is somewhat larger than the use of unmodified H_2^+ wave functions would indicate. The general conclusion in the case of H_2^+ that the symmetric wave function ψ_S leads to a bound state and the antisymmetric wave function ψ_A to an unbound one remains valid for H_2 .

In Sec. 7.3 the exclusion principle was formulated in terms of the symmetry and antisymmetry of wave functions, and it was concluded that systems of electrons are always described by antisymmetric wave functions (that is, by wave functions that reverse sign upon the exchange of any pair of electrons). However, the bound state in H_2 corresponds to both electrons being described by a symmetrical wave function ψ_S , which seems to contradict the above conclusion.

A closer look shows that there is really no contradiction. The complete wave function $\Psi(1, 2)$ of a system of two electrons is the product of a spatial wave function $\psi(1, 2)$ which describes the coordinates of the electrons and a spin function $s(1, 2)$ which describes the orientations of their spins. The exclusion principle requires that the complete wave function

$$\Psi(1, 2) = \psi(1, 2) s(1, 2)$$

be antisymmetric to an exchange of both coordinates and spins, not $\psi(1, 2)$ by itself.

An antisymmetric complete wave function Ψ_A can result from the combination of a symmetric coordinate wave function ψ_S and an antisymmetric spin function s_A or from the combination of an antisymmetric coordinate wave function ψ_A and a symmetric spin function s_S . That is, only

$$\Psi(1, 2) = \psi_S s_A \quad \text{and} \quad \Psi(1, 2) = \psi_A s_S$$

are acceptable.

If the spins of the two electrons are parallel, their spin function is symmetric since it does not change sign when the electrons are exchanged. Hence the coordinate wave function ψ for two electrons whose spins are parallel must be antisymmetric:

Spins parallel

$$\Psi(1, 2) = \psi_A s_S$$

On the other hand, if the spins of the two electrons are antiparallel, their spin function is antisymmetric since it reverses sign when the electrons are exchanged. Hence the coordinate wave function ψ for two electrons whose spins are antiparallel must be symmetric:

Spins antiparallel

$$\Psi(1, 2) = \psi_S s_A$$

Schrödinger's equation for the H_2 molecule has no exact solution. In fact, only for H_2^+ is an exact solution possible, and all other molecular systems must be treated approximately. The results of a detailed analysis of the H_2 molecule are shown in Fig. 8.8 for the case when the electrons have their spins parallel and the case when their spins are antiparallel. The difference between the two curves is due to the exclusion principle, which leads to a dominating repulsion when the spins are parallel.

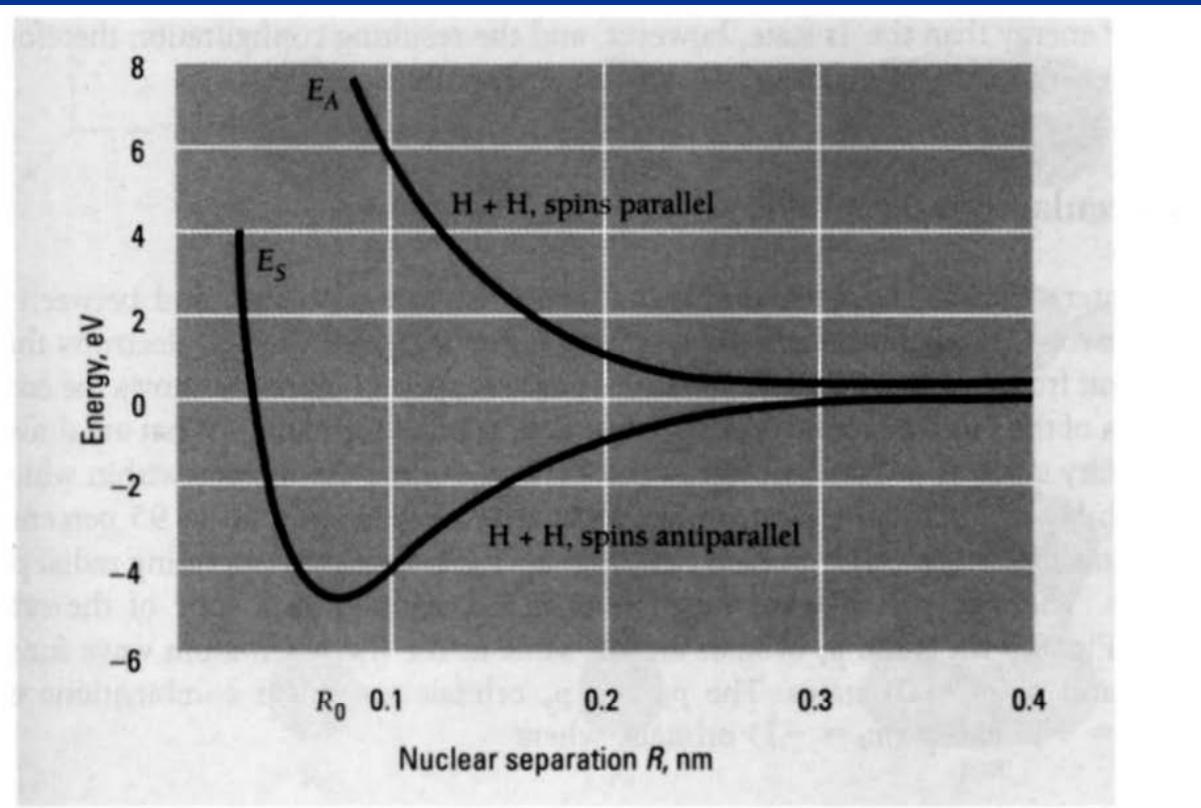


Figure 8.8 The variation of the energy of the system $\text{H} + \text{H}$ with their distances apart when the electron spins are parallel and antiparallel.

8.5 COMPLEX MOLECULES

Their geometry depends on the wave functions of the outer electrons of their atoms

Covalent bonding in molecules other than H_2 , diatomic as well as polyatomic, is usually a more complicated story. It would be yet more complicated but for the fact that any alteration in the electronic structure of an atom due to the proximity of another atom is confined to its outermost, or **valence**, electron shell. There are two reasons for this:

- 1 The inner electrons are much more tightly bound and hence less responsive to external influences, partly because they are closer to their parent nucleus and partly because they are shielded from the nuclear charge by fewer intervening electrons.
- 2 The repulsive interatomic forces in a molecule become predominant while the inner shells of its atoms are still relatively far apart.

The idea that only the valence electrons are involved in chemical bonding is supported by x-ray spectra that arise from transitions to inner-shell electron states. These spectra are virtually independent of how the atoms are combined in molecules or solids.

We have seen that two H atoms can combine to form an H_2 molecule; and, indeed, hydrogen molecules in nature always consist of two H atoms. The exclusion principle is what prevents molecules such as He_2 and H_3 from existing, while permitting such other molecules as H_2O to be stable.

Every He atom in its ground state has a 1s electron of each spin. If it is to join with another He atom by exchanging electrons, each atom will have two electrons with the same spin for part of the time. That is, one atom will have both electron spins up ($\uparrow\uparrow$) and the other will have both spins down ($\downarrow\downarrow$). The exclusion principle, of course, prohibits two 1s electrons in an atom from having the same spins, which is manifested in a repulsion between He atoms. Hence the He_2 molecule cannot exist.

A similar argument holds in the case of H_3 . An H_2 molecule contains two 1s electrons whose spins are antiparallel ($\uparrow\downarrow$). Should another H atom approach whose electron spin is, say, up, the resulting molecule would have two spins parallel ($\uparrow\uparrow\downarrow$), and this is impossible if all three electrons are to be in 1s states. Hence the existing H_2 molecule repels the additional H atom. The exclusion-principle argument does not apply if one of the three electrons in H_3 is in an excited state. All such states are of higher energy than the 1s state, however, and the resulting configuration therefore has more energy than $H_2 + H$ and so will decay rapidly to $H_2 + H$.

Molecular Bonds

The interaction between two atoms that gives rise to a covalent bond between them may involve probability-density distributions for the participating electrons that are different from those of Fig. 6.12 for atoms alone in space. Figure 8.9 shows the configurations of the s and p atomic orbitals important in bond formation. What are drawn are boundary surfaces of constant $|\psi|^2 = |R\theta\Phi|^2$ that outline the regions within which the probability of finding the electron has some definite value, say 90 or 95 percent. The diagrams thus show $|\theta\Phi|^2$ in each case; Fig. 6.11 gives the corresponding radial probabilities. The sign of the wave function ψ is indicated in each lobe of the orbitals.

In Fig. 8.9 the s and p_z orbitals are the same as the hydrogen-atom wave functions for s and p ($m_l = 0$) states. The p_x and p_y orbitals are linear combinations of the p ($m_l = +1$) and p ($m_l = -1$) orbitals, where

$$\psi_{p_x} = \frac{1}{\sqrt{2}}(\psi_{+1} + \psi_{-1}) \quad \psi_{p_y} = \frac{1}{\sqrt{2}}(\psi_{+1} - \psi_{-1}) \quad (8.2)$$

The $1/\sqrt{2}$ factors are needed to normalize the wave functions. Because the energies of the $m_l = +1$ and $m_l = -1$ orbitals are the same, the superpositions of the wave functions in Eq. (8.2) are also solutions of Schrödinger's equation (see the discussion at the end of Sec. 5.3).

Orbital n l m_l

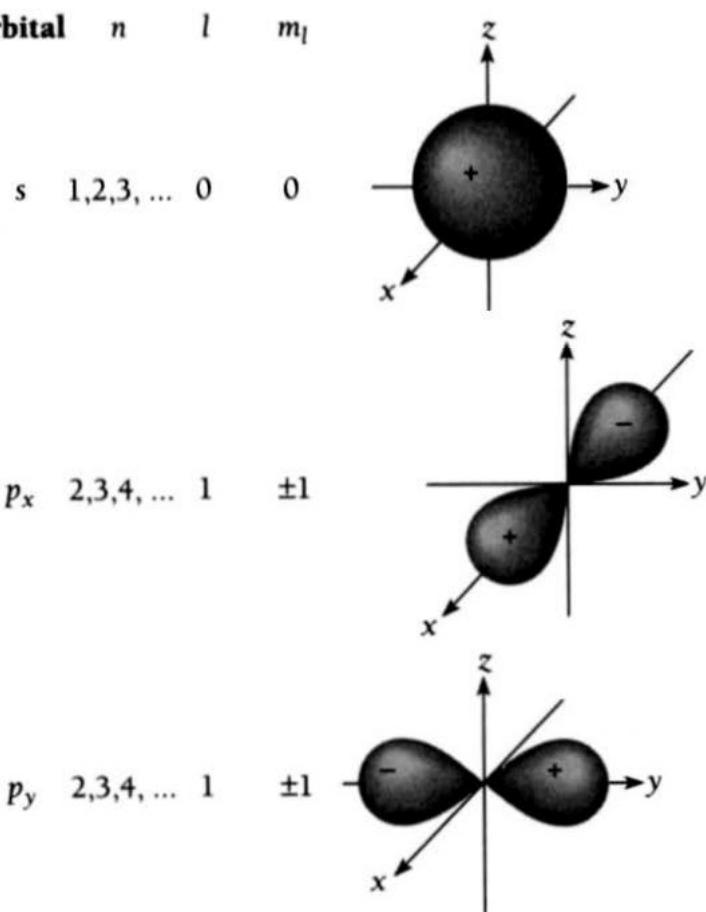
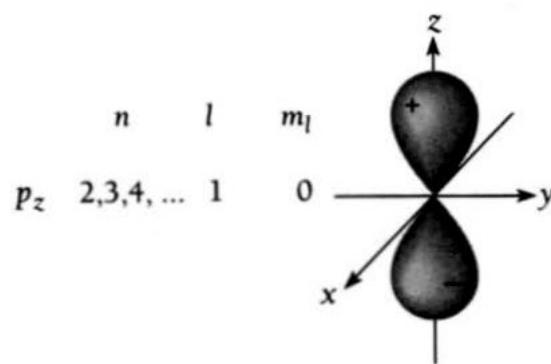


Figure 8.9 Boundary surface diagrams for s and p atomic orbitals. Each orbital can "contain" two electrons. There is a high probability of finding an electron described by one of these orbitals in the shaded regions. The sign of the wave function in each lobe is indicated



When two atoms come together, their orbitals overlap. If the result is an increased $|\psi|^2$ between them, the combined orbitals constitute a bonding molecular orbital. In Sec. 8.4 we saw how the 1s orbitals of two hydrogen atoms could join to form the bonding orbital ψ_s . Molecular bonds are classified by Greek letters according to their angular momenta L about the bond axis, which is taken to be the z axis: σ (the Greek equivalent of s) corresponds to $L = 0$, π (the Greek equivalent of p) corresponds to $L = \hbar$, and so on in alphabetic order.

Figure 8.10 shows the formation of σ and π bonding molecular orbitals from s and p atomic orbitals. Evidently ψ_s for H_2 is an $ss\sigma$ bond. Since the lobes of p_z orbitals are on the bond axis, they form σ molecular orbitals; the p_x and p_y orbitals usually form π molecular orbitals.

The atomic orbitals that combine to form a molecular orbital may be different in the two atoms. An example is the water molecule H_2O . Although one $2p$ orbital in O is fully occupied by two electrons, the other two $2p$ orbitals are only singly occupied and so can join with the 1s orbitals of two H atoms to form $sp\sigma$ bonding orbitals (Fig. 8.11). The mutual repulsion between the H nuclei (which are protons) widens the angles between the bond axes from 90° to the observed 104.5° .

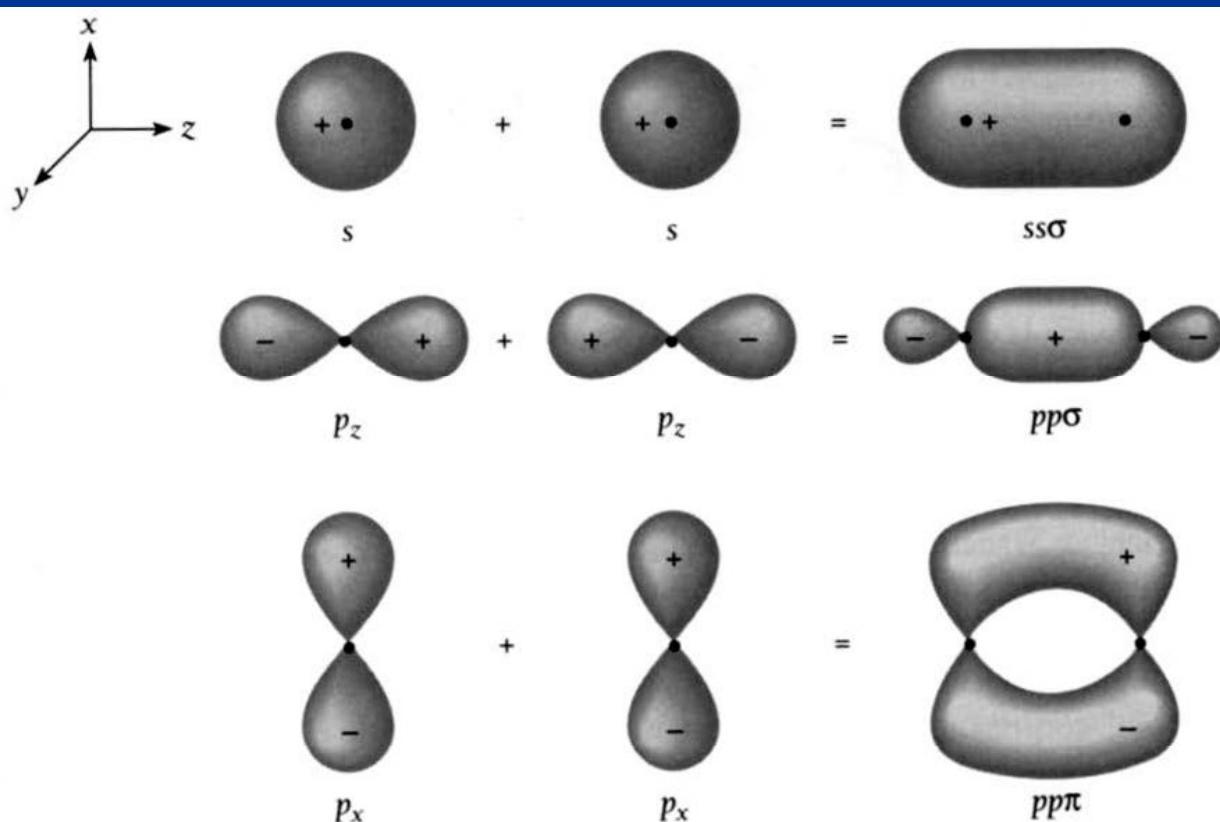


Figure 8.10 The formation of $ss\sigma$, $pp\sigma$, and $pp\pi$ bonding molecular orbitals. Two p_y atomic orbitals can combine to form a $pp\sigma$ molecular orbital in the same way as shown for two p_x atomic orbitals but with a different orientation.

