Obj: General Introduction to 312

Electromagnetic Radiation

Harmonic motion

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Office hour: SMW

8-9 am – the hour before class

10-11 am – the hour after class

(always check outside Build. 4 for me)

– or by appointment (Tel. or email)

Contents

Chap. 11: Quantum Mechanics
Atomic structuer

Chap. 12: Chemical Bond

Chap. 13: Foundations of spectroscopy

Chap. 14: Modern Applications
(not complete Chapter)

Chap. 15: Statistical Mechanics

Homework: <u>Submission</u> alone gives
~~problem/chap.~~ 1 points for each
submitted problem
after normalized to 10

Submission: Week after End of Chap.

<u>No Quizzes</u>: for quizzes: 3rd Major Exam

10 Attendance points: -1 for each absence

no makeup for Majors ~~o~~ or Final

<u>Exams</u>: Problems <u>similar</u> (not same) to
homework problems

Homework : 10 points (submission)
Attendance : 10 points
1. Major (Chap. 11): 16 points
2. Major (Chap. 12): 16 points
3. Major (Chap. 13): 16 points
Final (Chap. 11-15): 32 points

100 points

Electromagnetic Radiation

in vacuum: all types travel withe the same speed (c)

$c = 2.998 \cdot 10^{8} \frac{m}{s}$

$c = \lambda \cdot \nu$ = wavelength · frequency

nm or Å also m (SI)   Hz $= s^{-1}$

⊥ to direction of move:

plane withe the electric field $\vec{E}$

- ⊥ to that plane with magnetic field ~~B~~ $\vec{H}$ (transverse waves)

mol. rotations   mol.

long radio waves, microwaves, infra-

vibrations ←   electronic transitions →

red, visible: red → violet, ultraviolet,

X-rays, γ-rays: increasing λ

radioactive emission

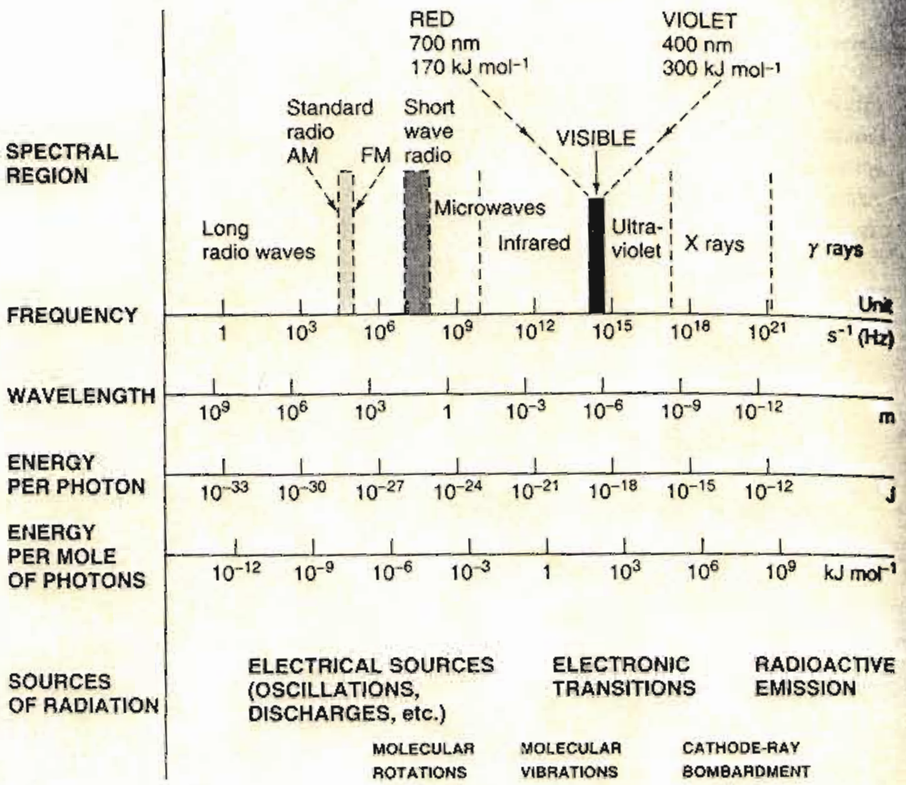


FIGURE 11.1
The electromagnetic spectrum.

floating on still water. If a ripple passes, the cork bobs up and down; its motion is perpendicular to the direction of the wave and it has the same frequency. Similarly an electromagnetic wave causes the particle to move *transverse* (i.e., at right angles) to the direction of propagation, and it is therefore called a *transverse* wave. By contrast, a sound wave is a *longitudinal* wave since the motion of the medium is in the direction of propagation. Both longitudinal and transverse waves are possible in a given medium, a fact that is used to locate the epicenters of earthquakes.

The analogy of a cork on water may be carried further. If the cork is made to oscillate up and down on the surface, a ripple wave is generated. Similarly, an oscillating electron induces electric and magnetic fields and generates an electromagnetic wave.

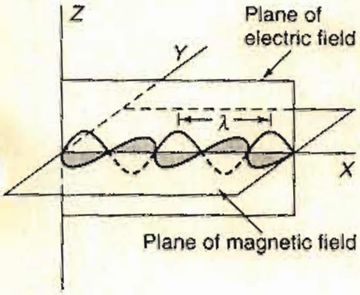


FIGURE 11.2
The propagation of one type of electromagnetic wave, showing the oscillation of the electric field and the magnetic field in planes at right angles to one another, at a given time. Standing waves, and plane-polarized waves, are of this type.

Simple Harmonic Motion

It is important to understand the physics and mathematics of wave motion, since this is essential to an understanding of atomic and molecular structure. Some fundamental principles are illustrated in Figure 11.3. Suppose that point C in Figure 11.3a moves counterclockwise on the circumference of the circle; we will call this the *positive* direction. We will be particularly interested in the motion of point P, the projection of point C on the Y axis, which is plotted in Figure 11.3b. Suppose that point C

sound waves: longitudinal ① -2

density variations parallel to the speed

- water waves

seismic waves

all bound to matter!

electromagnetic waves: radiation

1) in vacuum and matter (different speed at different λ in matter)

2) couple to matter (interaction)

coupling: charged particles (electrons) couple to the wave and oscillate with frequency of the field (wave)

like a cork floating in H_2O moves up and down when a water wave passes

Harmonic motion

can be visualized by a regular rotation of a point on a circle

the displacement of the point can be plotted as function of time

2π rad = full revolution round the circle

↓

radians

largest displacement: amplitude A

time for 1 revolution: period τ

ω: angular velocity, rad/s

$$\omega = \frac{2\pi \text{ rad}}{\tau}$$

frequency $\nu = \frac{1}{\tau} = \frac{\omega}{2\pi \text{ rad}}$

$$\omega = 2\pi \text{ rad} \cdot \nu$$

displacement $y = A \sin(\omega t)$

Phase: ωt (rad) $\qquad y = A \sin(\omega t + \delta)$

initial displacement δ = phase constant

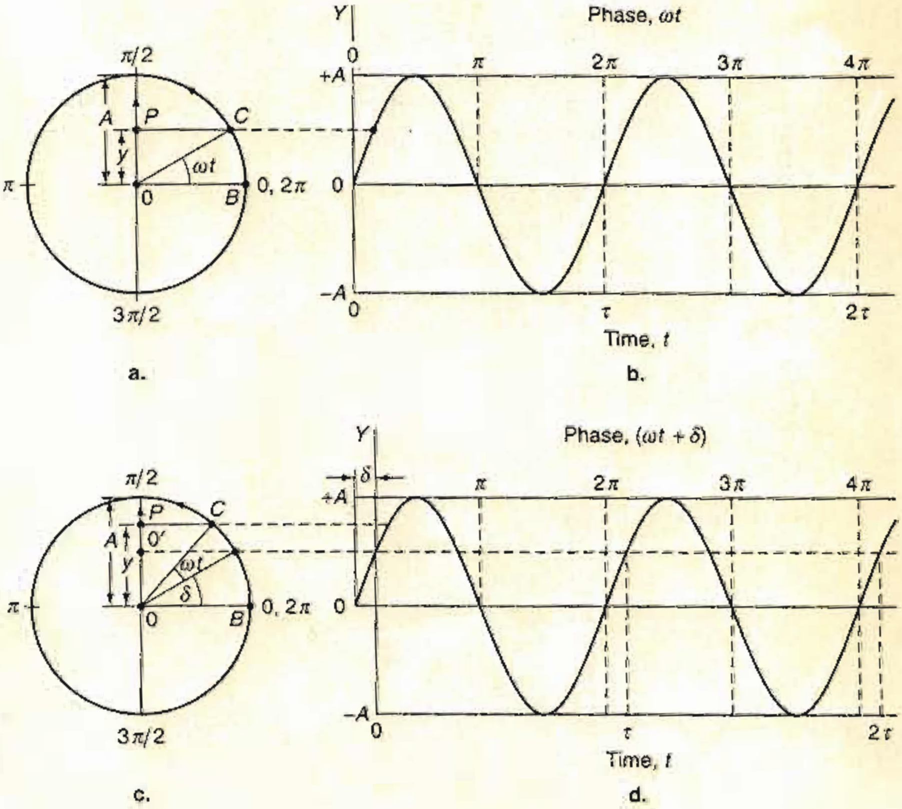


FIGURE 11.3
The generation of simple harmonic motion. (a) A point C undergoes circular motion in the anticlockwise direction. (b) The variation with time of the displacement y of point P; the projection of C on the y axis. (c) and (d) The same as (a) and (b) but with an initial phase displacement δ.

Amplitude: Period

is at B at zero time and moves with constant speed. During a complete revolution with the point C starting at B, the distance y between P and the origin starts from zero, becomes equal to A after a quarter revolution ($\frac{\pi}{2}$ rad), is zero again after half a revolution (π rad), is $-A$ at $\frac{3\pi}{2}$ rad, and is zero again after a complete revolution. This variation of y is shown in Figure 11.3b, the same pattern then continuing indefinitely. The maximum displacement A is known as the **amplitude.** The **period** τ is the time for one revolution, and since the angular path for one revolution is 2π rad, we have[1]

$$\tau = \frac{2\pi \text{ rad}}{\omega} \tag{11.2}$$

Frequency

where ω is the angular velocity; its SI unit is rad s^{-1}. The **frequency** is the reciprocal of the period,

$$\nu = \frac{1}{\tau} = \frac{\omega}{2\pi \text{ rad}} \tag{11.3}$$

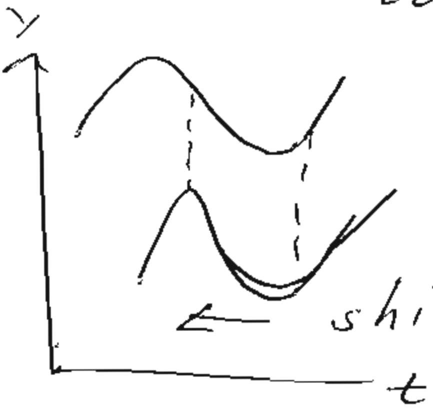
---

[1] A complete revolution is 2π rad. Note that the unit, the radian, must be included in Eqs. 11.2–11.4 to balance the units.

two harmonic motions are ①-4

<u>out of phase</u> when a shift is needed

to super impose them



← shift to superimpose!

acceleration of a point: $\frac{d^2y}{dt^2}$

$$y = A\sin(\omega t + \delta)$$

$$\dot{y} = \frac{dy}{dt} = \omega A\cos(\omega t + \delta)$$

$$\ddot{y} = \frac{d^2y}{dt^2} = -\omega^2 A\sin(\omega t + \delta) = -\omega^2 y$$

→ differential equation for a simple harmonic motion:

$$\frac{d^2y}{dt^2} = -\omega^2 y$$

Same motion as that of a mass on the end of a spring

restoring force: Hooke's law must be obeyed for harmonic motion:

$F = -ky$ k: force constant

Newton's 2. law:

mass · acceleration = force

$\rightarrow \quad F = m \dfrac{d^2y}{dt^2} \Rightarrow \ddot{y} = \dfrac{d^2y}{dt^2} = -\dfrac{k}{m} y$

sin and cos functions or their linear combinations give the function back when diffentiated 2x

solution of $\ddot{y} = -\frac{k}{m} y$:

$y = a \cdot \sin\left(\sqrt{\frac{k}{m}}\, t + b\right)$ a, b free constants

$\rightarrow \ddot{y} = -\frac{k}{m} a \sin\left(\sqrt{\frac{k}{m}}\, t + b\right) = -\frac{k}{m} y$

$\rightarrow$ y solves the equation

comparison: $a = A$, $b = \delta$

$$\Rightarrow \sqrt{\frac{k}{m}} = \frac{\omega}{\text{rad}}$$

$\rightarrow$ natural frequency: $\nu = \dfrac{\omega}{2\pi\,\text{rad}} = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$

kinetic energy E_k and potential energy E_p are continously varying (changing) with time

<u>but</u> $E_k + E_p = E_{tot} =$ const.

all time the same:

conservation of energy

E_p: work needed to bring the mass m from 0 to y against the force

$$\rightarrow E_p = \int_0^y (-F)\, dy$$

$-F$: force needed to overcome F

$$E_p = \int_0^y \underbrace{ky}_{-F}\, dy = \frac{1}{2} k y^2$$

$$E_k = \frac{1}{2} m u^2 = \frac{1}{2} m \dot{y}^2$$

↳ velocity

$$= \frac{1}{2} m \left(\frac{dy}{dt}\right)^2$$

at turning point:

(y maximal, $=A$ or minimal, $=-A$)

$u = 0$ (no velocity when turning)

$E_p^{t.p.} = \frac{1}{2}kA^2$, $E_k^{t.p.} = 0$

$\rightarrow E_{tot}^{t.p.} = \frac{1}{2}kA^2 =$ const. at all time

$\rightarrow E_{tot} \sim A^2$ for all harmonic motions

electromagnetic wave oscillation:

$E^{electrical} \sim |\vec{E}|^2$ E-field vector

$E^{magnetic} \sim |\vec{H}|^2$, H-field vector

↳ magnetic and electric energies in the wave

<u>Obj</u> Standing waves, black body radiation

along a wave energy is transported

<u>plane wave</u>. parallel wave trains
constant amplitudes (A)
planar wave front

A model is a [illegible] pulse on a stretched string, + vertical oscillation with ν = const.

traveling wave: $\rightarrow$ frequency ν = const.
vertical oscillations

move of phase with a phase velocity $u = \Delta x / \Delta t$

movement of the phase

this is the total energy:

$$E_{\text{total}} = \tfrac{1}{2}k_h A^2 \tag{11.18}$$

This result, that the energy is proportional to A^2, is true for any type of simple harmonic motion. For electromagnetic wave motion in a vacuum, for example, the electrical energy is proportional to the square of the electrical field vector (see Figure 11.2), and the magnetic energy is proportional to the square of the magnetic field vector.

Plane Waves and Standing Waves

Traveling Wave

So far we have considered oscillations at right angles to the direction of propagation of the wave. Energy must also be transported along the wave. A simple type of wave is the *plane wave,* which consists of parallel waves of constant amplitude and has a planar wave front; a useful model of a plane wave is provided by a string stretched horizontally. If it is given a single vertical pulse (Figure 11.4a), the pulse travels the length of the string. If a fixed-frequency vertical oscillation is applied, a *traveling wave* is generated. This is a wave whose amplitude at a particular position along the string changes periodically with time. Figure 11.4b shows two wave patterns captured at two different instants; these two *profiles* illustrate the fact that the transverse displacement is moving along the string.

Analysis of this type of wave motion leads to the result that the displacement y is given by the equation

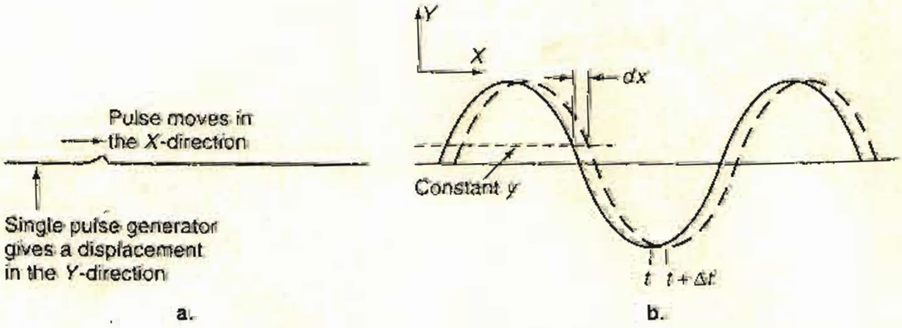
$$y = A \sin \frac{2\pi}{\lambda}(x \pm ut) \tag{11.19}$$

Phase Velocity

The quantity u is called the **phase velocity** because it is the velocity with which a given phase of the wave travels along the X axis. If the positive sign is taken, the wave is traveling to the right with velocity u (see Figure 11.4b); the negative sign means that it is traveling to the left. For electromagnetic radiation traveling in a vacuum the phase velocity is 2.998×10^8 m s^{-1}.

So far we have considered the length of the string to be infinite. A finite string vibrates in a pattern having evenly spaced **nodes** (points of zero displacement) and

FIGURE 11.4
(a) A single wave pulse traveling along a stretched string. (b) Two profiles of a traveling wave. The solid line shows the transverse displacement y at a position x at time t. The dashed line shows the same curve at a later time $t + \Delta t$.



$\rightarrow y = A \sin \frac{2\pi}{\lambda}(x \pm ut)$

with phase velocity u the wave travels along the string (x)
i.e. a given phase travels

to the right: $+u$
to the left: $-u$

for electromagnetic waves in a vacuum:

$$u = c = 2.998 \cdot 10^{8} \frac{m}{s}$$

it length l of the string is fixed on both sides: wave travels forth and back

→ superposition: the final pattern is sum of all interfering waves

interference: by forth and back travel
fixed places of 0 displacements: <u>nodes</u>
fixed places of maximum displacements: <u>antinodes</u>

integer # of nodes: standing wave!

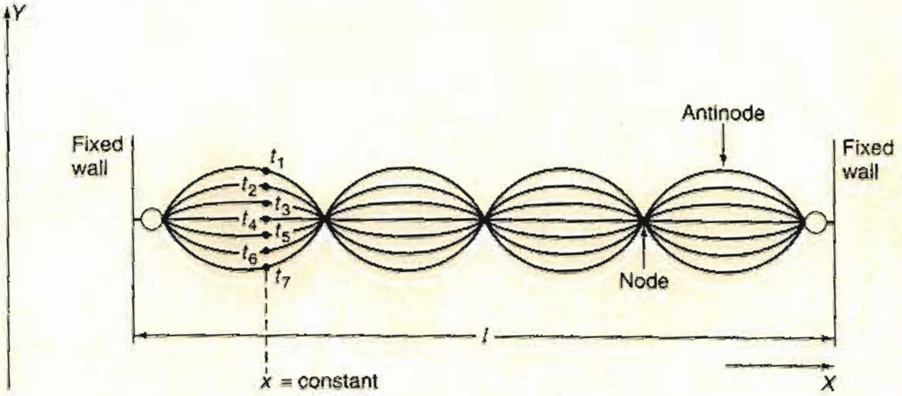


FIGURE 11.5
A typical standing wave in a stretched string fixed at both ends. This diagram shows individual profiles at different times t_1 through t_7. Each point vibrates at the same frequency but with different amplitudes. The amplitude is zero at a node and a maximum at an antinode.

antinodes (points of maximum displacement). An example is shown in Figure 11.5, in which individual profiles are superimposed to show the patterns at various times. The fixed ends are themselves nodes and may be the only nodes; there may be any integral number of nodes as shown in Figure 11.5. This wave form is called a **standing wave** or a *stationary wave*. This situation is dealt with by applying the **principle of superposition,** according to which when two or more waves are involved, the displacement at any position is the sum of the displacements at that position for each individual wave. A special case of this is when the crest of one wave coincides with the trough of another, so that the two cancel; there is then said to be *destructive interference*. Conversely, if crests coincide, the waves reinforce each other, and we then speak of *constructive interference*. The standing wave shown in Figure 11.5 is the sum of the displacements of waves that are traveling back and forth and are reflected at the ends of the string.

The equation for a standing wave, such as shown in Figure 11.5, is

$$y = A_s \sin \frac{n\pi x}{l} \tag{11.20}$$

where A_s is the amplitude of the standing wave, l is the length of the string, and n is a constant to be determined. This equation already satisfies the left-hand boundary condition that $y = 0$ when $x = 0$. It must also satisfy the right-hand boundary condition that $y = 0$ when $x = l$. Insertion of this condition into Eq. 11.20 leads to

$$\sin n\pi = 0 \tag{11.21}$$

Since the sine is zero only for the angles $0, \pi, 2\pi$ etc., it follows that *n must be an integer.*

The value of n is the number of antinodes in the string, as illustrated in Figure 11.6. When $n = 0$, there is zero displacement for all values of x, and no antinodes are present; this means that there is no vibration. When $n = 1$, the value of y is zero only if $x = 0$ or $x = l$; there are only two nodes, at the ends of the string, and there is an antinode in the middle. When $n = 2$, nodes occur at $x = 0$, $x = l/2$, and $x = l$, and there are two antinodes. It is easily seen that only those wavelengths are allowed for which l is an integral multiple of one-half the wavelength. Corresponding to these

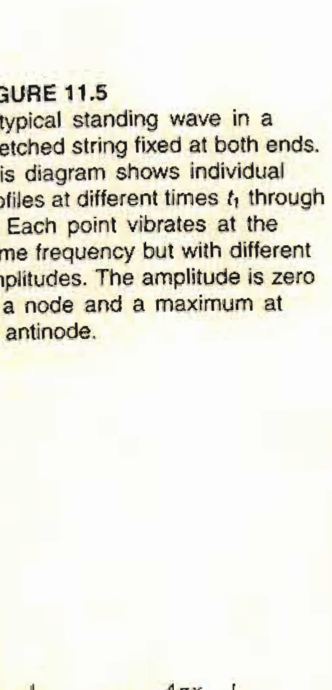
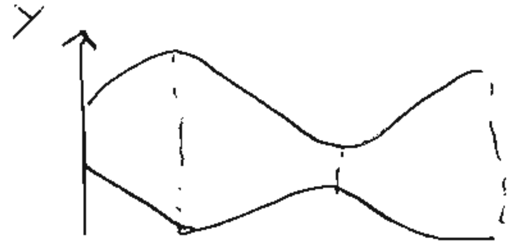


FIGURE 11.6
Some modes of vibration allowed for a standing wave in a stretched string fixed at both ends.

destructive interference:

waves out of phase:

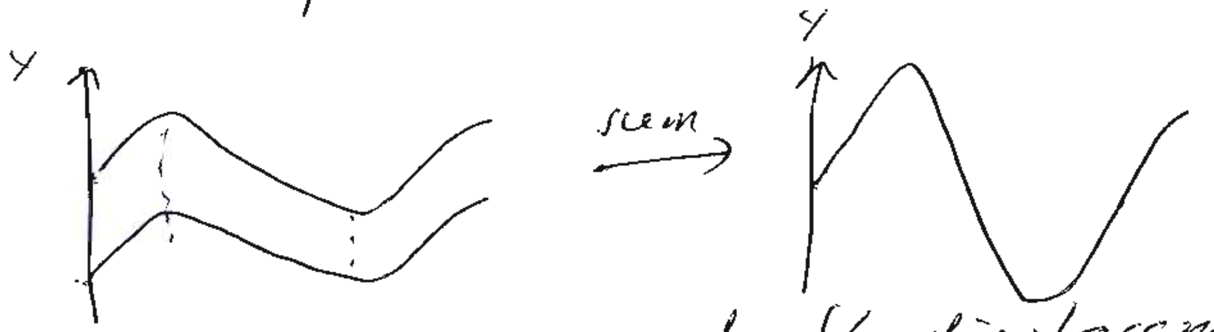


wave 1 $\xrightarrow{\text{sum}}$ 0

wave 2

no displacement

waves in phase:



double displacement

consider any pattern ~~#3~~ in figure:

standing wave: sum of the waves travelling forth & back

$$\rightarrow \quad y = A \sin\left(\frac{n\pi x}{\ell}\right)$$

A: amplitude of the standing wave, n: integer number

ℓ: length

y: displacement of the vibration at any point x

$x = 0$: $y = A_n \sin\left(\frac{n\pi}{\ell} 0\right) = 0$

ok : node

at $x = \ell$ must be also a node :

(no move because fixed)

$x = \ell$: $y = A_n \sin\left(\frac{n\pi}{\ell} \cdot \ell\right) = A_n \sin(n\pi)$

$= 0$ only if n is integer!

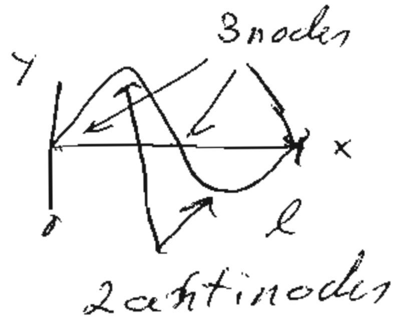
$n =$ # of antinodes (maxima)

in Figure: vibrations for a standing wave (in the string)

$n=0$: no vibration, no antinodes $\lambda = \infty$

$n=1$: 1 antinode, 2 nodes (ends) $\lambda = 2\ell$

$n=2$: 2 antinodes, 3 nodes $\lambda = \ell$



possible values of λ for standing waves on a string, length ℓ:

$$\ell = \frac{n}{2}\lambda$$

→ frequencies of vibrations

= modes of vibrations

<u>also</u> superposition of different modes is possible

linear combination of the waves

energy in a simple harmonic motion:

$$E \sim A^2$$

in our case: $E \sim y^2$ in a given point x

at <u>node</u>: $E = 0$

at <u>antinode</u>: $E = E_{max} \sim A^2$

Black body radiation

radiation emitted by a hot solid:

→ radiant energy density $\rho_\nu = f(\lambda)$

dull red glow: ≈ 950 K
(tungsten, W)

when the tungsten (W) gets hotter

→ bright red → orange → yellow
→ white (2300K)

sun is a black body: it absorbs
all incident radiation, what
comes from the sun is emitted
all inside (≈5500K on surface)

full equilibrium between incoming and
outgoing radiation

Kirchhoff a body that absorbs radiation
of all frequencies and reflects
nothing ⇒ black body

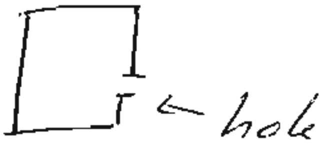
equilibrium:

incident radiation intensity

= emitted radiation intensity

<u>Wien</u>: good model for a black body:

cavity with a small hole in it



intensity depends only on $\underline{T}$ not on the material!

radiant energy density:

$$\varrho_\nu = \frac{\text{emitted energy at frequency } \nu}{\text{unit volume} \cdot \text{unit frequency range}}$$

before 1900: only measurements possible at visible and near UV ν-s

<u>Wien</u>: $\varrho_\nu = \alpha \nu^3 e^{-\frac{\beta\nu}{T}}$ α, β constants

→ fit to experiment

found after 1900: incorrect at small values of ν (infrared):

infrared catastrophy

Rayleigh-Jeans :

classical treatment:

continous distribution of vibrational energy over frequency ν

all ~~modi~~ oscillations in the black body, also at larger ν have the some average energy $k_B T$

k_B: Boltzmann's constant

but $k_B T$ too large at large ν

$$\rightarrow \rho_\nu = \frac{8\pi\nu^2}{c^3} k_B T$$

→ far too large at large ν

→ ultraviolet catastrophe

classical physics breaks down

Planck: old quantum theory: restriction of energy in higher ν

empirical: $\rho_\nu = \frac{\alpha\nu^3}{e^{\frac{\beta\nu}{T}} - 1}$ before Planck no theory!

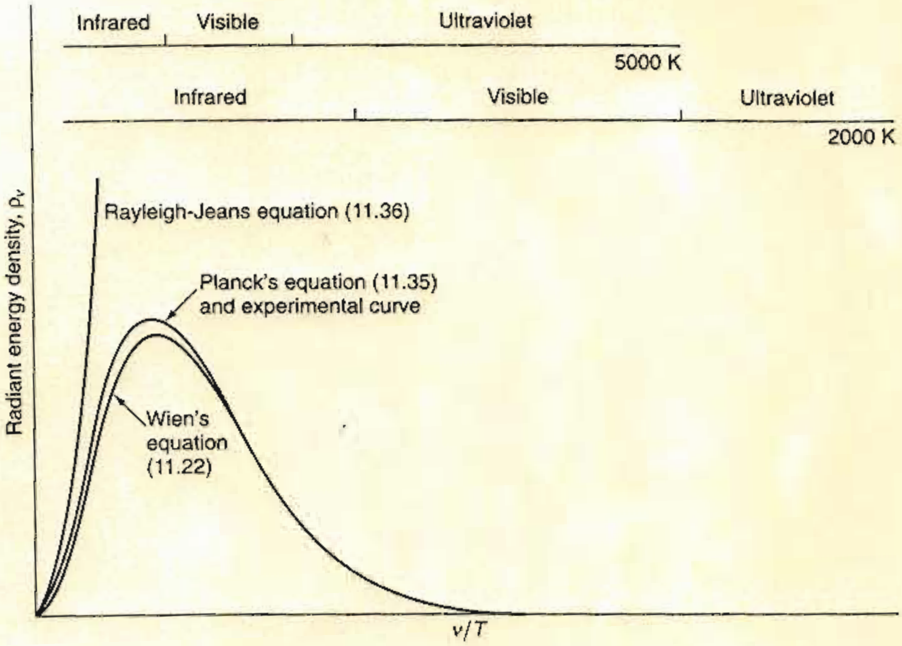


FIGURE 11.7
Plots of Wien's equation 11.22, Planck's equation 11.35, and the Rayleigh-Jeans equation 11.36. Since all three equations involve the ratio of the frequency ν to the temperature T, the radiant energy density ρ_ν is plotted against ν/T. The agreement with Planck's equation is within the experimental error at all temperatures measured. The approximate infrared, visible, and infrared ranges are shown at two temperatures.

where α and β are constants. A plot of his function, which passes through a maximum, is shown in Figure 11.7.

