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QUANTIZATION

P W Atkins

ESG

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ACKNOWLEDGEMENT

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Outline of contents	7	.....
Some features of classical mechanics	8	.....
Trajectories	8	.....
Vibrations	9	.....
Rotations	10	.....
The emergence of quantum theory	11	.....
Black-body radiation	12	.....
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Well-behaved and misbehaving functions	23	.....
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Quantization

1 TOPICS DISCUSSED IN THIS PRESENTATION

Side 1: The basic formulation of quantum mechanics.

The elementary predictions of classical mechanics

Experimental evidence for quantum theory

The Schrödinger equation

The wavefunction

Quantization

General features of quantum theory.

Side 2: Basic applications of quantum mechanics

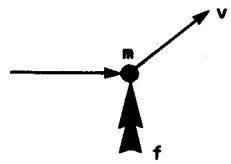
The quantum theory of translation

The quantum theory of vibration

The quantum theory of rotation

Angular momentum in quantum mechanics.

2 THE BASIC FEATURES OF CLASSICAL MECHANICS



1. Notation.

m	mass
v	velocity
p	Momentum ($p = mv$)
f	force

2. Newton's second law.

$$dp/dt = f(t)$$

That is: the rate of change of momentum is equal to the force acting at that instant.

3. The classical mechanics of translational motion.

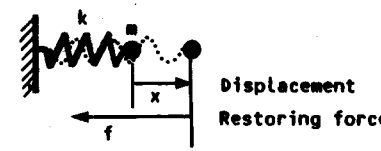
When a stationary particle of mass m is subjected to a constant force f, after a time t its position, speed and energy are given by

(A) $x(t) = x(0) + (f/2m)t^2$

(B) $v(t) = ft$

(C) $E(t) = \frac{1}{2}mv^2 = (f^2/2m)t^2$

3 THE CLASSICAL MECHANICS OF VIBRATIONAL MOTION



The condition for simple harmonic motion:

restoring force $\propto$ displacement

That is, $f = -kx$

k is called the force constant.

Potential energy: $V = \frac{1}{2}kx^2$

Kinetic energy: $T = \frac{1}{2}mv^2 = p^2/2m$

Total energy: $E = T + V = p^2/2m + \frac{1}{2}kx^2$

Frequency: $\nu = (1/2\pi)\sqrt{(k/m)}$

Maximum amplitude of displacement when its energy is E:

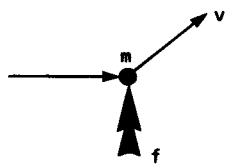
$$A = \sqrt{(2E/k)}$$

If the displacement is initially A, after the oscillator is released its position and momentum are given by

$$x(t) = A \cos \omega t$$
$$p(t) = m\omega A \sin \omega t$$

with $\omega = 2\pi\nu = \sqrt{(k/m)}$.

2 THE BASIC FEATURES OF CLASSICAL MECHANICS



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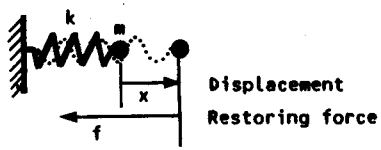

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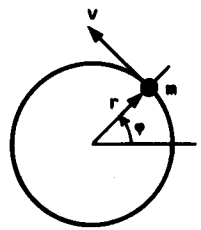
4 THE CLASSICAL MECHANICS OF ROTATIONAL MOTION.



1. Notation

- I Moment of inertia (mr^2 for a particle confined to a ring of radius r)
- J angular momentum (of magnitude mvr for a particle)
- ω angular velocity (rate of change of angle, $d\varphi/dt$)
- T torque (moment of force, magnitude fr)

2. Newton's second law.

$$dJ/dt = T$$

That is, rate of change of angular momentum is equal to the torque acting at that instant.