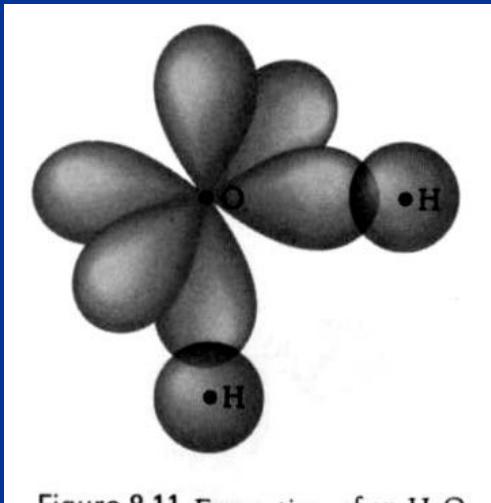


Figure 8.11 Formation of an H_2O molecule. Overlaps represent $s p\sigma$ covalent bonds. The angle between the bonds is 104.5° .

Hybrid Orbitals

The straightforward way in which the shape of the H_2O molecule is explained fails in the case of methane, CH_4 . A carbon atom has two electrons in its $2s$ orbital and one electron in each of two $2p$ orbitals. Thus we would expect the hydride of carbon to be CH_2 , with two $s p\sigma$ bonding orbitals and a bond angle of a little over 90° . The $2s$ electrons should not participate in the bonding at all. Yet CH_4 exists and is perfectly symmetrical in structure with tetrahedral molecules whose C—H bonds are exactly equivalent to one another.

The problem of CH_4 (and those of many other molecules) was solved by Linus Pauling in 1928. He proposed that linear combinations of *both* the 2s and 2p atomic orbitals of C contribute to *each* molecular orbital in CH_4 . The 2s and 2p wave functions are both solutions of the same Schrödinger's equation if the corresponding energies are the same, which is not true in the isolated C atom. However, in an actual CH_4 molecule the electric field experienced by the outer C electrons is affected by the nearby H nuclei, and the energy difference between 2s and 2p states then can disappear. **Hybrid orbitals** that consist of mixtures of s and p orbitals occur when the bonding energies they produce are greater than those which pure orbitals would produce. In CH_4 , the four hybrid orbitals are mixtures of one 2s and three 2p orbitals, and accordingly are called sp^3 hybrids (Fig. 8.12). The wave functions of these hybrid orbitals are

$$\begin{aligned}\psi_1 &= \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}) & \psi_3 &= \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) \\ \psi_2 &= \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}) & \psi_4 &= \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z})\end{aligned}$$

Figure 8.13 shows the resulting structure of the CH_4 molecule.

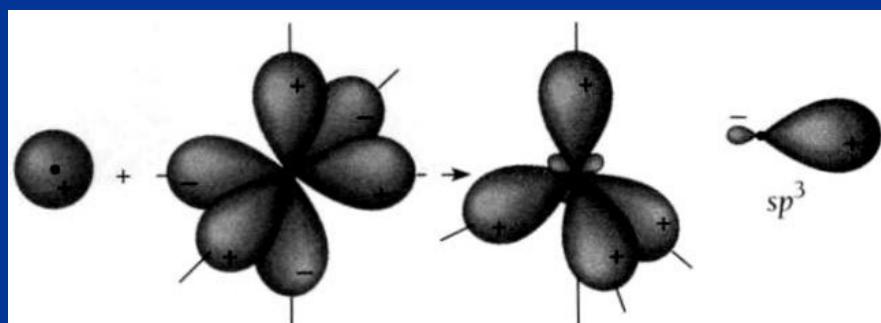


Figure 8.12 In sp^3 hybridization, an s orbital and three p orbitals in the same atom combine to form four sp^3 hybrid orbitals.

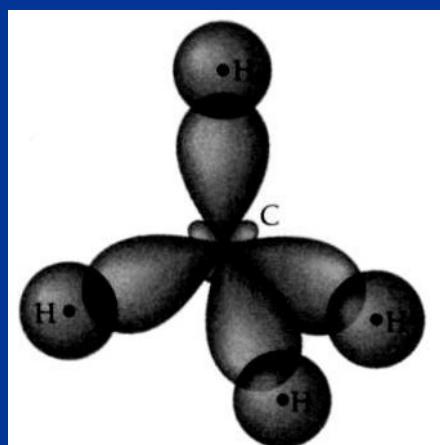
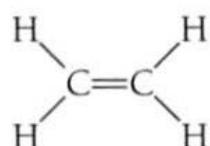


Figure 8.13 The bonds in the CH_4 (methane) molecule involve sp^3 hybrid orbitals.

Two other types of hybrid orbital in addition to sp^3 can occur in carbon atoms. In sp^2 hybridization, one outer electron is in a pure p orbital and the other three are in hybrid orbitals that are $\frac{1}{3}s$ and $\frac{2}{3}p$ in character. In sp hybridization, two outer electrons are in pure p orbitals and the other two are in hybrid orbitals that are $\frac{1}{2}s$ and $\frac{1}{2}p$ in character.

Ethylene, C_2H_4 , is an example of sp^2 hybridization in which the two C atoms are joined by two bonds, one a σ bond and one a π bond (Fig. 8.14). The conventional structural formula of ethylene shows these two bonds:

Ethylene



The electrons in the π bond are “exposed” outside the molecule, so ethylene and similar compounds are much more reactive chemically than compounds whose molecules have only σ bonds between their C atoms.

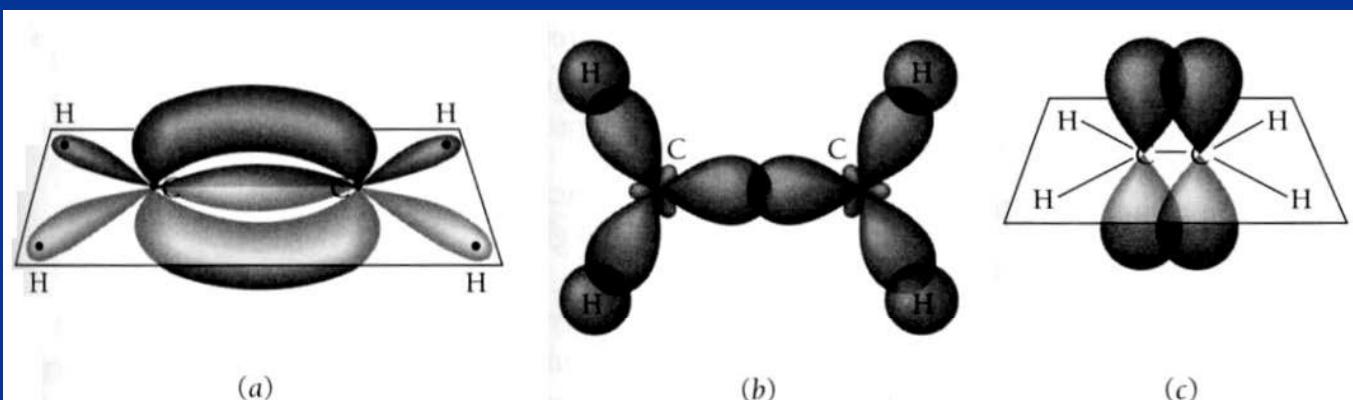


Figure 8.14 (a) The ethylene (C_2H_4) molecule. All the atoms lie in a plane perpendicular to the plane of the paper. (b) Top view, showing the sp^2 hybrid orbitals that form σ bonds between the C atoms and between each C atom and two H atoms. (c) Side view, showing the pure p_x orbitals that form a π bond between the C atoms.

In benzene, C_6H_6 , the six C atoms are arranged in a flat hexagonal ring, as in Fig. 8.15, with three sp^2 orbitals per C atom forming σ bonds with each other and with the H atoms. This leaves each C atom with one $2p$ orbital. The total of six $2p$ orbitals in the molecule combine into bonding π orbitals that are continuous above and below the plane of the ring. The six electrons involved belong to the molecule as a whole and not to any particular pair of atoms; these electrons are **delocalized**. An appropriate structural formula for benzene is therefore

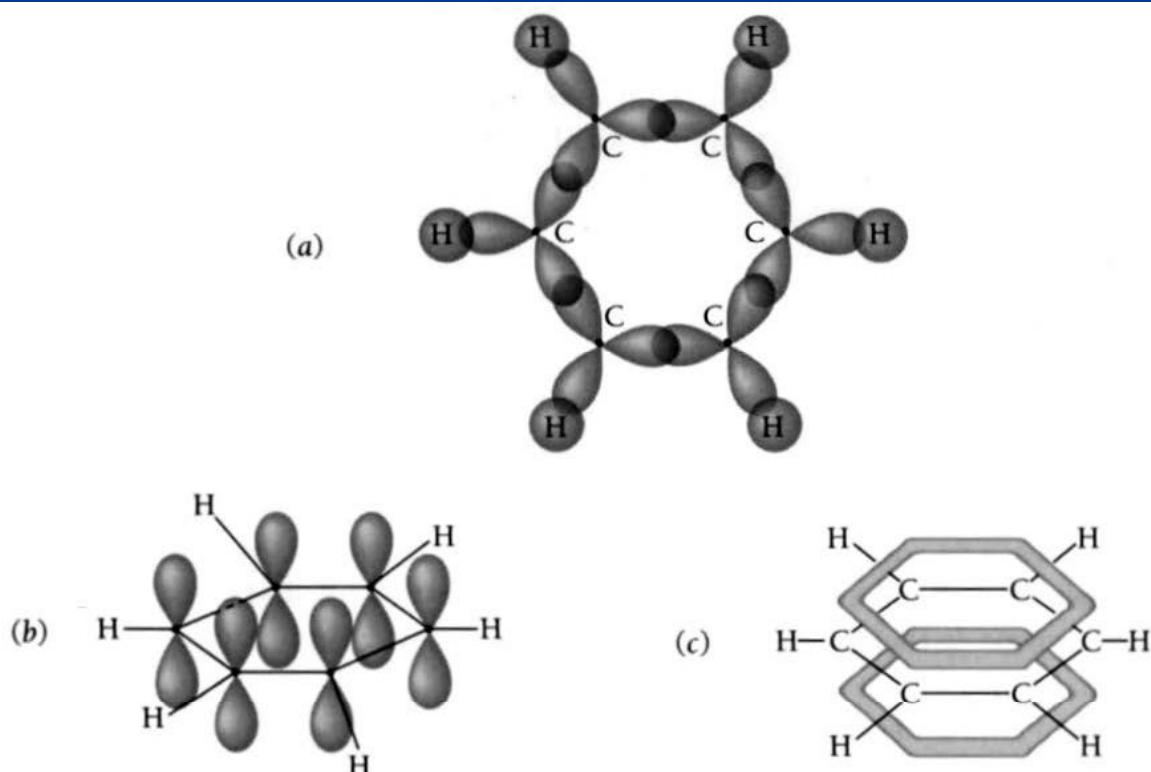
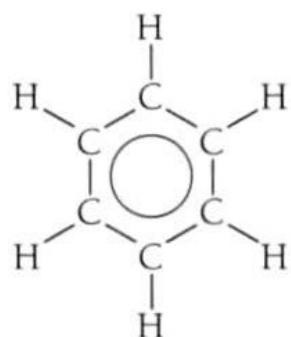


Figure 8.15 The benzene molecule. (a) The overlaps between the sp^2 hybrid orbitals in the C atoms with each other and with the s orbitals of the H atoms lead to σ bonds. (b) Each C atom has a pure p_x orbital occupied by one electron. (c) The bonding π molecular orbitals formed by the six p_x atomic orbitals constitute a continuous electron probability distribution around the molecule that contains six delocalized electrons.

8.6 ROTATIONAL ENERGY LEVELS

Molecular rotational spectra are in the microwave region

Molecular energy states arise from the rotation of a molecule as a whole, from the vibrations of its atoms relative to one another, and from changes in its electronic configuration:

1 *Rotational states* are separated by quite small energy intervals (10⁻³ eV is typical). The spectra that arise from transitions between these states are in the microwave region with wavelengths of 0.1 mm to 1 cm.

2 *Vibrational states* are separated by somewhat larger energy intervals (0.1 eV is typical). Vibrational spectra are in the infrared region with wavelengths of 1 μm to 0.1 mm.

3 *Molecular electronic states* have the highest energies, with typical separations between the energy levels of outer electrons of several eV. The corresponding spectra are in the visible and ultraviolet regions.

A detailed picture of a particular molecule can often be obtained from its spectrum, including bond lengths, force constants, and bond angles. For simplicity the treatment here will cover only diatomic molecules, but the main ideas apply to more complicated ones as well.

The lowest energy levels of a diatomic molecule arise from rotation about its center of mass. We may picture such a molecule as consisting of atoms of masses m_1 and m_2 a distance R apart, as in Fig. 8.16. The moment of inertia of this molecule about an axis passing through its center of mass and perpendicular to a line joining the atoms is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (8.3)$$

where r_1 and r_2 are the distances of atoms 1 and 2, respectively, from the center of mass. From the definition of center of mass,

$$m_1 r_1 = m_2 r_2 \quad (8.4)$$

Hence the moment of inertia may be written

Moment of inertia $I = \frac{m_1 m_2}{m_1 + m_2} (r_1 + r_2)^2 = m' R^2 \quad (8.5)$

Here **Reduced mass** $m' = \frac{m_1 m_2}{m_1 + m_2} \quad (8.6)$

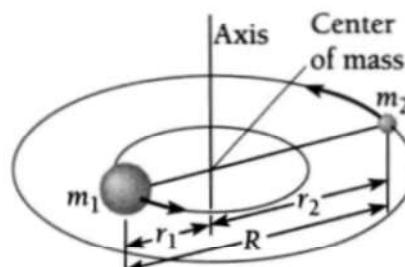


Figure 8.16 A diatomic molecule can rotate about its center of mass.

is the **reduced mass** of the molecule. Equation (8.5) states that the rotation of a diatomic molecule is equivalent to the rotation of a single particle of mass m' about an axis located a distance R away.

The angular momentum \mathbf{L} of the molecule has the magnitude

$$L = I\omega \quad (8.7)$$

where ω is its angular velocity. Angular momentum is always quantized in nature, as we know. If we denote the **rotational quantum number** by J , we have here

Angular momentum

$$L = \sqrt{J(J+1)}\hbar \quad J = 0, 1, 2, 3, \dots \quad (8.8)$$

The energy of a rotating molecule is $\frac{1}{2}I\omega^2$, and so its energy levels are specified by

Rotational energy levels

$$E_J = \frac{1}{2} I\omega^2 = \frac{L^2}{2I} = \frac{J(J+1)\hbar^2}{2I} \quad (8.9)$$

Example 8.1

The carbon monoxide (CO) molecule has a bond length R of 0.113 nm and the masses of the ^{12}C and ^{16}O atoms are respectively 1.99×10^{-26} kg and 2.66×10^{-26} kg. Find (a) the energy and (b) the angular velocity of the CO molecule when it is in its lowest rotational state.

Solution

(a) The reduced mass m' of the CO molecule is

$$\begin{aligned} m' &= \frac{m_1 m_2}{m_1 + m_2} = \left[\frac{(1.99)(2.66)}{1.99 + 2.66} \right] \times 10^{-26} \text{ kg} \\ &= 1.14 \times 10^{-26} \text{ kg} \end{aligned}$$

and its moment of inertia I is

$$\begin{aligned} I &= m'R^2 = (1.14 \times 10^{-26} \text{ kg})(1.13 \times 10^{-10} \text{ m})^2 \\ &= 1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \end{aligned}$$

The lowest rotational energy level corresponds to $J = 1$, and for this level in CO

$$\begin{aligned} E_{J=1} &= \frac{J(J+1)\hbar^2}{2I} = \frac{\hbar^2}{I} = \frac{(1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2} \\ &= 7.61 \times 10^{-23} \text{ J} = 4.76 \times 10^{-4} \text{ eV} \end{aligned}$$

This is not a lot of energy, and at room temperature, when $kT \approx 2.6 \times 10^{-2} \text{ eV}$, nearly all the molecules in a sample of CO are in excited rotational states.

(b) The angular velocity of the CO molecule when $J = 1$ is

$$\begin{aligned} \omega &= \sqrt{\frac{2E}{I}} = \sqrt{\frac{(2)(7.61 \times 10^{-23} \text{ J})}{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2}} \\ &= 3.23 \times 10^{11} \text{ rad/s} \end{aligned}$$

Rotations About the Bond Axis

We have been considering only rotation about an axis perpendicular to the bond axis of a diatomic molecule, as in Fig. 8.16—end-over-end rotations. What about rotations about the axis of symmetry itself?