The variation of the radiant energy density with the frequency was extensively investigated, especially by the German physicists Otto R. Lummer (1860–1925), Ernst Pringsheim (1859–1917), Heinrich Rubens (1865–1922), and Ferdinand Kurlbaum (1857–1927). At a given temperature the curves go through a maximum, as shown in Figure 11.7, and as the temperature is raised the maximum shifts to shorter wavelengths. This result was qualitatively predicted by Wien's equation 11.22, which at first seemed to be satisfactory. In 1900, however, Rubens and Kurlbaum made measurements over a wider frequency range than previously, going further into the infrared, that is, to lower frequencies. They found that whereas Wien's formula gave excellent agreement at the higher frequencies, at the lower frequencies it predicted radiant energy densities that were too low, the discrepancies becoming greater as the frequency was lowered.

The solution to the problem of the discrepancies at low frequencies was given in 1900 by the German physicist Max Karl Ernst Ludwig Planck (1858–1947). He first suggested, on a purely empirical basis, the equation

$$\rho_\nu = \frac{\alpha\nu^3}{\exp(\beta\nu/T) - 1} \tag{11.23}$$

This expression differs from Wien's equation 11.22 only by the inclusion of unity in the denominator; it predicts a curve which always lies above the Wien curve (Fig. 11.7). At higher frequencies, where unity in the denominator can be neglected, the equation reduces to Wien's equation.

difference of empirical law to
Wien: -1 in denominator

ν large: -1 can be neglected
$\rightarrow$ Wien's law ok for large ν

<u>Plank's explanation</u>:

energy cannot appear at all values,
but only in packets $nh\nu$
n: integer, h Planck's constant

<u>solid</u> contains atoms that vibrate
<u>all</u> with the same fundamental
frequency ν

<u>only</u> packets of energy possible
with values $nh\nu$, n integer

$\rightarrow$ N_0 oscillators with $E_0 = 0$
N_1 oscillators with $E_1 = h\nu$
N_2 oscillators with $E_2 = 2h\nu$
$\vdots$

Boltzmann equation:

$$N_n = N_0 e^{-\frac{nh\nu}{k_BT}} \quad , \quad k_B = \frac{R}{N_A}$$

N_A ↙ Avogadro's number

# of all oscillators N:

$$N = N_0 + N_0 e^{-\frac{h\nu}{k_BT}} + N_0 e^{-\frac{2h\nu}{k_BT}} + \cdots$$

$$= N_0 (1 + x + x^2 + \cdots) \qquad x = e^{-\frac{h\nu}{k_BT}}$$

$$x^2 = e^{-\frac{2h\nu}{k_BT}}$$

$$= \frac{N_0}{1-x}$$

$$\rightarrow N = \frac{N_0}{1 - e^{-\frac{h\nu}{k_BT}}}$$

total energy of all oscillators:

$$E = N_0 E_0 + N_1 E_1 + N_2 E_2 + \cdots$$

$$= N_0 \cdot 0 + N_1 h\nu + N_2 2h\nu + \cdots$$

$$= N_0 h\nu e^{-\frac{h\nu}{k_BT}} + N_0 2h\nu e^{-\frac{2h\nu}{k_BT}} + \cdots$$

$$= N_0 h\nu e^{-\frac{h\nu}{k_BT}} \left[1 + 2e^{-\frac{h\nu}{k_BT}} + \cdots \right]$$

$$= N_0 h\nu e^{-\frac{h\nu}{k_BT}} \Big[\underbrace{1 + 2x + 3x^2 + \cdots}_{= \frac{1}{(1-x)^2}} \Big]$$

$$x = e^{-\frac{h\nu}{k_BT}}$$

$$\rightarrow \quad E = \frac{N_0 h\nu \, e^{-\frac{h\nu}{k_BT}}}{\left[1-e^{-\frac{h\nu}{k_BT}}\right]^2}$$

$$N_0 = N\left[1-e^{-\frac{h\nu}{k_BT}}\right]$$

$$\Rightarrow \quad E = N h\nu \, \frac{e^{-\frac{h\nu}{k_BT}}}{1-e^{-\frac{h\nu}{k_BT}}} \left(\cdot \, \frac{e^{\frac{h\nu}{k_BT}}}{e^{\frac{h\nu}{k_BT}}}\right)$$

$$= N h\nu \, \frac{1}{e^{\frac{h\nu}{k_BT}}-1}$$

⇒ average energy:

$$\bar{\varepsilon} = \frac{E}{N} = \frac{h\nu}{e^{\frac{h\nu}{k_BT}}-1}$$

when $h\nu \ll k_BT$: $e^{\frac{h\nu}{k_BT}} \approx 1 + \frac{h\nu}{k_BT}$

⇒ $\bar{\varepsilon} \approx k_BT$ for large T

classical value

⇒ always:

$$\text{quantum theory} \xrightarrow[\substack{+\text{ small quanta} \\ (h \text{ small, } \nu \text{ small})}]{\text{large } T} \text{classical theory}$$

$$\varrho_\nu = \frac{8\pi\nu^2}{c^3}\,\bar{\varepsilon}$$

$$= \frac{8\pi\nu^2}{c^3}\,\frac{h\nu}{e^{\frac{h\nu}{k_BT}}-1}$$

$$= \text{experiment}$$

fit to experiment:

Planck obtained good (reliable) values for h, k_B and N_A ($k_B = \frac{R}{N_A}$) not known very well at that time

≃ 1900: quantum theory was not believed, besides ultraviolet catastrophy

Jeans said: "I know the value of h, it is $h = 0$"

= no quanta

up to 1905: Einstein's explanation of photoelectric effect!

Black Body Radiation

Introduction

During the 19th century, it was a widespread assumption, that all the basic concepts of physics were well known and explored by that time. One believed in general, that in the picture physics paints of nature, just a few minor details might be missing, but nothing fundamental.

However, within the 20th century it became more and more obvious that indeed something basic is missing in physics. An outstanding phenomenon indicating that is that of black body radiation.

A black body is an object which does not reflect any radiation, but all it emits is created in the black body itself. For this reason, e.g. the sun is a perfect black body: it does not reflect any incoming radiation, but absorbs it all and radiation coming from it is created entirely by the sun itself. Thus it is a black body by definition, although it does not look "black". A device that simulates a black body in the lab could be a black box with a small pinhole in one of its surfaces. It is black, in order to reflect no light from its outside. All light that falls through the pinhole, will become reflected, if at all, by the interior walls and has little or no chance to escape again through the pinhole. On the contrary it becomes absorbed and excites vibrations in the material which can emit radiation through the pinhole. In fact the radiation coming from the pinhole depends on the temperature, but not on the material from which the box is made.

Also the heated metal wire, emitting light, in a bulb is a black body. With increasing temperature the light emitted by a black body becomes higher in frequency, and if the temperature is high enough it starts to glow.

The problem that came from black bodies was that with the well known classical concepts of physics it turned out to be impossible to describe correctly the radiant energy density of black body radiation as a function of temperature and frequency. This radiant energy density $\rho(\nu,T)$ is the energy radiated by the body into a unit volume in unit frequency range. Thus the unit is $J/(Hz\ m^3)$, where $1\ Hz = 1\ s^{-1}$.

An attempt to obtain this radiant energy density by theory was made by Rayleigh and Jeans on the basis of classical physics. The classical assumptions were that in a black body all vibrational energy values are possible, i.e. that the vibrational frequencies are continous. Further, and that was one of the corner stones of classical physics, they assumed equipartitioning of energy between all possible vibrations in the emitting black body, i.e. all vibrational degrees of freedom contribute an energy of k_BT to the total energy, where $k_B = 1.38066 \times 10^{-23}$ J/K denotes Boltzmann's constant. With these classical basic assumptions they obtained for the radiant energy density the expression

$$\rho(\nu,T) = \frac{8\pi\nu^2}{c^3}\bar{E} = \frac{8\pi\nu^2}{c^3}k_BT$$

with $c = 2.99792458 \times 10^8$ m/s being the speed of light in vacuum, ν the frequency of the radiation, T the absolute temperature in K, and according to the equipartition principle k_BT is the average energy of an oscillator. To be able to perform a feasible plot of this function it is best to transform it into a dimensionless variable $x = h\nu/(k_BT)$, $h = 6.62608 \times 10^{-34}$ Js being Planck's constant. Thus one obtains the following form of the Rayleigh-Jeans law

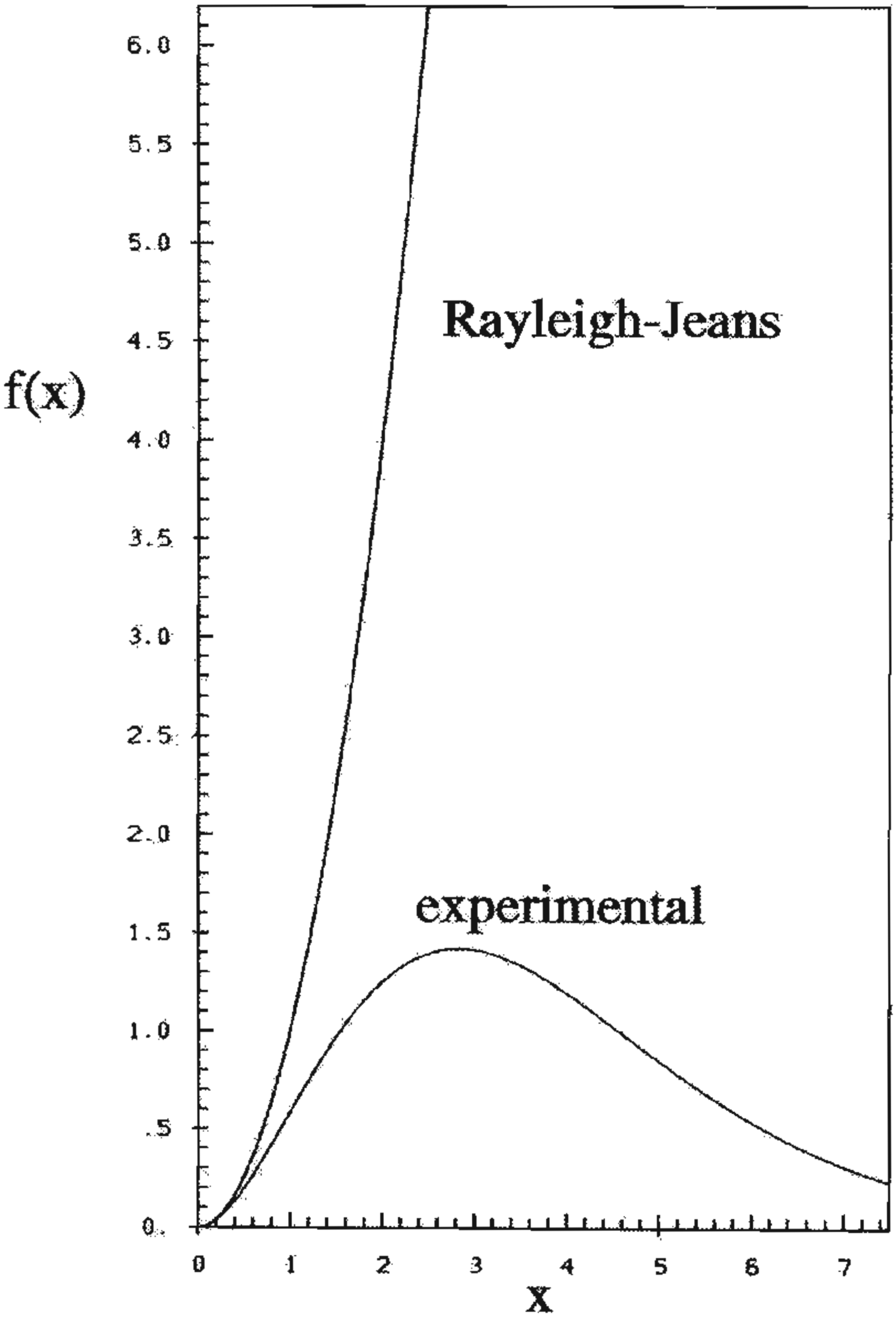
$$\rho(\nu,T) = \frac{8\pi}{c^3}\left(\frac{h\nu}{k_BT}\right)^2\left(\frac{k_BT}{h}\right)^2 k_BT = \frac{8\pi}{h^2}\left(\frac{k_BT}{c}\right)^3 x^2$$

Thus instead of the radiant energy density itself one can plot the function f(x) versus x:

$$f(x) = \left(\frac{c}{k_BT}\right)^3 \frac{h^2}{8\pi}\rho(\nu,T) = x^2\,;\ x = \frac{h\nu}{k_BT}$$

To allow a comparison one can plot into the same graf the experimental radiant energy density, made dimensionless with the same factor for different temperatures versus the same x. This plot is shown below. Obviously the experimental curve goes through a maximum with increasing x (increasing frequency and/or decreasing temperature) and then approaches zero for even higher frequencies, while the Rayleigh-Jeans law shows no maximum but a quadratic increase to infinity with increasing x.

Since increasing x means increasing frequency at constant temperature, this behavior of the law was named the "ultraviolet catastrophe". Catastrophe, because it became obvious that any classical treatment based on the above assumptions and assumed to be true must lead to such a false behavior. The reason for that is the equipartitioning of energy which allows unphysically large contributions of higher vibrational energies to the total energy. When a generally believed classical concept yields wrong results, that is a catastrophe, and it happens at high frequencies, hence "ultraviolet catastrophe"


6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.
f(x)
Rayleigh-Jeans
experimental
0
1
2
3
4
5
6
7
x

In 1900 Max Planck was able to solve the problem, however, by abandoning concepts so dear to classical physicists. As a first step he was trying to find out the form of a function that could reproduce the experimental one. He was able to find a functional form which could be fitted exactly to the experimentally found one. However, in order to identify the fitting parameters in his function with physical constants he needed a theoretical derivation of it from first principles.

To this end he started from work introduced by Ludwig Boltzmann earlier. Boltzmann used to introduce the idea that energy can come only in small packets, not in all possible amounts. However, Boltzmann used this idea only to make derivations mathematically easier and at the end of his derivations he always let the energy packet size go to zero and thus avoided to introduce energy quantization as a physical truth.

Planck did not do this last step and thus in his derivation energy quantization appeared as a physical reality and actually was giving the correct result. He assumed that for a vibration of a given frequency v, energy can exist only as whole number multiples of the smallest energy packet size hv, h being Planck's constant, h = 6.62608 x 10^{-34} Js. Such packets are called quanta of energy, one packet simply a quantum of energy (from a Latin phrase, meaning "how much?").

Planck assumed that all atoms of a solid (the black body) vibrate with the same fundamental frequency v. Since the energy can only come in integer multiples of the packet size, ihv, one would have in the black body N_0 atoms vibrating with frequency 0, having energy 0, N_1 atoms vibrating with frequency v, having energy hv, N_2 atoms vibrating with frequency 2v, having energy 2hv, and so on.

Planck assumed that the distribution of oscillators over the allowed frequencies iv, i being an integer, follows Boltzmann's distribution law. Thus the number of atoms N_i having frequency iv and therefore the energy ihv is

$$N_i = N_0 e^{-\frac{ih\nu}{k_B T}}\ ;\ k_B = \frac{R}{N_A}$$

N_0 is the number of atoms with zero vibrational energy, k_B Boltzmann's constant, R the gas constant, and N_A Avogadro's number. By summing over all energy states i, one obtains the total number of oscillators (atoms), N:

$$N = N_0 \left[1 + e^{-\frac{h\nu}{k_B T}} + e^{-\frac{2h\nu}{k_B T}} + \dots \right]$$

Since for an exponential exp(ix) = $[\exp(x)]^i$ holds this is equivalent to

$$N = N_0\left[\left(e^{-\frac{h\nu}{k_BT}}\right)^0+\left(e^{-\frac{h\nu}{k_BT}}\right)^1+\left(e^{-\frac{h\nu}{k_BT}}\right)^2+\ldots\right]$$

With the definition y = exp[-(hν)/(k$_B$T)] this can be written as

$$\frac{N}{N_0}=1+y+y^2+y^3+\ldots$$

This is a well known series of a function g(y) (see Appendix I for details):

$$g(y)=\frac{1}{1-y}$$

as can be found in formula collections. Thus

$$\frac{N}{N_0}=\frac{1}{1-y}=\frac{1}{1-e^{-\frac{h\nu}{k_BT}}}$$

The total energy E of our system can now be calculated, by summing over all the products of N$_i$, the number of oscillators with a given energy ihν, with that energies, ihν. This total energy E we need, because to obtain the radiant energy density we have to calculate the average energy of an oscillator by dividing the total energy with the total number N of oscillators (remember the Rayleigh-Jeans law). Thus the total energy is obtained by

$$E=N_0\bullet 0+N_1\bullet h\nu+N_2\bullet 2h\nu+\ldots$$

The first term has 0 as a factor and thus cancels out and for the others we can use again Boltzmann's distribution for the factors N$_i$:

$$E=N_0\left[h\nu\bullet e^{-\frac{h\nu}{k_BT}}+2h\nu\bullet e^{-\frac{2h\nu}{k_BT}}+3h\nu\bullet e^{-\frac{3h\nu}{k_BT}}+\ldots\right]$$

Each term of the sum contains the factor hν exp[-(hν)/(k$_B$T)] which we can write in front of the bracket:

$$E=N_0\bullet h\nu\bullet e^{-\frac{h\nu}{k_BT}}\left[1+2e^{-\frac{h\nu}{k_BT}}+3e^{-\frac{2h\nu}{k_BT}}+\ldots\right]$$

With the same definition of y as above, we can rewrite the sum in the bracket to

$$\left(1+2y+3y^2+\ldots\right)$$

This is again a well known series of a function G(y) as we can find also in formula collections (see Appendix I for details):

$$G(y) = \frac{1}{(1-y)^2} = 1 + 2y + 3y^2 + \ldots$$

giving the total energy as

$$E = \frac{N_0 \bullet h\nu \bullet e^{-\frac{h\nu}{k_B T}}}{\left[1 - e^{-\frac{h\nu}{k_B T}} \right]^2}$$

Dividing this by the total number of oscillators N yields the average energy of an oscillator:

$$\overline{E} = \frac{E}{N} = \frac{N_0}{N} \frac{h\nu \bullet e^{-\frac{h\nu}{k_B T}}}{\left[1 - e^{-\frac{h\nu}{k_B T}} \right]^2}$$

Above we have derived that

$$\frac{N}{N_0} = \frac{1}{1 - e^{-\frac{h\nu}{k_B T}}}$$

and thus

$$\frac{N_0}{N} = 1 - e^{-\frac{h\nu}{k_B T}}$$

When we introduce this into our equation for the average energy of an oscillator, it cancels with the square in the denominator:

$$\overline{E} = \frac{h\nu \bullet e^{-\frac{h\nu}{k_B T}}}{1 - e^{-\frac{h\nu}{k_B T}}}$$

Now we can multiply both nominator and denominator with exp[(hv)/(k_BT)]:

$$\overline{E} = \frac{h\nu \bullet e^{-\frac{h\nu}{k_B T}} e^{\frac{h\nu}{k_B T}}}{\left(1 - e^{-\frac{h\nu}{k_B T}} \right) e^{\frac{h\nu}{k_B T}}}$$

Since exp(-x) exp(+x) = 1 this yields

$$\overline{E} = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}$$

If we assume that x = (hv)/(k_BT) is very small (i.e. small frequency and large temperature) then e^x is approximately 1 + x and the average energy becomes the classical value $k_B T$, because hν, left in the denominator in this case, cancels with hν in the nominator. Multiplied with the appropriate factor this average energy in the classical limit of very small x gives the radiant energy density as obtained by Rayleigh and Jeans.

Note that this is an example of the correpondence principle: in the appropriate limits a quantum treatment must always reduce approximately to the classical limiting case. The classical equipartition principle assumes that each state is populated equally. However, this can only be true when the excited states have low energies (small frequency) so that the thermal energy is large enough (high temperature) to distribute the atoms equally over their excited states.

However, now we can write down the equation for the radiant energy density as obtained by Planck:

$$\overline{E} = \frac{8\pi \nu^2}{c^3} \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}$$

The form of the function is the same as Planck had found earlier empirically, so at this stage he could identify his fitting parameters with actual physical constants. Since these were not very well known at the time it was an important contribution to obtain their values from black body radiation. The values Planck obtained were actually rather close to the values used today.

Such constants were for example Planck's constant itself and Boltzmann's constant. Since $k_B = R/N_A$, he could also obtain a rather accurate value for Avogadro's number. Note that it is of no use to plot this function here, because it has exactly the same plot as the experimental results shown earlier.

Problems worked out in detail

a) Rewrite the expression for the radiant energy density ρ(v,T) into the form ρ = f(x)g(T), where v denotes frequency, x is the dimensionless variable x = (hv)/(k$_B$T), f(x) depends only on x and g(T) only on T.

$$\rho(v,T) = \frac{8\pi}{c^3} \frac{hv^3}{e^{(hv)/(k_B T)} - 1}$$

In the exponential there is already the variable x as required. But in the nominator we have to introduce $h^2/(k_B T)^3$ in order to obtain x^3 and thus we have to multiply the pre-factor by the inverse of this:

$$\rho(v,T) = \frac{8\pi}{c^3} \frac{(k_B T)^3}{h^2} \frac{x^3}{e^x - 1}$$

If we rearrange the pre-factor a little, we obtain

$$\rho(v,T) = \frac{8\pi}{h^2} \left(\frac{k_B T}{c} \right)^3 \frac{x^3}{e^x - 1}$$

which is of the desired form:

$$\rho(v,T) = f(x) \bullet g(T)$$

with

$$g(T) = \frac{8\pi}{h^2} \left(\frac{k_B T}{c} \right)^3$$

and

$$f(x) = \frac{x^3}{e^x - 1}$$

This form has the advantage that in order to find the frequency v_o where the radiant energy density is largest, we only need to find the maximum x_o of f(x) at T = const..

b) Form the derivative of f(x) with respect to x and obtain an equation for the determination of x_o, where f(x) is maximal.

Following the rules of differentiation we have

$$\frac{df(x)}{dx}=\frac{3x^2}{e^x-1}-\frac{x^3e^x}{(e^x-1)^2}$$

A maximum in $x=x_o$ we can have only when the derivative is zero:

$$\frac{3x_o^2}{e^{x_o}-1}-\frac{x_o^3e^{x_o}}{(e^{x_o}-1)^2}=0$$

If x_o not equal to zero (reasonable, because zero frequency or infinite temperature make not much sense) the denominator does not vanish and we can multiply the equation with it:

$$3x_o^2(e^{x_o}-1)-x_o^3e^{x_o}=0$$

Now we can divide the equation by the exponential and by x_o^2:

$$3(1-e^{-x_o})-x_o=0$$

Thus finally we have

$$x_o=3(1-e^{-x_o})$$

which can be solved, beginning with a start value, by iteration:

1. step: value for x_o^{old}

2. step:

$$x_o^{new}=3(1-e^{-x_o^{old}})$$

3. step: If x_o does not change up to the desired digit anymore the iteration is finished, if x_o still changes in the desired accuracy, replace the old value with the new one and go back to the 1. step.

c) With the help of a Fortran or any other program print the values of f(x) for x between 0.1 and say 3.0 in steps of 0.1. From these values determine a starting value for the above iteration.

A simple Fortran code for this could be a file, call it prog1.f (.f indicates that it is a source file), that can be typed using the "pico" editor in unix. Just type "pico prog1.f" and you can type in the program. Don't forget that in a fortran code the first 6 characters must be either blank or a statement label.

```
      Program one
      x=0.1
 1000 continue
      f=(x**3)/(exp(x)-1)
      write(6,*) x,f
      x=x+0.1
      if(x.gt.3.0) stop
      goto 1000
      stop
      end
```

After compilation, e.g. with "xlf":

```
xlf  -q AUTODBL=DBLPAD -o prog1.x  prog1.f
```

That statement compiles the source file prog1.f and writes the executable to the file prog1.x. The first part beginning with -q denotes double precision of the variables, which have 6 to 8 digits accuracy on an IBM computer in single precision, while with double precision up to 14 digits can be trusted.

The program needs no input only an output file and thus can be run by

```
prog1.x  >out1
```

After that the output file, readable by "pico out1" is:

```
 0.100000000000000006  0.950833194477504473E-02
 0.200000000000000011  0.361332445290159648E-01
 0.300000000000000044  0.771739896647722357E-01
 0.400000000000000022  0.130127666030063149
 0.500000000000000000  0.192686760317099776
 0.599999999999999978  0.262735750474748120
 0.699999999999999956  0.338346815226620801
 0.799999999999999933  0.417774705109040190
 0.899999999999999911  0.499450840045250644
 0.999999999999999889  0.581976706869326232
 1.09999999999999987   0.664116637093322248
 1.19999999999999996   0.744790050478079668
 1.30000000000000004   0.823063253572152709
 1.40000000000000013   0.898140884321207533
 1.50000000000000022   0.969357094162430655
 1.60000000000000031   1.03616655778551103
 1.70000000000000040   1.09813539807925697
```

```
1.80000000000000049   1.15493210983551475
1.90000000000000058   1.20631856071715560
2.00000000000000044   1.25214114199732540
2.10000000000000053   1.29232213483503200
2.20000000000000062   1.32685135056169523
2.30000000000000071   1.35577809580551945
2.40000000000000080   1.37920350545752868
2.50000000000000089   1.39727327865393791
2.60000000000000098   1.41017084526661551
2.70000000000000107   1.41811098299022320
2.80000000000000115   1.42133389810382327
2.90000000000000124   1.42009977645780849
3.00000000000000133   1.41468380526391080
```

One sees that the maximum of f(x) (the second number in a line) is at about 1.42 for x=2.800 (the first number of a line). Thus a suitable starting value for x in an iteration to find x_o would be 2.7.

Another possibility would be simply to use excel. Open excel and type 0.1 into the box A1, then =A1+0.1 into box A2. Click at the lower left corner (where a cross is displayed) of box A2, go down to A100 and you have your values for x from 0.1 to 10 in boxes A1 to A100. Now type in box B1 the equation for f(x): =(A1*A1*A1)/(EXP(A1)-1), klick again the lower left corner of the box, keep it clicked on and go down to A100. The equation will be longer than box B1, but you have to click the lower left corner of box B1. That gives the same numbers as above only with fewer digits. IMPORTANT: if you do not click exactly the lower left corner of the box, but maybe one of the lines, then excel will just copy the contents of the box. You get from this the maximum of f(x) at 1.421334 in box B28 for x=2.8 in box A28, suggesting 2.7 as starting value for the iteration.

d) Perform the iteration until x_o is more accurate than 10^{-8} in Fortran or until the digits shown in excel do not change anymore.

A program, e.g. named prog2.f could be:

```
      program two
      iter=0
      xold=2.7
 1000 continue
      xnew=3.*(1.-exp(-xold))
      iter=iter+1
      write(6,*) iter,xold,xnew,xnew-xold
      if(abs(xnew-xold).lt.1.0e-8) stop
```

```
xold=xnew
goto 1000
stop
end
```

This program has to be handled as above only with prog2.f and prog2.x and yields as out2:

```
 1 2.70000000000000018   2.79838346178075081  0.983834617807506362E-01
 2 2.79838346178075081   2.81727466826190565  0.188912064811548319E-01
 3 2.81727466826190565   2.82069416928843530  0.341950102652965882E-02
 4 2.82069416928843530   2.82130625864409668  0.612089355661371570E-03
 5 2.82130625864409668   2.82141560171382544  0.109343069728762288E-03
 6 2.82141560171382544   2.82143512761260951  0.195258987840674081E-04
 7 2.82143512761260951   2.82143861421819464  0.348660558513458341E-05
 8 2.82143861421819464   2.82143923679023434  0.622572039699065272E-06
 9 2.82143923679023434   2.82143934795713847  0.111166904126491772E-06
10 2.82143934795713847   2.82143936780717208  0.198500336168194735E-07
11 2.82143936780717208   2.82143937135160616  0.354443407957205636E-08
```

The first number being the number of the iteration, the second the old value of x_o, the third the new one and the last their difference. The program stops when the latter is less than 10^{-8}.

The final result for x_o is 2.8214394, the last digit still changing.

If you like to do the iteration with excel, first open excel. In box A1 write the starting value 2.7 and in box A2 the expression =3*(1-EXP(A1)). Then click the lower left corner (cross is displayed) and keeping the mouseclick, go down below box A10. The value from box A8 is 2.821439 and no more changing.

Thus at constant temperature the maximum of f(x) with x (equivalent to frequency) is at x_o=2.821439.

Homework

An integral of the radiant energy density over frequency yields the energy density radiated within the integration range. Such an integral can also be done over x, keeping in mind that $\nu=(k_BTx)/h$ and thus $d\nu=k_BTh^{-1}dx$. Therefore

$$\int_{\nu_1}^{\nu_2} \rho(\nu,T)d\nu = \frac{k_BT}{h} g(T) \int_{x_1}^{x_2} f(x)dx$$

Perform these integrals using Simpson's rule (see Appendix II for a derivation of Simpson's rule). The package you apply, whether Fortran, Excel or another program does not matter, however, it has to be Simpson's rule.

a) Integrate the radiant energy density over the complete frequency range, from x = 0 to infinity to obtain the total energy density radiated at 5000 K, the approximate surface temperature of the sun. Make sure that you have enough integration intervals and that you have extended your integration range far enough to obtain a 4 figure accuracy.

b) Perform the same type of integration in the microwave and infrared frequency range from a wavelength of $\lambda = 10^{-2}$ m to 7×10^{-7} m (speed of light in vacuum $c = 2.99792458 \times 10^8$ m/s), and with the result of a) determine the percentage of the energy density radiated at 5000 K as heat.

c) Perform the same type of integration in the frequency range of visible light from a wavelength of $\lambda = 7 \times 10^{-7}$ m to 4×10^{-7} m (speed of light in vacuum $c = 2.99792458 \times 10^8$ m/s), and with the result of a) determine the percentage of the energy density radiated at 5000 K as visible light.

d) Perform the same type of integration in the frequency range of harmful ultraviolet light from a wavelength of $\lambda = 4 \times 10^{-7}$ m to 10^{-9} m (speed of light in vacuum $c = 2.99792458 \times 10^8$ m/s), and with the result of a) determine the percentage of the energy density radiated at 5000 K as ultraviolet light.