3. Predictions.

When a stationary body of moment of inertia I (e.g. a particle of mass m on a ring of radius r) is subjected to a constant torque T, after a time t its position (angle), angular momentum and energy are given by

(A) $\varphi(t) = \varphi(0) + \frac{1}{2}Tt^2$

(B) $J(t) = Tt$

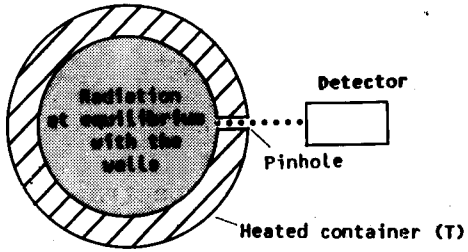
(C) $E(t) = p^2/2m = (pr)^2/2mr^2 = J^2/2I = (T^2/2I)t^2$

5 EXPERIMENTAL EVIDENCE FOR THE QUANTUM THEORY

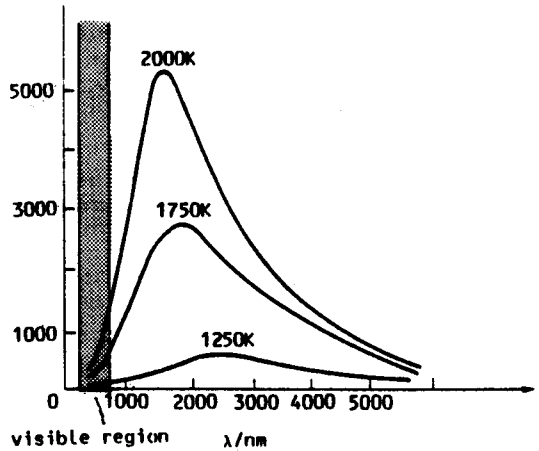
1. Black body radiation.
2. Heat capacities at low temperatures.
3. The photoelectric effect.
4. The Compton effect.
5. Atomic and molecular spectra.

6 BLACK BODY RADIATION: THE EXPERIMENTAL DATA.

1. A pinhole in a closed vessel acts as a black body:



2. The energy density inside the cavity depends on the wavelength and the temperature:



3. Two quantitative results were noticed:

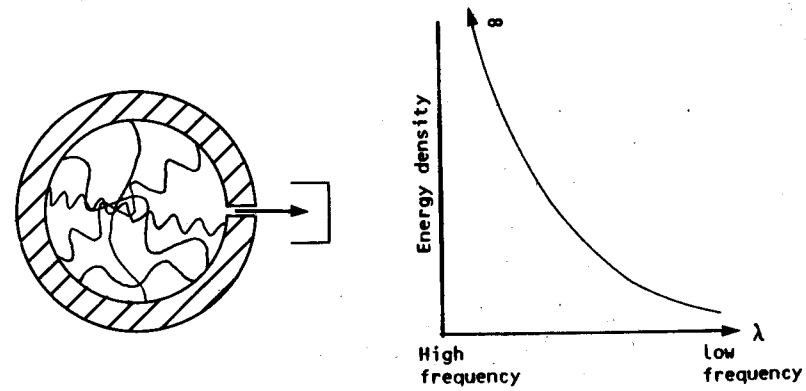
Wein's displacement law: The wavelength corresponding to the maximum energy density at a temperature T obeys $\lambda_{max} T$ = constant

Stefan's law: The energy density $\mathscr{U}$ inside the container at a temperature T obeys $\mathscr{U} = aT^4$

7 BLACK BODY RADIATION: THE THEORETICAL INTERPRETATION

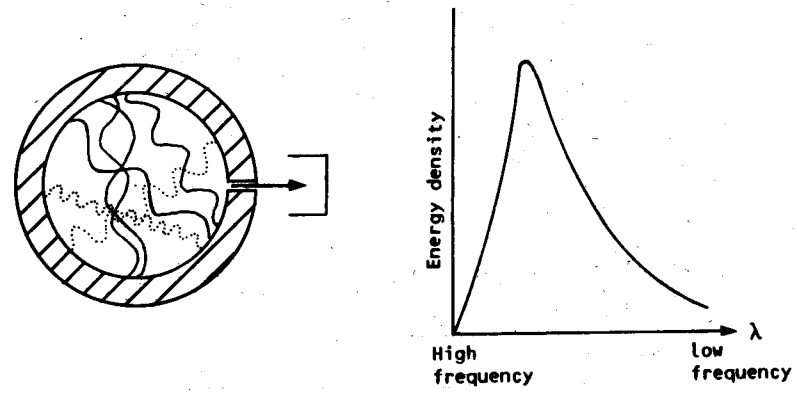
1. The Rayleigh-Jeans calculation

An oscillator of frequency ν has a mean energy kT. As a consequence, all oscillators, even those of very high frequency, are active at all temperatures.