Such rotations can be neglected because the mass of an atom is located almost entirely in its nucleus, whose radius is only $\sim 10^{-4}$ of the radius of the atom itself. The main contribution to the moment of inertia of a diatomic molecule about its bond axis therefore comes from its electrons, which are concentrated in a region whose radius about the axis is roughly half the bond length R but whose total mass is only about $\frac{1}{4000}$ of the total molecular mass. Since the allowed rotational energy levels are proportional to $1/I$, rotation about the symmetry axis must involve energies $\sim 10^4$ times the E_J values for end-over-end rotations. Hence energies of at least several eV would be involved in any rotation about the symmetry axis of a diatomic molecule. Bond energies are also of this order of magnitude, so the molecule would be likely to dissociate in any environment in which such a rotation could be excited.

Rotational Spectra

Rotational spectra arise from transitions between rotational energy states. Only molecules that have electric dipole moments can absorb or emit electromagnetic photons in such transitions. For this reason nonpolar diatomic molecules such as H₂ and symmetric polyatomic molecules such as CO₂ (O=C=O) and CH₄ (Fig. 8.13) do not exhibit rotational spectra. Transitions between rotational states in molecules like H₂, CO₂, and CH₄ can take place during collisions, however.

Even in molecules with permanent dipole moments, not all transitions between rotational states involve radiation. As in the case of atomic spectra, certain selection rules summarize the conditions for a radiative transition between rotational states to be possible. For a rigid diatomic molecule the selection rule for rotational transitions is

Selection rule

$$\Delta J = \pm 1 \quad (8.10)$$

In practice, rotational spectra are always obtained in absorption, so that each transition that is found involves a change from some initial state of quantum number J to the next higher state of quantum number $J + 1$. In the case of a rigid molecule, the frequency of the absorbed photon is

$$\nu_{J \rightarrow J+1} = \frac{\Delta E}{h} = \frac{E_{J+1} - E_J}{h}$$

$$= \frac{\hbar}{2\pi I}(J + 1) \quad (8.11)$$

$E_J = \frac{J(J + 1)\hbar^2}{2I}$

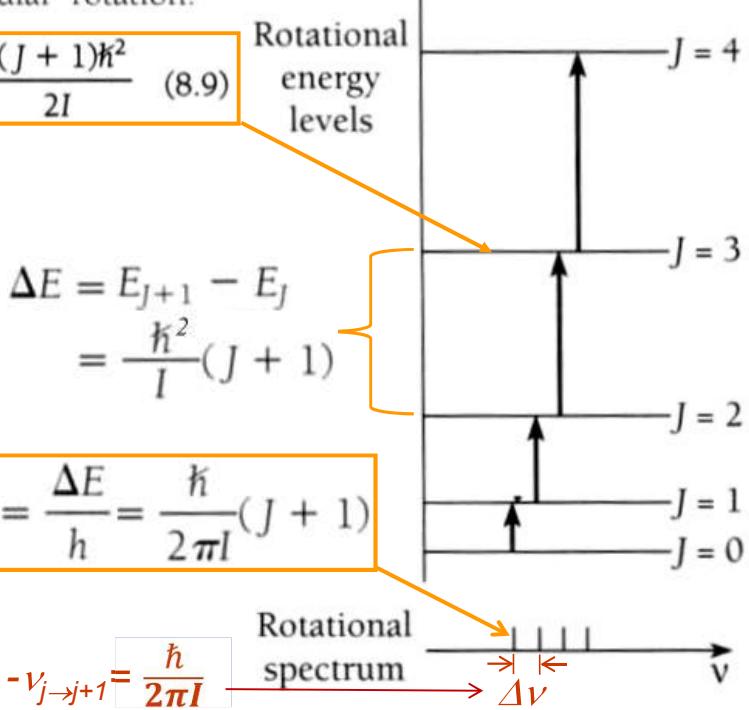
Rotational spectra

$$\Delta\nu = \nu_{j+1 \rightarrow j+2} - \nu_{j \rightarrow j+1} = \frac{\hbar}{2\pi I}$$

where I is the moment of inertia for end-over-end rotations. The spectrum of a rigid molecule therefore consists of equally spaced lines, as in Fig. 8.17. The frequency of each line can be measured, and the transition it corresponds to can often be found from the sequence of lines. From these data the moment of inertia of the molecule can be calculated. Alternatively, the frequencies of any two successive lines may be used to determine I if the lowest-frequency lines in a particular spectral sequence are not recorded.

Figure 8.17 Energy levels and spectrum of molecular rotation.

$$E_J = \frac{J(J+1)\hbar^2}{2I} \quad (8.9)$$



$$\begin{aligned}\Delta E &= E_{J+1} - E_J \\ &= \frac{\hbar^2}{I}(J+1)\end{aligned}$$

$$\nu_{j \rightarrow j+1} = \frac{\Delta E}{h} = \frac{\hbar}{2\pi I}(J+1)$$

$$\Delta\nu = \nu_{j+1 \rightarrow j+2} - \nu_{j \rightarrow j+1} = \frac{\hbar}{2\pi I}$$

$$\nu_{j \rightarrow j+1} = \frac{\hbar}{2\pi I}(J+1) \quad (8.11)$$

Example 8.2

In CO the $J = 0 \rightarrow J = 1$ absorption line occurs at a frequency of 1.15×10^{11} Hz. What is the bond length of the CO molecule?

Solution

First we find the moment of inertia of this molecule from Eq. (8.11):

$$I_{CO} = \frac{\hbar}{2\pi\nu}(J+1) = \frac{1.054 \times 10^{-34} \text{ J} \cdot \text{s}}{(2\pi)(1.15 \times 10^{11} \text{ s}^{-1})} = 1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

In Example 8.1 we saw that the reduced mass of the CO molecule is $m' = 1.14 \times 10^{-26}$ kg. From Eq. (8.5), $I = m'R^2$, we obtain

$$R_{CO} = \sqrt{\frac{I}{m'}} = \sqrt{\frac{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2}{1.14 \times 10^{-26} \text{ kg}}} = 1.13 \times 10^{-10} \text{ m} = 0.113 \text{ nm}$$

This is the way in which the bond length for CO quoted earlier was determined.

8.7 VIBRATIONAL ENERGY LEVELS

A molecule may have many different modes of vibration

When sufficiently excited, a molecule can vibrate as well as rotate. As before, we will consider only diatomic molecules.

Figure 8.18 shows how the potential energy of a molecule varies with the internuclear distance R . Near the minimum of this curve, which corresponds to the normal configuration of the molecule, the shape of the curve is very nearly a parabola. In this region, then,

Parabolic approximation

$$U = U_0 + \frac{1}{2}k(R - R_0)^2 \quad (8.12)$$

where R_0 is the equilibrium separation of the atoms.

The interatomic force that gives rise to this potential energy is given by differentiating U :

$$F = -\frac{dU}{dR} = -k(R - R_0) \quad (8.13)$$

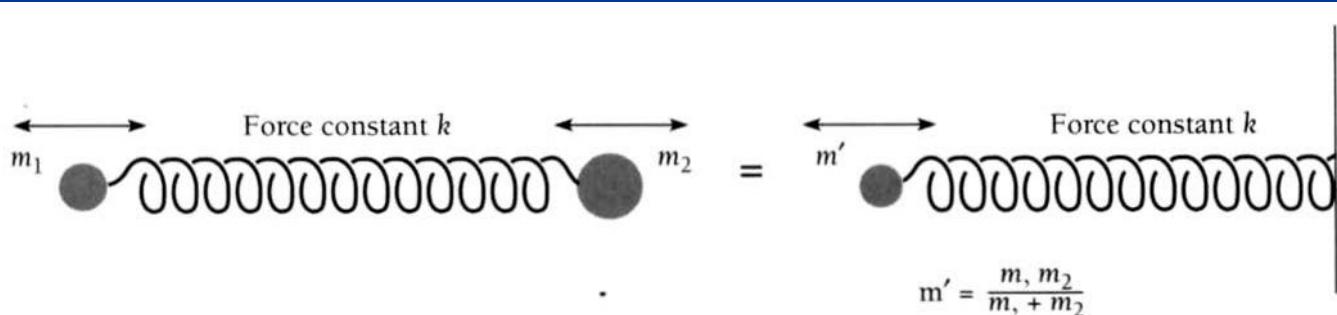


Figure 8.19 A two-body oscillator behaves like an ordinary harmonic oscillator with the same spring constant but with the reduced mass m' .

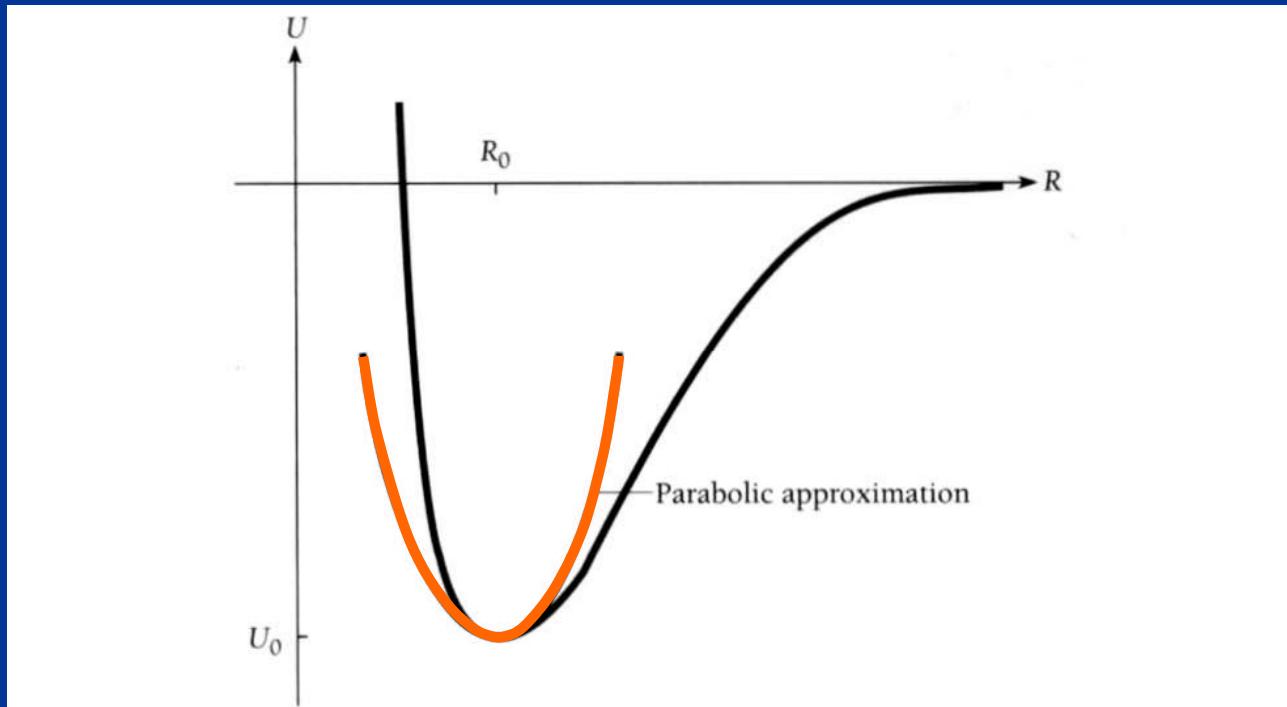


Figure 8.18 The potential energy of a diatomic molecule as a function of internuclear distance.

The force is just the restoring force that a stretched or compressed spring exerts—a Hooke's law force—and, as with a spring, a molecule suitably excited can undergo simple harmonic oscillations.

Classically, the frequency of a vibrating body of mass m connected to a spring of force constant k is

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (8.14)$$

What we have in the case of a diatomic molecule is the somewhat different situation of two bodies of masses m_1 and m_2 joined by a spring, as in Fig. 8.19. In the absence of external forces the linear momentum of the system remains constant, and the oscillations of the bodies therefore cannot effect the motion of their center of mass. For this reason m_1 and m_2 vibrate back and forth relative to their center of mass in opposite directions, and both reach the extremes of their respective motions at the same times. The frequency of oscillation of such a two-body oscillator is given by Eq. (8.14) with the reduced mass m' of Eq. (8.6) substituted for m :

Two-body oscillator

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} \quad (8.15)$$

When the harmonic-oscillator problem is solved quantum mechanically (see Sec. 5.9), the energy of the oscillator turns out to be restricted to the values

Harmonic oscillator

$$E_v = (v + \frac{1}{2})h\nu_0 \quad (8.16)$$

where v , the **vibrational quantum number**, may have the values

Vibrational quantum number

$$v = 0, 1, 2, 3, \dots$$

The lowest vibrational state ($v = 0$) has the zero-point energy $\frac{1}{2}h\nu_0$, not the classical value of 0. This result is in accord with the uncertainty principle, because if the oscillating particle were stationary, the uncertainty in its position would be $\Delta x = 0$ and its momentum uncertainty would then have to be infinite—and a particle with $E = 0$ cannot have an infinitely uncertain momentum. In view of Eq. (8.15) the vibrational energy levels of a diatomic molecule are specified by

Vibrational energy levels

$$E_v = (v + \frac{1}{2})\hbar \sqrt{\frac{k}{m'}} \quad (8.17)$$

The higher vibrational states of a molecule do not obey Eq. (8.16) because the parabolic approximation to its potential-energy curve becomes less and less valid with increasing energy. As a result, the spacing between adjacent energy levels of high v is less than the spacing between adjacent levels of low v , which is shown in Fig. 8.20. This diagram also shows the fine structure in the vibrational levels caused by the simultaneous excitation of rotational levels.

Vibrational Spectra

The selection rule for transitions between vibrational states is

$$\text{Selection rule} \quad \Delta v = \pm 1 \quad (8.18)$$

in the harmonic-oscillator approximation. This rule is easy to understand. An oscillating dipole whose frequency is ν_0 can absorb or emit only electromagnetic radiation of the same frequency and all quanta of frequency ν_0 have the energy $h\nu_0$. The oscillating dipole accordingly can only absorb $\Delta E = h\nu_0$ at a time, in which case its energy increases from $(v + \frac{1}{2})h\nu_0$ to $(v + \frac{1}{2} + 1)h\nu_0$. It can also emit only $\Delta E = h\nu_0$ at a time, in which case its energy decreases from $(v + \frac{1}{2})h\nu_0$ to $(v + \frac{1}{2} - 1)h\nu_0$. Hence the selection rule $\Delta v = \pm 1$.

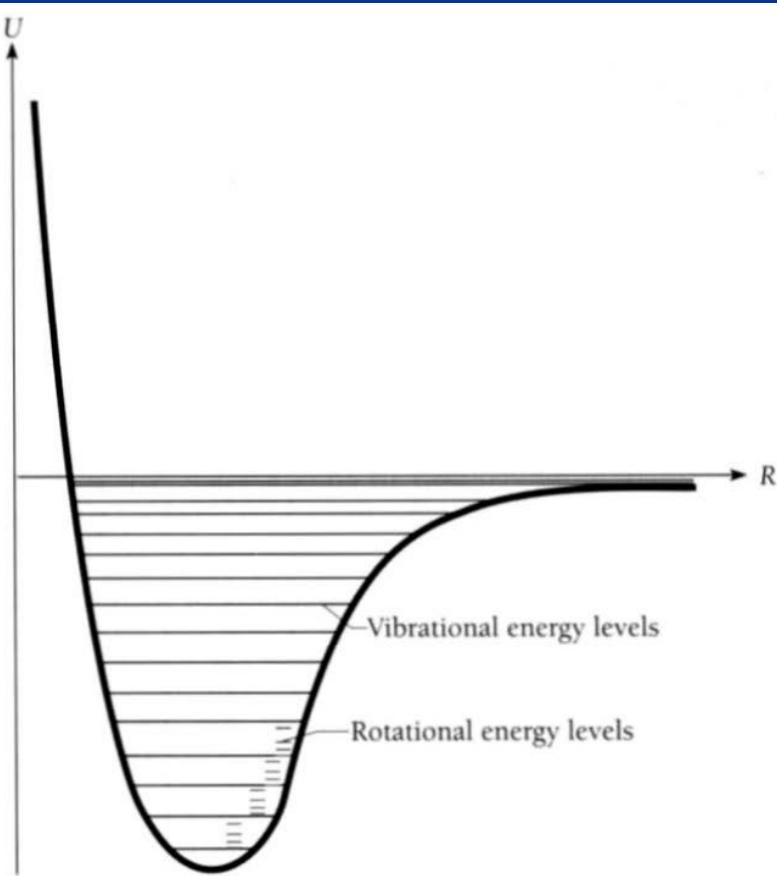


Figure 8.20 The potential energy of a diatomic molecule as a function of interatomic distance, showing vibrational and rotational energy levels.

Example 8.3

When CO is dissolved in liquid carbon tetrachloride, infrared radiation of frequency 6.42×10^{13} Hz is absorbed. Carbon tetrachloride by itself is transparent at this frequency, so the absorption must be due to the CO. (a) What is the force constant of the bond in the CO molecule? (b) What is the spacing between its vibrational energy levels?