To perform a Simpson integration in an interval between a and b of the variable, use 2N+1 equidistant points between a and b, including explicitely the borders a and b. Thus the distance h (here and below h is not Planck's constant) between 2 consecutive points must be $h = (b-a)/(2N)$. Then an approximation to the integral is the sum over all values f_j of the function, where j goes from 0 to 2N and $f_0 = f(a)$, $f_{2N} = f(b)$ and $f_j = f(a + j \times h)$. When you sum the values of the function, you must multiply f_0 and f_{2N} with the factor 1, f_j with the factor 4, if j is an odd number, and with the factor 2, if j is an even number. The accuracy is the larger, the larger N is:

$$\int_a^b f(x)dx \approx \frac{h}{3}[f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \ldots + f_{2N}]$$

with h = (b-a)/(2N).

To determine N, use problem a) with x between 0 and 10 and start by calculating the integral with N=10, repeat with N=20, N=30 and so on, until its first 4 figures do not change anymore when increasing N by 10.

To determine the sufficient range of x, solve a) first for x from 0 to 10, then from x from 0 to 20 and go on doubling the range of x, until the first 4 figures do not change anymore when doubling the range of x. To keep the accuracy you must double the number N every time when you double the range of x.

The value of N, sufficient for a) you can use in problems b), c) and d) also.

Note that for a=0 the value of the function is

$$f(0) = \lim_{a\to 0}\frac{a^3}{e^a - 1} = \lim_{a\to 0}\frac{\frac{d}{da}a^3}{\frac{d}{da}(e^a - 1)} = \lim_{a\to 0}\frac{3a^2}{e^a} = \frac{0}{1} = 0$$

because we have the case "0/0" and thus d'Hospital's rule applies.

Important: the appendices are no assignments. You only need to read them, when you really like to know the background of the subjects.

Appendix I: Summation of Infinite Serieses

The first eaxmple of an infinite series we were confronted with was

$$S = 1 + q + q^2 + \ldots = \sum_{k=0}^{\infty} q^k$$

with q being between 0 and 1. This property is very important to insure the convergence of the series. Also the operations we have to perform to do the summation are only allowed if the series is absolutely convergent. At first we take a factor q out of the series and we sum only from k=1:

$$S = 1 + \sum_{k=1}^{\infty} q^k = 1 + q\sum_{k=1}^{\infty} q^{k-1}$$

Now we change the summation index from k to k'=k-1 which we have to sum from k=1, corresponding to k'=0 to infinity:

$$S = 1 + \sum_{k'=0}^{\infty} q^{k'} = 1 + qS$$

Bringing qS to the left side yields

$$S - qS = (1 - q)\,S = 1$$

which yields the desired closed expression for S:

$$S = \frac{1}{1 - q}$$

The other infinite series we met requires some more manipulations to sum it up:

$$T = 1 + 2q + 3q^2 + 4q^3 + \ldots = \sum_{k=0}^{\infty} (k + 1)\,q^k$$

As first step we write the terms for k=0 and k=1 separately

$$T = 1 + 2q + \sum_{k=2}^{\infty} (k + 1)\,q^k$$

(k+1) we can rewrite in the form (2k-k+1):

$$T = 1 + 2q + \sum_{k=2}^{\infty} (2k - k + 1)\,q^k$$

Now we can split the summation into two of them

$$T = 1 + 2q + \sum_{k=2}^{\infty} 2\,kq^k - \sum_{k=2}^{\infty} (k - 1)\,q^k$$

Since 2q corresponds to a term with k=1 in the first summation we have

$$T = 1 + \sum_{k'=1}^{\infty} 2k'\,q^{k'} - \sum_{k'=2}^{\infty} (k' - 1)\,q^{k'}$$

In addition we have renamed the summation index k to k'. Now in the first summation we change the summation index to k=k'-1 or in turn k'=k+1 so that k'=1 corresponds now to k=0. Further, in the second sum we rename the index such that k+1=k'-1 or in turn k'=k+2 and k=k'-2. Thus k'=2 in the second sum corresponds now to k=0:

$$T = 1 + \sum_{k=0}^{\infty} 2(k + 1)\,q^{k+1} - \sum_{k=0}^{\infty} (k + 1)\,q^{k+2}$$

Now in the first summation we have the common factor 2q at all terms and in the second one the common factor q^2 at all terms:

$$T = 1 + 2q\sum_{k=0}^{\infty}(k + 1)\,q^{k} - q^{2}\sum_{k=0}^{\infty}(k + 1)\,q^{k}$$

Now both summations are simply T again

$$T = 1 + 2qT - q^{2}T$$

Again, all terms with T we collect on the left hand side:

$$(1 - 2q + q^{2})T = 1$$

In the bracket we have now a complete square:

$$(1 - q)^{2}T = 1$$

which yields our final expression

$$T = \frac{1}{(1 - q)^{2}}$$

Appendix II: Simpson's Rule

Simpson's rule is based on the idea, that you always can adjust an exact parabola to 3 values f_0, f_1 and f_2 of a function. After that you can easily integrate over this parabola.

The points at which the values of the function f are taken are chosen as equidistant. For only 3 points in an interval between a and b you chose a distance h = (b-a)/2, and thus $f_0 = f(a)$, $f_1 = f(a + h)$ and $f_2 = f(b) = f(a + 2 \times h)$. To adjust a parabola to these points, you can introduce a variable t, going from 0 to 2h:

$$p(t) = f_0 + \alpha t^{2} + \beta t$$

Then the adjustment yields a system of equations:

$$f_0 = p(t = 0) = f_0 \quad (0)$$

$$f_1 = p(t = h) = f_0 + \alpha h^2 + \beta h \quad (1)$$

$$f_2 = p(t = 2h) = f_0 + 4\alpha h^2 + 2\beta h \quad (2)$$

where equation (0) is trivial. The system is most easily solved by removing the parameter α, using 4 x (1) - (2):

$$4 f_1 - f_2 = 3 f_0 + 2\beta h$$

$$\beta = \frac{1}{2h}\left[-3 f_0 + 4 f_1 - f_2 \right]$$

With equation (1) this yields α:

$$\alpha = \frac{1}{h^2}\left[f_1 - f_0 - \beta h \right] = \frac{1}{h^2}\left[f_1 - f_0 + \frac{3}{2} f_0 - 2 f_1 + \frac{1}{2} f_2 \right]$$

$$\alpha = \frac{1}{h^2}\left[\frac{1}{2} f_0 - f_1 + \frac{1}{2} f_2 \right]$$

Now an integral from a to b over f(x)dx is approximated by one from 0 to 2h over p(t):

$$Q = \int_0^{2h} \left[\alpha t^2 + \beta t + f_0 \right] dt$$

$$= \frac{\alpha}{3}\left[t^3 \right]_0^{2h} + \frac{\beta}{2}\left[t^2 \right]_0^{2h} + f_0 \left[t \right]_0^{2h}$$

$$= \frac{8}{3}\alpha h^3 + 2\beta h^2 + 2 f_0 h$$

Substitution of our parameters yields

$$Q = \frac{8}{3} h \left[\frac{1}{2} f_0 - f_1 + \frac{1}{2} f_2 \right] + h\left[-3 f_0 + 4 f_1 - f_2 \right] + 2 f_0 h$$

$$= h\left[\frac{8}{6} f_0 - \frac{8}{3} f_1 + \frac{4}{3} f_2 - 3 f_0 + 4 f_1 - f_2 + 2 f_0 \right]$$

$$= h\left[\left(\frac{4}{3} - 3 + 2\right)f_0 + \left(-\frac{8}{3} + 4\right)f_1 + \left(\frac{4}{3} - \frac{3}{3}\right)f_2\right]$$

$$= h\left[\left(\frac{4}{3} - \frac{9}{3} + \frac{6}{3}\right)f_0 + \left(-\frac{8}{3} + \frac{12}{3}\right)f_1 + \frac{1}{3}f_2\right]$$

and finally for the approximated integral

$$Q = \frac{h}{3}[f_0 + 4f_1 + f_2]$$

However, this is not a good approximation, because our function f(x) is approximated by only 1 parabola in the whole integration range. Let us as next step put 5 equidistant points into the integration interval from a to b, f(a), f(a+h), f(a+2h), f(a+3h), and f(a+4h) = f(b), with h = (b-a)/4.

When we adjust 1 parabola to f(a), f(a+h) and f(a+2h) and a second one to f(a+2h), f(a+3h) and f(b), and sum over the two integral approximations, then the central point f_2 must be counted twice:

$$Q = \frac{h}{3}[f_0 + 4f_1 + f_2 + f_2 + 4f_3 + f_4]$$

$$= \frac{h}{3}[f_0 + 4f_1 + 2f_2 + 4f_3 + f_4]$$

In completely the same way, for 2N+1 points, we obtain

$$Q = \frac{h}{3}[f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \ldots + f_{2N}]$$

$$h = \frac{b - a}{2N}$$

So we can divide our summation into 3 of them:

$$Q_1 = f(a) + f(b) = f(a) + f(a + 2Nh)$$

$$Q_2 = \sum_{j=0}^{N-1} f[a + (2j + 1)h]$$

$$Q_3 = \sum_{j=1}^{N-1} f(a + 2jh)$$

Then finally the approximated integral becomes

$$Q = \frac{h}{3}[Q_1 + 4Q_2 + 2Q_3]$$

Solutions for Homework Section 01

a) A Fortran program that increases the number of intervals N in a Simpson integration from N=10 to 20, to 30 and so on up to n=100 and performs the integration of our function f(x) from x=0 to x=10 could be:

```
      program three
      n=0
      a=0.
      b=10.
 1000 continue
      n=n+10
      q1=0.
      q1=q1+(b**3)/(exp(b)-1.)
      q2=0.
      q3=0.
      h=(b-a)/(2.*n)
      nm=n-1
      do 1 j=1,nm
      if(j.ne.1) goto 10
      x=a+h
      q2=q2+x**3/(exp(x)-1.)
   10 continue
      x=a+(2.*j+1.)*h
      q2=q2+x**3/(exp(x)-1.)
      x=a+2.*j*h
      q3=q3+x**3/(exp(x)-1.)
    1 continue
      q=(h/3.)*(q1+4.*q2+2.*q3)
      write(6,*) 'n=',n,' a=',a,' b=',b
      write(6,*) 'Q = ',q
      if(n.eq.100) stop
      goto 1000
      stop
      end
```

This program gives the output file

```
 n= 10  a= 0.000000000000000000E+00  b= 10.0000000000000000
 Q =  6.43295926036646470
 n= 20  a= 0.000000000000000000E+00  b= 10.0000000000000000
 Q =  6.43198673107936614
 n= 30  a= 0.000000000000000000E+00  b= 10.0000000000000000
```

```
Q=  6.43193470352364471
n= 40  a= 0.000000000000000000E+00  b= 10.000000000000000
Q=  6.43192594891134650
n= 50  a= 0.000000000000000000E+00  b= 10.000000000000000
Q=  6.43192355653339209
n= 60  a= 0.000000000000000000E+00  b= 10.000000000000000
Q=  6.43192269720196386
n= 70  a= 0.000000000000000000E+00  b= 10.000000000000000
Q=  6.43192232882862314
n= 80  a= 0.000000000000000000E+00  b= 10.000000000000000
Q=  6.43192215003970791
n= 90  a= 0.000000000000000000E+00  b= 10.000000000000000
Q=  6.43192205488946556
n= 100  a= 0.000000000000000000E+00  b= 10.000000000000000
Q=  6.43192200051624319
```

Obviously for N=100 the integral is converged already to more than the required 4 figures. As next step we have to double the interval continously, where each doubling of the interval requires a doubling of N also.

A Fortran program for this task would be:

```
      program four
      n=100
      a=0.
      b=10.
 1000 continue
      q1=0.
      q1=q1+(b**3)/(exp(b)-1.)
      q2=0.
      q3=0.
      h=(b-a)/(2.*n)
      nm=n-1
      do 1 j=1,nm
      if(j.ne.1) goto 10
      x=a+h
      q2=q2+x**3/(exp(x)-1.)
   10 continue
      x=a+(2.*j+1.)*h
      q2=q2+x**3/(exp(x)-1.)
      x=a+2.*j*h
      q3=q3+x**3/(exp(x)-1.)
    1 continue
```

```
q=(h/3.)*(q1+4.*q2+2.*q3)
write(6,*) 'n=',n,' a=',a,' b=',b
write(6,*) 'Q = ',q
b=2.*b
n=2*n
if(n.eq.6400) stop
goto 1000
stop
end
```

It is nearly identical to the previous one and the output is

```
n= 100  a= 0.000000000000000000E+00  b= 10.0000000000000000
Q =  6.43192200051624319
n= 200  a= 0.000000000000000000E+00  b= 20.0000000000000000
Q =  6.49392028411445477
n= 400  a= 0.000000000000000000E+00  b= 40.0000000000000000
Q =  6.49393950643320572
n= 800  a= 0.000000000000000000E+00  b= 80.0000000000000000
Q =  6.49393950643349260
n= 1600  a= 0.000000000000000000E+00  b= 160.000000000000000
Q =  6.49393950643349260
n= 3200  a= 0.000000000000000000E+00  b= 320.000000000000000
Q =  6.49393950643349260
```

Obviously for integration from x=0 to x=80 with N=800 intervals the integral is equal to 6.4939395 (it has no units) and of sufficient accuracy.

The function g(T) is at 5000 K, together with the factor from the change of the integration variable:

$$g(T) = \frac{8\pi}{h^2}\left(\frac{k_B T}{c}\right)^3$$

$$g = \frac{8 \bullet 3.141593}{(6.62608 \bullet 10^{-34}\ J\ s)^2}\left(\frac{1.38066 \bullet 10^{-23}\ \frac{J}{K} \bullet 5000\ K}{2.99792458 \bullet 10^8\ \frac{m}{s}}\right)^3$$

$$= 6.989316 \bullet 10^{-16}\ \frac{J\ s}{m^3}$$

$$\frac{k_B T}{h} \bullet g = 6.989316 \bullet 10^{-16} \frac{J\,s}{m^3} \bullet \frac{1.38066 \bullet 10^{-23} \bullet \frac{J}{K}\,5000\,K}{6.62608 \bullet 10^{-34}\,J\,s}$$

$$\frac{k_B T}{h} \bullet g = 0.0728173 \frac{J}{m^3}$$

Thus the energy density radiated by the sun is 6.4939395 x 0.0728173 J/m^3 = 0.4728713 J/m^3. This might look not too much, but remember, it means about 0.5 GJ/km^3, i.e. a volume of a km^3 having the same thickness in a larger distance from the sun will receive the same energy in a much larger area.

b), c), d) A Fortran program for that could look like:

```
      program five
      n=800
      c=2.99792458e8
      bk=1.38066e-23
      hh=6.62608e-34
      tt=5000.
      etot=0.4728713
      factor=0.0728173
      do 2000 i=1,3
      read(5,*) rlam1,rlam2
      write(6,*) 'limits: lambda1 = ',rlam1,' m, lambda2 = ',rlam2,' m'
      a=hh*c/(rlam1*bk*tt)
      b=hh*c/(rlam2*bk*tt)
      q1=(a**3)/(exp(a)-1.)
      q1=q1+(b**3)/(exp(b)-1.)
      q2=0.
      q3=0.
      h=(b-a)/(2.*n)
      nm=n-1
      do 1 j=1,nm
      if(j.ne.1) goto 10
      x=a+h
      q2=q2+x**3/(exp(x)-1.)
   10 continue
      x=a+(2.*j+1.)*h
```

```
      q2=q2+x**3/(exp(x)-1.)
      x=a+2.*j*h
      q3=q3+x**3/(exp(x)-1.)
    1 continue
      q=(h/3.)*(q1+4.*q2+2.*q3)
      write(6,*) 'n=',n,' a=',a,' b=',b
      write(6,*) 'Q = ',q
      e=q*factor
      perc=e*100./etot
      write(6,*) 'radiated energy density = ',e,' J/m**3'
      write(6,*) 'relative to total energy = ',perc,' %'
 2000 continue
      stop
      end
```

This program does the job for b), c) and d) in one run. It requires an inputfile inp5, containing the wavelength ranges in m:

```
0.02,7.e-7,
7.e-7,4.e-7,
4.e-7,1.e-9,
```

Then the statement

```
prog5.x <inp5 >out5
```

produces the output file:

```
 limits: lambda1 =  0.2000E-01  m, lambda2 =0.7000E-06  m
 n= 800  a= 0.143876755327498440E-03  b= 4.11076443792852686
 Q =  4.00732224608373588
 radiated energy density =  0.291802386189753238  J/m**3
 relative to total energy =  61.7086268906049540  %
 limits: lambda1 =  0.70000E-06  m, lambda2 =  0.40000E-06  m
 n= 800  a= 4.11076443792852686  b= 7.19383776637492200
 Q =  2.05326392040877170
 radiated energy density =  0.149513134871581660  J/m**3
 relative to total energy =  31.6181453329017117  %
 limits: lambda1 =  0.40000E-06  m, lambda2 =  0.10000E-08  m
 n= 800  a= 7.19383776637492200  b= 2877.53510654996853
 Q =  0.435086908340634293
 radiated energy density =  0.316818539307124683E-01  J/m**3
 relative to total energy =  6.69988936328182128  %
```

The result tells us, that as expected still 61.7 % of the sun's energy is radiated as heat, while the brightness of the sun is due to 31.6 % of the energy radiated in the visible frequency region. The dangerous ultraviolet part of the sun light contains still 6.7 % of its total energy output. Note that the percentages sum up to 100.0 % and thus there is no deadly radiation of still higher frequency.

To do these calculations with Fortran is the best and most easy way to do it, especially to learn Simpson integration. It could be done with the help of Excel or also more sophisticated packages. But that would mean first of all, that the details lay hidden in the packages, what is not the goal of this homework.

Obj Photoelectric effect
Bohr's model

Photoelectric Effect

Light of large enough frequency ν falls on a metal

→ emission of surface electrons

in metal: electrons are bound with energy W (work function)

wave theory

radiation energy $\sim (\text{Intensity})^2$

→ all frequencies ν can supply W in a long enough time

(energy $\sim (\text{Intensity})^2$ ~~sur~~ adds up with irradiation time)

but: only if $\nu > \nu_{thr}$ (threshold frequency)

only # of emitted electrons $\sim (\text{Intensity})^2$

Einstein : light is a beam of particles when interacting with a single electron

it behaves as a wave only in interactions with the bulk of a material : diffraction, reflection

- particles of light : photons, each with energy $h\nu$

→ energy of 1 photon must be $h\nu \geq W$ for e^--emission

and $h\nu_{thr} = W$

- energy $h\nu$ of photon used to break the electron free (W), the rest to accelerate it to speed u:

$$h\nu = \frac{1}{2} m_e u^2 + W$$

threshold: $\nu_{thr} = \frac{W}{h}$

$(\text{Intensity})^2 \sim$ number of photons
$\sim$ number of e^- emitted

1 photon → 1 electron

before: quantization of oscillators

now: quantization of radiation

Also in photoelectric effect:

- classical physics → wrong results
- quantization → correct results

Wave/particle dualism:

When light interacts with individual electrons: photons (behavior as particles)

when it interacts with the bulk of a material: behavior as waves

Zero-point energy

Einstein and Stern:

Specific heat of H_2 at low T:

Even at T = 0K (all motion should stop) the molecules (oscillators) have an energy of $\frac{1}{2}h\nu$ → motion is left at 0K

→ quantum effect!

~~Bohr's~~ Bohr's atomic theory

Rutherford: e^- orbits around the proton (p^+) like a planet orbits round the sun (classical)

but: classical Electrodynamics:

oscillating (accelerated) charges Loose energy by emission of radiation

→ e^- would fall into the nucleus

→ classically H atom not stable!

Bohr's postulate: e^- in H are only stable in certain stationary states

stationary states: discrete (quantized) values of angular momentum L

$$\text{unit}(L) = \frac{\text{mass}\cdot(\text{distance } \cancel{r \text{ from center}})^2}{\text{time}}$$

→ unit: energy · time as in h (Js)

$$L = mvr$$

<u>postulate</u> an orbit is stable

only if $mur = n\frac{h}{2\pi} = n\hbar$ $\quad m \equiv m_e$

n integer ≥ 1, $\hbar \equiv \frac{h}{2\pi}$

classical: in a cirkular orbit of an e^- around the proton, the centripetal force must balance the attraction by p^+ (Coulomb)

reduced mass: $\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M}$ $\quad M = m_p$, $m = m_e$

$$= \frac{M+m}{mM}$$

$$\rightarrow \mu = \frac{mM}{m+M} \approx m \qquad M \approx 1000\,m$$

centripetal force = Coulomb force

$$\frac{\mu u^2}{r} = \frac{Ze^2}{4\pi \varepsilon_0 r^2}$$

nuclear charge: Ze, $H: Z = 1$

ε_0: permittivity of the vacuum

r: radius of the circular orbit of the e^- round the p^+

$$\mu u r = n\frac{h}{2\pi}$$

$$\rightarrow \quad u = \frac{nh}{2\pi\mu r}$$

$$\frac{\mu u^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \quad ; \quad u^2 = \frac{Ze^2}{4\pi\varepsilon_0 \mu r}$$

$$r = \frac{Ze^2}{4\pi\varepsilon_0 \mu u^2} = \frac{Ze^2}{4\pi\varepsilon_0 \mu \frac{n^2h^2}{4\pi^2\mu^2 r^2}}$$

$$= \frac{Ze^2 \pi \mu r^2}{\varepsilon_0 n^2 h^2}$$

$$\rightarrow \quad 1 = \frac{Ze^2 \pi \mu r}{\varepsilon_0 n^2 h^2}$$

$$\rightarrow \boxed{r = \frac{h^2 \varepsilon_0}{\pi \mu Z e^2} n^2} = \frac{n^2}{Z} a_0$$

$$a_0 = \frac{h^2\varepsilon_0}{\mu \pi e^2}$$ Bohr's radius

=atomic unit

= 52.92 pm

kinetic energy of the e^- in H;

$$E_k = \frac{1}{2}\mu u^2 = \frac{Ze^2}{8\pi\varepsilon_0 r} = \frac{Z^2e^2}{8\pi\varepsilon_0 a_0}\frac{1}{n^2} \quad \left(r = \frac{n^2 a_0}{Z}\right)$$

potential energy:

$$E_p = -\int_r^{\infty} \frac{Ze^2}{4\pi\varepsilon_0 r^2} dr = -\frac{Ze^2}{4\pi\varepsilon_0}\int_r^{\infty}\frac{dr}{r^2} = \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}\Big|_r^{\infty}$$

$$= \frac{Ze^2}{4\pi\varepsilon_0}\left(\underset{\downarrow 0}{\frac{1}{\infty}} - \frac{1}{r}\right) = -\frac{Ze^2}{4\pi\varepsilon_0 r} = -\frac{Z^2e^2}{4\pi\varepsilon_0 a_0}\frac{1}{n^2}$$

$\rightarrow E_p = -2E_k$ virial theorem

total: $E_t = E_k + E_p = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0} \frac{1}{n^2}$

energy relative to completely <u>free</u> electron (removed from the atom)

$n=1$: $E_t(n=1) = -2.1798 \cdot 10^{-18}\,J = -13.605\,eV$

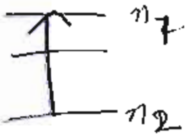
ionization energy of H: $+13.605\,eV$

electron goes from n_2 to n_7

$\rightarrow$ photon of energy $h\nu$ is

emitted: $n_1 \leftarrow n_2$

or absorbed: $n_1 \rightarrow n_2$



emission: $\nu = \frac{E_2 - E_1}{h}$

absolute value of $\Delta E = E_{final} - E_{initial}$

here: $E_{final} = E_1 < E_{initial} = E_2$

E_1 more negative than E_2 in emission

$$\bar{\nu} = \frac{1}{\lambda} = \frac{Z^2 e^2}{8\pi\varepsilon_0 a_0 hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$\downarrow$

wavenumber

$\frac{1}{n_1} > \frac{1}{n_2}$

$\lambda = \frac{c}{\nu}$; $\frac{1}{\lambda} = \bar{\nu} = \frac{\nu}{c} = \frac{|\Delta E|}{hc}$ since $n_1 < n_2$

Rydberg constant:

$$R = \frac{Z^2 e^2}{8\pi \varepsilon_0 a_0 hc} \quad (\text{for } H,\ Z=1)$$

$$\rightarrow \bar{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

this is the empirical formula (from experiment)

for H: $R = \frac{e^2}{8\pi\varepsilon_0 a_0 hc}$ fits very well to experimental value

Theory works well <u>only</u> for 1-electron atoms or ions:

$H,\ He^{+},\ Li^{2+},\ Be^{3+},\ B^{4+},\ ----$

it does <u>not</u> work at all for atoms or ions with more than 1 electron

→ new theory needed

→ modern Quantum Mechanics (QM)

<u>Correspondence principle</u>: all QM must ~~led~~ lead to classical theories under conditions where classical behavior is found!

Spectral Series

After Bohr had developed his theory of hydrogenlike atoms he did not at first consider applying it to spectra, which he thought would be too difficult to interpret. However, a colleague pointed out to him the existence of certain regularities in atomic spectra, of which Bohr had surprisingly been unaware.

The emission spectrum of hydrogen consists of sharp lines, as shown in Figure 11.8a, and some useful empirical relationships had been discovered. In 1885 Johann Jakob Balmer (1825–1898), who taught mathematics at a girls' high school in Basel, Switzerland, developed an empirical equation for the lines now known as the Balmer series (Figure 11.8). Other similar series were later predicted by empirical equations developed by the American physicist Theodore Lyman (1874–1954) and the German physicist Friedrich Paschen (1865–1940). These equations were all generalized by the Swedish physicist Johannes Robert Rydberg (1854–1919) and by the Swiss physicist Walter Ritz (1878–1909).

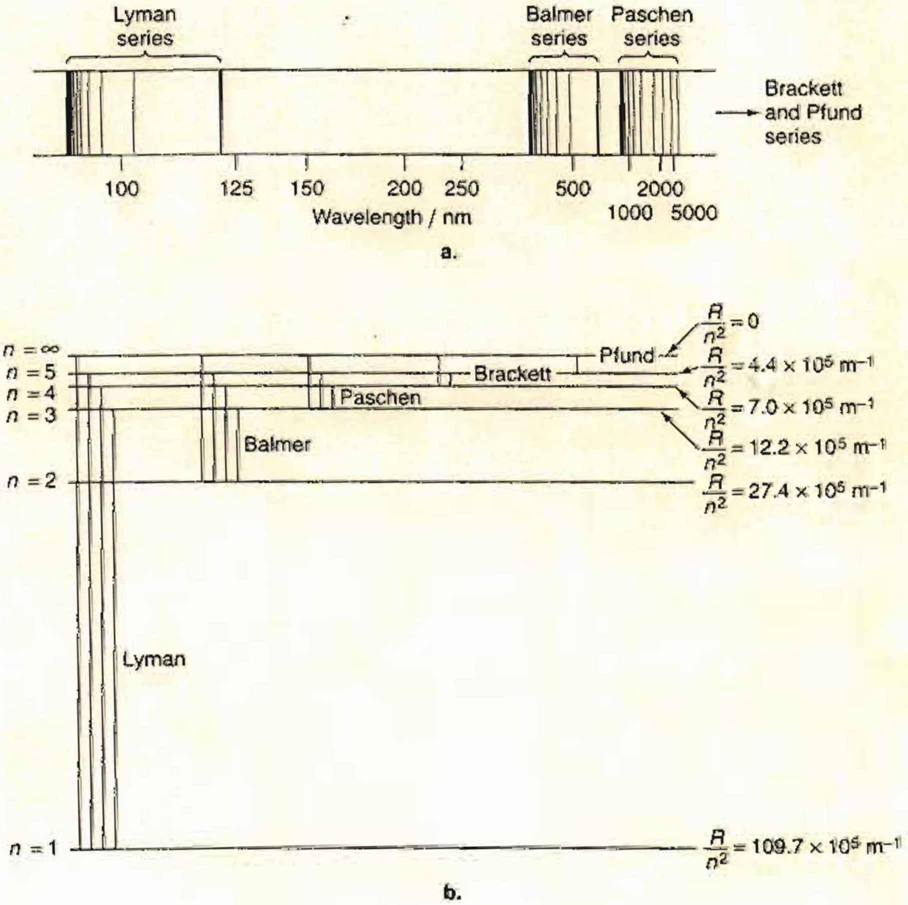


FIGURE 11.8
(a) The hydrogen spectrum in the visible and the near-ultraviolet and near-infrared regions, showing the Lyman, Balmer, and Paschen series. (b) The interpretation of the series as given by the Balmer-Rydberg-Ritz formula. The horizontal lines show R/n^2 values (the spectral terms) for various values of n. The transitions involved in the various series are shown.

black body radiation,
photoelectric effect:
radiation has wave <u>and</u> particle (photons)
properties (electromagnetic radiation)

Foundation of QM:
electrons, tiny particles have also a
wave nature

- Compton: monochromatic (only 1 value of ν)
X-rays on graphite (e.g.):
observed: 2 values of ν, the original ν
<u>and</u> a smaller one
→ some photons hit electrons and transfer
energy and momentum to them
- no classical explanation: momentum con
→ Xrays contain particles

<u>de Broglie</u> when light can behave as
particle and as wave,
can e^- behave as waves also?

wavelength of a particle at speed u?