2. Planck's calculation

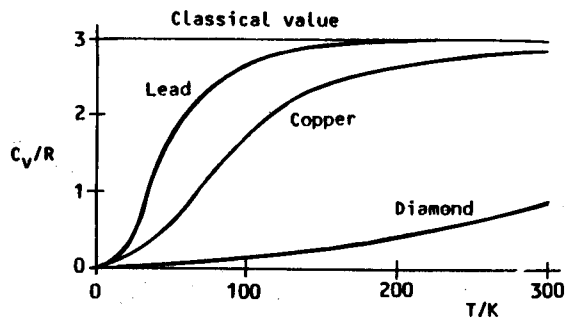
An oscillator of frequency ν can possess only an energy that is some integral multiple of hν , where h is a fundamental constant ($h = 6.626 \times 10^{-34}$ J s). The consequence is that high frequency oscillators are not excited.



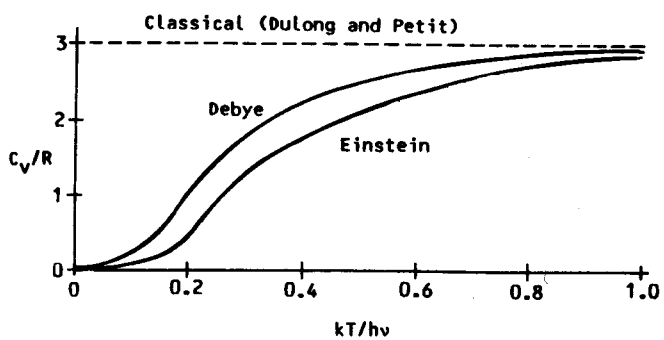
8 HEAT CAPACITIES AT LOW TEMPERATURES

Heat capacity is defined as $C = dq/dT$, where dq is the amount of heat needed to raise the temperature of an object by dT.

Experimental results at room temperature and below are as follows:



Einstein regarded the solid as a collection of oscillators, of frequency ν, and, following Planck, allowed their energies to be only some integral multiple of $h\nu$. Debye improved the calculation. They obtained the following results:



9 THE PHOTOELECTRIC EFFECT

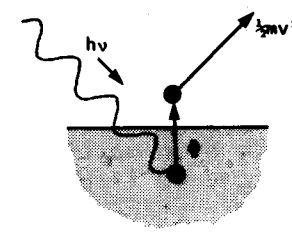
The experimental information is as follows:

1. No electrons are ejected, regardless of the intensity of the light, unless its frequency exceeds a threshold value characteristic of each metal.

2. Even at low light intensities, electrons are ejected immediately if the frequency is above threshold.

3. The kinetic energy of the ejected electrons is linearly proportional to the frequency ν of the incident light.

Einstein's interpretation is as follows:



Conservation of energy:

Energy of incident photon = energy to remove electron + kinetic energy of ejected electron

$$h\nu = \Phi + \tfrac{1}{2}mv^2$$

Conclusion: A light beam may be regarded as a stream of photons. The energy of a photon is $h\nu$. High intensity beams are dense streams of photons.

10 THE COMPTON EFFECT

When light strikes electrons it is scattered from them with a change of wavelength from λ to $\lambda + \delta\lambda$.

Classically a range of wavelengths is expected in the scattered light.

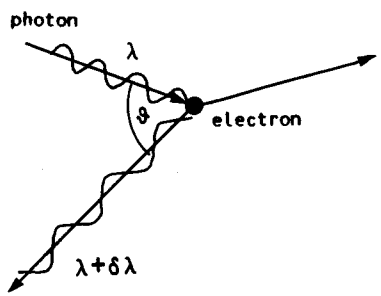
Experimentally it is found that the wavelength is increased by a single, definite amount which depends only on the angle through which the light is scattered.