Solution

(a) As we know, the reduced mass of the CO molecule is $m' = 1.14 \times 10^{-26}$ kg. From Eq. (8.15), $\nu_0 = \frac{1}{2\pi} \sqrt{k/m'}$, the force constant is

$$k = 4\pi^2 \nu_0^2 m' = (4\pi^2)(6.42 \times 10^{13} \text{ Hz})^2(1.14 \times 10^{-26} \text{ kg}) = 1.86 \times 10^3 \text{ N/m}$$

This is about 10 lb/in.

(b) The separation ΔE between the vibrational levels in CO is

$$\Delta E = E_{v+1} - E_v = h\nu_0 = (6.63 \times 10^{-34} \text{ J} \cdot \text{s})(6.42 \times 10^{13} \text{ Hz}) = 4.26 \times 10^{-20} \text{ J} = 0.266 \text{ eV}$$

This is considerably more than the spacing between its rotational energy levels. Because $\Delta E > kT$ for vibrational states in a sample at room temperature, most of the molecules in such a sample exist in the $v = 0$ state with only their zero-point energies. This situation is very different from that characteristic of rotational states, where the much smaller energies mean that the majority of the molecules in a room-temperature sample are excited to higher states.

Vibration-Rotation Spectra

Pure vibrational spectra are observed only in liquids where interactions between adjacent molecules inhibit rotation. Because the excitation energies involved in molecular rotation are much smaller than those involved in vibration, the freely moving molecules in a gas or vapor nearly always are rotating, regardless of their vibrational state. The spectra of such molecules do not show isolated lines corresponding to each vibrational transition, but instead a large number of closely spaced lines due to transitions between the various rotational states of one vibrational level and the rotational states of the other. In spectra obtained using a spectrometer with inadequate resolution, the lines appear as a broad streak called a vibration-rotation band.

To a first approximation, the vibrations and rotations of a molecule take place independently of each other, and we can also ignore the effects of centrifugal distortion and anharmonicity. Under these circumstances the energy levels of a diatomic molecule are specified by

$$\text{Diatomc molecule } E_{v,J} = \left(v + \frac{1}{2}\right) h \sqrt{\frac{k}{m'}} + J(J+1) \frac{\hbar^2}{2I} \quad (8.19)$$

$$E_{v,J} = \left(v + \frac{1}{2}\right) h \sqrt{\frac{k}{m'}} + J(J+1) \frac{\hbar^2}{2I}$$

Figure 8.21 shows the $J = 0, 1, 2, 3$, and 4 levels of a diatomic molecule for the $v = 0$ and $v = 1$ vibrational states, together with the spectral lines in absorption that are consistent with the selection rules $\Delta v = \pm 1$ and $\Delta J = \pm 1$.

The $v = 0 \rightarrow v = 1$ transitions fall into two categories, the **P branch** in which $\Delta J = -1$ (that is, $J \rightarrow J - 1$) and the **R branch** in which $\Delta J = +1$ ($J \rightarrow J + 1$). From Eq. (8.19) the frequencies of the spectral lines in each branch are given by

$$\nu_P = \frac{E_{1,J-1} - E_{0,J}}{h} = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} + [(J-1)J - J(J+1)] \frac{\hbar}{4\pi I}$$

P branch $\nu_P = \nu_0 - J \frac{\hbar}{2\pi I} \quad J = 1, 2, 3, \dots \quad (8.20)$

$$\nu_R = \frac{E_{1,J+1} - E_{0,J}}{h} = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} + [(J+1)(J+2) - J(J+1)] \frac{\hbar}{4\pi I}$$

R branch $\nu_R = \nu_0 + (J+1) \frac{\hbar}{2\pi I} \quad J = 0, 1, 2, \dots \quad (8.21)$

There is no line at $\nu = \nu_0$ because transitions for which $\Delta J = 0$ are forbidden in diatomic molecules.

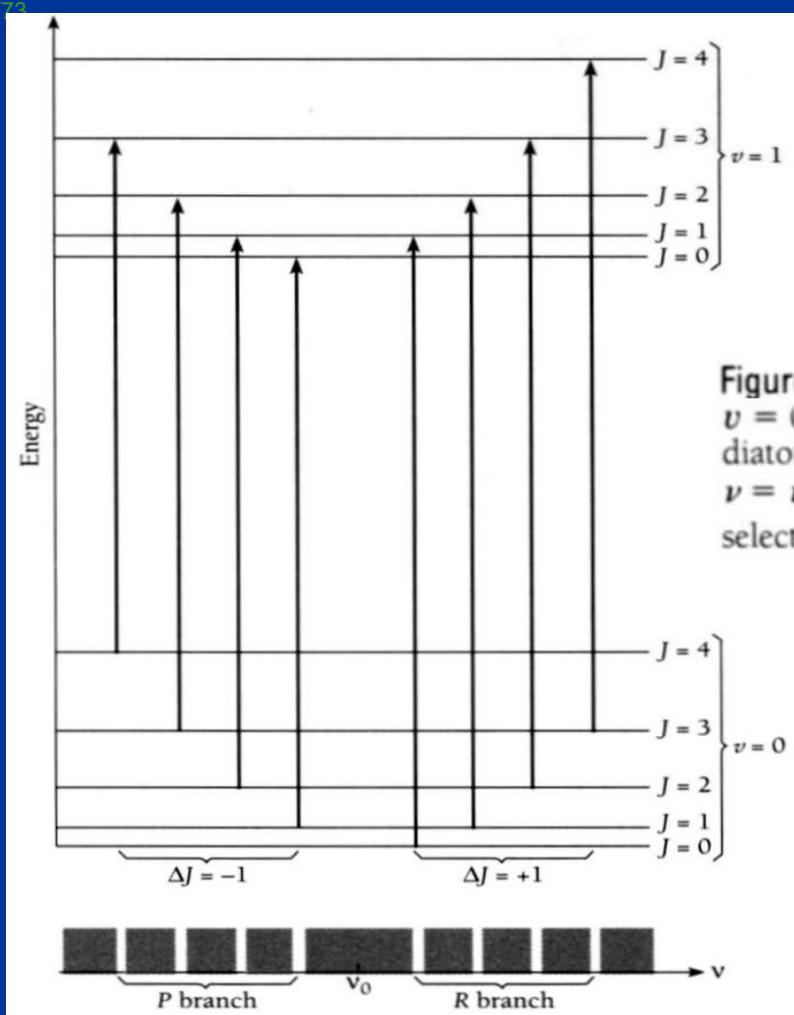


Figure 8.21 The rotational structure of the $v = 0 \rightarrow v = 1$ vibrational transitions in a diatomic molecule. There is no line at $\nu = \nu_0$ (the Q branch) because of the selection rule $\Delta J = \pm 1$.

The spacing between the lines in both the P and the R branch is $\Delta\nu = \hbar/2\pi l$. Hence the moment of inertia of a molecule can be found from its infrared vibration-rotation spectrum as well as from its microwave pure-rotation spectrum. Figure 8.22 shows the $v = 0 \rightarrow v = 1$ vibration-rotation absorption band in CO.

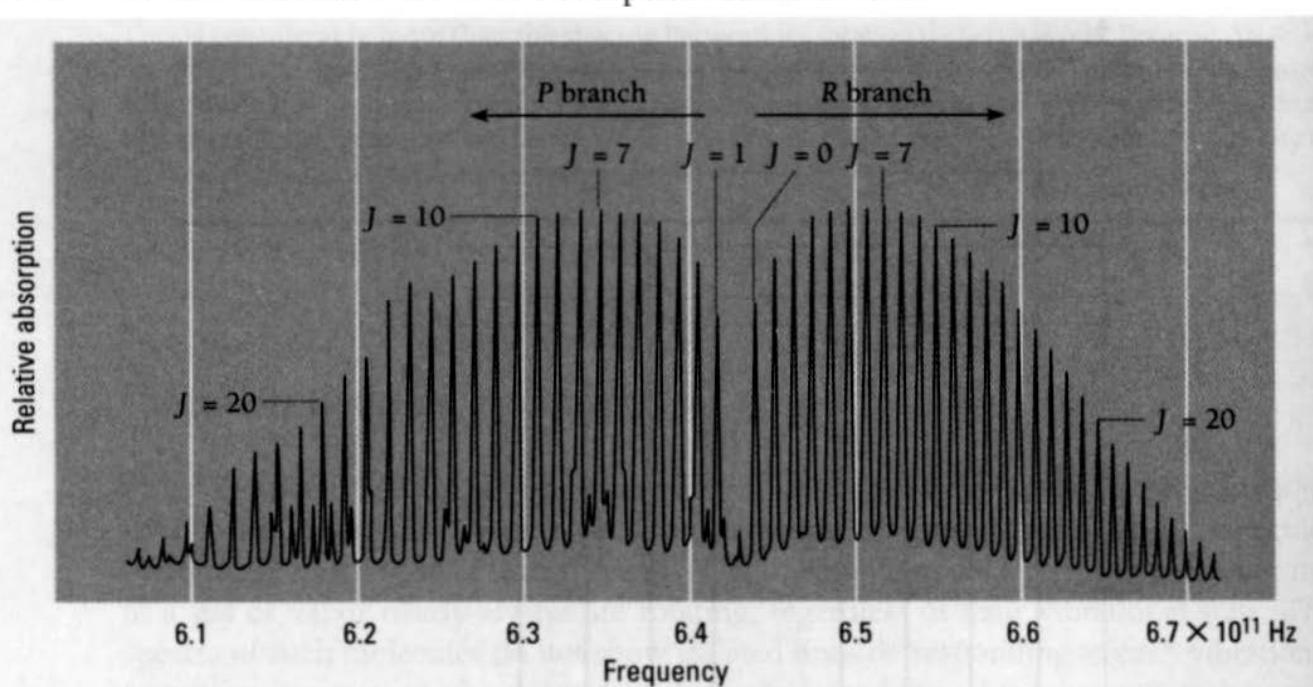


Figure 8.22 The $v = 0 \rightarrow v = 1$ vibration-rotation absorption band in CO under high resolution. The lines are identified by the value of J in the initial rotational state.

A complex molecule may have many different modes of vibration. Some of these modes involve the entire molecule (Figs. 8.23 and 8.24), but others involve only groups of atoms whose vibrations occur more or less independently of the rest of the molecule. Thus the —OH group has a characteristic vibrational frequency of 1.1×10^{14} Hz and the —NH_2 group has a frequency of 1.0×10^{14} Hz.

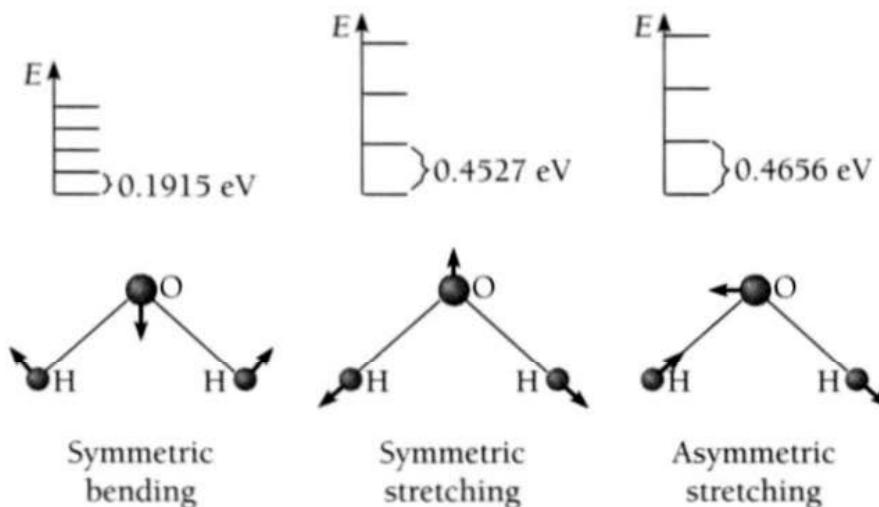


Figure 8.23 The normal modes of vibration of the H_2O molecule and the energy levels of each mode.

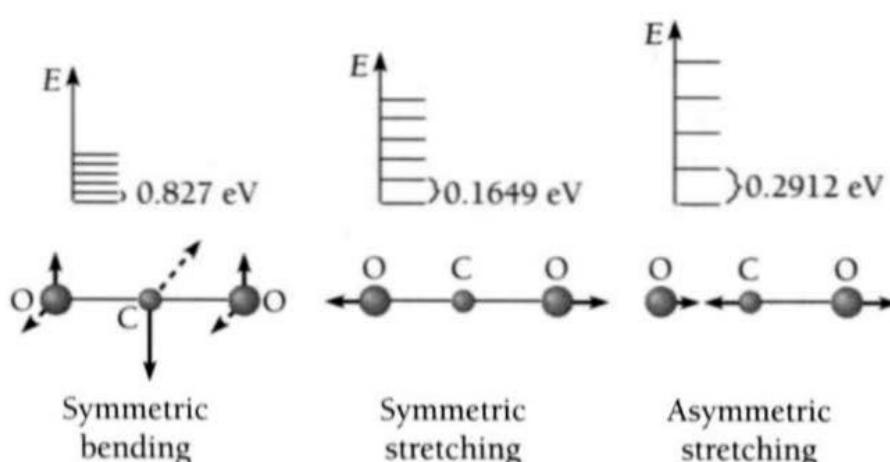


Figure 8.24 The normal modes of vibration of the CO_2 molecule and the energy levels of each mode. The symmetric bending mode can occur in two perpendicular planes.

The characteristic vibrational frequency of a carbon-carbon group depends upon the number of bonds between the C atoms: the ---C---C--- group vibrates at about 3.3×10^{13} Hz, the ---C=C--- group vibrates at about 5.0×10^{13} Hz, and the ---C\equiv C--- group vibrates at about 6.7×10^{13} Hz. (As we would expect, the more carbon-carbon bonds, the larger the force constant k and the higher the frequency.) In each case the frequency does not depend strongly on the particular molecule or the location in the molecule of the group, which makes vibrational spectra a valuable tool in determining molecular structures.

An example is thioacetic acid, whose structure might conceivably be either $\text{CH}_3\text{CO---SH}$ or $\text{CH}_3\text{CS---OH}$. The infrared absorption spectrum of thioacetic acid contains lines at frequencies equal to the vibrational frequencies of the C=O and ---SH groups, but no lines corresponding to the C=S or ---OH groups. The first alternative is evidently the correct one.

8.8 ELECTRONIC SPECTRA OF MOLECULES

How fluorescence and phosphorescence occur

The energies of rotation and vibration in a molecule are due to the motion of its atomic nuclei, which contain virtually all the molecule's mass. The molecule's electrons also can be excited to higher energy levels than those corresponding to its ground state. However, the spacing of these levels is much greater than the spacing of rotational or vibrational levels.

Electronic transitions involve radiation in the visible or ultraviolet parts of the spectrum. Each transition appears as a series of closely spaced lines, called a band, due to the presence of different rotational and vibrational states in each electronic state (Fig. 8.25).

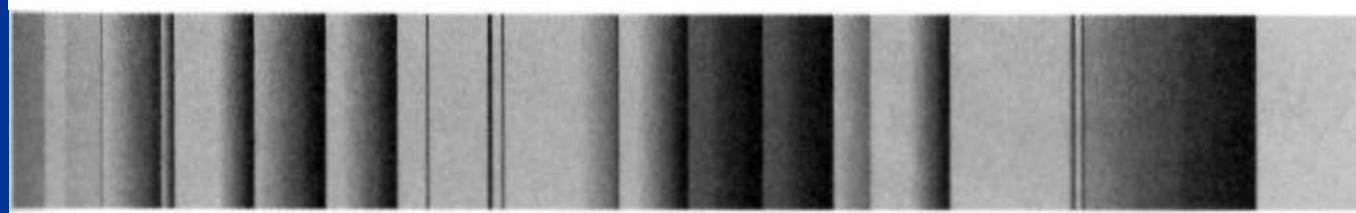


Figure 8.25 A portion of the band spectrum of PN.

All molecules exhibit electronic spectra, since a dipole moment change always accompanies a change in the electronic configuration of a molecule. Therefore homonuclear molecules, such as H₂ and N₂, which have neither rotational nor vibrational spectra because they lack permanent dipole moments, nevertheless have electronic spectra whose rotational and vibrational fine structures enable moments of inertia and bond force constants to be found.

Electronic excitation in a polyatomic molecule often leads to a change in the molecule's shape, which can be determined from the rotational fine structure in its band spectrum. The origin of such changes lies in the different characters of the wave functions of electrons in different states, which lead to correspondingly different bond geometries. For example, the molecule beryllium hydride, BeH₂, is linear (H—Be—H) in one state and bent (H—Be) in another.



A molecule in an excited electronic state can lose energy and return to its ground state in various ways. The molecule may, of course, simply emit a photon of the same frequency as that of the photon it absorbed, thereby returning to the ground state in a single step. Another possibility is **fluorescence**. Here the molecule gives up some of its vibrational energy in collisions with other molecules, so that the downward radiative transition originates from a lower vibrational level in the upper electronic state (Fig. 8.26). Fluorescent radiation is therefore of lower frequency than that of the absorbed radiation.