Special relativity:

$$E^2 = \underset{\text{momentum}}{\underset{\downarrow}{p^2}} c^2 + \underset{\text{restmass: mass at } u=0}{\underset{\downarrow}{m_0^2}} c^4$$

light: $m_0 = 0$, speed always c and

$m_0 = 0$ at $u = 0$ and all other $u < c$

→ light: $E = p \cdot c = p \underbrace{\lambda \nu}_{=c}$

and $E = h\nu \Rightarrow p\lambda\nu = h\nu$

$pc = h\nu \rightarrow \lambda = \frac{h}{p}$, $p = \frac{h}{\lambda} = \frac{h\nu}{c}$

p: momentum of photons

particles: momentum $p = mu$ $(m \neq 0)$

analogy to photons: $\lambda = \frac{h}{p} = \frac{h}{mu}$

for particles

e^- under a potential of 100 V

$$E_k = \frac{1}{2} m u^2 = U \cdot q = 100 \text{V} \cdot 1.602 \cdot 10^{-19} \text{As (C)}$$

$$= 1.602 \cdot 10^{-17} \text{J}$$

$$1 \text{VAs} = 1 \text{J}$$

$$u = \sqrt{\frac{2 E_k}{m}} = 5.93 \cdot 10^6 \frac{\text{m}}{\text{s}}$$

$$\lambda = \frac{h}{mu} = \frac{6.626 \cdot 10^{-34} \text{Js}}{9.11 \cdot 10^{-31} \text{kg} \cdot 5.93 \cdot 10^6 \frac{\text{m}}{\text{s}}}$$

$$= 123 \text{pm}$$

if there is a thermal average speed at temperature T: $\frac{1}{2} m u_{av}^2 = k_B T \rightarrow u$

wave nature of e^- can be seen by diffraction on a crystal

now used to study molecular structures (electron microscope)

a <u>standing</u> wave and thus a stable orbit, can only exist, when the wave fits into the orbit (constructive interference)

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Note that J. J. Thomson won a 1906 Nobel Prize for showing that the electron is a particle, while his son G. P. Thomson shared the 1937 prize with C. J. Davisson for showing that it is a wave.

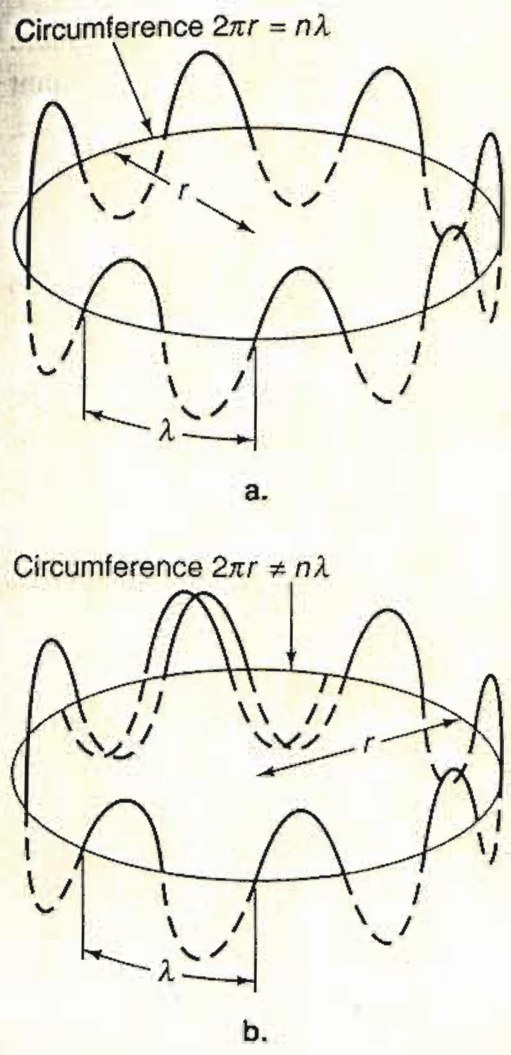


FIGURE 11.9
The de Broglie wave associated with an electron in a Bohr orbit of radius r. (a) Constructive interference: the wave fits into the orbit. (b) Destructive interference: the wave does not fit an integral number of times into the orbit. If in this diagram we continued the waves indefinitely, they would completely obliterate one another, the net amplitude becoming zero.

be diffracted by using a crystal as a diffrac
experimentally in 1927 by the English ph
1975) and A. Reid and by the American p
1958) and Lester Halbert Germer. The
employed as a technique for investigating

The realization that electrons have wa
tion of Bohr's hypothesis of stationary orb
associated with an electron in a Bohr orb
equal to an integer n multiplied by the w
an integral number of times, and *constru*
for this is

$$2\pi r$$

Destructive interference occurs with wa
and the orbit is not a stationary one. The
constructive interference thus leads to a
given by Eq. 11.56 into Eq. 11.57 gives

$$2\pi r$$

or

$$mur = n\frac{h}{2\pi} =$$

The quantity mur is the orbital angular n
an integral number of $h/2\pi$. We can now
once to this quantization condition.

The Uncertainty Principle

Scientists have often found it useful to
Gedanke, thought) experiments. These
if not impossible to perform but that ca
results that are quite reliable. A very s
out in 1926 by Werner Heisenberg, who
to be followed in order to make a sim
momentum of a small particle such a
impossible to make accurate measurem
for measuring one of them will necess
measurement of the other one to be im
is used to make an accurate determina
we must use radiation of short waveler
defined. Radiation of short wavelength,
we have seen in the Compton effect tha

orbits where the wave does not fit, destructive interference

→ instable

fit only, if $2\pi r = n\lambda = \frac{nh}{mu}$

$$\rightarrow \quad mur = \frac{nh}{2\pi}$$

$$\rightarrow \quad L = n\hbar \quad n \text{ integer}$$

→ Bohr's postulate follows directly from the wave nature of an electron!

Obj Quantum Mechanics:

uncertainty principle
Schrödinger's wave mechanics
Normalitation

Heisenberg's uncertainty principle

$$\Delta q \cdot \Delta p \geqslant \frac{1}{2}\hbar = \frac{h}{4\pi}$$

$p = mu \Rightarrow \Delta q \cdot \Delta u \geqslant \frac{1}{2}\frac{\hbar}{m}$

small m: large uncertainty
e and other particles

macroscopic: m very large
→ small uncertainty
(correspondence)

$\Delta t = \frac{\Delta q}{u}$ time to travel position uncertainty

$E = \frac{1}{2} m u^2$ (free particle)
$p = mu$

$\Rightarrow E = \frac{1}{2} u p$

$\rightarrow \Delta E = \frac{1}{2} u \Delta p$

$\Delta p = \frac{\Delta E}{u}$ ($\frac{1}{2}$ unimportant)

$\Delta q = u \Delta t$

$\Rightarrow \Delta q \cdot \Delta p = u \cdot \Delta t \cdot \frac{\Delta E}{u} = \Delta t \cdot \Delta E \geq \frac{1}{2}\hbar$ ④ - 2

α-particles in radioactive decay

E measured precisely

→ emission time not precise

(statistical decay laws)

e^- transition from ground state

→ sharp line → certainty in energy

⇒ Δt long when ΔE small

⇒ long life times of groundstates

excited states: short life times

→ Δt small

→ ΔE large → broad lines

exact position determination

→ small wavelength line needed

small λ implies high photon energy

→ change of momentum of e^- when measurement of position with small Δq

→ Δq small ⇒ Δp large

Schrödinger's wave mechanics

equivalent to Heisenberg's matrix mechanics

no derivation, only plausibility arguments:

electromagn. wave in vacuum,

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 y}{\partial t^2} \qquad y: E, H$$

Schrödinger: $y \rightsquigarrow \psi(x,t)$

wave function describing e^-

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

solution: $\psi(x,t) = C e^{\frac{2\pi i x}{\lambda}} \cdot e^{-2\pi i \nu t}$

de Broglie: $\lambda \rightsquigarrow \frac{h}{p_x} \qquad \nu \rightsquigarrow \frac{E}{h}$

$$\psi(x,t) = C e^{\frac{2\pi i p_x}{h}x} e^{-\frac{2\pi i E t}{h}}$$

$$\frac{\partial \psi}{\partial t} = -\frac{2\pi i}{h} E\psi$$

$$\Rightarrow \quad -\frac{\hbar}{i}\frac{\partial \psi}{\partial t} = E\psi$$ operator equation

energy operator: $\hat{E}$:

$$\hat{E} = -\frac{\hbar}{i}\frac{\partial}{\partial t}$$

operates on ψ and gives $E\psi$ when ψ is an eigenfunction

eigenfunction: $\hat{O} f = o f$ o eigenvalue

$\hat{E}\psi = E\psi$ no division by ψ possible

$$\frac{\partial\psi}{\partial x} = \frac{2\pi i p_x}{h}\psi$$

$$\frac{\hbar}{i}\frac{\partial\psi}{\partial x} = p_x\psi$$

linear momentum operator:

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\hat{p}_x\psi = p_x\psi$$

total energy: $E_t = E_k + E_p$

$$= \frac{p_x^2}{2m} + E_p$$

$$\frac{p_x^2}{2m} = \frac{(mu_x)^2}{2m} = \frac{1}{2}mu_x^2$$

E_t: ~~Hamilt~~ Hamilton function

$$i^2 = (\sqrt{-1})^2 = -1$$ ④-5

→ Hamilton operator: insert $\hat{p}_x$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + E_p$$

$$\hat{H}\psi = E_t\psi$$

and $-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = E_t\psi$

$$\Rightarrow \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + E_p\right]\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}$$

3 dimensions: $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Laplace operator

→ time-dependent Schrödinger equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + E_p(x,y,z,t)\right]\psi = -\frac{\hbar}{i}\frac{\partial\psi}{\partial t}$$

$$\psi = \psi(x,y,z,t)$$

for atomic, molecular structures

t-dependence of ψ not important:

stationary states: $E_p(x)$

time - independent

$$\psi(x,y,z,t) = \psi(x,y,z)\, e^{-\frac{2\pi i E t}{h}}$$

$$\rightarrow \quad \frac{\partial \psi}{\partial t} = -\frac{2\pi i}{h} E\psi \qquad \hat{H}\psi = -\frac{h}{2\pi i}\frac{\partial \psi}{\partial t}$$

in $\hat{H}$: no time dependence, because E_p does not depend on time

cancel $e^{-\frac{2\pi i E}{h}t}$ on both sides

→ time independent Schr. equation:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + E_p(x,y,z)\right]\psi(x,y,z) = E\psi(x,y,z)$$

$$\hat{H}\psi = E\psi$$

E_p given for a system, $\hat{H}\psi = E\psi$ can in principle be solved

→ stationary state solutions (like standing waves on a string)

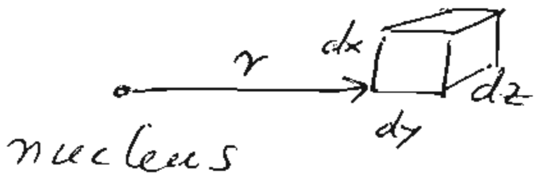
solutions ψ: { wave functions
eigenfunctions of $\hat{H}$
characteristic functions

for each ψ: defined E-value:

eigen value, characteristic value

conservative systems: time independent

~~Wach~~ What is ψ?



if ψ real function (no i):

$\psi^2(x,y,z)\,dV \sim$ probability to find an e^- in volume element $dV = dx\,dy\,dz$ at r <u>Born</u>

→ ψ^2: probability density of e^- or probability distribution

→ several conditions for a possible eigenfunction must be fulfilled:

1) single valued: only 1 value of ψ at a point
2) finite everywhere: never ∞
3) continous function: density does not jump
4) ψ must be square integrable:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^2(x,y,z)\,dx\,dy\,dz \quad \underline{\text{finite}} \begin{cases} \text{not } 0 \\ \text{not } \infty \end{cases}$$

ψ <u>can</u> be complex, then ψ^2 also complex and prob. density ~ $\psi\psi^*$ ④-8

$\psi = a + ib \quad \psi^* = a - ib$

$\psi^*\psi$ is real: $(a+ib)(a-ib)$

$\underline{i^2 = -1} \qquad = a^2 + iba - iba + b^2 = a^2 + b^2$

$\psi\psi^* dV$ ~ probability to find e^- in dV at r

Normalization: $\psi\psi^* dV$ = probability
if ψ is normalized

if ψ is a solution of $\hat{H}\psi = E\psi$, then $N\psi$ is also for all N

$\hat{H}(N\psi) = N\hat{H}\psi = NE\psi$, N cancels

probality to find e^- in <u>all</u> space must be 1 (somewhere it must be!)

all space: sum over all dV → integration

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi\psi^* \, dx\, dy\, dz = 1$$

$\hat{=} \quad \int \psi\psi^* d\tau = 1$ normalization condition

$d\tau = dx \cdot dy \cdot dz$, $\int$ over all space

usually for a solution: ϕ:

$\int \phi^*\phi \, d\tau = b$ ~~$\int \phi\phi^* d\tau = N$~~ ~~$\int \psi^*\psi \, d\tau = N$~~

→ normalized function:

$$\psi = \frac{1}{\sqrt{6}}\phi$$

$$\rightarrow \int \psi^* \psi \, d\tau = \int \frac{\phi^*}{\sqrt{6}} \frac{\phi}{\sqrt{6}} d\tau = \frac{1}{6}\int \phi^* \phi \, d\tau = \frac{6}{6} = 1$$

normalization process

<u>then</u> normalized ψ gives exactly the probability P to find electron in $d\tau = dx\,dy\,dz$ at r

$$P = \psi \psi^* d\tau$$

$$P(x, y, z) = \psi(x,y,z)\psi^*(x,y,z)\,dx\,dy\,dz$$

~~prb~~ probability density ρ:

- $\rho(x,y,z) = \psi(x,y,z)\psi^*(x,y,z)$

$$\rho(\underline{r}) = \psi(\underline{r})\,\psi^*(\underline{r})$$

$\underline{r}$: vector from O to point (x, y, z)

$$\begin{aligned} P(\underline{r}) &= \psi(\underline{r})\psi^*(\underline{r})\,dV \\ &= \psi(\underline{r})\,\psi^*(\underline{r})\,dx\,dy\,dz \\ &= \psi(\underline{r})\,\psi^*(\underline{r})\,d\tau \end{aligned}$$

Obj: QM postulates

QM developed from analogy of particles to waves from wave-equ.

also possible - more general, from

Quantum Mechanical Postulates

I. The state of a particle is described completely by an appropriate wave function $\psi(x,y,z,t)$

II. The possible $\psi(x,y,z,t)$ are solutions of the corresponding Schrödinger equation (right E_p)

System given → pot. energy E_p

if E_p is time independent (Coulomb)

then: $\left[-\frac{\hbar^2}{2m}\nabla^2 + E_p(x,y,z)\right]\psi = E\psi$

boundary conditions important!

III. Every observable quantity (position, momentum, energy) can be represented by a linear operator.

operator: $\hat{O} f = g$

like $\hat{O} = \frac{d}{dx} \Rightarrow \hat{O} x^2 = \frac{\partial}{dx} x^2 = 2x$

$\hat{x} : \hat{x} f = x \cdot f$

kinetic energy: $\hat{E}_k = -\frac{\hbar^2}{2m} \nabla^2$

Linear operator:

$$\hat{O}(a\psi + b\phi) = a\hat{O}\psi + b\hat{O}\phi$$

$\frac{d}{dx}[af(x) + b\cancel{f}g(x)] = a\frac{df}{dx} + b\frac{dg}{dx}$ linear

$\sqrt{f+g} \neq \sqrt{f} + \sqrt{g}$ $\quad \sqrt{}$ not linear

physical observables: only linear operators

if not linear: no superpositions of wave functions possible

2 operators commute:

$$\hat{O}_1(\hat{O}_2\psi) = \hat{O}_2(\hat{O}_1\psi)$$

↑ acts first

eigenfunctions of operator: $\hat{O}\psi = o\psi$

eigenvalue

_if_ 2 operators commute → same eigenfunctions: $\hat{O}_1\psi = o_1\psi$ and $\hat{O}_2\psi = o_2\psi$

$$\hat{O}_1\hat{O}_2\psi = \hat{O}_1 o_2\psi = o_2\hat{O}_1\psi = o_2 o_1\psi$$

$$\|$$

$$\hat{O}_2\hat{O}_1\psi = \hat{O}_2 o_1\psi = o_1\hat{O}_2\psi = o_1 o_2\psi$$

do position ($\hat{x} = x$) and momentum ($\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$) operators commute?

1) $\hat{x}\hat{p}_x(2x) = x\frac{\hbar}{i}\frac{\partial}{\partial x}(2x) = \frac{2\hbar x}{i}$

$\neq$

$\hat{p}_x\hat{x}(2x) = \frac{\hbar}{i}\frac{\partial}{\partial x}(x2x) = \frac{2\hbar}{i}\frac{\partial}{\partial x}(x^2) = \frac{4\hbar x}{i}$

if they commute, they must do for _every_ function, also for $f = 2x$

2) $\hat{p}_x e^{ikx} = \frac{\hbar}{i}\frac{\partial}{\partial x}e^{ikx} = \frac{\hbar}{i}ike^{ikx} = \hbar k\, e^{ikx}$

→ e^{ikx} eigenfunction of $\hat{p}_x$

$\hat{x}e^{ikx} = xe^{ikx}$ e^{ikx} is _no_ eigenfunction of $\hat{x}$

→ $\hat{x}$ and $\hat{p}_x$ do not commute if 2 operators commute they have the same eigenfunctions (states)

→ both quantities have precise values (eigenvalues)

$\hat{x}, \hat{P}_x$ do <u>not</u> commute

→ no precise measurements of both quantities at the same time possible

→ uncertainty principle

IV QM-operators are obtained from the classical equation for a quantity by certain procedures:

- in equ.: $x \rightarrow \hat{x}$, $P_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$ $E \rightarrow -\frac{\hbar}{i}\frac{\partial}{\partial t}$

time dependence

conservative system: $\hat{H} = \hat{E}_k + \hat{E}_p$

$$= -\frac{\hbar^2}{2m}\nabla^2 + E_p$$

$$E_k = \frac{1}{2}mu^2 = \frac{1}{2}\frac{p^2}{m} \rightarrow \hat{E}_k = \frac{1}{2}\frac{p^2}{m} = \underset{\uparrow \, i^2}{-}\frac{\hbar^2}{2m}\nabla^2$$

energy: $\hat{H}\psi = E\psi$, momentum $\hat{p}\phi = p\phi$

more general

V When the equation $\hat{O}\psi = o\psi$ (for any observable o), then the eigenvalues o are all possible results of an individual measurement of o

$\hat{H}\psi = E\psi$ gives all possible energies

VI The mean value $\bar{O}$ or its expectation value, of an observable averaged over the results of a large number of measurements is

$$\bar{O} = \langle \hat{O} \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{O} \psi \, d\tau}{\int_{-\infty}^{\infty} \psi^* \psi \, d\tau}$$

also if ψ is not eigenfunction of $\hat{O}$

Wave function ψ: $\hat{H}\psi = E\psi$

ψ normalized

then in state ψ:

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi \, d\tau$$

Operators which describe physical observables must be <u>hermitian</u>:

hermitian, if $\int \psi_1^* \hat{O} \psi_2 \, d\tau = \int \psi_2 \hat{O}^* \psi_1^* \, d\tau$

because eigenvalues of hermitian operators are real

$\langle \hat{O} \rangle = \int_{-\infty}^{\infty} \psi^* \hat{O} \psi \, d\tau$ ($= o$ if ψ is normalized eigenfunction of $\hat{\theta}$)

$$\langle \hat{O} \rangle^* = \int_{-\infty}^{\infty} \psi \hat{O}^* \psi^* \, d\tau \underset{\substack{\uparrow \\ \hat{O}\text{ hermitian}}}{=} \int_{-\infty}^{\infty} \psi^* \hat{O} \psi \, d\tau$$

$= \langle \theta \rangle \Rightarrow \langle \hat{O} \rangle, o$ real if $\hat{O}$ is hermitian

Orthogonality of wave functions

Normalization: $\int_{-\infty}^{\infty} \phi^* \phi \, d\tau = b$

→ normalized function $\psi = \frac{1}{\sqrt{b}} \phi$

so that $\int_{-\infty}^{\infty} \psi^* \psi \, d\tau = \frac{1}{b} \int_{-\infty}^{\infty} \phi^* \phi \, d\tau = 1$

Orthogonality

2 eigenfunction of a hermition Operator for 2 different eigenvalues:

$\hat{O}\psi_1 = o_1\psi_1 \qquad \hat{O}\psi_2 = o_2\psi_2 \qquad o_1 \neq o_2$

$\Rightarrow \int \psi_1^* \psi_2 \, d\tau = \int \psi_2^* \psi_1 \, d\tau = 0$ Orthogonality

$\int \psi_2^* \hat{O} \psi_1 \, d\tau = \int \psi_2^* o_1 \psi_1 \, d\tau = a_1 \int \psi_2^* \psi_1 \, d\tau$

|| hermitian operator ||

$\int \psi_1 \hat{O}^* \psi_2^* \, d\tau = \int \psi_1 o_2^* \psi_2^* \, d\tau = o_2^* \int \psi_2^* \psi_1 \, d\tau$

hermitian $\Rightarrow o_2^* = o_2$ real

$\Rightarrow o_1 \int \psi_2^* \psi_1 \, d\tau = o_2 \int \psi_2^* \psi_1 \, d\tau$

$o_1 \neq o_2$, $\Rightarrow$ the integral (same) must be 0

it can happen that differen eigenf. ψ_1, ψ_2 belong to the same eigenvalue o: $\hat{O}\psi_1 = o\psi_1$, $\hat{O}\psi_2 = o\psi_2$ degenerate states ψ_1, ψ_2

the ψ_1, ψ_2 can be orthogonal, but the can also result non-orthogal from solution of $\hat{O}\psi = o\psi$

if ψ_1, ψ_2 are 2 degenerate eigenfunctions of $\hat{O}$, then any linear combination of them is also eigenfunction of $\hat{O}$ with the same eigenvalue

$c_1\psi_1 + c_2\psi_2$ linear combination

c_1, c_2 any constant number

$$\rightarrow \hat{O}(c_1\psi_1 + c_2\psi_2) = c_1\hat{O}\psi_1 + c_2\hat{O}\psi_2$$

$$= c_1 o \psi_1 + c_2 o \psi_2$$

$$= o(c_1\psi_1 + c_2\psi_2)$$

also eigenfunction but <u>only</u> if ψ_1, ψ_2 degenerate

non-orthogonal degenerate eigenf. $\xrightarrow[\text{combination}]{\text{linear}}$ orthogonal degenerate eigenf.

$\hat{H}$: ψ_1, ψ_2 both to eigenvalue E

E: two-fold degenerate energy level

if $\psi_1, \psi_2, \dots, \psi_n$ all to eigenvalue E

E: n-fold degenerate energy level

can be made orthogonal!

assume ψ_1, ψ_2 are orthogal, normalized eigenfunctions of $\hat{H}$ to different eigenvalues $o_1 \neq o_2$

then $\psi_3 = c_1\psi_1 + c_2\psi_2$ is not eigenfunction of $\hat{H}$, but can be useful

$$\hat{H}\psi_3 = o_1 c_1 \psi_1 + o_2 c_2 \psi_2$$ not eigenf. since $o_1 \neq o_2$

ψ_3, to be useful should be

normalized

$$\int_{-\infty}^{\infty} \psi_3^* \psi_3 \, d\tau = 1 = \int_{-\infty}^{\infty} (c_1^* \psi_1^* + c_2^* \psi_2^*)(c_1 \psi_1 + c_2 \psi_2) \, d\tau$$

$$= c_1^* c_1 \underbrace{\int_{-\infty}^{\infty} \psi_1^* \psi_1 \, d\tau}_{1} + c_1^* c_2 \underbrace{\int_{-\infty}^{\infty} \psi_1^* \psi_2 \, d\tau}_{0}$$

$$+ c_2^* c_1 \underbrace{\int_{-\infty}^{\infty} \psi_2^* \psi_1 \, d\tau}_{0} + c_2^* c_2 \underbrace{\int_{-\infty}^{\infty} \psi_2^* \psi_2 \, d\tau}_{1}$$

$$= c_1^* c_1 + c_2^* c_2$$

$\Rightarrow$ if $\boxed{c_1^* c_1 + c_2^* c_2 = 1} = |c_1|^2 + |c_2|^2$

then $\psi_3 = c_1 \psi_1 + c_2 \psi_2$ is normalized!

but is <u>not</u> eigenfunction to $\hat{H}$

because $o_1 \neq o_2$!

Obj Application to simple systems
→ exact solutions
and related to important problems
- free particle
- particle in the box

The free particle

particle, mass m, moving in x-dir.
free: no force → E_p = const. = 0
since force $F = -\frac{\partial E_p}{\partial x} = 0$
if E_p = const.

$$\rightarrow E_{tot} = E_k + E_p = E_k = \frac{1}{2} m u_x^2$$

$$= \frac{P_x^2}{2m} = H$$

Hamilton function

operator $\hat{H}$:

only x ⇒ d not ∂

$$\hat{H} = \frac{1}{2m} \hat{P}_x^2 = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx}\right)^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\hat{H}\psi = E\psi \Rightarrow -\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

$$\hbar \equiv \frac{h}{2\pi}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0$$

ψ that gives back ψ with a factor when 2~~x~~ times differentiated is solution

possible: $\psi = A e^{i\alpha x}$

$$\frac{d\psi}{dx} = i\alpha A e^{i\alpha x}$$

$$\frac{d^2\psi}{dx^2} = i^2\alpha^2 A e^{i\alpha x} = -\alpha^2\psi$$

from equation (compare):

here $\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0$

$$\Rightarrow \alpha^2 = \frac{2m}{\hbar^2} E = \frac{8\pi^2 m}{h^2} E$$

$$\rightarrow \alpha = \pm \frac{\sqrt{2mE}}{\hbar}$$

$$\Rightarrow \psi_1 = A e^{i\frac{\sqrt{2mE}}{\hbar}x} \qquad \psi_2 = B e^{-i\frac{\sqrt{2mE}}{\hbar}x}$$

particle probability density ρ:

$$\rho \sim |\psi|^2 = \psi^*\psi$$

$$|\psi_1|^2 = A e^{i\frac{\sqrt{2mE}}{\hbar}x} A^* e^{-i\frac{\sqrt{2mE}}{\hbar}x} = AA^* = |A|^2$$

$$e^{ia} e^{-ia} = e^{i(a-a)} = e^0 = 1$$

$\rho(x) \sim |A|^2 = \text{const.}$

equal ~~to~~ probability to find particle anywhere along x non-localized parti~~e~~cle !

postulat V: if ψ eigenfunction of $\hat{P}_x$

then momentum P_x sharp!

then: $\hat{P}_x \psi = P_x \psi$ must hold

$$\psi_{1,2} = A_{1,2}\, e^{\pm i \frac{\sqrt{2mE}}{\hbar} x}$$

$$\hat{P}_x \psi_{1,2} = \hat{P}_x A_{1,2}\, e^{\pm i \frac{\sqrt{2mE}}{\hbar} x} = \frac{\hbar}{i} \frac{d}{dx} A_{1,2}\, e^{\pm i \frac{\sqrt{2mE}}{\hbar} x}$$

$$= \frac{\hbar}{i} \left(\pm i \frac{\sqrt{2mE}}{\hbar} \right) \psi_{1,2}$$

→ $\psi_{1,2}$ are eigenfunctions of $\hat{P}_x$

→ sharp, ~~precise~~ accurate measurement of P_x

but particle can be everywhere along x

→ uncertainty principle: $\hat{x}, \hat{P}_x$ do not commute

⇒ P_x sharp value, x completely uncertain

$$P_x = \frac{\hbar}{i} \left(\pm i \frac{\sqrt{2mE}}{\hbar} \right) = \pm \sqrt{2mE}$$

movement left (-) or right (+)

no quantization of energy or momentum

we can give m any value of E_k or p_x we like

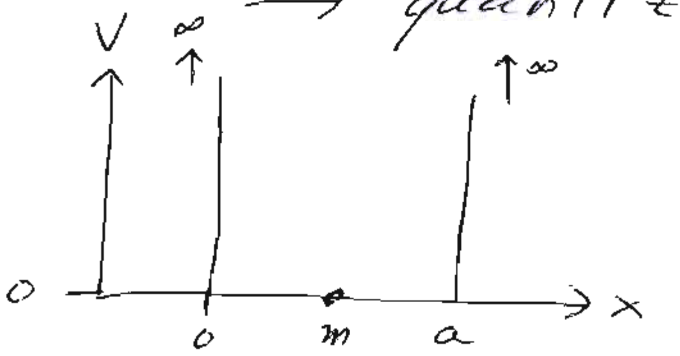
as in photoelectric effect:

$$h\nu = W + E_k \,,\; E_k = h\nu - W$$

Particle in the box

if we confine particle in a region between $x=0$ and $x=a$

→ quantization!



$$E_p = \begin{cases} \infty, & -\infty < x \le 0 \\ 0, & 0 < x < a \\ \infty, & a < x < \infty \end{cases}$$

inside box: $E_p = 0$: same equation as free particle

outside box: $E_p \to \infty$ particle cannot be there ⇒ probability dens.

$$\rho \sim |\psi|^2 = 0$$

$$\Rightarrow \psi = 0 \text{ for } x \le 0,\ x \ge a$$

→ ψ like free particle in the box, and 0 outside box

$$\Rightarrow \psi(x=0) = \psi(x=a) = 0 \; !$$

no jumps of ψ at $x=0$ and $x=a$

not possible with ψ_1 or ψ_2 alone!

because: e-function never exact $= 0$

$\rightarrow$ only $A=0$ or $B=0$ can give 0 at $x=0$ and $x=a$

but ψ_1, ψ_2: degenerate eigen functions for the same E

$\rightarrow$ $\psi_1 + \psi_2$ also solution with same E

$$\Rightarrow \quad \psi = A e^{i\alpha x} + B e^{-i\alpha x} \qquad \alpha = \frac{\sqrt{2mE}}{\hbar}$$

A, B arbitrary, free

$$x = 0: \quad e^{\pm i\alpha\cdot 0} = e^{0} = 1$$

$$\psi(x=0) = A + B$$

since $\psi(x=0) = 0$ must be

$$\Rightarrow A + B = 0 \Rightarrow A = -B$$

$$\rightarrow \psi = A\left(e^{i\alpha x} - e^{-i\alpha x}\right)$$

cancel: $\cos(-\alpha x) = \cos(\alpha x)$

Euler theorem:

$$\psi = A\left[\underline{\cos(\alpha x)} + i\sin(\alpha x) - \underline{\cos(\overset{-\alpha x}{\cancel{\alpha x}})} \underbrace{- i\sin(-\alpha x)}_{\rightarrow\, i\sin(\alpha x)}\right]$$

$$\sin(-\alpha x) = -\sin(\alpha x)$$

$\rightarrow \psi = 2i A \sin(\alpha x)$

$\psi(x = a) = 0$

$\rightarrow \psi(x=a) = 2iA \sin(\alpha a) = 0$

$\Rightarrow \alpha a = \pm n\pi \qquad n = 0, 1, 2, \ldots$

$\alpha = \pm \frac{n\pi}{a}$

because then

$\psi(x=a) = 2iA \sin(\pm n\pi) = 0$

$$\Rightarrow \qquad \psi = \begin{cases} 0 & -\infty < x \le 0,\ a \le x < \infty \\ \psi & 0 < x < a \end{cases}$$

$\psi = \pm 2i A \sin\left(n \frac{\pi x}{a}\right) \qquad 0 < x < a$

A from normalization : $\int_{-\infty}^{\infty} |\psi|^2 dx = 1$

$$1 = \int_{-\infty}^{0} 0\, dx + \int_{0}^{a} \psi^* \psi\, dx + \int_{a}^{\infty} 0\, dx$$

~~$= 1 \cdot i^2 = -1$~~

$$= \int_0^a \psi^* \psi\, dx = 4 \underset{A^*A}{} \underbrace{\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx}_{a/2}$$

~~$\psi\psi^* = 4i^2 A^2 \sin^2$~~

$\rightarrow 4 \underset{A^*A}{A^2} \frac{a}{2} = 1 \qquad \sqrt{A^*A} = \sqrt{\frac{1}{2a}}$

for real wavefunction $A = \pm\sqrt{\frac{\pm 1}{2a}} = \pm\sqrt{\frac{1}{2a}}\, i$

choose $A = \sqrt{\frac{1}{2a}}\, i$

free choice for real ψ:

$$A = \pm \sqrt{\frac{1}{2a}}\, i$$

$$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad n = 1, 2, 3, \dots$$

<u>$n=0$</u>: $\psi_{n=0} = 0 \Rightarrow$ no particle in the state!

sign of ψ not important, because all properties depend only on $|\psi|^2$

E-quantization: $\alpha = \frac{n\pi}{a}$

$$\cancel{\Rightarrow E_n = \frac{\hbar^2}{2ma^2}} \qquad \frac{\sqrt{2mE_n}}{\hbar} = \frac{n\pi}{a}$$

$$\Rightarrow 2mE_n = \hbar^2 \frac{n^2\pi^2}{a^2}$$

$$E_n = \frac{\hbar^2\pi^2}{2ma^2} n^2 = \frac{h^2\pi^2 n^2}{8\pi^2 a^2 m}$$

$$E_n = \frac{h^2}{8ma^2} n^2$$ possible stationary state ~~eng~~ energies

$E_n \sim n^2$, # of antinodes (extrema ~~maxima~~): n

# of nodes (places with $\psi = 0$): $n-1$

$x=0$, $x=a$ not counted!