Quantum theory takes the view that the light should be regarded as particles of energy $h\nu$ and momentum h/λ,
$\lambda = c/\nu$, (A)
Then treating the electron-photon interaction as a collision in which energy and momentum are conserved leads to the expression:

$$\delta\lambda = (h/m_e c)(1 - \cos\vartheta)$$

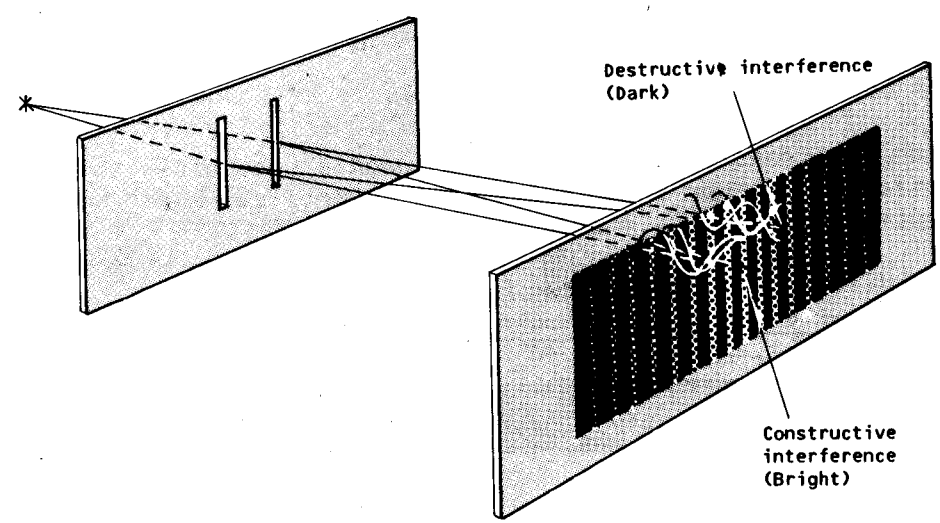
which is verified experimentally.

$h/m_e c$ is called the Compton wavelength of the electron. Its magnitude is 2.426×10^{-12} m.



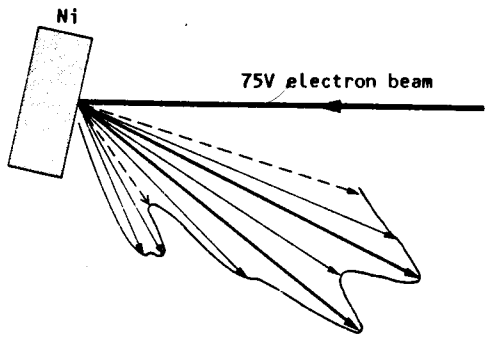
11 THE DIFFRACTION OF WAVES

The characteristic property of waves is their diffraction by a screen. The pattern of light and dark is readily explained by the interference of waves taking different paths: constructive interference (where the waves augment each other) leads to a bright band; destructive interference (where the waves cancel) accounts for a dark band.



12 THE DIFFRACTION OF ELECTRONS

Davisson and Germer found that electrons could be diffracted by the planes of atoms in a crystal lattice:



When electrons are accelerated through a potential difference V they acquire a kinetic energy eV, and hence a momentum $p = \sqrt{(2m_e eV)}$.

The diffraction results can be explained on the basis that an electron with a momentum p behaves as a wave of wavelength λ, where

(A) $\lambda = h/p$, the de Broglie relation.

The de Broglie relation is a general relation applicable to all types of particle (electrons, protons, photons, atoms, molecules, balls, etc.).

13 ATOMIC AND MOLECULAR SPECTRA

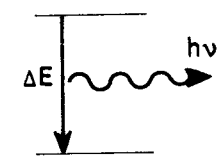
A typical atomic spectrum (emission from Hg):

A typical molecular spectrum (absorption by ScF):

Explanation: The spectra can be accounted for on the basis that

1. The energies of atoms and molecules are confined to certain discrete values.

2. The atom or molecule can shed its energy only in discrete steps, ΔE.



3. The change of energy ΔE is radiated, the frequency of the radiation ν being given by

$\Delta E = h\nu$, the Bohr frequency condition.