Fluorescence excited by ultraviolet light has many applications, for instance to help identify minerals and biochemical compounds. In a **fluorescent lamp**, a mixture of mercury vapor and an inert gas such as argon inside a glass tube gives off ultraviolet radiation when an electric current is passed through it. The inside of the tube is coated with a fluorescent material called a phosphor that emits visible light when excited by the ultraviolet radiation. The process is much more efficient than using a current to heat a filament to incandescence, as in ordinary light bulbs.

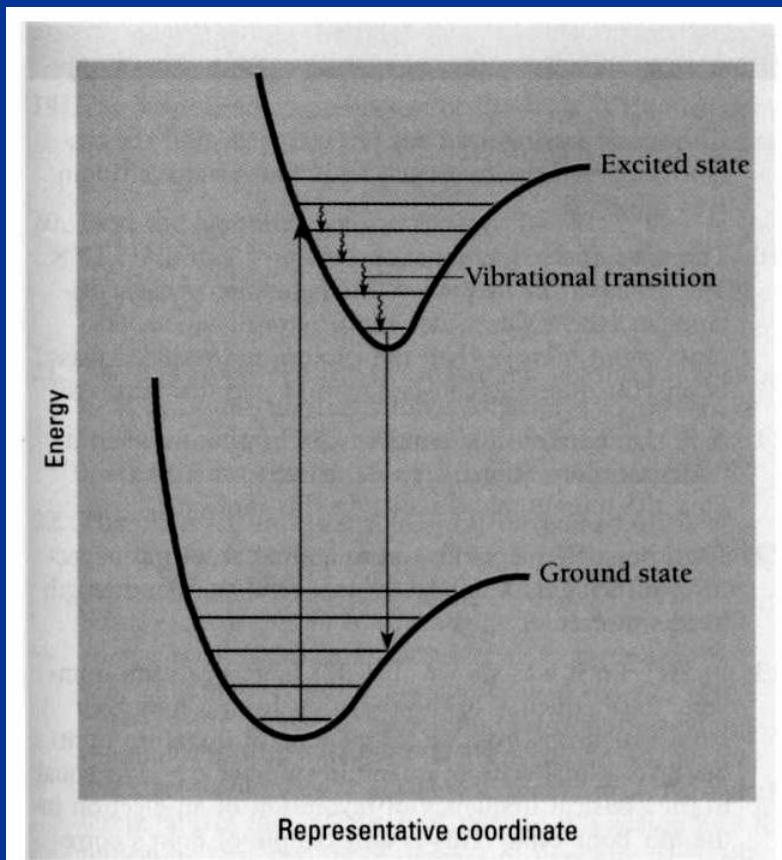
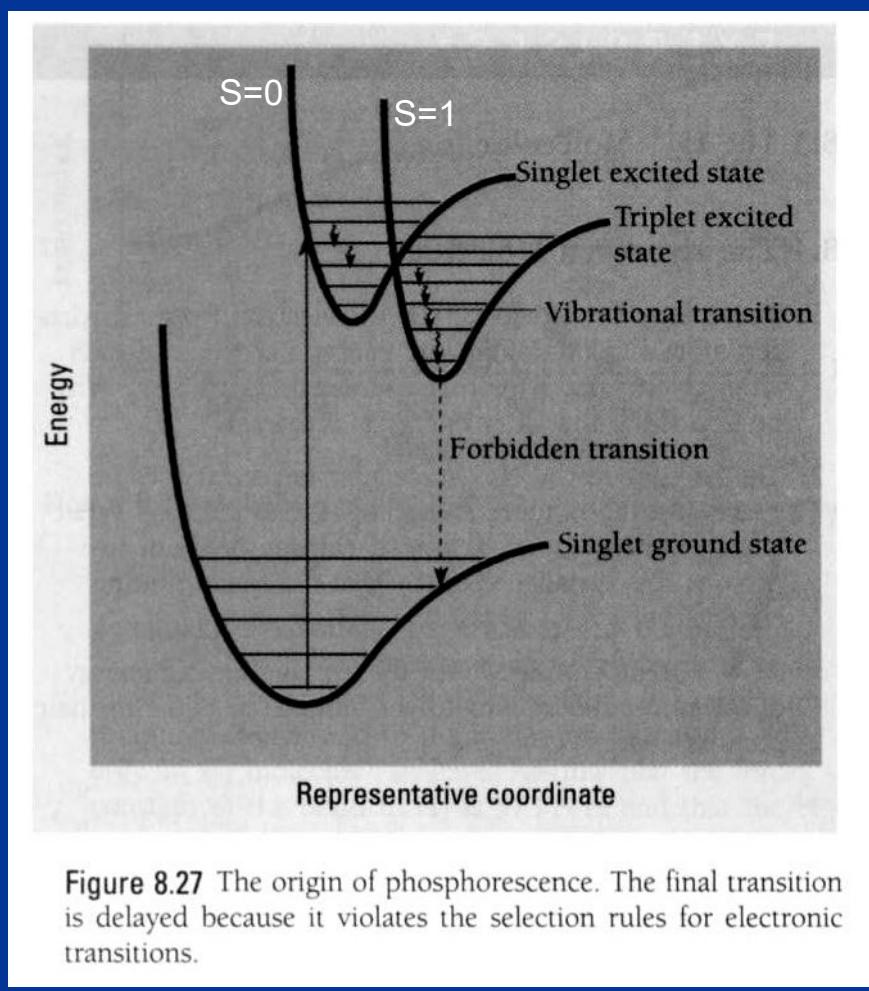


Figure 8.26 The origin of fluorescence. The emitted radiation is lower in frequency than the absorbed radiation.

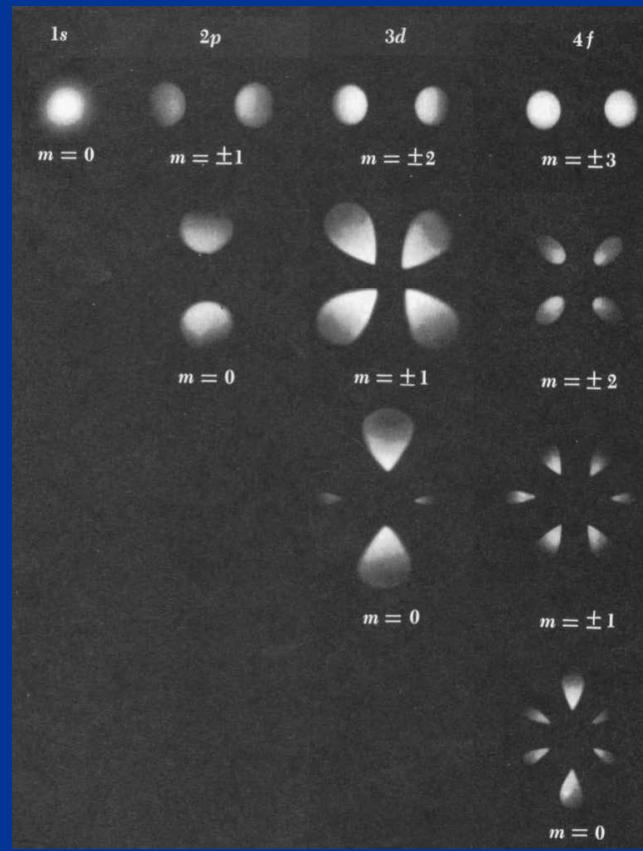
In molecular spectra, radiative transitions between electronic states of different total spin are prohibited. Figure 8.27 shows a situation in which the molecule in its singlet (total spin quantum number $\mathbf{S} = 0$) ground state absorbs a photon and is raised to a singlet excited state. In collisions the molecule can undergo radiationless transitions to a lower vibrational level that may happen to have about the same energy as one of the levels in the triplet ($\mathbf{S} = 1$) excited state. There is then a certain probability for a shift to the triplet state to occur. Further collisions in the triplet state bring the molecule's energy below that of the crossover point, so that it is now trapped in the triplet state and ultimately reaches the $v = 0$ level.

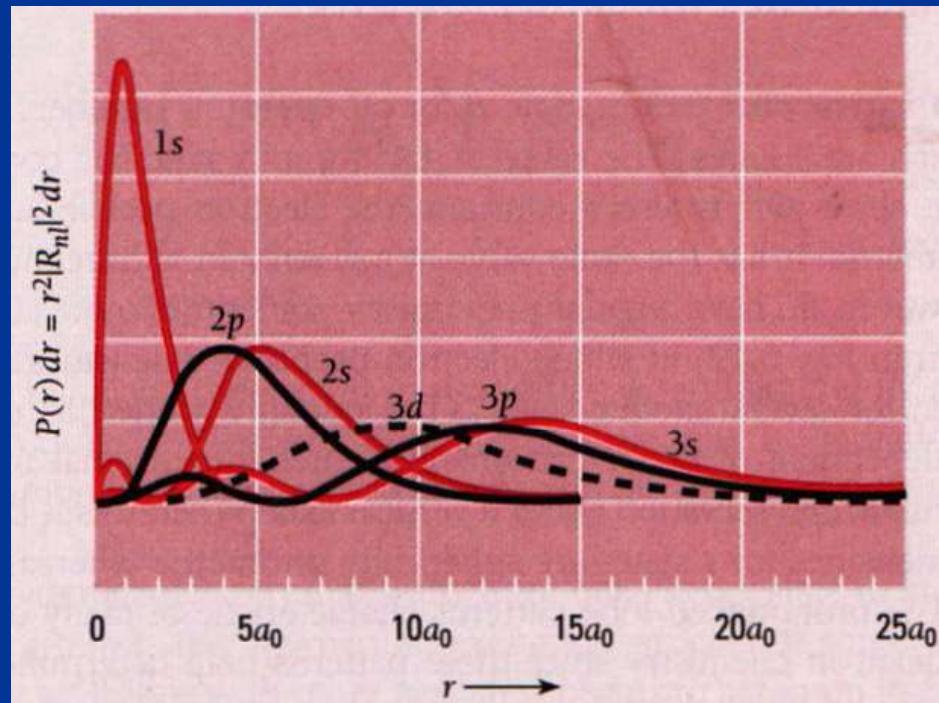
A radiative transition from a triplet to a singlet state is “forbidden” by the selection rules, which really means not that it is impossible but that it has only a small likelihood of occurring. Such transitions accordingly have long half-lives, and the resulting **phosphorescent radiation** may be emitted minutes or even hours after the initial absorption.



Tunable Dye Lasers

The existence of bands of extremely closely spaced lines in molecular spectra underlies the operation of the **tunable dye laser**. Such a laser uses an organic dye whose molecules are “pumped” to excited states by light from another laser. The dye then fluoresces in a broad emission band. From this band, light of the desired wavelength λ can be selected for laser amplification with the help of a pair of facing mirrors, one of them partly transparent. The separation of the mirrors is set to an integral multiple of $\lambda/2$. As in the case of the lasers discussed in Sec. 4.10, the trapped laser light forms an optical standing wave that emerges through the partly transparent mirror. A dye laser of this kind can be tuned to a precision of better than one part in a million by adjusting the spacing of the mirrors.





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9.1 STATISTICAL DISTRIBUTIONS

Three different kinds

What statistical mechanics does is determine the most probable way in which a certain total amount of energy E is distributed among the N members of a system of particles in thermal equilibrium at the absolute temperature T . Thus we can establish how many particles are likely to have the energy ϵ_1 , how many to have the energy ϵ_2 , and so on.

The particles are assumed to interact with one another and with the walls of their container to an extent sufficient to establish thermal equilibrium but not so much that their motions are strongly correlated. More than one particle state may correspond to a certain energy ϵ . If the particles are not subject to the exclusion principle, more than one particle may be in a certain state.

A basic premise of statistical mechanics is that the greater the number W of different ways in which the particles can be arranged among the available states to yield a particular distribution of energies, the more probable is the distribution. It is assumed that each state of a certain energy is equally likely to be occupied. This assumption is plausible but its ultimate justification (as in the case of Schrödinger's equation) is that the conclusions arrived at with its help agree with experiment.

The program of statistical mechanics begins by finding a general formula for W for the kind of particles being considered. The most probable distribution, which corresponds to the system's being in thermal equilibrium, is the one for which W is a maximum, subject to the condition that the system consists of a fixed number N of particles (except when they are photons or their acoustic equivalent called **phonons**) whose total energy is some fixed amount E . The result in each case is an expression for $n(\epsilon)$, the number of particles with the energy ϵ , that has the form

**Number of particles
of energy ϵ** $n(\epsilon) = g(\epsilon)f(\epsilon)$ (9.1)

where $\underline{g(\epsilon)}$ = number of states of energy ϵ
 $=$ statistical weight corresponding to energy ϵ
 $\underline{f(\epsilon)}$ = distribution function
 $=$ average number of particles in each state of energy ϵ
 $=$ probability of occupancy of each state of energy ϵ

When a continuous rather than a discrete distribution of energies is involved, $g(\epsilon)$ is replaced by $g(\epsilon) d\epsilon$, the number of states with energies between ϵ and $\epsilon + d\epsilon$.

We shall consider systems of three different kinds of particles:

- 1 Identical particles that are sufficiently far apart to be distinguishable, for instance, the molecules of a gas. In quantum terms, the wave functions of the particles overlap to a negligible extent. The **Maxwell-Boltzmann distribution function** holds for such particles.
- 2 Identical particles of 0 or integral spin that cannot be distinguished one from another because their wave functions overlap. Such particles, called **bosons** in Chap. 7, do not obey the exclusion principle, and the **Bose-Einstein distribution function** holds for them. Photons are in this category, and we shall use Bose-Einstein statistics to account for the spectrum of radiation from a blackbody.
- 3 Identical particles with odd half-integral spin ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$) that also cannot be distinguished one from another. Such particles, called **fermions**, obey the exclusion principle, and the **Fermi-Dirac distribution function** holds for them. Electrons are in this category, and we shall use Fermi-Dirac statistics to study the behavior of the free electrons in a metal that are responsible for its ability to conduct electric current.

9.2 MAXWELL-BOLTZMANN STATISTICS

Classical particles such as gas molecules obey them

The Maxwell-Boltzmann distribution function states that the average number of particles $f_{MB}(\epsilon)$ in a state of energy ϵ in a system of particles at the absolute temperature T is

Maxwell-Boltzmann distribution function

$$f_{MB}(\epsilon) = A e^{-\epsilon/kT} \quad (9.2)$$

The value of A depends on the number of particles in the system and plays a role here analogous to that of the normalization constant of a wave function. As usual, k is Boltzmann's constant, whose value is

Boltzmann's constant

$$k = 1.381 \times 10^{-23} \text{ J/K} = 8.617 \times 10^{-5} \text{ eV/K}$$

Combining Eqs. (9.1) and (9.2) gives us the number $n(\epsilon)$ of identical, distinguishable particles in an assembly at the temperature T that have the energy ϵ :

Maxwell-Boltzmann

$$n(\epsilon) = A g(\epsilon) e^{-\epsilon/kT} \quad (9.3)$$

Example 9.2

Obtain a formula for the populations of the rotational states of a rigid diatomic molecule.

Solution

For such a molecule Eq. (8.9) gives the energy states in terms of the rotational quantum number J as

$$\epsilon_J = J(J + 1) \frac{\hbar^2}{2I}$$

More than one rotational state may correspond to a particular J because the component L_z in any specified direction of the angular momentum L may have any value in multiples of \hbar from $J\hbar$ through 0 to $-J\hbar$, for a total of $2J + 1$ possible values. Each of these $2J + 1$ possible orientations of L constitutes a separate quantum state, and so

$$g(\epsilon) = 2J + 1$$

$$g(\epsilon) = 2J + 1$$

If the number of molecules in the $J = 0$ state is n_0 , the normalization constant A in Eq. (9.3) is just n_0 , and the number of molecules in the $J = J$ state is

$$n_J = Ag(\epsilon)e^{-\epsilon/kT} = n_0(2J + 1)e^{-J(J+1)\hbar^2/kT} \quad \text{2I}$$

In carbon monoxide, to give an example, this formula shows that the $J = 7$ state is the most highly populated at 20°C. The intensities of the rotational lines in a molecular spectrum are proportional to the relative populations of the various rotational energy levels. Figure 8.22 shows the vibration-rotation band of CO for the $v = 0 \rightarrow v = 1$ vibrational transition with lines identified according to the J value of the initial rotational level. The P and R branches both have their maxima at $J = 7$, as expected.