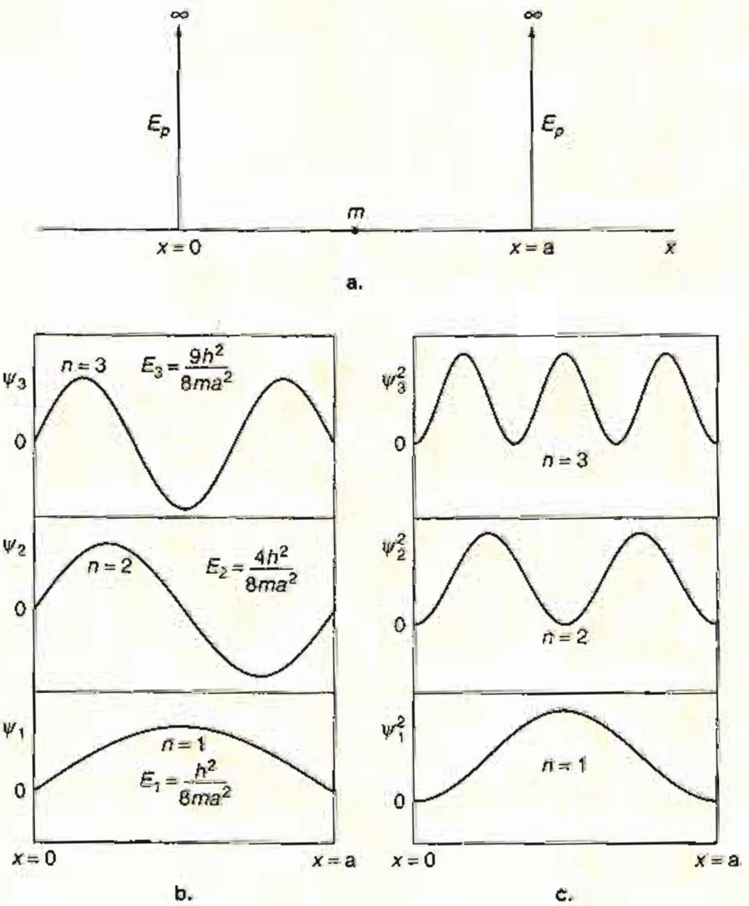


FIGURE 11.11
(a) A particle confined to a one-dimensional box of length a. The potential energy is infinite for $x < 0$ and $x > a$. (b) The form of some of the wave functions for the particle in a one-dimensional box and the corresponding energies. (c) The form of the probability densities ψ^2.

The second boundary condition, that $\psi = 0$ when $x = a$, gives

$$0 = 2iA \sin\left(\frac{\sqrt{8\pi^2 mE}}{h}a\right) \tag{11.138}$$

The factor $2iA$ cannot be zero, but the sine of an angle is zero when the angle is an integral multiple of π. Thus

$$\frac{\sqrt{8\pi^2 mE_n}}{h}a = \pm n\pi \tag{11.139}$$

where $n = 0, 1, 2, \ldots, \infty$. We have now written E_n instead of E since there is a different energy E_n for each value of n. The wave function (Eq. 11.137) therefore becomes

$$\psi_n = \pm 2iA \sin\frac{n\pi x}{a} \tag{11.140}$$

Note that the ± sign can go outside the sine function since $\sin(-n\pi x/a) = -\sin(n\pi x/a)$.

$E_n \sim n^2$ and $E_n \sim \frac{1}{ma^2}$

$\Rightarrow \Delta E_{n,n\pm1} \sim \frac{1}{ma^2}$

$\Rightarrow$ heavy particle (m large)

large box (a large)

→ levels very close and

differences $\Delta E_{n,n\pm1}$ cannot be seen

no quantization can be observed

→ this is the classical case for

macroscopic systems (m, a large)

→ correspondence principle

atomic dimensions: m small, a small

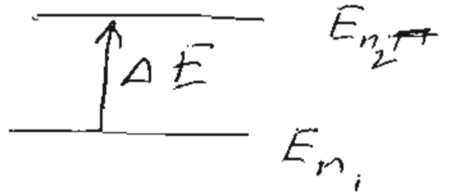
→ $\Delta E_{n,n\pm1}$ large and quantization

can easily be measured

how many levels with $E_n \leq E_0$ exist?

E_0 arbitrary:

$$E_n = \frac{h^2 n^2}{8ma^2} \leq E_0 \Rightarrow n^2 \leq \frac{8ma^2}{h^2} E_0$$



$$\Delta E = E_2 - E_1$$
$$= \frac{h^2}{8ma^2}(n_2^2 - n_1^2) = h\nu$$

light that can be absorbed and brings particle from n_1 to n_2 level

$$\rightarrow \quad \nu = \frac{h}{8ma^2}(n_2^2 - n_1^2)$$

$$\lambda = \frac{c}{\nu} = \frac{8ma^2c}{h}\,\frac{1}{n_2^2 - n_1^2}$$

<u>example</u> electron e^- in a box of atomic dimension $a \approx 4 \cdot 10^{-10}\,m$

wave length λ for $n=1 \rightarrow n=2$ transition?

$$E_1 = 3{,}77 \cdot 10^{-19}\ J \qquad n=1$$

$$E_2 = E_1 n^2 = 4E_1 \qquad n=2$$

$$\Delta E = E_2 - E_1 = 3E_1 = 1{,}33 \cdot 10^{-18}\ J$$

$$\lambda = \frac{c}{\nu} \underset{\substack{\uparrow \\ h\nu = \Delta E}}{=} \frac{hc}{\Delta E} = 176\ nm \quad \text{ultraviolet}$$

$m = 1g$ in $a = 0,10\ m$

$\rightarrow \Delta E = 1.65 \cdot 10^{-63}\ J$

$\rightarrow \lambda = 1.21 \cdot 10^{87}\ m$

~~com~~ cannot be measured

$\lambda \approx 10^{74}$ light years

> universe (= observed galaxies)

3-dimensional box, sides a, b, c

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

cube : $a = b = c$

$$E = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

many degenerate levels

ground state : $n_1 = n_2 = n_3 = 1$; $E_g = \frac{3h^2}{8ma^2}$

1. level higher groundstate :

n_1	n_2	n_3	$n_1^2 + n_2^2 + n_3^2$
2	1	1	6
1	2	1	6
1	1	2	6

same E

3 fold degenerate

1,2,3 : 123 , 132 , 213
231 , 312 , 321 6 fold degenerate

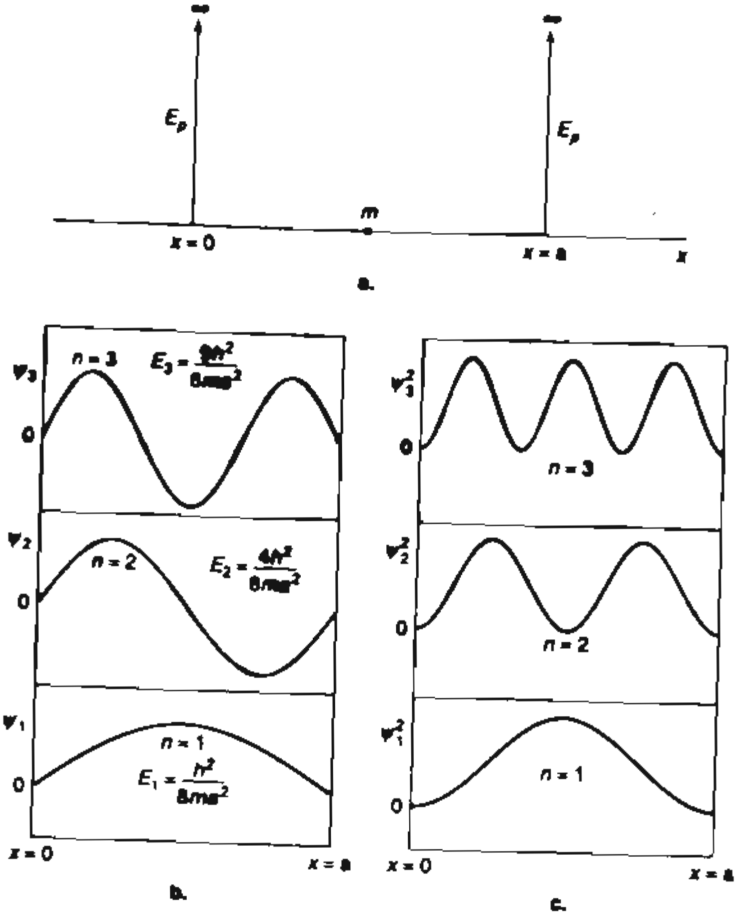


FIGURE 11.11
(a) A particle confined to a one-dimensional box of length a. The potential energy is infinite for $x < 0$ and $x > a$. (b) The form of some of the wave functions for the particle in a one-dimensional box and the corresponding energies. (c) The form of the probability densities ψ^2.

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Note that the ± sign can go outside the sine function since $\sin(-n\pi x/a) = -\sin(n\pi x/a)$.

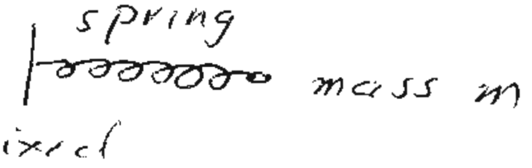
Obj harmonic oscillator
hydrogen like atoms

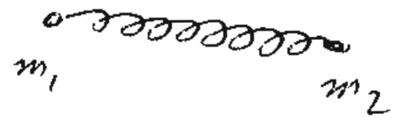
Harmonic oscillator

~~Si~~ simplest model for molecular vibration

diatomic: 2 masses m_1, m_2, connected by a bond

simplest approximation: harmonic motion
bond as a spring

before


here


same equations, only not m, but reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$

$x=0$: equilibrium: spring not extended
not compressed
length x_0

$x>0$: spring extended

$x<0$: spring compressed

bond-length: $x + x_0$

$$E_p = \frac{1}{2}\underset{\substack{\downarrow \\ \text{force constant}}}{k}x^2$$ Hooke's law for springs

$$E_k = \frac{p_x^2}{2\mu} \leftarrow \mu \text{ instead of } m$$

$$H = \frac{p_x^2}{2\mu} + \frac{1}{2}kx^2 = E_{tot}$$ as Hamilton function: only p_x and x as variables

$$\hat{H} = \frac{\hat{p}_x^2}{2\mu} + \frac{1}{2}\hat{x}^2 \qquad \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}, \quad \hat{x} = x$$

only x, no (underlined) y, z

$\hat{H}\psi = E\psi$:

$$\Big[\underset{\substack{\uparrow \\ i^2}}{-}\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\Big]\psi = E\psi$$

solutions Hermite polynomials

solutions exist <u>only</u> for certain (quantized) energies:

$$E_v = \cancel{h\nu}\,\hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right) = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right)$$

$v = 0, 1, 2, \ldots$ vibrational quantum number natural frequency of harmonic oscillator: $\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

Wave no.: cm^{-1}: $\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$ $\quad \lambda = \frac{c}{\nu}$

$E_v = h\nu_0 (v + \frac{1}{2})$ equidistant

lowest possible energy. $E_0 = \frac{1}{2} h\nu_0$

classical: a $\overset{\text{bond}}{\text{spring}}$ can have 0 energy

and does not move at all

<u>QM</u>: <u>no</u> move $\Rightarrow x = 0,\ P_x = 0$

both ~~prec~~ precisely known

<u>not</u> possible because of uncertainty principle

$\rightarrow E_0 = \frac{1}{2} h\nu_0$ zero-point energy

lower not possible!

also at T= 0K movement with E_0

even v: symmetric wave function
odd v: antisymmetric wave function

classically forbidden region:

extension or compression beyond turning point ($E_k = 0$)

there: $E = E_p = \frac{1}{2} k x_t^2$ ($E_k = 0$ at x_t)

→ turning point: classical maximum of x:

$$X_t = \sqrt{\frac{2E}{k}}$$

classically: x_t initial extension we give the spring

classical probability:

$\underline{X = 0}$ ⇒ $E_p(0) = 0$, $E_k = E$

E_k max → fastest passing
→ lowest probability

$\underline{X = X_t}$ $E_p = E$, $E_k(x_t) = 0$, slowest move
highest probability

probability $\sim \psi_0^* \psi_0$ largest at $x = 0$
smallest at $x = x_t$

$\underline{\text{Larger } v}$ ⇒ $\psi_v^* \psi_v^*$ approaches classical form: correspondence

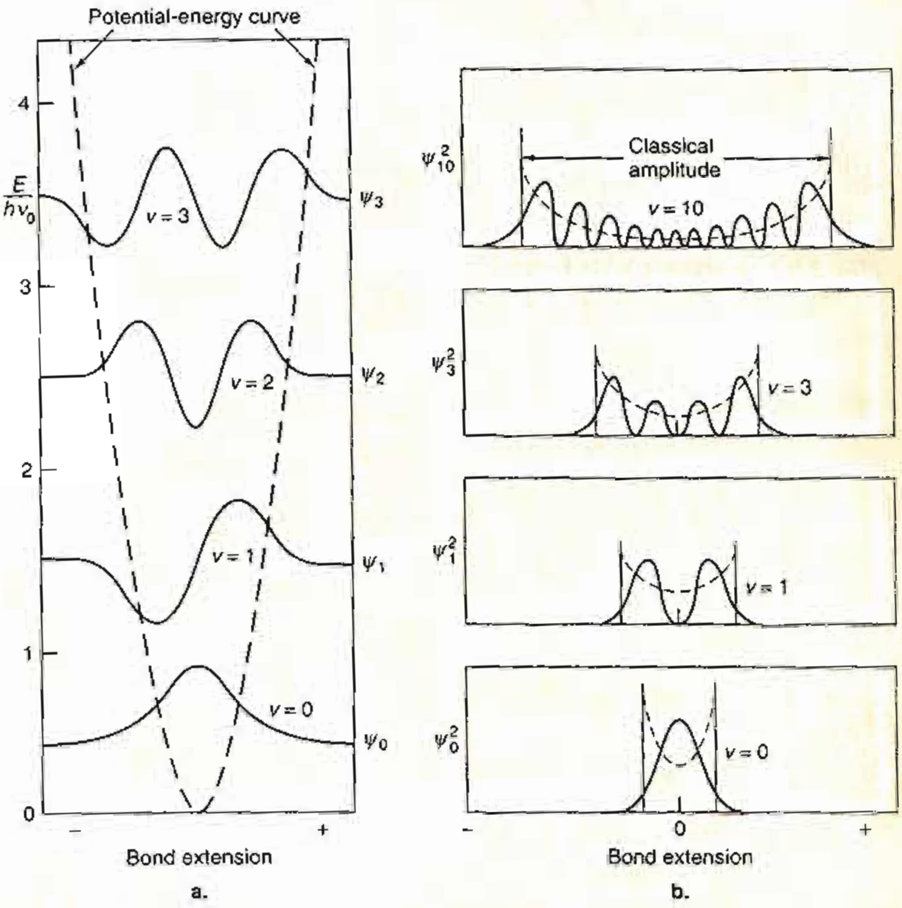


FIGURE 11.12
(a) The form of some wave functions for a harmonic oscillator. (b) Some probability density functions for a harmonic oscillator. The corresponding classical functions are shown as dashed lines.

several values of v are shown in Figure 11.12b. Also shown on this diagram are the corresponding classical probability functions. The differences between the classical and the quantum-mechanical behavior are very striking. For $v = 0$, for example, we see that the highest probability according to the quantum-mechanical treatment is when the system is passing through its equilibrium position ($x = 0$). In classical mechanics, on the other hand, the probability is *lowest* at the equilibrium position, since the system has its highest velocity at this position and therefore passes through it rapidly; the vibrational motion is slowest at the extremities of the vibration, and the probability is therefore the highest at these extremities. As the vibrational quantum number increases, however, the quantum-mechanical probabilities become closer to the classical ones, and the highest probabilities are close to the turning points of the vibrations.

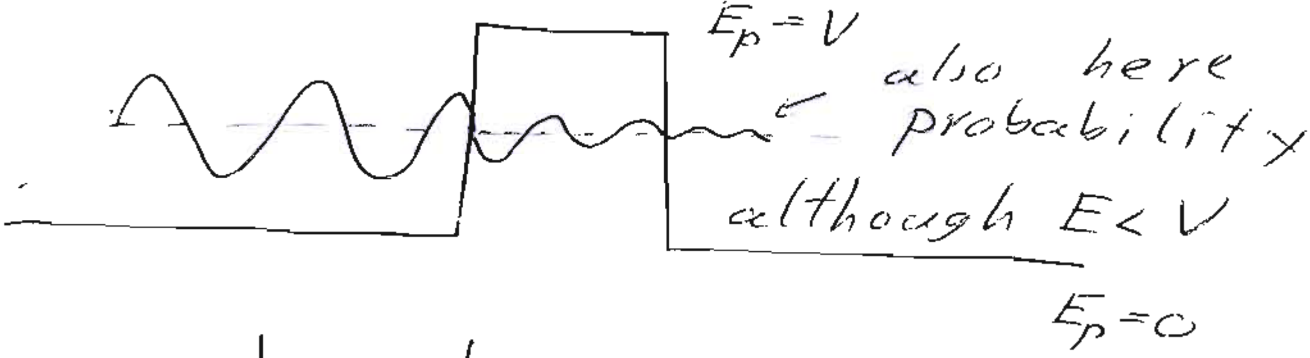
Another important difference between the quantum-mechanical and classical probabilities is that the quantum-mechanical treatment gives a finite probability that the bond is extended to a greater extent than the value permitted by classical theory. In a classical vibration the extension is restricted to a certain fixed value, but the nodes:

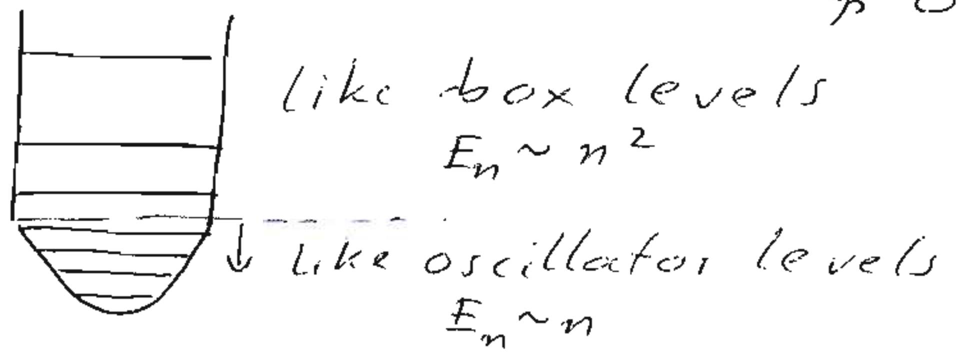
v nodes, $v+1$ antinodes

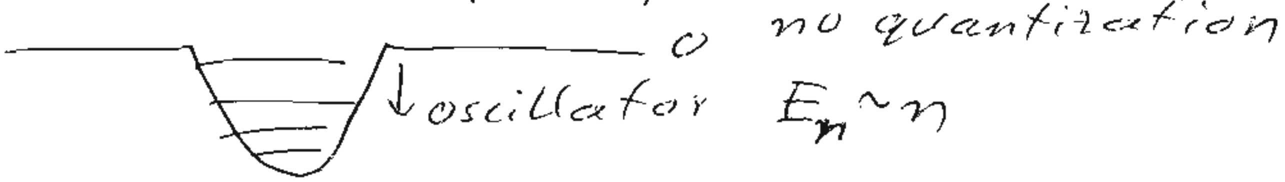
classical: x cannot be larger than x_t (not enough energy)

quantum: probability extends beyond turning point

- tunnel effect







Hydrogen like atoms ($1e^-$)

Bohr: only for $1e^-$ atoms or ions

$H, He^+, Li^{2+}, Be^{3+} \ldots$

reduced mass $\mu = \frac{\overset{e^-}{m} \, M \leftarrow \text{nucleus}}{m + M}$

$$M \gg m \Rightarrow \mu \approx \frac{mM}{M} = m(e)$$

Coulomb potential:

$$E_p = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

r: e-p distance

ε_0: permittivity of the vacuum

spherical symmetry, central field (no depundence on direction, only on distance r)

$$H = \frac{1}{2\mu}\left(p_x^2 + p_y^2 + p_z^2\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{H} = -\frac{h^2}{8\pi^2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

spherical symmetry: polar coordinates r, ϑ, φ instead of x, y, z

quantum-mechanical curves in Figure 11.12b show that there is a certain probability of an even greater extension. There are a number of situations where quantum mechanics permits a system to penetrate into regions that are forbidden in classical mechanics, and the effect is known as the **tunnel effect.** This effect is particularly important in chemical kinetics, and more is said about it in Section 14.9 in connection with transition-state theory (see Figure 14.9).

Tunneling

11.7 QUANTUM MECHANICS OF HYDROGENLIKE ATOMS

Bohr's theory of the hydrogen atom was a great step forward, but it failed to provide a satisfactory basis for the understanding of more complex atoms. Much greater success has been achieved through quantum mechanics. We will consider treatment of a hydrogen-like atom, having a nucleus of charge Ze and a single electron. Since the mass of the electron is very much smaller than that of the nucleus, the reduced mass μ, given by Eq. 11.148, is almost exactly equal to the mass of the electron.

The potential energy of the electron at a distance r from the nucleus arises entirely from the Coulombic attraction and is given by

$$E_p = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{11.158}$$

where ϵ_0 is the permittivity of a vacuum. The energy is independent of the direction, so that we have a *symmetrical field* or a *central field*.

The Hamiltonian for the system involves the components of momentum along the three axes and is

$$H = \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{11.159}$$

The Hamiltonian operator is obtained by making the substitutions of Table 11.1 and is

$$\hat{H} = -\frac{h^2}{8\pi^2\mu}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{11.160}$$

The time-independent Schrödinger equation $\hat{H}\psi = E\psi$ is therefore

$$-\frac{h^2}{8\pi^2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi = E\psi \tag{11.161}$$

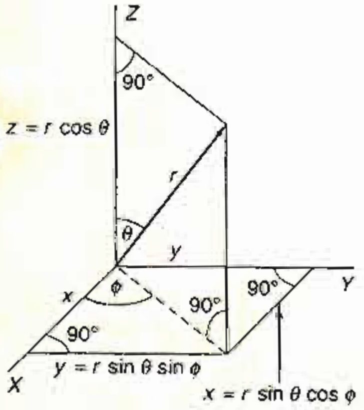


FIGURE 11.13
The relation between Cartesian and spherical polar coordinates.

Since the system is spherically symmetrical, it is most convenient to use spherical polar coordinates, which are related to Cartesian coordinates as shown in Figure 11.13. When the Laplacian operator ∇^2 is converted to polar coordinates, the Schrödinger equation takes the form

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi = 0 \tag{11.162}$$

$$0 \leq r < \infty$$

$$0 \leq \varphi < 2\pi$$

$$0 \leq \vartheta \leq \pi$$

$$z = r \cos\vartheta$$

$$x = r \sin\vartheta \cos\varphi$$

$$y = r \sin\vartheta \sin\varphi$$

$$d\tau = dx\,dy\,dz$$

$$= r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi$$

do not try to learn Schrödinger equation in polar coordinates (look up in book!)

it follows from

$$\nabla^2(x,y,z) \longrightarrow \nabla^2(r,\vartheta,\varphi)$$

in polar coordinates Schrödinger equation can be separated,

$$\psi(r,\vartheta,\varphi) = R(r) \cdot \Theta(\vartheta) \cdot \phi(\varphi)$$

1 equation for each variable!

Separation

if in $\hat{H}(x,y)\psi(x,y) = E\psi(x,y)$

$$\hat{H}(x,y) = \hat{H}_1(x) + \hat{H}_2(y)$$

then equation can be solved:

$$\hat{H}_1(x)\psi(x,y) + \hat{H}_2(y)\psi(x,y) = E\psi(x,y)$$

can be solved with

$$\psi(x,y) = X(x)\cdot Y(y)$$

$$\Rightarrow\ y\,\hat{H}_1(x)X(x) + x\,\hat{H}_2(y)Y(y) = EX(x)Y(y)$$

$$\frac{1}{X(x)}\hat{H}_1(x)X(x) + \frac{1}{Y(y)}\hat{H}_2(y)Y(y) = \overset{E}{\cancel{EX(x)Y(y)}}$$

$$\underbrace{\frac{1}{X(x)}\hat{H}_1(x)X(x) - E}_{\text{only function of } x} = \underbrace{-\frac{1}{Y(y)}\hat{H}_2(y)Y(y)}_{\text{only function of } y}$$

must be true for all x on the left *and* for all y on the right

$\Rightarrow$ both sides must be equal to a constant a

$$\Rightarrow \frac{1}{X(x)} \hat{H}_1(x) X(x) - E = a$$

$$\Rightarrow \hat{H}_1(x) X(x) = (a+E) X(x)$$

$$-\frac{1}{Y(y)} \hat{H}_2(y) Y(y) = a$$

$$\Rightarrow \hat{H}_2(y) Y(y) = -a Y(y)$$

2 equations on 1 variable each

particle in 3-dimensional box:

$$\psi(x,y,z) = X(x) \cdot Y(y) \cdot Z(z)$$

$\rightarrow$ for X, Y, Z 3 linear box equations

Schrödinger equation for H:

$$\psi(r,\vartheta,\varphi) = R(r) \cdot \Theta(\vartheta) \cdot \phi(\varphi)$$

$$\frac{1}{r^2R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\Theta r^2\sin\vartheta}\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right)$$

$$+\underbrace{\frac{1}{r^2\sin^2\vartheta}\cdot\frac{1}{\phi}\frac{d^2\phi}{d\varphi^2}}_{\text{③}}+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)=0$$

term ③ has $\frac{1}{\phi}\frac{d^2\phi}{d\varphi^2}$

only term with φ and ϕ

$\Rightarrow$ term 3 must be constant

free choice of constant:

$$\frac{1}{\phi}\frac{d^2\phi}{d\varphi^2}=-m_\ell^2$$ ϕ equation

magnetic quantum no.