14 THE SCHRODINGER EQUATION

For a particle of mass m and energy E free to move in one dimension where it experiences a potential energy V(x),

$$(-\hbar/2m)(d^2/dx^2)\Psi(x) + V(x)\Psi(x) = E\Psi(x).$$

$\hbar$ ("h cross" or "h bar") is a convenient modification of Planck's constant, $\hbar = h/2\pi$. The function $\Psi(x)$ is called the wavefunction.

15 THE CLASSICAL WAVE EQUATION

The equation for the spatial variation of the amplitude f(x) of a wave of wavelength λ is

$$\text{(A)} \quad (d^2f/dx^2) + (2\pi/\lambda)^2 f(x) = 0$$

The Schrödinger equation can be rearranged into the form

$$\text{(B)} \quad (d^2\Psi/dx^2) + \underbrace{(2m/\hbar^2)\{E - V(x)\}}_{\text{(C)}}\Psi(x) = 0$$

The two equations can be identified if we set

$$\text{(D)} \quad (2\pi/\lambda)^2 = (2m/\hbar^2)\{E - V(x)\}$$

16 WAVELENGTH, MOMENTUM AND ENERGY

When a particle is not acted on by a force it is in a region of constant potential energy V. If its total energy is E its kinetic energy is

(A) Kinetic energy = E − V.

But we also have

(B) Kinetic energy = $\frac{1}{2}mv^2 = p^2/2m$.

Therefore

(C) $p^2/2m = E - V$, or $p = \sqrt{\{2m(E - V)\}}$.

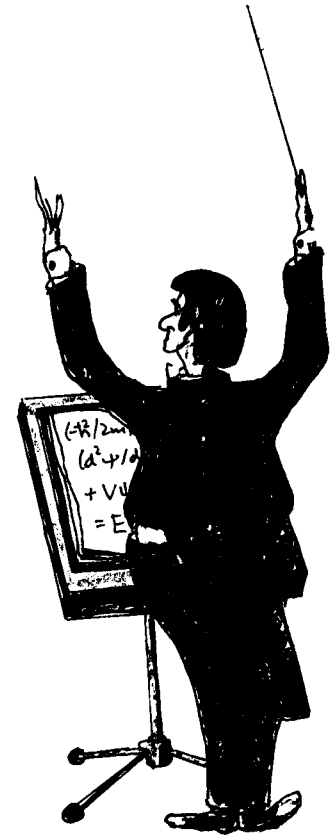
The condition for the wave equation and the Schrödinger equation to be the same is therefore

(D) $(2\pi/\lambda)^2 = p^2/\hbar^2$ or $1/\lambda = p/h$,

that is, the de Broglie relation.

In summary, if the de Broglie relation is combined with the classical wave equation, we arrive at the Schrödinger equation.

17



The spectra of atoms and molecules are, in a sense, music.

18 THE BORN INTERPRETATION OF THE WAVEFUNCTION

1. An electromagnetic wave has an electric field $\mathscr{E}$ which varies through space as

$$\mathscr{E} = \mathscr{E}_0 \cos(2\pi x/\lambda), \text{ or } \mathscr{E}(x) \text{ in general.}$$

The intensity of light is related to the amplitude $\mathscr{E}(x)$ by the relation

$$\text{intensity} \propto \mathscr{E}(x)^2 \quad (\text{or } \mathscr{E}^*(x)\mathscr{E}(x) \text{ if } \mathscr{E}(x) \text{ is complex}).$$