9.3 MOLECULAR ENERGIES IN AN IDEAL GAS

They vary about an average of $\frac{3}{2}kT$

We now apply Maxwell-Boltzmann statistics to find the distribution of energies among the molecules of an ideal gas. Energy quantization is inconspicuous in the translational motion of gas molecules, and the total number of molecules N in a sample is usually very large. It is therefore reasonable to consider a continuous distribution of molecular energies instead of the discrete set $\epsilon_1, \epsilon_2, \epsilon_3, \dots$. If $n(\epsilon) d\epsilon$ is the number of molecules whose energies lie between ϵ and $\epsilon + d\epsilon$, Eq. (9.1) becomes

Number of molecules with energies between ϵ and $\epsilon + d\epsilon$

$$n(\epsilon) d\epsilon = [g(\epsilon) d\epsilon] f(\epsilon) = Ag(\epsilon)e^{-\epsilon/kT} d\epsilon \quad (9.4)$$

The first task is to find $g(\epsilon) d\epsilon$, the number of states that have energies between ϵ and $\epsilon + d\epsilon$. This is easiest to do in an indirect way. A molecule of energy ϵ has a momentum p whose magnitude p is specified by

$$p = \sqrt{2m\epsilon} = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

Each set of momentum components p_x, p_y, p_z specifies a different state of motion. Let us imagine a **momentum space** whose coordinate axes are p_x, p_y, p_z , as in Fig. 9.1. The number of states $g(p) dp$ with momenta whose magnitudes are between p and $p + dp$ is proportional to the volume of a spherical shell in momentum space p in radius and dp thick, which is $4\pi p^2 dp$. Hence

Number of momentum states

$$g(p) dp = Bp^2 dp \quad (9.5)$$

where B is some constant.

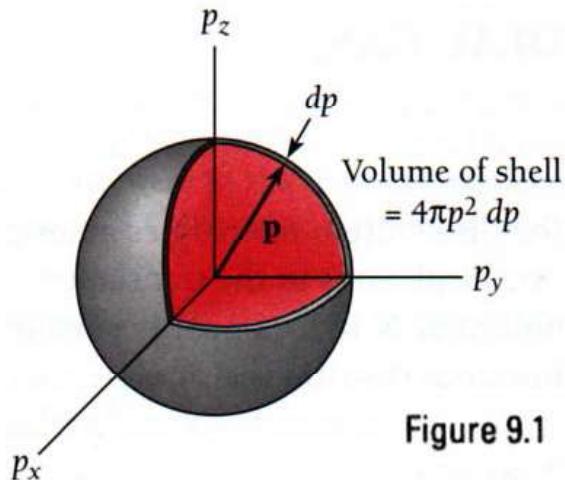


Figure 9.1

Since each momentum magnitude p corresponds to a single energy ϵ , the number of energy states $g(\epsilon) d\epsilon$ between ϵ and $\epsilon + d\epsilon$ is the same as the number of momentum states $g(p) dp$ between p and $p + dp$, and so

$$g(\epsilon) d\epsilon = Bp^2 dp \quad (9.6)$$

Because

$$p^2 = 2m\epsilon \quad \text{and} \quad dp = \frac{m d\epsilon}{\sqrt{2m\epsilon}}$$

Eq. (9.6) becomes

Number of energy states

$$g(\epsilon) d\epsilon = 2m^{3/2} B \sqrt{\epsilon} d\epsilon \quad (9.7)$$

The number of molecules with energies between ϵ and $d\epsilon$ is therefore

$$n(\epsilon) d\epsilon = C \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.8)$$

where $C (= 2m^{3/2} AB)$ is a constant to be evaluated.

$$n(\epsilon) d\epsilon = A g(\epsilon) e^{-\epsilon/kT} d\epsilon \quad (9.4)$$

To find C we make use of the normalization condition that the total number of molecules is N , so that

Normalization
$$N = \int_0^\infty n(\epsilon) d\epsilon = C \int_0^\infty \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.9)$$

From a table of definite integrals we find that

$$\int_0^\infty \sqrt{x} e^{-ax} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

Here $a = 1/kT$, and the result is $N = \frac{C}{2} \sqrt{\pi} (kT)^{3/2}$

$$C = \frac{2\pi N}{(\pi kT)^{3/2}} \quad (9.10)$$

and, finally,

Molecular energy distribution
$$n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.11)$$

Molecular energy distribution
$$n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.11)$$

This formula gives the number of molecules with energies between ϵ and $\epsilon + d\epsilon$ in a sample of an ideal gas that contains N molecules and whose absolute temperature is T .

Equation (9.11) is plotted in Fig. 9.2 in terms of kT . The curve is not symmetrical about the most probable energy because the lower limit to ϵ is $\epsilon = 0$ while there is, in principle, no upper limit (although the likelihood of energies many times greater than kT is small).

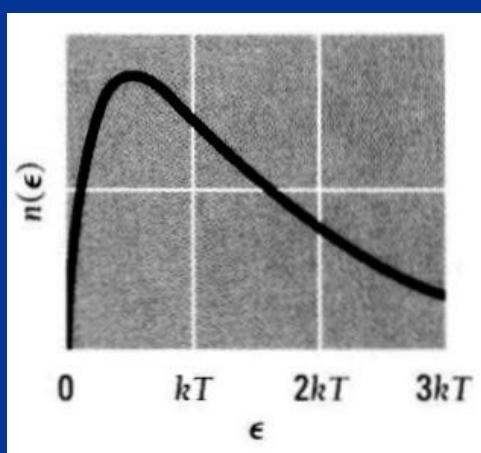


Figure 9.2 Maxwell-Boltzmann energy distribution for the molecules of an ideal gas. The average molecular energy is $\bar{\epsilon} = \frac{3}{2}kT$.

Average Molecular Energy

To find the average energy per molecule we begin by calculating the total internal energy of the system. To do this we multiply $n(\epsilon) d\epsilon$ by the energy ϵ and then integrate over all energies from 0 to ∞ :

$$E = \int_0^{\infty} \epsilon n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^{\infty} \epsilon^{3/2} e^{-\epsilon/kT} d\epsilon$$

Making use of the definite integral

$$\int_0^{\infty} x^{3/2} e^{-ax} dx = \frac{3}{4a^2} \sqrt{\frac{\pi}{a}}$$

we have

Total energy of N gas molecules $E = \left[\frac{2\pi N}{(\pi kT)^{3/2}} \right] \left[\frac{3}{4}(kT)^2 \sqrt{\pi kT} \right] = \frac{3}{2} N k T$ (9.12)

The average energy of an ideal-gas molecule is $\underline{E/N}$, or

Average molecular energy $\bar{\epsilon} = \frac{3}{2} k T$ (9.13)

which is independent of the molecule's mass: a light molecule has a greater average speed at a given temperature than a heavy one. The value of $\bar{\epsilon}$ at room temperature is about 0.04 eV, $\frac{1}{25}$ eV.

Equipartition of Energy

A gas molecule has three **degrees of freedom** that correspond to motions in three independent (that is, perpendicular) directions. Since the average kinetic energy of the molecule is $\frac{3}{2}kT$, we can associate $\frac{1}{2}kT$ with the average energy of each degree of freedom: $\frac{1}{2}mv_x^2 = \frac{1}{2}mv_y^2 = \frac{1}{2}mv_z^2 = \frac{1}{2}kT$. This association turns out to be quite general and is called the **equipartition theorem**:

The average energy per degree of freedom of any classical object that is a member of a system of such objects in thermal equilibrium at the temperature T is $\frac{1}{2}kT$.

Degrees of freedom are not limited to linear velocity components—each variable that appears squared in the formula for the energy of a particular object represents a degree of freedom. Thus each component ω_i of angular velocity (provided it involves a moment of inertia I_i) is a degree of freedom, so that $\frac{1}{2}I_i\omega_i^2 = \frac{1}{2}kT$. A rigid diatomic molecule of the kind described in Sec. 8.6 therefore has five degrees of freedom, one each for motions in the x , y , and z directions and two for rotations about axes perpendicular to its symmetry axis.

$$n(\epsilon) d\epsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{\epsilon} e^{-\epsilon/kT} d\epsilon \quad (9.11)$$

Distribution of Molecular Speeds

The distribution of molecular speeds in an ideal gas can be found from Eq. (9.11) by making the substitutions

$$\epsilon = \frac{1}{2}mv^2 \quad d\epsilon = mv \, dv$$

The result for the number of molecules with speeds between v and $v + dv$ is

Molecular-speed distribution $n(v) dv = 4\pi N \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT} dv \quad (9.14)$

This formula, which was first obtained by Maxwell in 1859, is plotted in Fig. 9.3.

The speed of a molecule with the average energy of $\frac{3}{2}kT$ is

RMS speed $v_{\text{rms}} = \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}} \quad (9.15)$

since $\frac{1}{2}mv^2 = \frac{3}{2}kT$. This speed is denoted v_{rms} because it is the square root of the average of the squared molecular speeds—the root-mean-square speed—and is not the same as the simple arithmetical average speed \bar{v} .

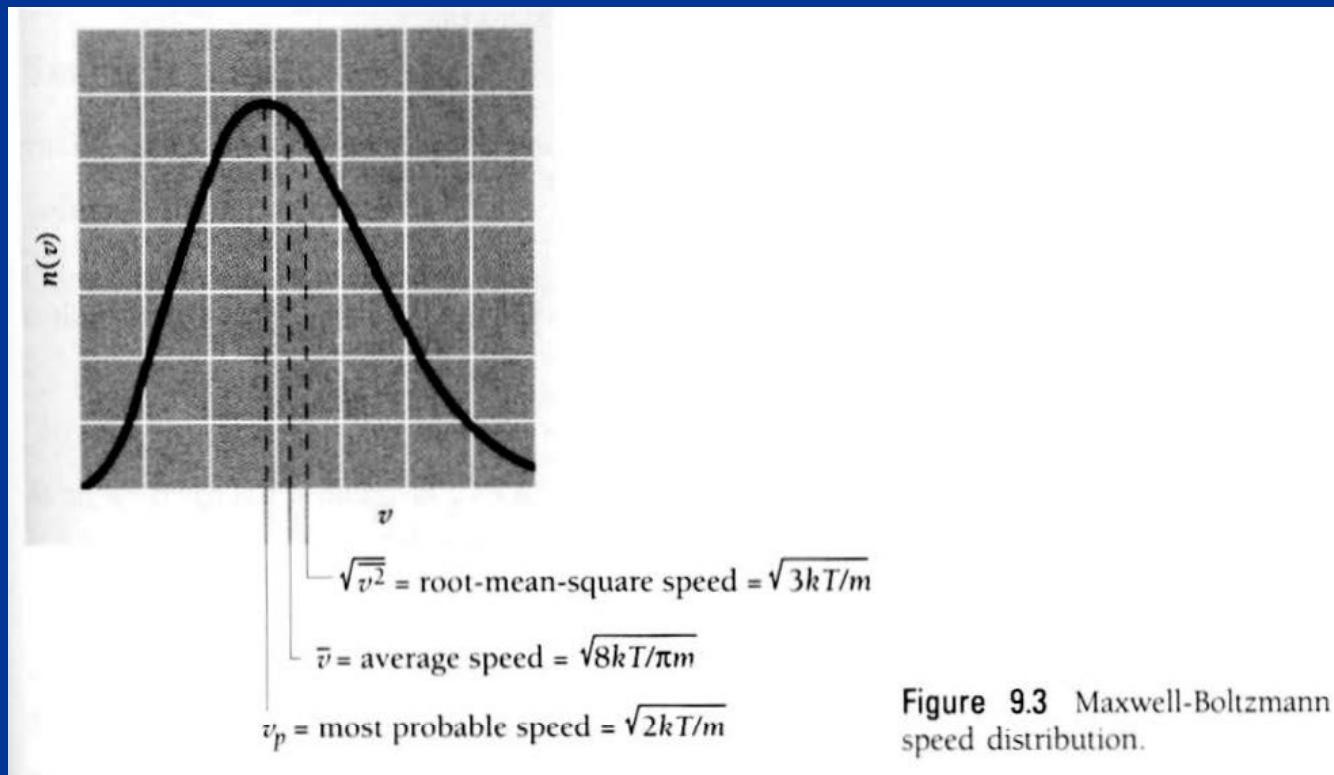


Figure 9.3 Maxwell-Boltzmann speed distribution.

Because the speed distribution of Eq. (9.14) is not symmetrical, the most probable speed v_p is smaller than either \bar{v} or v_{rms} . To find v_p , we set equal to zero the derivative of $n(v)$ with respect to v and solve the resulting equation for v . The result is

Most probable speed

$$v_p = \sqrt{\frac{2kT}{m}} \quad (9.16)$$

Molecular speeds in a gas vary considerably on either side of v_p . Figure 9.4 shows the distribution of speeds in oxygen at 73 K (-200°C), in oxygen at 273 K (0°C), and in hydrogen at 273 K. The most probable speed increases with temperature and decreases with molecular mass. Accordingly molecular speeds in oxygen at 73 K are on the whole less than at 273 K, and at 273 K molecular speeds in hydrogen are on the whole greater than in oxygen at the same temperature. The average molecular energy is the same in both oxygen and hydrogen at 273 K, of course.

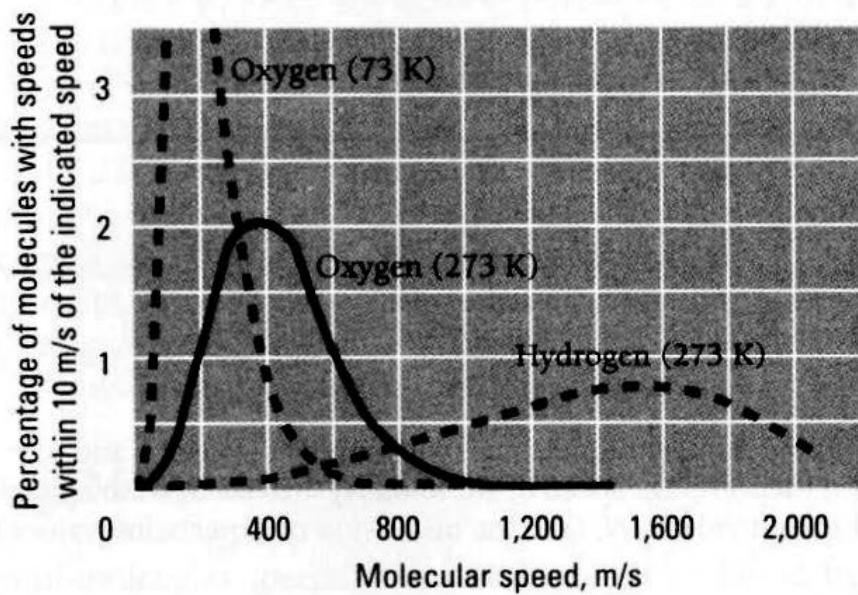
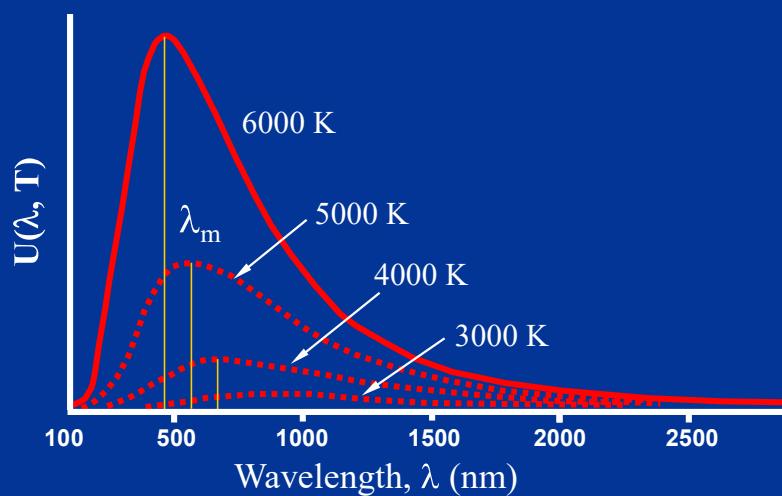


Figure 9.4 The distributions of molecular speeds in oxygen at 73 K, in oxygen at 273 K, and in hydrogen at 273 K.

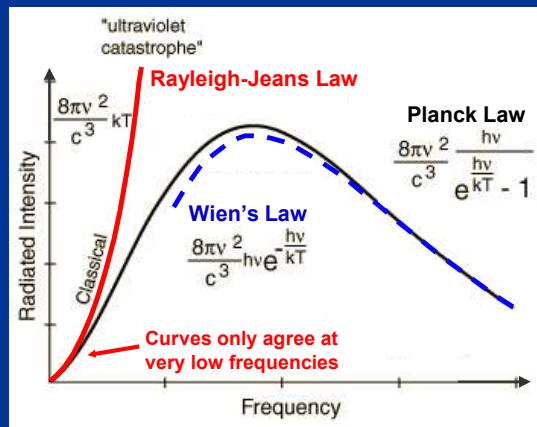
9.5 RAYLEIGH-JEANS FORMULA

The classical approach to blackbody radiation



In classic physics, the blackbody emission was described by two contradictory theorems:

- Rayleigh-Jeans radiation law, valid in the low frequency region
- Wien's law, valid in the high frequency region



Think a cavity made of metal

$$U(v, T) = \frac{g(v) \times \bar{u}}{V} \quad \bar{u} = \int_0^{\infty} u n(u) du$$

$E=0$ at $x=0, L$; otherwise there is a current flowing on the wall !