$\Rightarrow$ term ③:

$$\frac{1}{r^2\sin^2\vartheta}\cdot\frac{1}{\phi}\frac{d^2\phi}{d\varphi^2}=-\frac{m_\ell^2}{r^2\sin^2\vartheta}$$

gives after some work:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)r^2$$

$$=\frac{m_e^2}{\sin^2\vartheta}-\frac{1}{\sin\vartheta}\frac{1}{\Theta}\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right)$$

$$\underset{\underline{\text{only } r}}{\overset{}{\text{Left}\downarrow}}=\text{constant}=\underset{\underline{\text{only } \vartheta}}{\text{right}\downarrow}$$

l: angular momentum quantum no.

separation constant $= l(l+1)$

$$\Rightarrow$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu}{h^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)r^2=l(l+1)$$

<u>R - equation</u> n follows from solution

$$\frac{1}{\sin\vartheta}\frac{d}{d\vartheta}\left(\sin\vartheta\frac{d\Theta}{d\vartheta}\right)-\frac{m_e^2\Theta}{\sin^2\vartheta}+l(l+1)\Theta=0$$

<u>Θ equation</u>

don't learn these!

Obj: go on with H-atom

ϕ equation: $\frac{d^2\phi}{d\varphi^2} = -m_\ell^2\phi$

as free particle equation

$\rightarrow$ $\phi = Ae^{im_\ell\varphi}$ A: normalization

$\phi(\varphi=0) = \phi(\varphi=2\pi) = \phi(\varphi=4\pi) \dots$

because full turn (2π) = same position

$\rightarrow$ quantization: $m_\ell = 0, \pm 1, \pm 2, \dots$

$$\int_0^{2\pi} \phi_{m_\ell}\phi^*_{m_\ell}\,d\varphi = A^2\int_0^{2\pi} e^{im_\ell\varphi}e^{-im_\ell\varphi}\,d\varphi$$

$$= A^2\int_0^{2\pi} d\varphi = 2\pi A^2 = 1 \quad \underline{\text{must be}}$$

$$\rightarrow A = \frac{1}{\sqrt{2\pi}}$$

$$\phi_{m_\ell} = \frac{1}{\sqrt{2\pi}}\,e^{im_\ell\varphi}$$

$\phi_0 = \frac{1}{\sqrt{2\pi}}$, ϕ_{m_ℓ} $(m_\ell > 0)$ complex linear combination of functions ⑧-2

to same $-m_\ell^2$ (eigenvalue) also eigenfunction

to the same $-m_\ell^2$

$$\phi_x = \frac{1}{\sqrt{2}}(\phi_1 + \phi_{-1}) = \frac{1}{2\sqrt{\pi}}(e^{i\varphi} + e^{-i\varphi})$$

$$= \frac{1}{\sqrt{\pi}}\cos\varphi$$

$\cos\varphi$ factor at $x = r\sin\vartheta\cos\varphi$

$\rightarrow \phi_x$

$$e^{i\varphi} + e^{-i\varphi} = \cos\varphi + i\sin\varphi + \cos\varphi - i\sin\varphi$$

$$= 2\cos\varphi$$

$$\phi_y = \frac{1}{\sqrt{2}}(\phi_1 - \phi_{-1}) = \frac{1}{2\sqrt{\pi}}(e^{i\varphi} - e^{-i\varphi})$$

$$= \frac{i}{\sqrt{\pi}}\sin\varphi$$

in $\phi_y^*\phi_y$ i cancels out $(i\cdot(-i) = 1)$

$\rightarrow$ drop i

$$\rightarrow \phi_y = \frac{1}{\sqrt{\pi}}\sin\varphi$$

TABLE 11.2 Solution of the Φ Equation

Value of m_l	Solution in Complex Form	Real Form
0	–	$\Phi_0 = \dfrac{1}{\sqrt{2\pi}}$
1	$\Phi_1 = \dfrac{1}{\sqrt{2\pi}}e^{i\phi}$	$\Phi_x = \dfrac{1}{\sqrt{2}}(\Phi_1 + \Phi_{-1}) = \dfrac{\cos\phi}{\sqrt{\pi}}$
−1	$\Phi_{-1} = \dfrac{1}{\sqrt{2\pi}}e^{-i\phi}$	$\Phi_y = \dfrac{1}{\sqrt{2}}(\Phi_1 - \Phi_{-1}) = \dfrac{\sin\phi}{\sqrt{\pi}}$
2	$\Phi_2 = \dfrac{1}{\sqrt{2\pi}}e^{i2\phi}$	$\Phi_{x^2-y^2} = \dfrac{1}{\sqrt{2}}(\Phi_2 + \Phi_{-2}) = \dfrac{\cos 2\phi}{\sqrt{\pi}}$
−2	$\Phi_{-2} = \dfrac{1}{\sqrt{2\pi}}e^{-i2\phi}$	$\Phi_{xy} = \dfrac{1}{\sqrt{2}}(\Phi_2 - \Phi_{-2}) = \dfrac{\sin 2\phi}{\sqrt{\pi}}$

The reasons for the $x^2 - y^2$ and xy subscripts are as follows:

1. $\cos 2\phi = \cos^2\phi - \sin^2\phi$; from Figure 11.13, $\cos^2\phi = x^2/r^2 \sin^2\theta$ and $\sin^2\phi = y^2/r^2 \sin^2\theta$; thus $\cos 2\phi$ has the same dependence on ϕ as $x^2 - y^2$.
2. $\sin 2\phi = 2\sin\phi\cos\phi = xy/r^2 \sin^2\theta$; thus $\sin 2\phi$ has the same dependence on ϕ as xy

(as we see from Figure 11.13) corresponds to the X axis. Similarly we can take the difference $\Phi_1 - \Phi_{-1}$ divided by $\sqrt{2}$:

$$\Phi_y = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_{-1}) = \frac{1}{2\sqrt{\pi}}(e^{i\phi} - e^{-i\phi}) = \frac{i\sin\phi}{\sqrt{\pi}} \tag{11.176}$$

Since we are usually interested in probability densities $\Phi\Phi^*$, is it common to drop the i in this expression, since it disappears when we take the complex conjugate. The function is therefore written as

$$\Phi_y = \frac{\sin\phi}{\sqrt{\pi}} \tag{11.177}$$

The value of this function is a maximum when $\phi = \pi/2$, which is along the Y axis.

Table 11.2 lists Φ functions for the first three values of $\pm m_l$.

Solution of the Θ Equation

The solution of the Θ equation (Eq. 11.168) is mathematically more difficult, and we will present only a very brief outline, with emphasis on the main results. For details the reader is referred to textbooks of quantum mechanics.[6]

We may introduce a transformation into Eq. 11.168 by putting

$$\xi = \cos\theta \quad \text{and} \quad P_l(\xi) = \Theta \tag{11.178}$$

and obtain

$$(1-\xi)^2\frac{d^2P_l(\xi)}{d\xi^2} - 2\xi\frac{dP_l(\xi)}{d\xi} + \left[l(l+1) - \frac{m_l^2}{(1-\xi^2)}\right]p_l(\xi) = 0 \tag{11.179}$$

---

[6] A particularly clear treatment is given by L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*, New York: McGraw-Hill, 1935 (Dover reprint, 1985).

TABLE 11.3 Solution of the Θ Equation

l	m_l	Function
0	0	$\Theta_{00} = \frac{\sqrt{2}}{2}$
1	0	$\Theta_{10} = \frac{\sqrt{6}}{2}\cos\theta$
1	+1, −1	$\Theta_{1\pm1} = \frac{\sqrt{3}}{2}\sin\theta$
2	0	$\Theta_{20} = \frac{\sqrt{10}}{4}(3\cos^2\theta - 1)$
2	+1, −1	$\Theta_{2\pm1} = \frac{\sqrt{15}}{2}\sin\theta\cos\theta$
2	+2, −2	$\Theta_{2\pm2} = \frac{\sqrt{15}}{4}\sin^2\theta$

Insertion of a value into a recursion formula gives a new value back until the series of new values is naturally limited by mathematical constraints of the formula.

When m_l is zero, this equation is the *Legendre equation*, named after the French mathematician Adrien Marie Legendre (1752–1833). Solutions for the Legendre equation are possible only *when l is zero or has positive integral values*. These solutions are known as the *Legendre polynomials of degree l*. When m_l is not zero, a solution can only be obtained if m_l has one of the integral values $-l, -l+1, \ldots, 0, \ldots, l-1, l$. The solutions are then the *associated Legendre functions* and are usually expressed by means of a *recursion formula*.

The conclusion is therefore that l can only be zero or have a positive integral value and that the m_l values are determined by the value of l:

$$l = 0, 1, 2, 3, \ldots \tag{11.180}$$

$$m_l = -l, -l+1, \ldots, -1, 0, 1, \ldots, l-1, l \tag{11.181}$$

We shall see that the solution of the R equation imposes an upper limit on the value of l.

Table 11.3 gives solutions of the Θ equation for l values of 0, 1, and 2 and the corresponding permitted m_l values. Because the sine and cosine functions can have positive and negative values, there are positive and negative regions of the wave functions. The functions in Table 11.3 are orthogonal to one another (as required for eigenfunctions of a Hermitian operator) and have been normalized.

Solution of the *R* Equation

The R equation, Eq. 11.167, may be cast into the form of a type of equation studied in the nineteenth century by the French mathematician Edmond Laguerre (1834–1886). Its solution leads to the conclusion that there is a quantum number n that can have positive integral values starting with unity:

$$n = 1, 2, 3, \ldots \tag{11.182}$$

The relationship between n and l is that the maximum value that l can have is one less than the value of n:

$$l = 0, 1, \ldots, n-1 \tag{11.183}$$

TABLE 11.4 Solutions of the *R* Equation

Quantum Numbers		
n	*l*	Function
1	0	$R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	$R_{20} = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	$R_{21} = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}$
3	0	$R_{30} = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{4Zr}{a_0} + \frac{4Z^2r^2}{9a_0^2}\right)e^{-Zr/3a_0}$
3	1	$R_{31} = \frac{1}{9\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(4 - \frac{2Zr}{3a_0}\right)\frac{2Zr}{3a_0}e^{(-Zr/3a_0)}$
3	2	$R_{32} = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{2Zr}{3a_0}\right)^2 e^{-Zr/3a_0}$

The quantity a_0 is the same as the first Bohr radius, defined by Eq. 11.45.

The solutions of the *R* equation, under these restrictions, are the *Laguerre polynomials*. The wave functions for the first three values of n and the possible values of l are given in Table 11.4.

Complete Wave Functions

Orbitals

The complete wave functions, known also as **orbitals,** are obtained by multiplying together the appropriate functions that are given in Tables 11.2, 11.3, and 11.4. Some examples are given in Table 11.5. The way they are constructed is shown by the following example.

EXAMPLE 11.7 Obtain a complete wave function for an electron having $n = 3, l = 1, m_l = 0$ (a 3p orbital).

Solution In order to determine an expression for Ψ_{nlm}, we can multiply the radial wave function for an $n = 3$, $l = 1$ orbital from Table 11.4 (R_{31}) by the Θ function for $l = 1$, $m_l = 0$ from Table 11.3 (Θ_{10}) and then by the Φ function for $m_l = 0$ from Table 11.2 (Φ_0). The final expression is

$$\psi_{310} = \frac{1}{27\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\left(\frac{Zr}{a_0}\right)e^{-Zr/3a_0}\cos\theta$$

Note that two other equally acceptable solutions for the 3p orbitals could have been obtained by taking the products $R_{31}\Theta_{11}\Phi_x$ or $R_{31}\Theta_{1-1}\Phi_y$. These give identical orbitals to the one described except for orientation.

TABLE 11.5 Selected Complete Hydrogen Atom Wave Functions ψ_n, l, m, for the Hydrogen Atom ($Z = 1$)

Quantum Numbers n	l	m_l	Function
1	0	0	$\psi_{1s} = \psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$
2	0	0	$\psi_{2s} = \psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\psi_{2p_z} = \psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	+1	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\cos\phi$
2	1	−1	$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\sin\phi$
3	0	0	$\psi_{3s} = \psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[6 - 6\left(\frac{2r}{3a_0}\right) + \left(\frac{2r}{3a_0}\right)^2\right] e^{-r/3a_0}$

The significance of the notation 1s, 2s, $2p_z$, etc., is considered later.

11.8 PHYSICAL SIGNIFICANCE OF THE ORBITAL QUANTUM NUMBERS

The mathematical solution of the Schrödinger equation for hydrogenlike atoms has thus revealed that there are three orbital quantum numbers n, l, and m_l; their magnitudes are related to one another by Eqs. 11.180, 11.183, and 11.181, respectively. A special notation has been introduced to designate the quantum numbers n and l and the orbitals to which they correspond. The principal quantum number n is given first, followed by a letter that indicates the quantum number l, as follows:

$l = 0$	s
$l = 1$	p
$l = 2$	d
$l = 3$	f

From then on we follow the letters in alphabetical order (g, h, etc.). The letters s, p, d, and f relate to the descriptions "sharp," "principal," "diffuse," and "fundamental" that the early spectroscopists had given to series of lines in atomic spectra. As an example of the use of this notation, a 3p orbital is one for which $n = 3$ and $l = 1$. We will see later that m_l values can be indicated by the addition of subscripts to the letters, but this is frequently unnecessary.

The Principal Quantum Number n

Inspection of Eqs. 11.165, 11.167, and 11.168 shows that the only one that contains the energy E is Eq. 11.167, the R equation. It therefore allows that the energies for a hydrogenlike atom depend only on the solutions of the R equation and not at all on

The orbital quantum numbers ⑧-3

3 of them:

principal quantum no. $n = 1, 2, 3, \dots$

angular momentum quantum no.:

$$l = 0, 1, 2, 3, \dots, (n-1)$$

s p d f

3p means: $n = 3, l = 1$

magnetic quantum no.:

$$-l \leq m_l \leq +l \qquad -l, \dots, -1, 0, 1, \dots, l$$

n is the only no. in energy equation:

equation for $R(r)$ contains E

→ in H or ions with 1 electron

E depends only on n

equation for $R_{n,l}(r)$ with different $n \rightarrow$

$$E_n = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0}\,\frac{1}{n^2}$$

Same as in Bohr's theory

lowest energy → groundstate

$n = 1$: E_1 most negative

exponential factors

→ wavefunctions approach 0 for $r \to \infty$

no. of radial nodes ($R_{n\ell} = 0$): $n - \ell - 1$

→ 0 radial nodes for 1s

1 for 2s

2 for 3s

probability for e⁻ to be in $d\tau = dx\,dy\,dz$:

$$\psi\psi^* d\tau = |\psi|^2 d\tau$$

divide by $d\tau$: probability density ρ

$$\rho = \frac{\text{probability}}{\text{unit volume}} = |\psi|^2$$

real function: $\rho = \psi^2$

$$\rho_{1s} = \psi_{1s}^2 = \frac{1}{\pi a_0^3} \cdot e^{-\frac{2r}{a_0}}$$

more of interest:

in volume between 2 spheres:

$$dV = \frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3$$

$$= 4\pi r^2 dr \quad \text{neglect } (dr)^2, (dr)^3$$

probab. to find e^- between the 2 spheres at r:

$$4\pi r^2 \psi_{1s}^2 \, dr$$

probability density per unit of radial distance: $4\pi r^2 \psi_{1s}^2$ radial distribution function

maximum for 1s at $r = a_0 = 52.92$ pm

most probable ~~position~~ distance of e^- from the nucleus

<u>Bohr</u> e^- moves on a precise circle with radius a_0 around nucleus

<u>QM</u> e^- most probable at $r = a_0$

ψ_{2s}^2, $\psi_{2s}^2 4\pi r^2$ 2 maxima

ψ_{ns}^2 n maxima, n-1 nodes (0)
(besides $r=0$)

$4\pi r^2 R_{2p}^2$ $(l \neq 0)$: no simple significance because of direction asymmetry of the orbitals

<u>1s</u> e^- <u>most likely</u> at distance a_0 from nucleus

<u>but</u>: the expectation value of r in ψ_{1s} is differnt from that because 1s not symmetric in $r < a_0$ to $r > a_0$

distance to by expected (average of ∞ measurements):

$$\langle r_{1s} \rangle = \int \psi_{1s}^{*} r \, \psi_{1s} = \int_0^\infty \psi_{1s} r \, \psi_{1s} \, r^2 dr \underbrace{\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\vartheta \, d\vartheta}_{4\pi}$$

$$dx\,dy\,dz = r^2 \sin\vartheta \, dr \, d\vartheta \, d\varphi$$

$$\langle r_{1s} \rangle = \frac{1}{\pi a_0^3} \int_0^\infty r e^{-\frac{2r}{a_0}} dr = \frac{3}{2} a_0$$

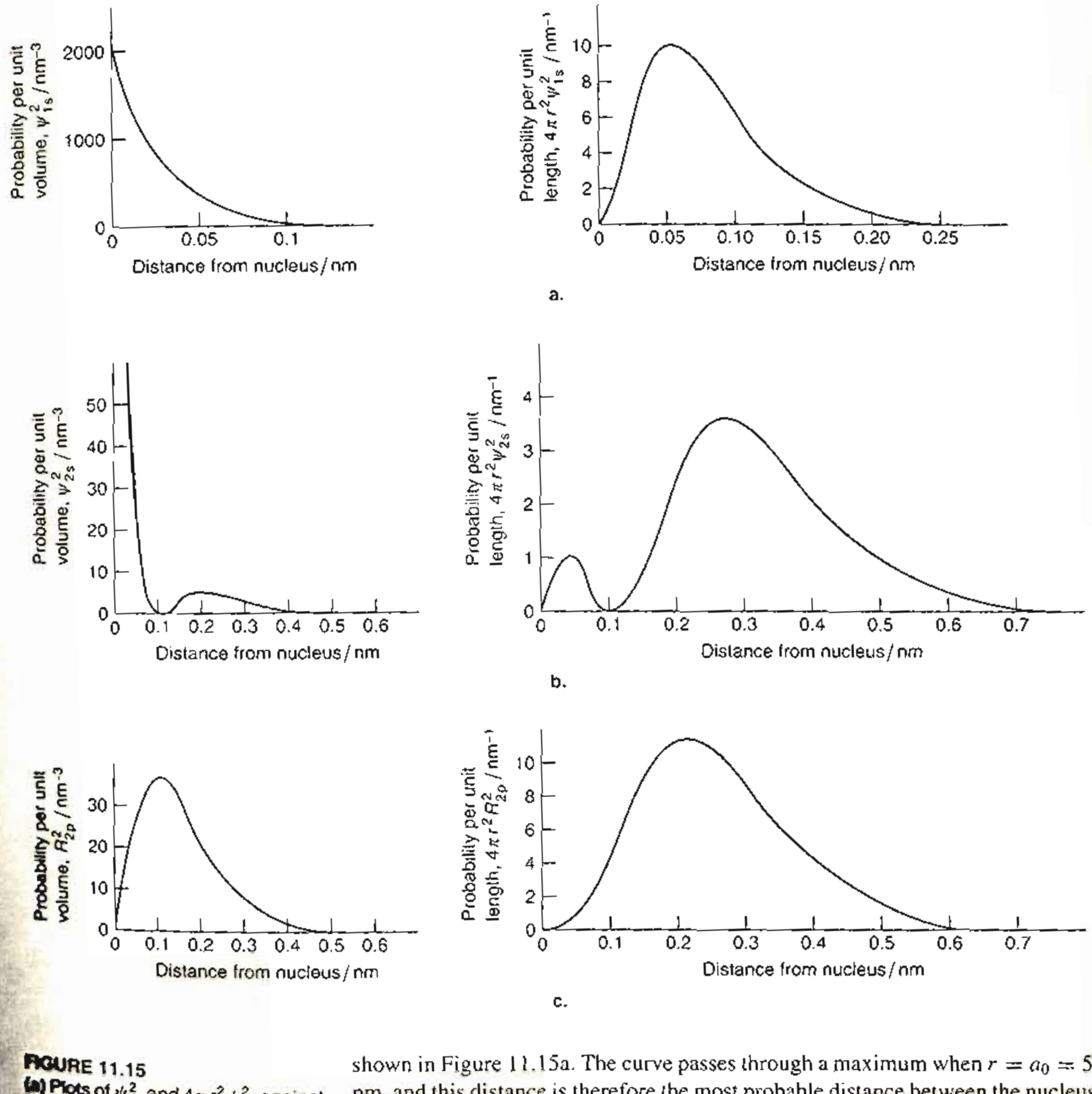


FIGURE 11.15
(a) Plots of ψ_{1s}^2 and $4\pi r^2\psi_{1s}^2$ against the distance r from the nucleus, for a 1s electron in the hydrogen atom. (b) Plots of ψ_{2s}^2 and $4\pi r^2\psi_{2s}^2$ against r, for a 2s electron. (c) Plots of R_{2p}^2 and $4\pi r^2 R_{2p}^2$, for a 2p electron.

shown in Figure 11.15a. The curve passes through a maximum when $r = a_0 = 52.92$ pm, and this distance is therefore the most probable distance between the nucleus and the electron. This emphasizes a very important similarity, and also a very important difference, between the Bohr theory and the wave-mechanical theory. In the Bohr theory the electron in the ground (1s) state of the hydrogen atom moves in a *precise orbit* of radius a_0, while in quantum mechanics this distance is only the *most probable distance;* the electron can be at other distances from the nucleus.

Figure 11.15b shows plots of ψ_{2s}^2 and of $4\pi r^2\psi_{2s}^2$ for an electron in the 2s state. The latter shows two maxima. Similar plots can be given for 3s, 4s, etc., states, and

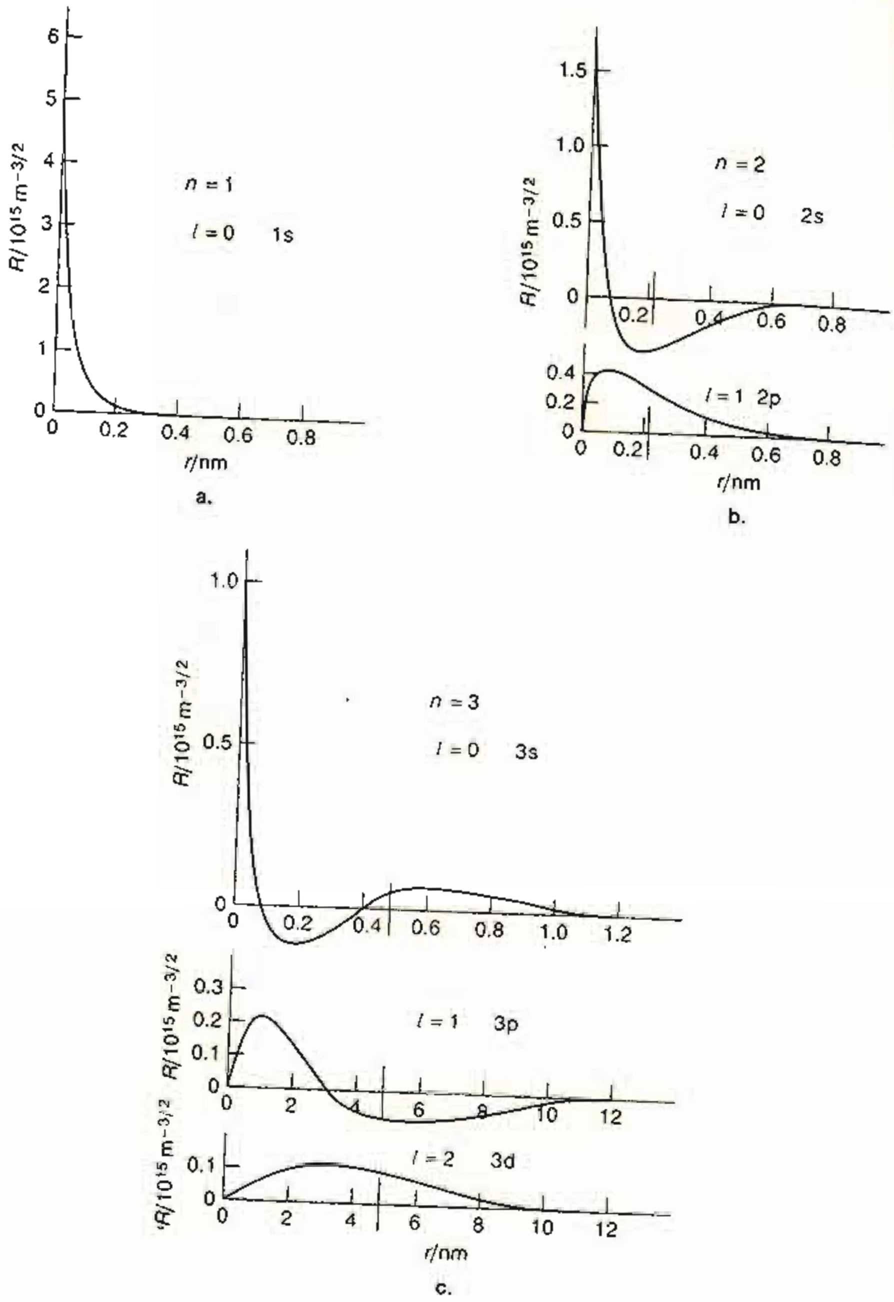


FIGURE 11.14
Radial wave functions $R(r)$ for the hydrogen atom, plotted against distance r from the nucleus. (a) The curve for $n = 1$; ℓ must be 0. (b) The curves for $n = 2$; ℓ can be 0 or 1. (c) The curves for $n = 3$; ℓ can be 0, 1, or 2.

$\langle r_{1s} \rangle = \frac{3}{2} a_0$

because of asymmetry around a_0, more measurements will give $r > a_0$ values than $r < a_0$ values

→ average, expected distance

> most probable distance

general: $\langle r_{ns} \rangle = \frac{3}{2} n^2 a_0$

l, m_l : $\Theta(\vartheta), \phi(\varphi)$

plots of the usual balloons:

$$[\Theta(\vartheta) \cdot \phi(\varphi)]^2$$

length of the line from origin to the plotted ~~see~~ figure surface is the relative probability to find e^- in this direction from nucleus!

no connection with distance from nucleus!

Angular Dependence of the Wave Function: The Quantum Numbers ℓ and m_ℓ

The Θ and Φ wave functions are best considered together, since both are concerned with the angular dependence of the orbitals. Plots of $[\Theta(\theta)\Phi(\phi)]^2$ for various l and m_l values are shown in Figure 11.16. It is to be emphasized that these plots are in no way related to distance from the nucleus but only to the variation of the wave function with the angles θ and ϕ. This is illustrated explicitly for the p_z orbital, for which the angles θ and ϕ are shown and in which the plot is shown in its three-dimensional form. For given values of θ and ϕ, the length of the line joining the origin to the surface of the solid figure is the relative probability that the electron is to be found in that direction. For this p_z orbital the *maximum* probability is along the Z axis. The other diagrams are given in a simpler form, but they are to be interpreted in the same way.