Wave equation for one-dimensional electromagnetic waves:

$$\frac{\partial^2 E}{\partial x^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2}$$

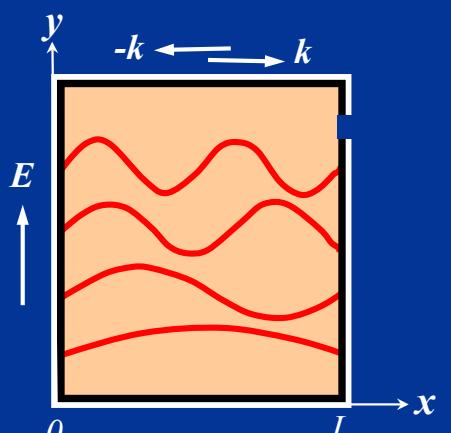
The solutions have the plane-wave form:

$$E = E_0 \sin(kx) \cdot \sin(\omega t) \quad \text{with } c = \omega/k$$

(here $\omega = 2\pi\nu$ is the angular frequency, $k = 2\pi/\lambda$ the wave vector)

When $x=L$, $E = E_0 \sin(kL) \cdot \sin(\omega t) = 0$ for any t , hence $kL = n\pi$ ($n=1, 2, 3, \dots$),

i.e. $k = n\pi/L$



So, for the standing waves: $E = E_0 \sin(n\pi x/L) \cdot \sin(\omega t)$

Similarly, for electromagnetic waves in a 3-dimensional cubic cavity:

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} + \frac{\partial^2 E}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2}$$

and the solutions for the standing waves are:

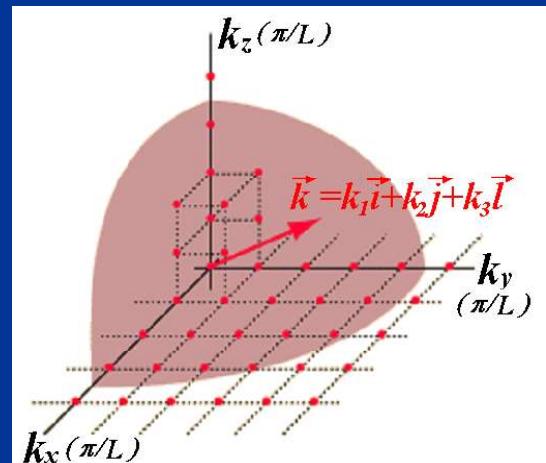
$$E = E_0 \sin(k_x x) \cdot \sin(k_y y) \cdot \sin(k_z z) \cdot \sin(\omega t)$$

where, $k_x = n_x \pi / L$, $k_y = n_y \pi / L$, $k_z = n_z \pi / L$

(n_x, n_y, n_z are integers: 1, 2, 3, ...)

$$\text{and } c = \omega/k \quad \text{with } (k^2 = k_x^2 + k_y^2 + k_z^2)$$

Let $\vec{k} = k_x \vec{i} + k_y \vec{j} + k_z \vec{l}$, which is the 3-dimensional wave-vector.



For each of \mathbf{k} , there are many combinations (modes) of k_x, k_y, k_z to meet $k^2 = k_x^2 + k_y^2 + k_z^2$ and all of them are on the first octant of a sphere with radius of \mathbf{k} .

All the modes with k between k and $k + \delta k$ fall inside the shell, whose internal radius is k and external radius $k + \delta k$.

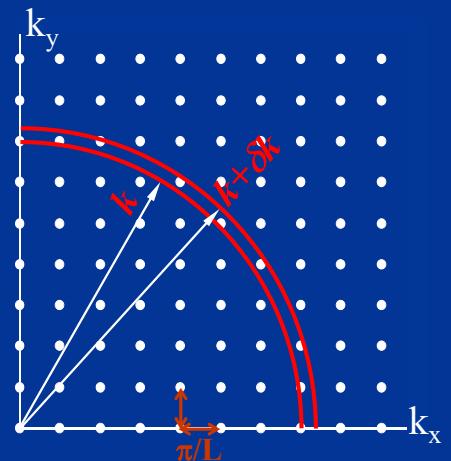
Every mode (i.e. a spot in the picture) take a space of $(\pi/L) \times (\pi/L) \times (\pi/L)$ on average

Hence the number of modes inside the shell is:

$$\delta N = \frac{1}{8} \times \frac{4}{3} \pi (k + \delta k)^3 - \frac{4}{3} \pi k^3 = \frac{L^3}{6\pi^2} [(k + \delta k)^3 - k^3]$$

ignore $(\delta k)^2$ and higher orders, $(k + \delta k)^3 \approx k^3 + 3k^2\delta k$

$$\text{So } \delta N = \frac{L^3}{2\pi^2} k^2 \delta k, \text{ replace } k \text{ with } v = \omega/2\pi = c \cdot k/2\pi, \text{ then } \delta N(v) = \frac{4\pi L^3}{c^3} v^2 \delta v$$



When $\delta v \rightarrow 0$, we have the density of modes: $g(v) = \frac{dN(v)}{dv} = \frac{4\pi L^3}{c^3} v^2$ (i.e. the number of standing waves at a given frequency v)

If the averaged energy for the standing waves is \bar{u} , then the energy density of blackbody radiation, i.e. energy per unit volume per frequency, is:

$$U(v, T) = 2 \times g(v) \times \bar{u} \times \frac{1}{L^3} = \frac{8\pi v^2}{c^3} \bar{u}$$

(the factor of 2 is because each electromagnetic wave has two polarisations)

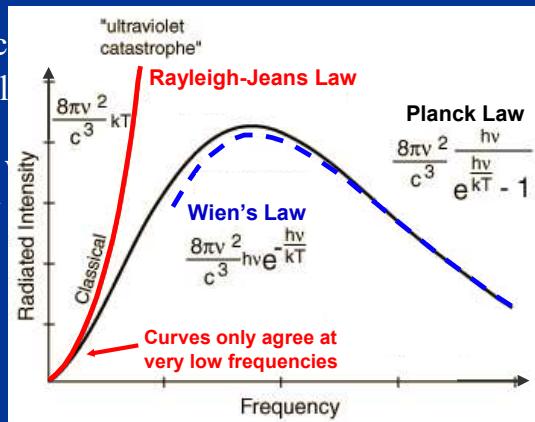
Now we need to work out average energy of the radiation system — \bar{u}

According to classic theory, the energy of each electron u , is the square of its amplitude and can be any value.

The large numbers of the standing electromagnetic cavity are the entities of a same kind, which follow

distribution: $Ae^{-\frac{u}{kT}}$

$$\text{Hence the average energy is: } \bar{u} = \frac{\int_0^\infty ue^{-\frac{u}{kT}} du}{\int_0^\infty e^{-\frac{u}{kT}} du}$$



$$\text{Let } x = -u/kT \text{ the denominator: } \int_0^\infty e^{-\frac{u}{kT}} du = kT \int_0^\infty e^{-x} dx = -kT e^{-x} \Big|_0^\infty = kT$$

$$\text{the numerator: } \int_0^\infty ue^{-\frac{u}{kT}} du = (kT)^2 \int_0^\infty xe^{-x} dx = (kT)^2 (xe^{-x} \Big|_0^\infty + \int_0^\infty e^{-x} dx) = (kT)^2$$

$$\text{So, } \bar{u} = \frac{(kT)^2}{kT} = kT, \quad U(\nu, T) = \frac{8\pi\nu^2}{c^3} \bar{u} = \frac{8\pi\nu^2}{c^3} kT \quad \text{Rayleigh-Jeans radiation law}$$

Planck's Assumption (1901):

- The energy exchange between the electrons in the cavity wall and electromagnetic waves only occur in discrete amounts.
- The minimum unit of energy exchange, which is called as “quantum of energy”, is $h\nu$. Here, $h=6.626 \times 10^{-34}$ (J·s) is the Plank's constant, ν the frequency of electromagnetic waves.

$$\bar{u} = \frac{\int_0^\infty ue^{-\frac{u}{kT}} du}{\int_0^\infty e^{-\frac{u}{kT}} du}$$

i.e. $\boxed{u = nh\nu, n=0, 1, 2, 3, \dots}$

So, the average energy is now: $\bar{u} = \frac{\sum_{n=0}^{\infty} nh\nu e^{-\frac{nh\nu}{kT}}}{\sum_{n=0}^{\infty} e^{-\frac{nh\nu}{kT}}}$

compare to classic

Let $Y = \sum_n e^{-nh\nu x}, x = 1/kT$, then $\bar{u} = -\frac{d}{dx} \ln Y$

$$Y = \sum_n e^{(-h\nu x)n} = \lim_{n \rightarrow \infty} \frac{1 - e^{(-h\nu x)(n+1)}}{1 - e^{(-h\nu x)}} = \frac{1}{1 - e^{-h\nu x}}$$

$$\bar{u} = -\frac{d}{dx} \ln \left[\frac{1}{1 - e^{-h\nu x}} \right] = \frac{d}{dx} \ln(1 - e^{-h\nu x}) = \frac{h\nu e^{-h\nu x}}{1 - e^{-h\nu x}} = \frac{h\nu}{e^{h\nu x} - 1}$$

$$x = 1/kT, \quad \bar{u} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1},$$

$$U(\nu, T) = \frac{8\pi\nu^2}{c^3} \bar{u} = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

Planck Law !

Plank's law
$$U(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

Rayleigh-Jeans and Wien's laws are special cases of Plank's law

We know: $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$

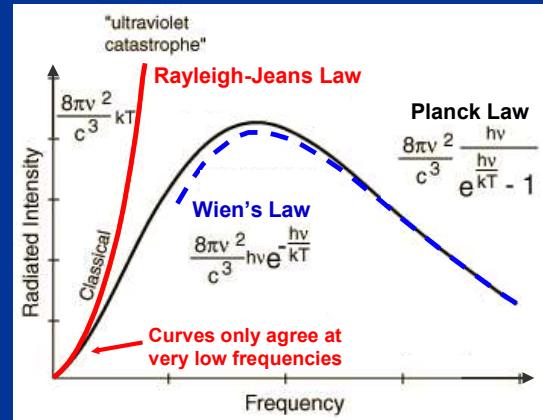
If x is small, $e^x \approx 1 + x$, and so for $h\nu/kT \ll 1$ we have

$$\frac{h\nu}{e^{h\nu/kT} - 1} \approx \frac{h\nu}{1 + \frac{h\nu}{kT} - 1} \approx \frac{h\nu}{\frac{h\nu}{kT}} = kT \quad h\nu \ll kT$$

Thus at low frequencies Planck's formula becomes

$$U(\nu, T) \approx \frac{8\pi h}{c^3} \nu^3 \left(\frac{kT}{h\nu} \right) d\nu \approx \frac{8\pi kT}{c^3} \nu^2$$

which is the Rayleigh-Jeans formula.



When $h\nu/kT \gg 1$, then

$$e^{h\nu/kT} \gg 1 \quad e^{h\nu/kT} - 1 \approx e^{h\nu/kT}$$

$$\frac{h\nu}{e^{h\nu/kT} - 1} \approx h\nu e^{-h\nu/kT} \quad U(\nu, T) \approx \frac{8\pi\nu^2}{c^3} h\nu e^{-\frac{h\nu}{kT}}$$

which is Wien's law.

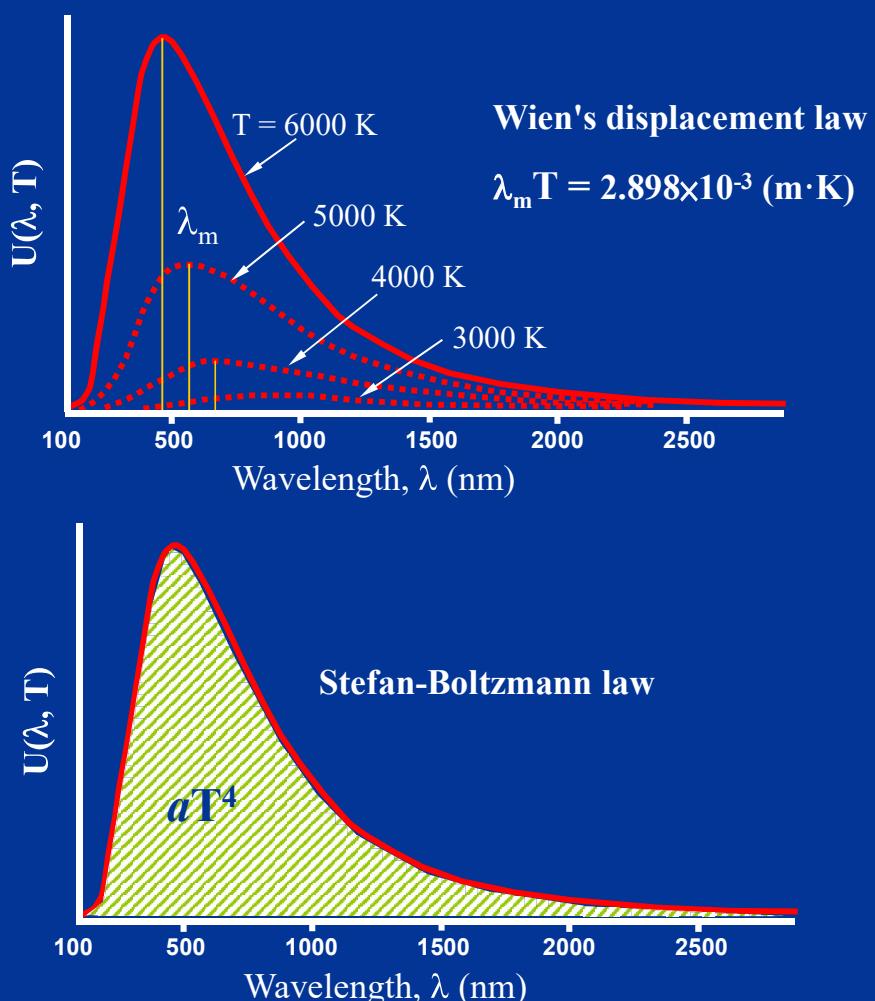
Wien's Displacement Law

An interesting feature of the blackbody spectrum at a given temperature is the wavelength λ_{\max} for which the energy density is the greatest. To find λ_{\max} we first express Eq. (9.38) in terms of wavelength and solve $du(\lambda)/d\lambda = 0$ for $\lambda = \lambda_{\max}$. We obtain in this way

$$\frac{hc}{kT\lambda_{\max}} = 4.965$$

which is more conveniently expressed as

Wien's displacement law $\lambda_{\max} T = \frac{hc}{4.965k} = 2.898 \times 10^{-3} \text{ m} \cdot \text{K}$ (9.40)



Stefan-Boltzmann Law

Another result we can obtain from Eq. (9.38) is the total energy density u of the radiation in a cavity. This is the integral of the energy density over all frequencies,

$$u = \int_0^\infty u(\nu) d\nu = \frac{8\pi^5 k^4}{15c^3 h^3} T^4 = aT^4$$

where a is a universal constant. The total energy density is proportional to the fourth power of the absolute temperature of the cavity walls. We therefore expect that the energy R radiated by an object per second per unit area is also proportional to T^4 , a conclusion embodied in the **Stefan-Boltzmann** law:

Stefan-Boltzmann law $R = e\sigma T^4$ (9.41)

The value of **Stefan's constant** σ is

Stefan's constant $\sigma = \frac{ac}{4} = 5.670 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4$

The emissivity e depends on the nature of the radiating surface and ranges from 0, for a perfect reflector which does not radiate at all, to 1, for a blackbody. Some typical values of e are 0.07 for polished steel, 0.6 for oxidized copper and brass, and 0.97 for matte black paint.

9.4 QUANTUM STATISTICS

Bosons and fermions have different distribution functions

Bose-Einstein and Fermi-Dirac Distribution Functions

The probability $f(\epsilon)$ that a boson occupies a state of energy ϵ turns out to be

**Bose-Einstein
distribution
function**

$$f_{BE}(\epsilon) = \frac{1}{e^{\alpha e^{\epsilon/kT}} - 1} \quad (9.26)$$

and the probability for a fermion turns out to be

**Fermi-Dirac
distribution
function**

$$f_{FD}(\epsilon) = \frac{1}{e^{\alpha e^{\epsilon/kT}} + 1} \quad (9.27)$$

The quantity α depends on the properties of the particular system and may be a function of T .

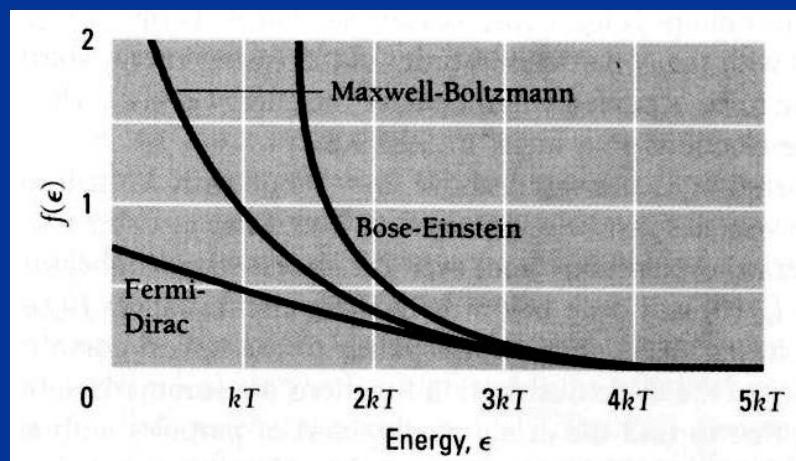


Figure 9.5 A comparison of the three distribution functions for $\alpha = -1$. The Bose-Einstein function is always higher than the Maxwell-Boltzmann one, which is a pure exponential, and the Fermi-Dirac function is always lower. The functions give the probability of occupancy of a state of energy ϵ at the absolute temperature T .

$$f_{FD}(\epsilon) = \frac{1}{e^{\alpha} e^{\epsilon/kT} + 1} \quad (9.27)$$

Denote the energy for $f_{FD}=1/2$ as ϵ_F , then we have:

$$\begin{aligned} f_{FD}(\epsilon_F) &= \frac{1}{e^{\alpha} e^{\epsilon_F/kT} + 1} = \frac{1}{2}, & 2 &= e^{\alpha} e^{\epsilon_F/kT} + 1, & e^{-\alpha} &= e^{\epsilon_F/kT} \\ \epsilon_F &= -\alpha kT, & \alpha &= -\epsilon_F/kT \\ f_{FD}(\epsilon) &= \frac{1}{e^{\alpha} e^{\epsilon/kT} + 1} = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} \end{aligned}$$

Fermi energy

$$\epsilon_F = -\alpha kT \quad (9.28)$$

This energy, called the **Fermi energy**, is a very important quantity in a system of fermions, such as the electron gas in a metal. In terms of ϵ_F the Fermi-Dirac distribution function becomes

Fermi-Dirac

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} \quad (9.29)$$

To appreciate the significance of the Fermi energy, let us consider a system of fermions at $T = 0$ and investigate the occupancy of states whose energies are less than ϵ_F and greater than ϵ_F . What we find is this:

$$T = 0, \epsilon < \epsilon_F: \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

$$T = 0, \epsilon > \epsilon_F: \quad f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon-\epsilon_F)/kT} + 1} = \frac{1}{e^{\infty} + 1} = 0$$

Thus at absolute zero all energy states up to ϵ_F are occupied, and none above ϵ_F (Fig. 9.6a). If a system contains N fermions, we can calculate its Fermi energy ϵ_F by filling up its energy states with the N particles in order of increasing energy starting from $\epsilon = 0$. The highest state to be occupied will then have the energy $\epsilon = \epsilon_F$. This calculation will be made for the electrons in a metal in Sec. 9.8.

As the temperature is increased above $T = 0$ but with kT still smaller than ϵ_F , fermions will leave states just below ϵ_F to move into states just above it, as in Fig. 9.6b. At higher temperatures, fermions from even the lowest state will begin to be excited to higher ones, so $f_{FD}(0)$ will drop below 1. In these circumstances $f_{FD}(\epsilon)$ will assume a shape like that in Fig. 9.6c, which corresponds to the lowest curve in Fig. 9.5.

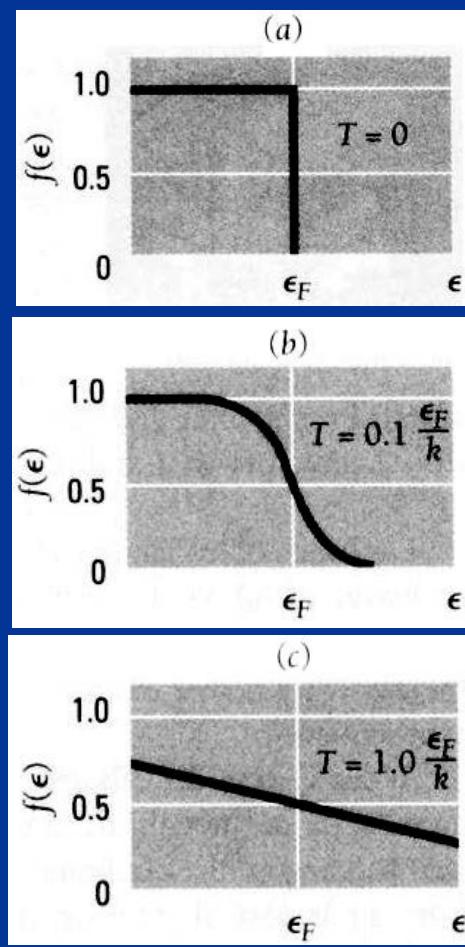


Figure 9.6 Distribution function for fermions at three different temperatures. (a) At $T = 0$, all the energy states up to the Fermi energy ϵ_F are occupied. (b) At a low temperature, some fermions will leave states just below ϵ_F and move into states just above ϵ_F . (c) At a higher temperature, fermions from any state below ϵ_F may move into states above ϵ_F .

9.7 SPECIFIC HEATS OF SOLIDS

Classical physics fails again

A 1-dimensional classic harmonic oscillator at temperature T has an average energy = kT

A 3-dimensional classic harmonic oscillator = $3kT$

A mole of solid has N_0 (Avogadro's number) of atoms, and has energy

$$E = 3N_0 kT$$

Classical internal energy of solid

$$E = 3N_0kT = 3RT \quad (9.42)$$

where $R = N_0k = 8.31 \times 10^3 \text{ J/kmol} \cdot \text{K}$ is the universal gas constant.

The specific heat at constant volume is given in terms of E by

Specific heat at constant volume

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V$$

and so here

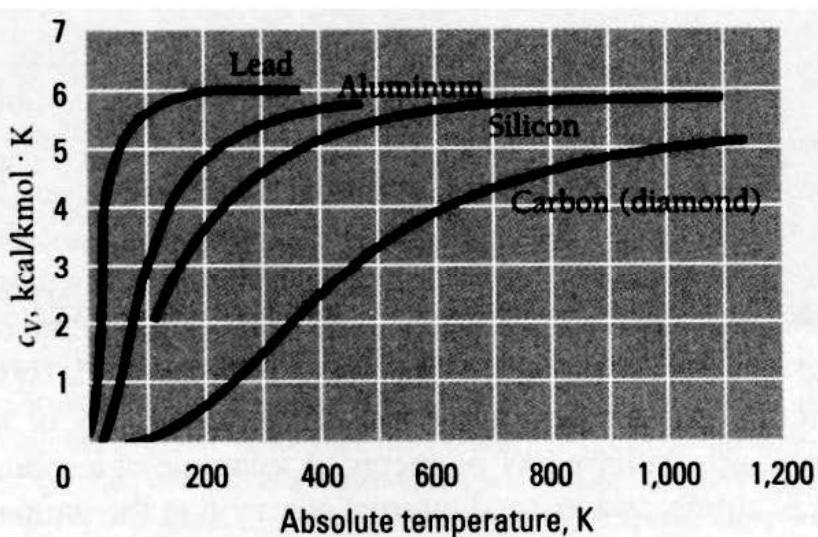
Dulong-Petit law

$$c_V = 3R = 5.97 \text{ kcal/kmol} \cdot \text{K} \quad (9.43)$$

Over a century ago Dulong and Petit found that, indeed, $c_V \approx 3R$ for most solids at room temperature and above, and Eq. (9.43) is known as the **Dulong-Petit law** in their honor.

However, the Dulong-Petit law fails for such light elements as boron, beryllium, and carbon (as diamond), for which $c_V = 3.34, 3.85$, and $1.46 \text{ kcal/kmol} \cdot \text{K}$ respectively at 20°C . Even worse, the specific heats of *all* solids drop sharply at low temperatures and approach 0 as T approaches 0 K. Figure 9.9 shows how c_V varies with T for several elements.

Figure 9.9 The variation with temperature of the molar specific heat at constant volume c_V for several elements.



Einstein's Formula

In 1907 Einstein discerned that the basic flaw in the derivation of Eq. (9.43) lies in the figure of kT for the average energy per oscillator in a solid. This flaw is the same as that responsible for the incorrect Rayleigh-Jeans formula for blackbody radiation.

Average energy per quantum oscillator

$$\bar{\epsilon} = \frac{h\nu}{e^{h\nu/kT} - 1} \quad (9.44)$$

and not $\bar{\epsilon} = kT$. The total internal energy of a kilomole of a solid therefore becomes

Internal energy of solid

$$E = 3N_0\bar{\epsilon} = \frac{3N_0h\nu}{e^{h\nu/kT} - 1} \quad (9.45)$$

and its molar specific heat is

Einstein specific heat formula

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = 3R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \quad (9.46)$$

[Link](#)

9.8 FREE ELECTRONS IN A METAL

Average occupancy per state

$$f_{FD}(\epsilon) = \frac{1}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.29)$$

What we also need is an expression for $g(\epsilon) d\epsilon$, the number of quantum states available to electrons with energies between ϵ and $\epsilon + d\epsilon$.

Free electrons in metal can be treated as “particle in a box”, because they have the same potential, i.e. inside the metal $U=0$, outside the metal $U=\infty$.

So, their wave functions are standing waves, which are the same as those inside the blackbody cavity, and they have the same $g(\epsilon)d\epsilon$

$$g(v) = \frac{dN(v)}{dv} = \frac{4\pi L^3}{c^3} v^2$$

replace with V

(phase velocity of electron wave)

$$g(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} = \frac{dN(v)}{dv} \cdot \frac{dv}{d\epsilon} = g(v) \frac{dv}{d\epsilon} = \frac{4\pi L^3}{V^3} v^2 \frac{dv}{d\epsilon}$$

[Link](#)

$$g(\epsilon) = \frac{4\pi L^3}{V^3} v^2 \frac{dv}{d\epsilon} = \frac{4\pi L^3}{V^3 h^3} (hv)^2 \frac{d(hv)}{d\epsilon} = \frac{4\pi L^3}{V^3 h^3} \epsilon^2$$

$\epsilon = hv$

$$V = \lambda v = \frac{h}{p} \cdot \frac{\epsilon}{h} = \frac{\epsilon}{p} = \frac{\epsilon}{\sqrt{2m\epsilon}} = (2m)^{-1/2} \epsilon^{1/2}$$

We have

$$g(\epsilon) = \frac{8\sqrt{2}\pi L^3 m^{3/2}}{h^3} \sqrt{\epsilon}$$

As in the case of standing waves in a cavity the exact shape of the metal sample does not matter, so we can substitute its volume V for L^3 to give

Number of electron states
$$g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \sqrt{\epsilon} d\epsilon \quad (9.47)$$

Fermi Energy

As shown previously, at $T=0$ K,

$$f_{FD}(\epsilon) = 0 \quad \text{if } \epsilon > \epsilon_F; \quad f_{FD}(\epsilon) = 1 \quad \text{if } \epsilon < \epsilon_F$$

So, total number of electrons N is:

$$N = \int_0^{\epsilon_F} g(\epsilon) d\epsilon = \frac{8\sqrt{2}\pi V m^{3/2}}{h^3} \int_0^{\epsilon_F} \sqrt{\epsilon} d\epsilon = \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} \epsilon_F^{3/2}$$

and so

Fermi energy
$$\epsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{2/3} \quad (9.48)$$

The quantity $N/V = n_e$ is the density of free electrons,

$$\epsilon_F \propto n_e^{2/3}$$

9.9 ELECTRON-ENERGY DISTRIBUTION

Why the electrons in a metal do not contribute to its specific heat except at very high and very low temperatures

With the help of Eqs. (9.29) and (9.47) we have for the number of electrons in an electron gas that have energies between ϵ and $\epsilon + d\epsilon$

$$n(\epsilon) d\epsilon = g(\epsilon)f(\epsilon) d\epsilon = \frac{(8\sqrt{2}\pi V m^{3/2}/h^3) \sqrt{\epsilon} d\epsilon}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.49)$$

If we express the numerator of Eq. (9.49) in terms of the Fermi energy ϵ_F we get

Electron energy distribution $n(\epsilon) d\epsilon = \frac{(3N/2) \epsilon_F^{-3/2} \sqrt{\epsilon} d\epsilon}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.50)$

This formula is plotted in Fig. 9.10 for $T = 0$, 300, and 1200 K.

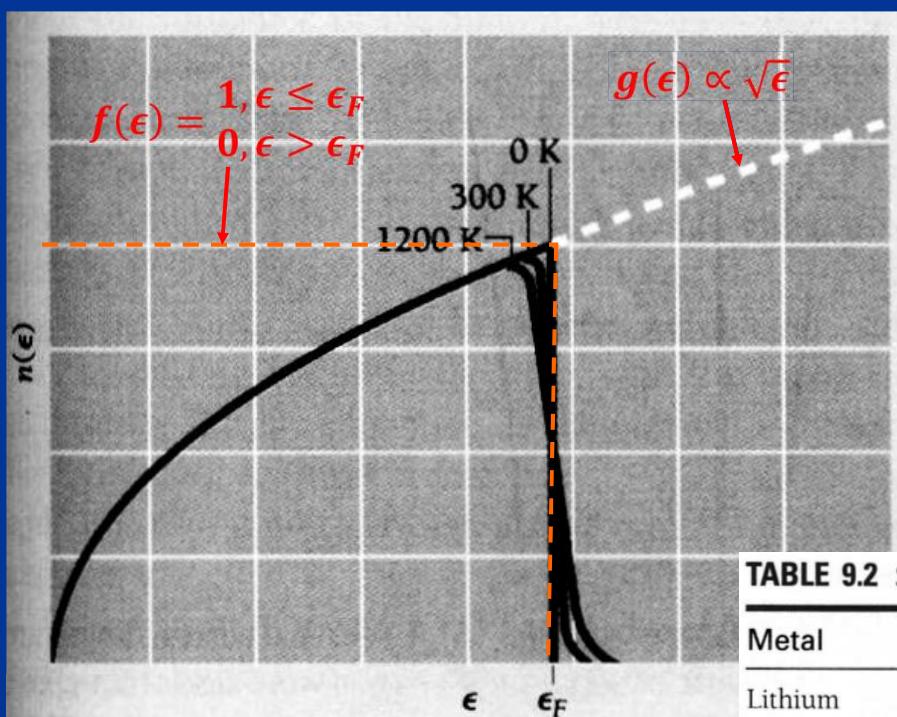


Figure 9.10 Distribution of electron energies in a metal at various temperatures.

TABLE 9.2 Some Fermi Energies

Metal	Fermi energy, eV	
Lithium	Li	4.72
Sodium	Na	3.12
Aluminum	Al	11.8
Potassium	K	2.14
Cesium	Cs	1.53
Copper	Cu	7.04
Zinc	Zn	11.0
Silver	Ag	5.51
Gold	Au	5.54

$$n(\epsilon) d\epsilon = \frac{(3N/2) \epsilon_F^{-3/2} \sqrt{\epsilon} d\epsilon}{e^{(\epsilon - \epsilon_F)/kT} + 1} \quad (9.50)$$

It is interesting to determine the average electron energy at 0 K. To do this, we first find the total energy E_0 at 0 K, which is

$$E_0 = \int_0^{\epsilon_F} \epsilon n(\epsilon) d\epsilon$$

Since at $T = 0$ K all the electrons have energies less than or equal to the Fermi energy ϵ_F , we may let

$$e^{(\epsilon - \epsilon_F)/kT} = e^{-\infty} = 0$$

and

$$E_0 = \frac{3N}{2} \epsilon_F^{-3/2} \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = \frac{3}{5} N \epsilon_F$$

The average electron energy $\bar{\epsilon}_0$ is this total energy divided by the number N of electrons present, which gives

Average electron energy at $T = 0$

$$\bar{\epsilon}_0 = \frac{3}{5} \epsilon_F \quad (9.51)$$

A detailed calculation shows that the specific heat of the electron gas in a metal is given by

Electron specific heat

$$c_{Ve} = \frac{\pi^2}{2} \left(\frac{kT}{\epsilon_F} \right) R \quad (9.52)$$

At room temperature, kT/ϵ_F ranges from 0.016 for cesium to 0.0021 for aluminum for the metals listed in Table 9.2, so the coefficient of R is very much smaller than the classical figure of $\frac{3}{2}$.

$$E = \frac{3}{5} N \epsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_f} \right)^2 \dots \right] \quad (\epsilon_F = kT_f)$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{1}{2} \pi^2 N k \left(\frac{T}{T_f} \right) \dots$$

TABLE 9.2 Some Fermi Energies

Metal	Fermi energy, eV	
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