All s orbitals ($l = 0$) have spherical symmetry, as shown in Figure 11.16a. When $l = 1$ (a p orbital), the quantum number m_l can have the value $-1, 0$, or

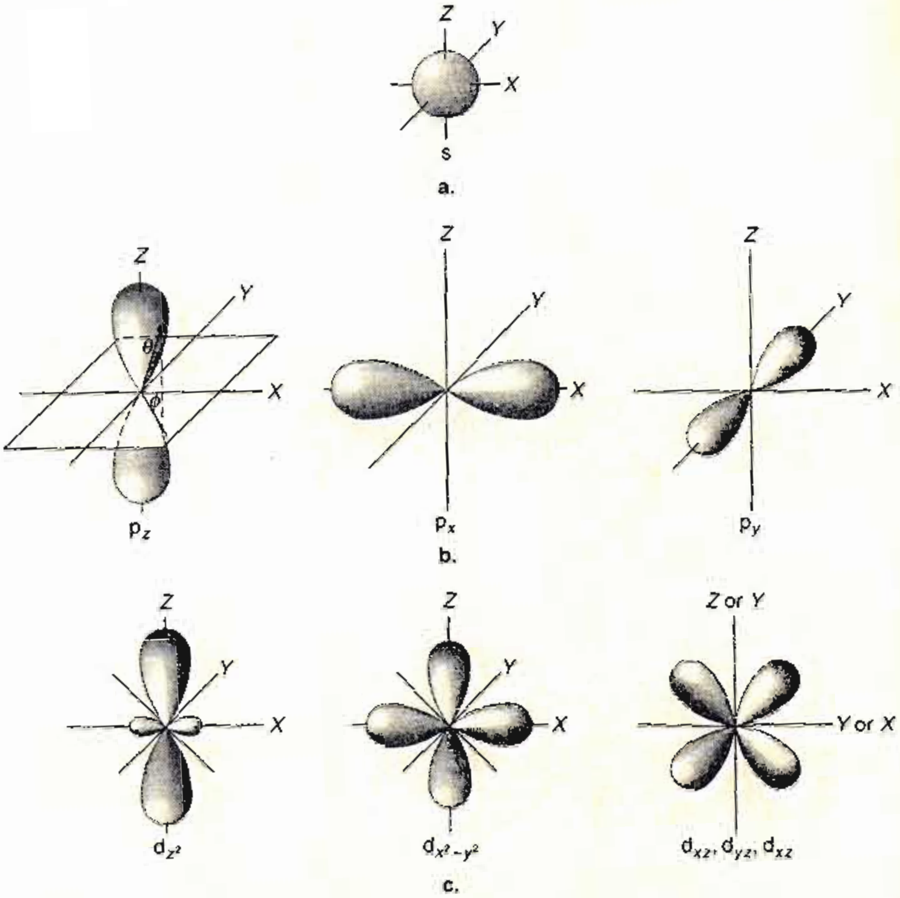


FIGURE 11.16
Plots of $[\Theta(\theta)\Phi(\phi)]^2$. (a) An s orbital ($\ell = 0$). (b) Three p orbitals; the p_z plot is shown enlarged for clarity in three-dimensional form. (c) The d_{z^2}, $d_{z^2-y^2}$, d_{xz}, d_{yz}, and d_{xy} orbitals.

p_z: maximum probability in z-direction

$s\ (l=0, m_l=0)$: spherical symmetry
same probability in all directions

p: $(l=1, m_l=-1,0,1)$
directed along x, y, z

d: $(l=2, m_l=-2,-1,0,1,2)$
5 different d-orbitals in a d set

example: ϕ_{y} $\Theta_{l=2, m_l=\pm 1}$

$$\Theta_{2,\pm 1}$$

$$= \frac{1}{2}\sqrt{\frac{15}{\pi}}\ \underbrace{\sin\vartheta}\ \underbrace{\cos\vartheta}_{z}\ \underbrace{\sin\varphi}$$

$$z = r\cos\vartheta$$

$$y = r\sin\vartheta\sin\varphi$$

$$\rightarrow d_{yz}$$

<u>$l=3$</u> f orbitals
not easy to draw

Unsöld theorem

it for a given value of ℓ and over all m_ℓ is ~~ter~~ summed:

$$\sum_{m_\ell=-\ell}^{\ell}\left[\Theta_{\ell,m_\ell}(\vartheta)\,\phi_{m_\ell}(\varphi)\right]^2 = \text{const.}\quad \forall\ \vartheta,\varphi$$

$\Rightarrow$ noble gas atoms,

where all orbitals to a given ℓ are occupied with e^-

are ~~sh~~ ~~+~~ spherically symmetric

Obj rigid rotor and

Angular and Magnetic Momentum

Angular momentum L

magnetic moment M

l determines magnitude of L and shape of orbital

m_l determines direction of L and direction of the orbital

right hand rule of L:

fingers in direction of the move

→ thumb in direction of L

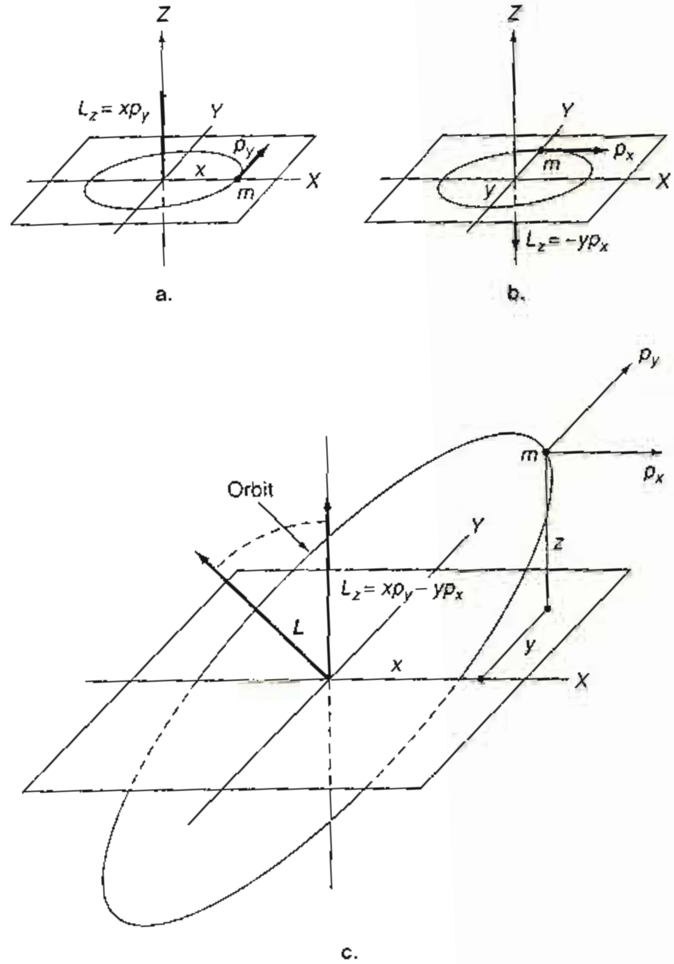


FIGURE 11.17
(a) A particle of mass m undergoing circular motion in the XY plane in an anticlockwise direction. (b) Clockwise motion in the XY plane. (c) The general case, showing the components of velocity and of linear momentum, and the component of angular momentum along the Z axis. In vector notation, $\mathbf{L} = \mathbf{T} \times \mathbf{p}$.

then, by definition, positive along the Z axis and is given by

$$L_z = p_y x = mu_y x \tag{11.191}$$

The sign of the angular momentum is determined by the *right-hand rule;* the curved fingers of the right hand are caused to point in the direction of the linear momentum vector, and the thumb then points in the direction of the angular momentum vector. Figure 11.17b shows the situation when the particle is on the Y axis; a positive momentum p_x then means that it is moving in the clockwise direction, so that the angular momentum L_z is now $-yp_x$. We can generalize these results for a particle moving in any direction (Figure 11.17c). If its momentum components are p_x and p_y and its position coordinates are x and y, the resultant component of angular momentum along the Z axis is given by

$$L_z = xp_y - yp_x \tag{11.192}$$

$L_z = P_y\, x = m u_y x$

if motion ⊥ z

and particle on x-axis

→ anti-clockwise

~~L_z~~ $L_z = P_y\, x$ upward

clock wise $L_z = -y P_x$

~~onx~~ on y-axis downward

any move directions: ~~[illegible]~~

$$L_z = x P_y - y P_x$$

$$\rightarrow \hat{L}_z = \frac{\hbar}{i}\left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}\right)$$

$$= \frac{\hbar}{i} \frac{\partial}{\partial \varphi} = \frac{h}{2\pi i} \frac{\partial}{\partial \varphi}$$

similar $\hat{L}_x$, $\hat{L}_y$

<u>vector</u>: $\vec{\hat{L}} = \vec{r} \times \vec{\hat{p}}$

$\underline{\hat{L}} = \underline{r} \times \underline{\hat{p}}$ also vector total angular momentum:

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

$$= -\hbar^2 \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial}{\partial\vartheta} \right) + \right.$$

$$\left. + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial\varphi^2} \right]$$

same as φ, ϑ part of $\hat{H}$

for H-atom

$\hat{L}_z$ same as φ part alone

→ $\hat{H}$ commutes with $\hat{L}_z$ and $\hat{L}^2$

→ they have same eigenfunctions

$$\hat{L}^2 \Theta\phi = \ell(\ell+1)\Theta\phi\hbar^2 = \hbar^2 \ell(\ell+1)\Theta\phi$$

L^2 can be measured precisely

together with energy E:

$$L^2 = \ell(\ell+1)\hbar^2$$

$$\hat{L}_z \phi = m_\ell \hbar \phi$$

$$L_z = m_\ell \hbar = m_\ell \frac{h}{2\pi}$$

also L_z has precise values, its eigenvalues

$\hat{H}, \hat{L}^2, \hat{L}_z$ have same eigenfunctions

for $\hat{L}^2$ only ϑ, φ important, $R_{nl}(r) = \text{const.}$

for $\hat{L}_z$ only φ is important, $R_{nl}(r), \Theta_{lm_l}(\vartheta) = \text{const.}$

the operators commute:

$$\hat{H}\hat{L}^2 = \hat{L}^2\hat{H}, \quad \hat{H}\hat{L}_z = \hat{L}_z\hat{H}, \quad \hat{L}_z\hat{L}^2 = \hat{L}^2\hat{L}_z$$

and measurements give the eigenvalues

As z we can choose any direction (if $\vec{E}$ or $\vec{B}$ field, then z-direction in field direction)

but: after z is fixed and L_z measured, then L_x, L_y cannot be measured exactly, because $\hat{L}_x, \hat{L}_y, \hat{L}_z$ do not commute

exact measurement:

E, L^2, L_z, or E, L^2, L_x, or E, L^2, L_y

magnetic moment

moving charge (e^-) → magnetic field

~~magen~~ magnetic field directed opposite to $\hat{L}$ because of − charge → left hand rule for magn. moment

magnetic moment operators $\hat{M}^2, \hat{M}_z$ are equal $\hat{L}^2, \hat{L}_z$ times a factor

→ same eigenfunction

→ l, m_l determine magnetic moment

$l=1 \quad L = \sqrt{l(l+1)}\,\hbar = \sqrt{2}\,\hbar$

on z-axis H-field interacting with magnetic moment

$$m_l = 0, \pm 1 \Rightarrow L_z = 0, \pm\hbar \ (m_l \hbar)$$

in H-field: M, L precess around field axis (cones)

such that L^2, L_z^2 = const. according to the quantum number

$\underline{l=2}$: ~~$L = \sqrt{2}\,\hbar$~~

$$L = \sqrt{l(l+1)}\,\hbar = \sqrt{6}\,\hbar$$

$L_z = 0, \pm\hbar, \pm 2\hbar$ 5 directions of cones for precession

$\ell = 1$

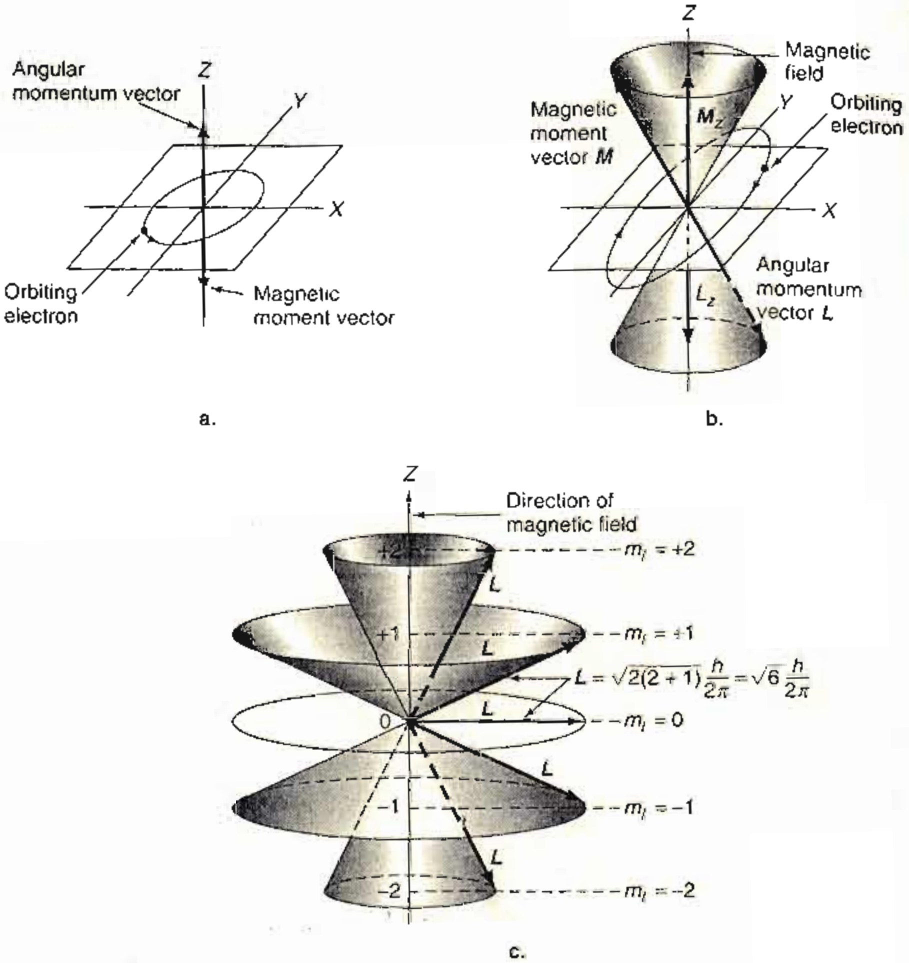


FIGURE 11.18
(a) An electron moving in an orbit in the XY plane, showing the angular momentum and magnetic moment vectors along the Z axis. (b) An orbiting electron in a magnetic field that lies along the Z axis, for $l = 1$. The Z component of the magnetic moment is shown aligned with the field and the angular momentum against it. The cones represent precession about the Z axis. (c) The five possible orientations of the orbital angular momentum vector, for $l = 2$, in a magnetic field. The magnetic moment lies in the opposite direction.

commute with $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$ and, therefore, have the same set of eigenfunctions. The same quantum numbers l and m_l therefore relate to the magnetic moment.

Gyromagnetic Ratio

Bohr Magneton

The magnetic moment differs in the *units* used for its measurement. We will discuss this further in Section 14.2 in connection with the Zeeman effect. Here we will simply state that the ratio of the magnetic moment to the angular momentum is known as the **gyromagnetic ratio,** or the **magnetogyric ratio.** For an electron of charge e and mass m_e this ratio is $-e/m_e$. The SI unit of magnetic moment is ampere metre^2 (A m^2), but it is usual to employ the **Bohr magneton,** which is equal to 9.2734×10^{-24} A m^2.

The importance of the magnetic moment is that it dictates the orientation of the orbital in a magnetic field, which may be that due to neighboring atoms. Figure 11.18b shows one arrangement that can arise when a p orbital ($l = 1$) is in a magnetic field along the Z axis. The Z components of the angular momentum and of the magnetic moment, opposite to one another, must have quantized values, corresponding to the

$\underline{l=1}$ $m_l=-1$: field and M_z aligned

→ lowest energy

field and L_z antiparallel

$m_l=+1$: field and M_z antiparallel

→ highest energy

field and L_z parallel

$m_l=0$: no interaction

field $\underline{H} \perp M_z$

gyromagnetic ratio or
magnetogyric ratio:

$$\frac{M}{L} = -\frac{e}{m_e} \qquad [M] = Am^2$$

Bohr's magneton as unit:

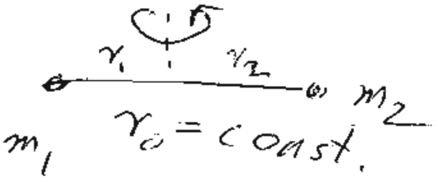
$9{,}2734 \cdot 10^{-24}\ Am^2$

$$M = -\frac{e}{m_e} L \qquad [L] = Js$$

$$[M] = \frac{As}{kg}\,\frac{kg\,m^2}{s^2}\,s = Am^2$$

Rigid linear rotor

Diatomic molecule:



r_0 = const.
= rigid

~~so~~ moment of inertia: $I = m_1 r_1^2 + m_2 r_2^2$
$= \mu r_0^2$

same equation is in orbitals
for $\theta\phi$

angular momentum: $L = I\vec{\omega}$ angular velocity

kinetic energy: $E_k = \frac{1}{2} I\omega^2$

$\omega = 2\pi\nu$, $\nu = \frac{1}{T}$ unit $\frac{rad}{s}$

$E_t = E_k = \frac{L^2}{2I}$ $\quad L^2 = I^2\omega^2$

$E_k = \frac{I\omega^2}{2} = \frac{L^2}{2I}$

$\hat{H} = \hat{L}^2$ already known

$\hat{H}\psi = E\psi \longrightarrow \psi = \theta\phi$

$L^2 = J(J+1)\frac{\hbar^2}{2}$ $\quad J = 0, 1, 2, ..$

J other symbol than l, used in rotors

$$E = \frac{L^2}{2I} = J(J+1)\frac{\hbar^2}{2I}$$

quantization ⇒ rotational spectra of molecules

no zero-point motion as in oscillator

<u>linear</u> no L_x, L_y because x, y axis can be chosen arbitrary

<u>but</u> $L_z = 0$, when z is the axis of the molecule

Obj
- Spin quantum numbers
- Many e^- atoms
- Pauli exclusion principle
- Hund's rule
- Aufbau principle
- Approximations

Spin quantum numbers

Stern-Gerlach experiment: Ag atoms in a magnetic field

Ag: all shells filled: $M_L = 0$

half filled one is an s^1 electron $M_L = 0$
unpaired

however: the atoms are deflected in field

→ e^- are rotating (spinning)

rotating e^- = moving, ~~accelerated~~ charge

= current = magnetic moment

relativistic effect (Dirac not Schrödinger theory): Dirac: spin comes out

Schrödinger: spin must be introduced

Spin angular momentum S,

analogous to orbital angular mom. L

Quantization: $S = \sqrt{s(s+1)}\,\hbar \overset{s=\frac{1}{2}}{=} \sqrt{\frac{3}{4}}\,\hbar$

as $\sqrt{l(l+1)}\,\hbar$ for L

however: $l = 0, 1, 2, \ldots, n-1$

but here $s = \frac{1}{2}$ only

S_z along z-axis (arbitrary), just as L_z: $S_z = m_s\hbar = \pm\frac{1}{2}\hbar$, $m_s = \pm\frac{1}{2}$

spin quantum no.

orbiting electron: $\underline{L} \to \sqrt{l(l+1)}\,\hbar$

L_z

$\underline{M}_L \to -\sqrt{l(l+1)}\,\hbar\,\frac{e}{m_e}$

M_z

e^- alone creates $\underline{S}$, S_z, $\cancel{M}_s$, $\cancel{M}_z$

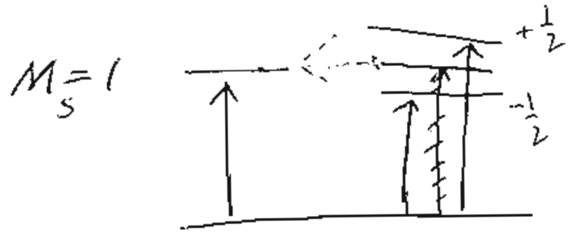
$\cancel{M}$, $\underline{M}$: same direction or opposite ~~a~~ as $\underline{H}$

~~higher~~ ~~lower~~

~~higher~~ energy ~~lower~~ energy

~~lower~~ ~~higher~~

lower higher



line doubling because of s

closely spaced

must be artificially introduced into nonrelativistic QM

comes out of relativistic QM

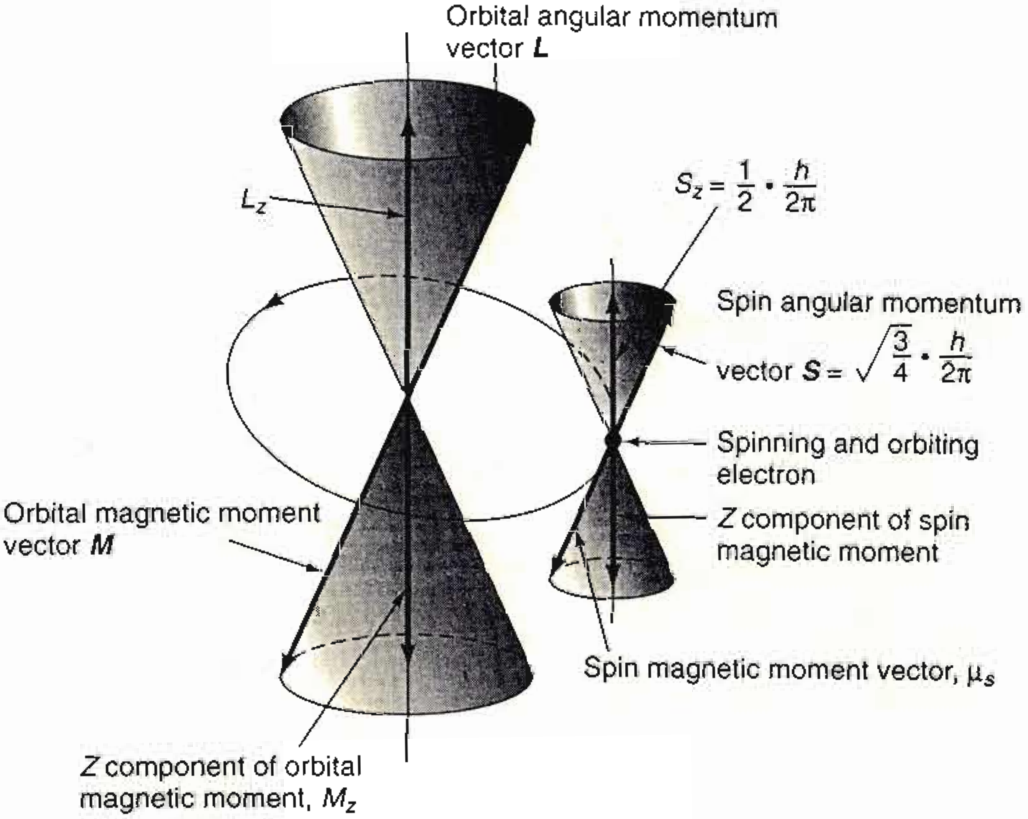
also experimentally found

EPR electron paramagnetic resonance

splitting ~ B

magnetic flux

~~$\nu = cc$~~ $\nu = c\bar{\nu}$, $\bar{\nu} = \frac{1}{\lambda}$



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angular momentum along the Z axis is quantized in a similar way to L_z,

$$S_z = m_s \frac{h}{2\pi} \tag{11.210b}$$

but the **spin quantum number** m_s can have only the values $+\frac{1}{2}$ and $-\frac{1}{2}$.

The orbital angular momentum of an orbital electron and also the spin angular momentum are shown in Figure 11.19. The orbiting electron produces a magnetic moment vector in the direction indicated, and the electron may be considered to spin on its own axis in the magnetic field produced by the orbital motion. The magnetic moment due to the spin may be oriented in the same direction as the magnetic field produced by the orbiting electron (as shown in the figure) or in the opposite direction. The former gives a somewhat higher energy than the latter. We shall see in Section 13.2 that the resulting splitting of energy levels gives closely spaced lines in atomic spectra.

We are now in a position to add two additional postulates to the six that we introduced in Section 11.5:

Postulate VII states that

$\Rightarrow$ 2 more postulates:

VII existence of spin angular momentum operator $\underline{\hat{S}}$ and its z-component $\hat{S}_z$ just as $\underline{\hat{L}}$ and $\hat{L}_z$

VIII $\hat{\underline{S}}^2$ and $\hat{S}_z$ have only 2 eigenfunctions α, β ; $s = \frac{1}{2}$, $m_s = \pm\frac{1}{2}$

s: spin quantum no.

m_s: magnetic spin quantum no.

$\hat{S}_z \alpha = \frac{1}{2}\hbar\alpha \qquad \hat{S}_z \beta = -\frac{1}{2}\hbar\beta$

$\hat{S}^2 \alpha = \frac{1}{2}(\frac{1}{2}+1)\hbar^2\alpha = \frac{3}{4}\hbar^2\alpha$

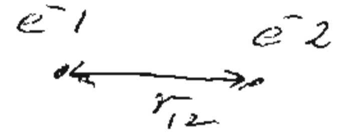
$\hat{S}^2 \beta = \frac{3}{4}\hbar^2\beta$

z axis arbitrary <u>when</u> there is no magnetic field

Many electron atoms

eg. 2 ; e⁻ 1 and 2

terms like $\frac{1}{r_{12}}$ in the Hamiltonian to describe e⁻-e repulsion



because $\frac{1}{r_{ij}}$ terms such equations cannot be separated

→ no exact ~~sol~~ solutions for more than 1 e^-

→ complicated approximations needed

The Aufbau principle (very short)

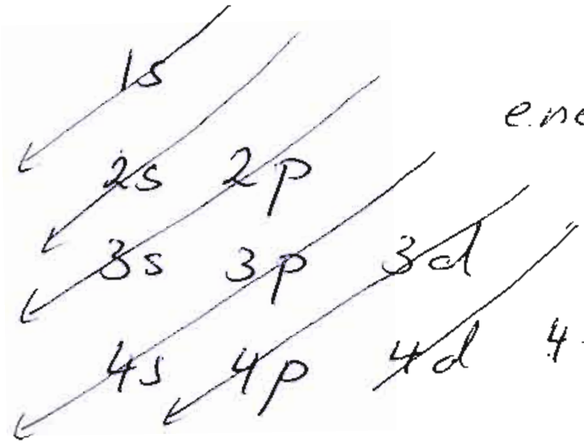
In many electron atoms the energy of an electron depends on n <u>and</u> l, not only on n

and on how many electrons are present

→ periodic table

from spectroscopic data and quantum mechanical calulations

order of orbitals in energy depends on how many electrons are present.



energy sequence of orbitals (filling pattern with e^-)

Pauli exclusion principle

how many electrons can fit into 1 orbital characterized by (n, l, m_l)?

principle In any atom no 2 e^- can have the same 4 quantum numbers:

$$(n, l, m_l, m_s)$$

2 electrons can be different in all 4 numbers, but must be different at least in 1 of them

3 equal → 2 electrons can have $m_s = \pm\frac{1}{2}$

$(n, l, m_l, \pm\frac{1}{2})$ spin up

only 2 electrons in 1 orbital ↑↓ spin down sub shells

ns : 1 orbital 2e

np : 3 orbitals 6e ($m_\ell = -1, 0, +1$)

nd : 5 orbitals 10e ($m_\ell = -2, -1, 0, +1, +2$)

nf : ~~8~~7 orbitals 14e ($m_\ell = -3, -2, -1, 0, 1, 2, 3$)

$n\ell$: $(2\ell+1)$ orbitals $2(2\ell+1)$ electrons

→ periodic table

Hund's rule

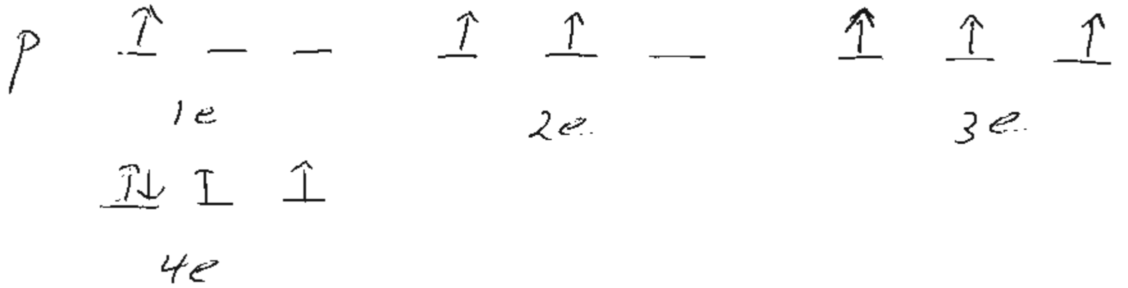
C : 6e : $1s^2 2s^2 2p^2$

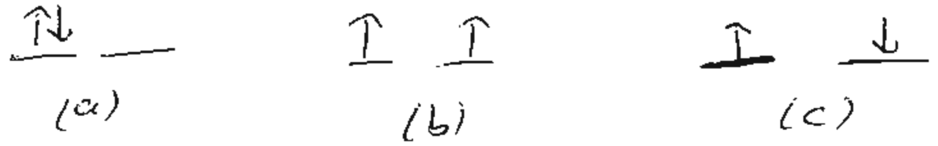
~~How~~ how are 2 electrons distributed among the 3 ~~gen~~ degenerate p orbitals?

possibility :

$p: \underline{\uparrow\downarrow}\ \underline{\quad}\ \underline{\quad}$ or $\underline{\uparrow}\ \underline{\downarrow}\ \underline{\quad}$ or $\underline{\uparrow}\ \underline{\uparrow}\ \underline{\quad}$

rule : ~~a~~ degenerate subshell is filled with e such that as many electrons as possible have parallel spins (unpaired)





1) in (a) $2e^-$ in the same orbital
$\rightarrow$ repulsion
in (b), (c) $2e^-$ in orbitals pointing into di~~f~~fferent directions
$\rightarrow$ less repulsion
$\rightarrow$ (b), (c) better than (a)

2) Pauli: $\psi(1,2) = -\psi(2,1)$ for electrons
case (b): spins $\alpha(1)\alpha(2)$ or $\beta(1)\beta(2)$ symm.
$\rightarrow$ space function antisymm.

$$\psi_b(1,2) = \left[\psi_1(r_1)\,\psi_2(r_2) - \psi_1(r_2)\,\psi_2(r_1)\right]\alpha(1)\alpha(2)$$
$$= -\psi_b(2,1)$$

$\psi_b(r_1 = r_2) = 0$

case (c): spin $\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right)$

$$\rightarrow \psi_c(1,2) = \left[\psi_1(r_1)\,\psi_2(r_2) + \psi_1(r_2)\,\psi_2(r_1)\right]\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$

$\psi_c(r_1 = r_2) \neq 0$

$\Rightarrow$ (b) has less repulsion and is more stable

⑩-8

p: 1e ↑ __ __
2e ↑ ↑ __
3e ↑ ↑ ↑
4e ↑↓ ↑ ↑

↑↓ __ __ (a)   ↑ ↑ __ (b)   ↑ ↓ __ (c)

<u>reasons</u>   nonsense in book:

1) orbitals with different m_ℓ have different directions

→ in cases (b) and (c) the electrons are more apart from each other

→ less repulsion than in case (a)

2) parallel spins   ok

→ magnetic moments aligned

→ more repulsion between magnetic moments in (b)

for north-south pole attraction (a), (c) better

3) in (c) not enough repulsion left to keep the e⁻ in separate orbitals

<u>balance</u> : (b) is best

spin-correlation: tendency of electrons with the same spin to avoid each other (separate orbitals)

<u>experimental determination:</u>

magnetic moment

B: $1s^2 2s^2 2p^1$

C: $1s^2 2s^2 2p^2$ double magnetic moment than B because of the 2 parallel spin p-electrons
(Hund's rule)

Approximations in QM

Simple exercise to set up the Schrödinger equation for <u>any</u> atom

$$\Big[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_k \frac{\hbar^2}{2M_k}\nabla_k^2$$

all electrons i all nuclei k

$$-\sum_{ik} \frac{Z_k e^2}{4\pi\varepsilon_0}\frac{1}{r_{ik}}$$

all electrons i attracted by all nuclei k

$$+\frac{1}{2}\sum_{\substack{k,k'\\k\neq k'}} \frac{Z_k Z_{k'} e^2}{4\pi\varepsilon_0}\frac{1}{r_{kk'}}$$

each nucleus k repels all other nuclei k' ($k \neq k'$)

$$+\frac{1}{2}\sum_{\substack{i,j\\i\neq j}} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r_{ij}}\Big]\psi$$

each electron i repels all other electrons j ($i \neq j$)

$$= E\psi$$

$\frac{1}{r_{kk'}}$, $\frac{1}{r_{ij}}$ causes that the equation is not separable

ψ is a function of 3 coordinates for each electron and 3 for each nucleus

→ approximations and thus computers needed

Born-Oppenheimer approx.

nuclei are much more heavy and thus much slower moving than electrons.:

Keep nuclear positions fixed

atoms: central field approximation

inner electrons just shield the nuclear charge from the outer ones

represented as $Z_{eff} e < Z_k e$

→ central symmetric field

→ outmost electron as in a 1e atom with a Zeff nucleus

Application: ionization energy estimates

potential energy $E_p = -\frac{Z^2 e^2}{4\pi\varepsilon_0 a_0} \frac{1}{n^2} = 2E_t$

$a_0 = 52.92$ pm: Bohr length, atomic unit of length atomic unit of energy:

Hartree: $1H = \underset{\text{atomic unit}}{1a.u.} = \frac{e^2}{4\pi\varepsilon_0 a_0}$

$= 27.2\ eV = 4.36 \cdot 10^{-18}\ J$

total $E_n = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0}\frac{1}{n^2} = -Z^2 \underset{\text{(Bohr)}}{R_y} \frac{1}{n^2}$

energy relative to a free electron

<u>spectra</u>: $\Delta E_{n_1 \to n_2} = -R_y\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = R_y\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

ionization energy $I = -E_n$

$$= \underbrace{\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0}}_{1/2H = 1/2\,au} \frac{1}{n^2}$$

$$= \frac{Z^2}{2n^2} \cdot \underset{au}{4.36 \cdot 10^{-18}}\ J$$

(J/mol: multiply by Avogadro's number)

$I = \frac{Z^2}{2n^2}$ au, central field

$I = \frac{Z_{eff}^2}{2n^2}$ au

1. I of He is 24.6 eV Z_{eff} in He?

$\frac{24.6\,eV}{27.2\,\frac{eV}{au}} \cancel{au} = 0.904$ au

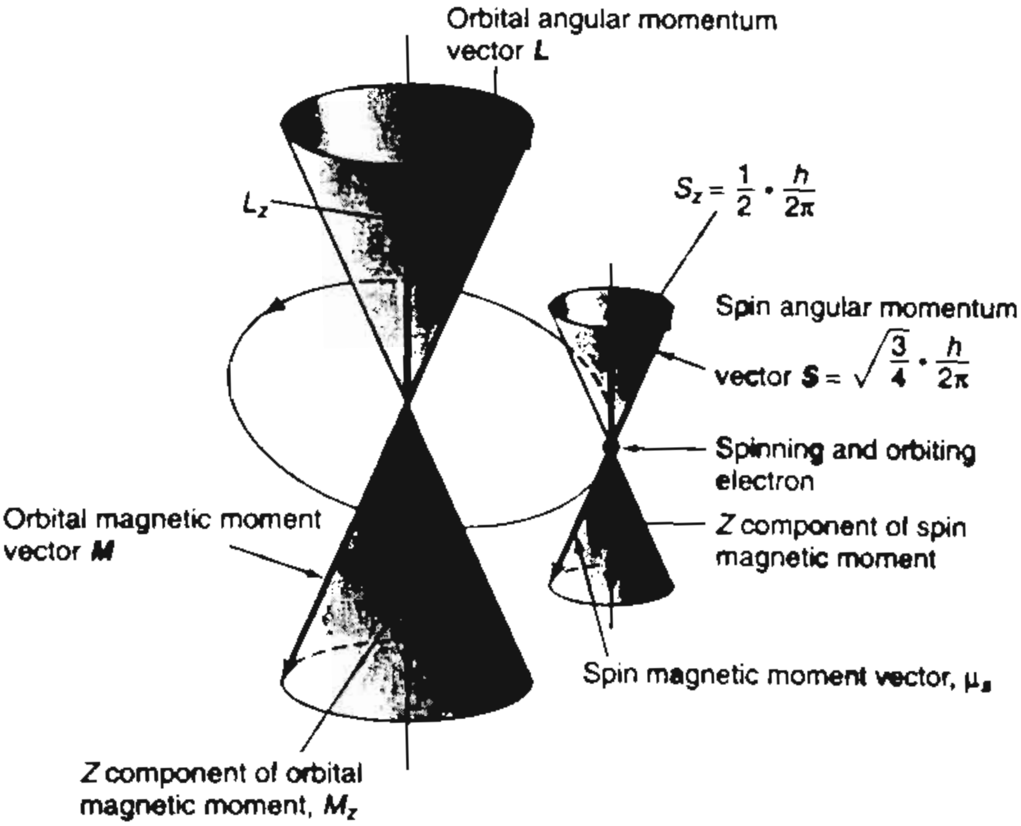
$n=1$ for 1s in He $\rightarrow 0.904 = \frac{Z_{eff}^2}{2}$

$\rightarrow z_{eff} = 1,34 < 2$

$2s^1$ in Li : $I = 5,38\,eV$

$$\frac{5,38\,eV}{27,2\,\frac{eV}{au}} = 0,198\,au$$

$$n=2 \Rightarrow 0,198 = \frac{z_{eff}^2}{\underset{\overset{\nearrow}{2n^2}}{8}} \quad , z_{eff} = 1,26 \ll 3$$



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angular momentum along the Z axis is quantized in a similar way to L_z,

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We are now in a position to add two additional postulates to the six that we introduced in Section 11.5:

Obj Approximation methods

Variation works well for groundstate energies

to solve: $\hat{H}\psi = E\psi$

multiply by ψ^* from left

$$\psi^* \cdot | \hat{H}\psi = E\psi$$

$$\psi^* \hat{H}\psi = E\psi^*\psi$$

$$\rightarrow \int \psi^* \hat{H}\psi \, d\tau = E\int \psi^*\psi \, d\tau$$

$$E = \frac{\int \psi^* \hat{H}\psi \, d\tau}{\int \psi^*\psi \, d\tau}$$

needed only if ψ is not normalized

normalization: $A\psi$ instead of ψ

with $A^2 \int \psi^*\psi \, d\tau = 1$

$$\rightarrow A = \frac{1}{\sqrt{\cancel{\psi^*}\int \psi^*\psi \, d\tau}}$$

normalized function: $\dfrac{\psi}{\sqrt{\int \psi^*\psi \, d\tau}}$

normalize $\psi = A x^2$

between $x = 0$ and $x = a$

$$\int \psi^2 dx = A^2 \int_0^a x^4 dx = A^2 \frac{x^5}{5}\Big|_0^a$$

ψ is real

$\rightarrow \psi^2$ not $\psi^* \psi$

$$= A^2\left(\frac{a^5}{5} - \frac{0^5}{5}\right) = A^2 \frac{a^5}{5}$$

$$= 1$$

$$\Rightarrow A^2 = \frac{5}{a^5} \quad , \quad A = \frac{\sqrt{5}}{\sqrt{a^5}}$$

normalized: $\frac{\sqrt{5}}{\sqrt{a^5}} x^2$

also gives the ~~n~~ energy of wave-functions which are <u>not</u> solutions:

$$E = \frac{\int \psi^* \hat{H} \psi \, d\tau}{\underbrace{\int \psi^* \psi \, d\tau}}$$

$\longrightarrow$ 1 if ψ normalized

in general:

$$\langle F \rangle = \frac{\int \psi^* \hat{F} \psi \, d\tau}{\int \psi^* \psi \, d\tau}$$

e.g. $\langle r \rangle = \frac{\int \psi^* r \psi \, d\tau}{\int \psi^* \psi \, d\tau}$

(11') −3

free particle in a box

from 0 to a:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad 1 \text{ dimension}$$

trial function $\psi = Ax^2$

$$\rightarrow E = -\int_0^a A^2 x^2 \frac{\hbar^2}{2m}\frac{d^2}{dx^2} x^2 \, dx$$

$$= -\frac{A^2\hbar^2}{2m}\int_0^a x^2 \frac{d^2}{dx^2} x^2 \, dx$$

$$\frac{d}{dx} x^2 = 2x \qquad \frac{d}{dx}(2x) = 2$$

$$\rightarrow E = -\frac{A^2\hbar^2}{2m} 2 \int_0^a x^2 dx$$

$$= -\frac{A^2\hbar^2}{m}\left[\frac{x^3}{3}\right]_0^a$$

$$= -\frac{A^2\hbar^2 a^3}{3m}$$

$$= -\frac{5\hbar^2 a^3}{3ma^5} = -\frac{5\hbar^2}{3ma^2} = -1.7\frac{\hbar^2}{ma^2}$$

$$\xrightarrow{} -4.9\frac{\hbar^2}{ma^2}$$

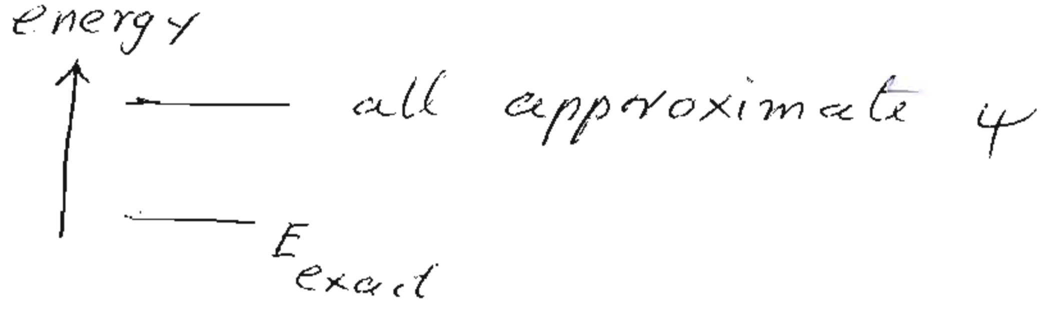
$$A^2 = \frac{5}{a^5}$$

box: $E_1 = \frac{h^2}{8ma^2}$ "

$$= \frac{4\pi^2\hbar^2}{8ma^2}$$

Variation principle

every ψ which is not the wave-function of a system, i.e. which is not a solution of $\hat{H}\phi = E_n\phi$ gives an energy E that is higher than the exact E_n



$\Rightarrow$ the lower is E, the better is the approximation

choose an approximation ψ with ~~a~~ free parameters

calculate E as function of the parameters.

determine the parameters such that E is smallest (minimum of E)

atoms: linear combinations of hydrogen functions as ~~par~~ approximation:

$$\psi = (a\varphi_1 + b\psi_2 + \cdots)$$

and find (a, b, ..) such that E is smallest (still sure higher than the exact energy)

= variation method

Configuration Interaction

CI adding (linear combination) excited electronic states ~~to~~ to the ground state wave function and determine the coefficient such that ~~en~~ the energy is minimal

nowadays: calculations with several millions excited configurations are done.

Perturbation Theory

Suppose that there is a similar, but simpler system than the unknown one ($\hat{H}$), that has an $\hat{H}^o$ which can be solved:

$$\hat{H}^o \psi^o = E^o \psi^o \quad \text{unperturbed}$$

assume that adding a perturbation $\hat{H}'$ with a factor λ to $\hat{H}^o$ give the desired $\hat{H}$:

$$\hat{H} = \hat{H}^o + \lambda \hat{H}'$$

then: $\psi = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \ldots$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots$$

simple: 1. order energy:

$$E = E^{(0)} + \underset{\substack{\downarrow \\ \text{e.g. a field strength} \\ \text{or simply } 1}}{\lambda} \int \psi^{(0)*} \hat{H}' \psi^{(0)} d\tau$$

higher orders get fast complicated

Self consistent field (SCF) method

Hartree - Fock

for atoms <u>and</u> molecules

start with some guess for ψ

→ calculate an effective, averaged field, ~~that~~ with which all other electrons interact with the given one

repeat for all electrons

with this average potential solve the Schrödinger equation numerically on a computer

→ new ψ → again form the effective potential and so on, until the results do not change anymore: self consistency

Slater orbitals

effective nuclear charge $Z_{eff} = Z - \sigma$

σ shielding constant for each electron

slater rules

consider an electron with quantum number (principal) n_0

1) electrons with $n > n_0$ contribute nothing to σ

2) $n_0 s$ shields other $n_0 s$ with 0,30

other electrons in n_0 shield with 0,35 for each one

3) $n = n_0 - 1$: 0,85 for each ns or np electron

1,00 for each nd or nf electron

4) $n < n_0 - 1$ contribution of 1.00 for each electron

Z_{eff} for 2p-e in N: $1s^2 2s^2 2p^3$, $Z=7$

$$\sigma = \overset{n = n_0 - 1}{2 \cdot 0.85\,(1s^2)} + \overset{n = n_0}{4 \cdot 0.35\,(2s^2 2p^2)}$$

$$= 1.70 + 1.40 = 3.10$$

→ Z_{eff} for one 2p electron:

$$Z_{eff} = Z - \sigma = 7 - 3.10 = 3.90$$

Slater orbitals for each electron:

r in au: units of a_0

$$\psi_{ns}(r) = r^{n-1} e^{-\frac{Z_{eff} r}{n}}$$

$$\psi_{np_x}(r) = x\, r^{n-2} e^{-\frac{Z_{eff} r}{n}}$$

can be used as first guess for an SCF calculation and for order of magnitude guesses.

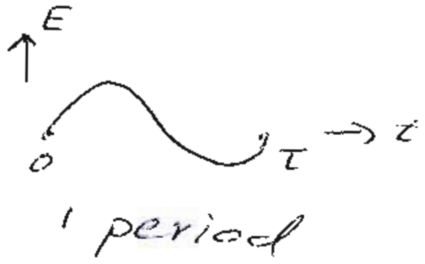
~~Per~~ Precise calc.: super computers

Review Chap. 11

1st Major

Electromagnetic radiation,
old quantum theory

$\lambda\nu = c$, $\nu = \frac{1}{\tau}$



angular velocity $\omega = 2\pi\nu = \frac{2\pi}{\tau}$

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ natural frequency

k: force constant

more in use than ν: energy $E = h\nu$

or $\bar{\nu} = \frac{1}{\lambda}$ (cm^{-1}) $\nu = c\bar{\nu}$

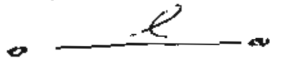
harmonic motion:

$$\frac{d^2y}{dt^2} = \frac{F}{m} \qquad \frac{d^2y}{dt^2} = -\frac{k}{m}y$$

$$y = a\sin\left(\sqrt{\frac{k}{m}}\,t + b\right)$$

plane wave: $y = 2\sin\frac{2\pi}{\lambda}(x \pm ut)$

u: phase velocity: move of a phase



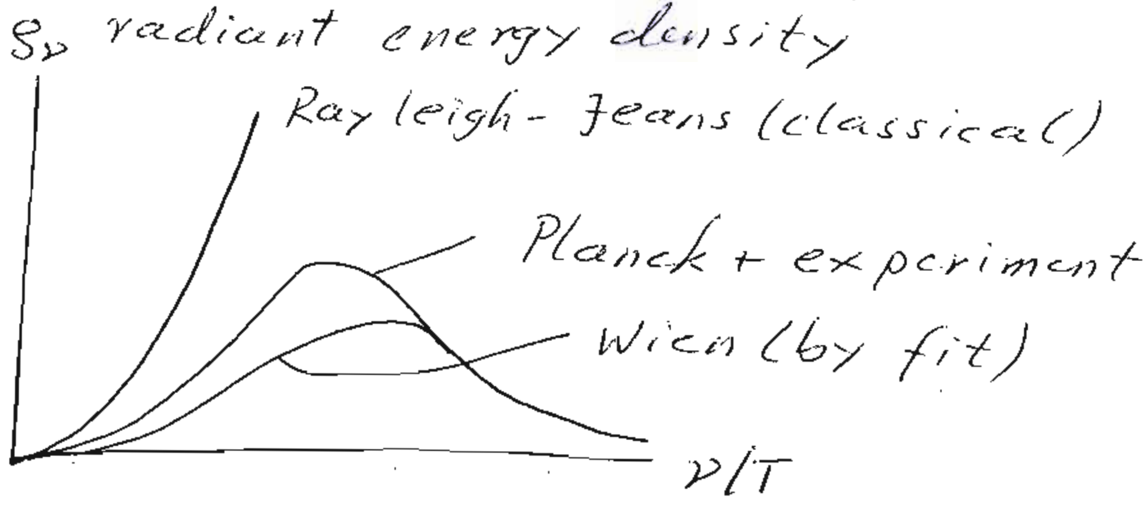
string

standing wave: $y = A\sin\frac{n\pi x}{l}\sin(2\pi\nu t + b)$

n: integer

Black body radiation

Planck: energy <u>only</u> in packets $h\nu$



Einstein: light as beam of photons, each with energy $h\nu$

$$h\nu = \frac{1}{2}mu^2 + W$$

u: e⁻-speed

W ↳ energy needed to cut an e⁻ free from a metal: work function

threshold frequency: $h\nu_0 = W$

light + bulk → wave
light + particle → particle

<u>Bohr's theory</u>

<u>classical</u>: e orbits round the nucleus like a planet round the sun
not stable

<u>Bohr</u> only special orbits stable

orbit stable when

angular momentum $L = mvr = n\hbar$

$n = 0, 1, 2, \ldots$

$$E_n = -R_y \frac{Z^2 hc}{n^2} \qquad R_y = \frac{e^2}{8\pi\varepsilon_0 a_0 hc}$$

E_n: ionization energy

good only for 1e atoms!

$H, He^{+}, Li^{2+}, Be^{3+}, B^{4+} \ldots$

line spectra, $Z=1$ for H:

$$\Delta E = -R_y hc \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$\Delta E = h\nu = h\frac{c}{\lambda} \qquad \frac{1}{\lambda} = \tilde{\nu} = \frac{\Delta E}{hc}$$

$$\tilde{\nu} = R_y \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Correspondence Principle

all QM must reduce to classical theory for classical experimental results cases

e.g. large masses

Large boxes

Foundations of QM

de ~~Brg~~ Broglie wavelength for particles: $\lambda = \frac{h}{mu}$

→ Bohr H-atom: particle must be a standing wave on a circle (orbit, stable)

$$\rightarrow 2\pi r = n\lambda = \frac{nh}{mu}$$

uncertainty principle

$$\Delta q \cdot \Delta p = \Delta E \Delta t \geq \frac{\hbar}{2}$$

Schrödinger's wave mechanics

reading assignment: plausibility

QM: Operators for physical quantities

$$\hat{x} \rightarrow x \quad , \quad \hat{P}_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$$

$$\nabla^2 = \left(\hat{P}_x^2 + \hat{P}_2^2 + \hat{P}_z^2\right)/(-\hbar^2) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

time-dependent systems: $E \rightarrow -\frac{\hbar}{i}\frac{\partial}{\partial t}$

conservative systems $E \rightarrow \hat{H}$

$$H = E_K + E_P = \frac{p^2}{2m} + E_P(x,t)$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + E_P(x,t)$$

wave function ψ:

$$\hat{H}\psi(x,t) = -\frac{\hbar}{i}\frac{\partial\psi(x,t)}{\partial t}$$

time independent (conservative):

$$\hat{H}\psi(x) = E\psi(x)$$

$$\psi(x,t) = \psi(x)\cdot e^{i\frac{Et}{\hbar}}$$

probability to find an e^- in $dV, d\tau$:

$P = \psi^*\psi \, d\tau \qquad d\tau = dx\,dy\,dz$

probability density:

$$\rho = \psi^*\psi$$

$\int\psi^*\psi \, d\tau = 1$ because it is prob. to find e^- any where in all space

any wave function: $\psi \to A\psi$

A such that $A^2\int\psi^*\psi \, d\tau = 1$

$$A = \frac{1}{\sqrt{\int\psi^*\psi \, d\tau}}$$

Postulates

solution of $\hat{H}\psi = E\psi$ gives the state of the system

ψ must be normalizable

(= square integrable):

$$\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz\, \psi^* \psi (x,y,z) = \text{finite number}$$

every physical observable is ~~der~~ described by a linear operator

when 2 operators commute:

$$\hat{O}_1 \hat{O}_2 \psi = \hat{O}_2 \hat{O}_1 \psi$$

then they have the same eigenfunctions and no uncertainty when measurement of their observables

$\Rightarrow$ every operator that commutes with $\hat{H}$ has observables that can be measured precisely

$$\langle F \rangle = \frac{\int \psi^* \hat{F} \psi \, d\tau}{\underbrace{\int \psi^* \psi \, d\tau}_{=1 \text{ if normalized}}}$$

if ψ eigenfunction of $\hat{F}$:

$$\hat{F}\psi = f\psi$$

then all measurements give precisely f and $\langle F \rangle = f$

if ψ not eigenfunction of $\hat{F}$:

then $\langle F \rangle$ is the average of an infinite number of measurements

r does not commute with $\hat{H}$

$\Rightarrow$ since $\hat{H}\psi = E\psi \sim \langle r \rangle = \int \psi^* r \psi \, d\tau$ is average or expectation value

if ψ_1, ψ_2 eigenfunctions of $\hat{F}$ with different eigenvalues (non degenerate)

then: $\int \psi_1^* \psi_2 \, d\tau = 0$ orthogonality

if ψ_1, ψ_2 eigenfunctions of $\hat{F}$ with the same eigenvalue (degenerate)

then all $a\psi_1 + b\psi_2$ are also eigenfunctions of $\hat{F}$ with the same eigenvalue and can be chosen to be orthogonal

free particle

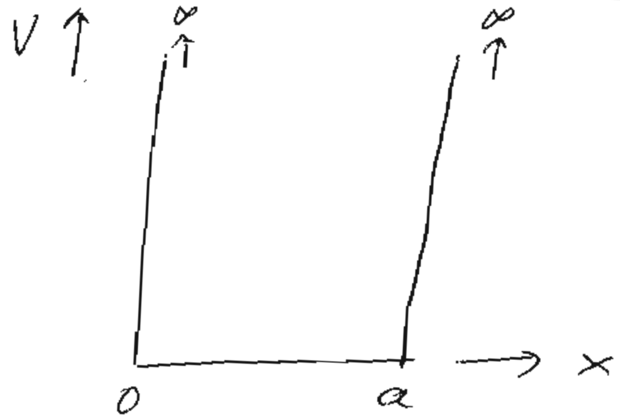
$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$ no quantization if no box

$$\psi = A e^{\pm \frac{i}{\hbar}\sqrt{8\pi^2 m E}\, x}$$

delocalized along x-axis

momentum: precise, sharp: $P_x = \pm\sqrt{2mE}$

particle in a box



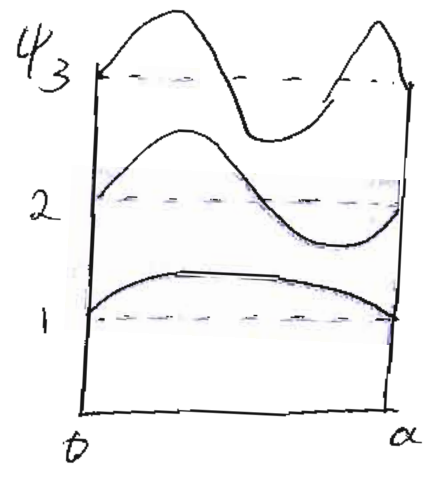
all integrals are from 0 to a, since

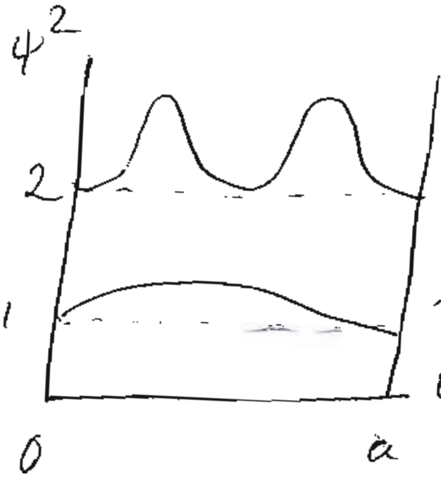
$\psi(x\leq 0) = \psi(x \geq a) = 0$

$$E_n = \frac{h^2}{8ma^2} n^2 \qquad n = 1, 2, 3, \cdots$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

3-dim. box: $E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$





of ~~maxi~~ maxima in ψ^2: n

$$E = -\frac{\hbar^2}{2m}\int_0^a \psi^* \frac{d^2}{dx^2}\psi \, dx$$

transitions: $\Delta E = \frac{h^2}{8ma^2}(n_2^2 - n_1^2)$ $n_1 \to n_2$

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

Harmonic oscillator

reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$

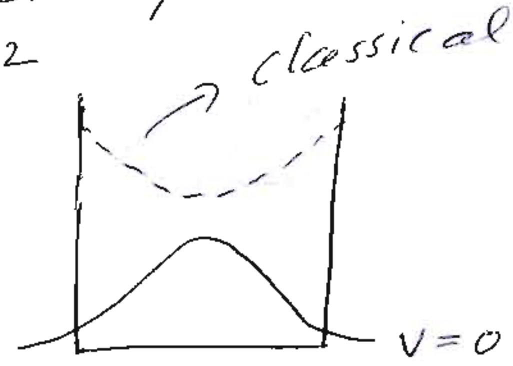
$E_p = \frac{1}{2}kx^2$ $\nu_0 = \sqrt{\frac{k}{\mu}}$

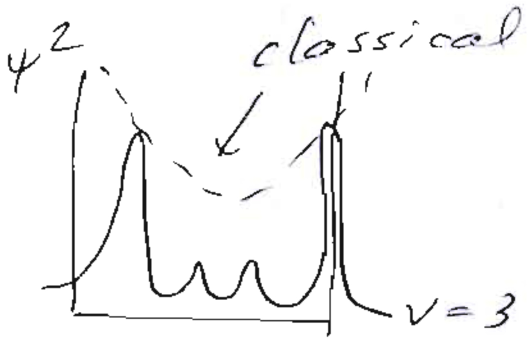
$E_v = h\nu_0 (v + \frac{1}{2})$ $v = 0, 1, 2$

$\nu = \bar{\nu} c$

$E_v = h\bar{\nu}_0 c\,(v + \frac{1}{2})$

zero-point energy $E_0 = \frac{1}{2}h\nu_0 = \frac{1}{2}hc\bar{\nu}_0$





approach to classical density for large v

all ψ_v with even v are even functions:

$$\psi_v(-x) = \psi_v(x) \quad v \text{ even}$$

all ψ_v with odd v are odd functions: $\psi_v(-x) = -\psi_v(x)$ v odd

ψ_0:

ψ_1

Hydrogen

separation if $\hat{H} = \hat{H}_1(x) + \hat{H}_2(y)$

then $\psi = \psi_1(x) \cdot \psi_2(y)$

polar coordinates:

$$\psi = R(r)\,\phi(\varphi)\,\theta(\vartheta)$$

→ quantum numbers n, l, m_l

$n = 1, 2, 3, \ldots$ integer

$l = 0, 1, \ldots, n-1$

$m_l = -l, \ldots, -1, 0, 1, \ldots, l$

hydrogen: E_n

many electrons $E_{n,l}$

n: determines size of ψ

l: " shape of ψ

m_l: " direction of the shape

for the form of ψ-s, sketches of $\langle r_{1s} \rangle$, of R^2 and $4\pi r^2 R^2$ and of $[\Theta(\vartheta)\Phi(\varphi)]^2$ in general must be known

Angular momentum

$$L = \sqrt{l(l+1)}\,\hbar \qquad L_z = m_l \hbar$$

magnetic moment: $\mu = -\frac{e}{m_e} L$

Bohr magnetons $\frac{e}{m_e}$ as units

Ang. momentum, rigid rotor, spin, many electron atoms, approximations must be studied for 1st Major

We have thus split the Schrödinger equation (Eq. 11.164) into three equations, one involving Φ and ϕ (Eq. 11.165), one involving R and r (Eq. 11.167), and one involving Θ and θ (Eq. 11.168). These equations must now be solved so as to eliminate the differentials. We will first solve the Φ equation so as to obtain the allowed values of m_l. These will then be used to solve the Θ equation so as to obtain the allowed l values. Finally, the l values will be used to solve the R equation.

Solution of the Φ Equation

Equation 11.165 is of a familiar form (compare Eq. 11.125) and its solution is

$$\Phi = Ae^{im_l\phi} \tag{11.169}$$

where A is a normalization constant. The function Φ must have the same value at $\phi = 0$, $\phi = 2\pi$, $\phi = 4\pi, \ldots$, because these angles correspond to the same position; this requires that

$$m_l = 0, \pm 1, \pm 2, \pm 3, \ldots \tag{11.170}$$

The positive and negative values relate to distinct solutions. The quantity m_l has thus become a quantum number because of the mathematical constraints on the system and not in any arbitrary way.

The value of A is obtained by applying the normalization condition, the range of ϕ being 0 to 2π:

$$\int_0^{2\pi} \Phi_{m_l}\Phi^*_{m_l}\, d\phi = A^2 \int_0^{2\pi} e^{im_l\phi}e^{-im_l\phi}\, d\phi = A^2 2\pi = 1 \tag{11.171}$$

Therefore $A = 1/\sqrt{2\pi}$ and the solution becomes

$$\Phi = \frac{1}{\sqrt{2\pi}}e^{im_l\phi} \tag{11.172}$$

When $m_l = 0$, the value of Φ_0 is $1/\sqrt{2\pi}$, but for other values of m_l the solutions involve imaginary exponents. This is awkward, and it is more usual to employ a linear combination of the functions, $\Phi_{m_l} \pm \Phi_{-m_l}$; as we have seen (Eq. 11.116), linear combinations of wave functions having the same eigenvalue are also solutions of wave equations. For example,

$$\text{for } m_l = 1, \qquad \Phi_1 = \frac{1}{\sqrt{2\pi}}e^{i\phi} \tag{11.173}$$

$$\text{for } m_l = -1, \qquad \Phi_{-1} = \frac{1}{\sqrt{2\pi}}e^{-i\phi} \tag{11.174}$$

We can take the sum of these and divide by $\sqrt{2}$ to preserve the normalization,

$$\Phi_x = \frac{1}{\sqrt{2}}(\Phi_1 + \Phi_{-1}) = \frac{1}{2\sqrt{\pi}}(e^{i\phi} + e^{-i\phi}) = \frac{\cos\phi}{\sqrt{\pi}} \tag{11.175}$$

We designate this orbital Φ_x since $\cos\phi$ has its maximum value when $\phi = 0$, which