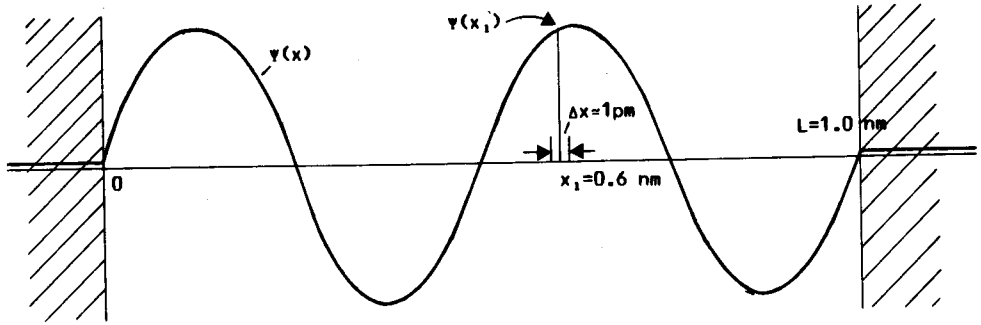
The probability of finding a photon in a selected region is therefore proportional to the intensity, and therefore to $\mathscr{E}(x)^2$.

2. The wavefunction Ψ varies through space as

$$\Psi = \Psi_0 \cos(2\pi x/\lambda)$$

in simple cases and as $\Psi(x)$ in general. By analogy we assert that the probability of finding a particle in a selected region is proportional to $\Psi(x)^2$, and to $\Psi^*(x)\Psi(x)$ if $\Psi(x)$ is complex.

19 THE WAVEFUNCTION FOR A PARTICLE TRAPPED BETWEEN TWO WALLS



The form of the wavefunction throughout the region is

(A) $\Psi(x) = (2/L)^{\frac{1}{2}} \sin(4\pi x/L)$, $L = 1$ nm (10^{-9} m, 1000 pm)

and is zero inside the walls.

The amplitude of the wavefunction at the point x_1 is

(B) $\Psi(x_1) = (2/L)^{\frac{1}{2}} \sin(4\pi x_1/L)$.

Since the point $x_1 = 0.6$ nm, the numerical value of the wavefunction there is

(C) $\Psi(x_1) = (2/1.0\text{ nm})^{\frac{1}{2}} \sin(4\pi \times 0.6\text{ nm}/1.0\text{ nm})$
$= (2/\text{nm})^{\frac{1}{2}} \sin 7.54$ (7.54 radians, that is.)
$= 1.34\text{ nm}^{-\frac{1}{2}}$.

(D) $\Psi(x_1)^2 = 1.81\text{ nm}^{-1}$.

Note that $\Psi(x)^2$ is a probability density.

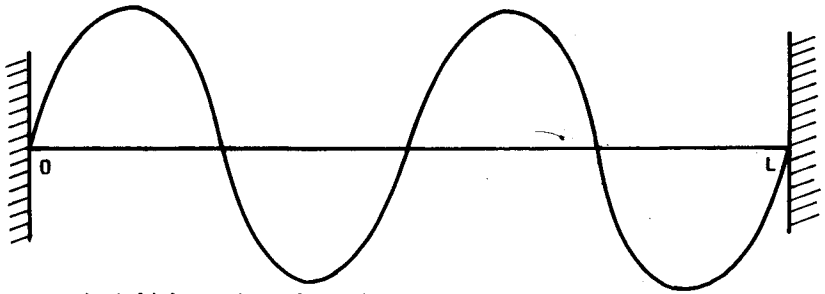
The probability of finding the particle in the region of length Δx at the point x_1 is the product of the length of the region and the probability density there:

(E) Probability of the particle being in Δx at x_1

$$P(x_1) = \Psi(x_1)^2 \Delta x = (1.81\text{ nm}^{-1}) \times (10^{-3}\text{ nm})$$
$$= 1.81 \times 10^{-3} = 1/553.$$

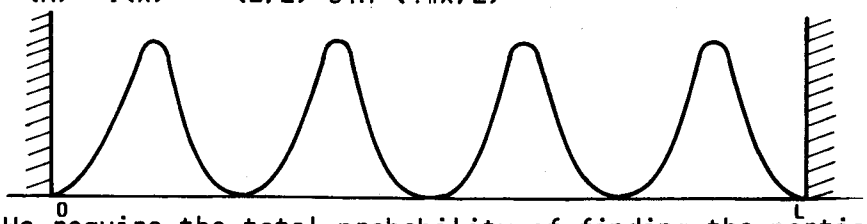
20 THE PROBABILITY OF FINDING THE PARTICLE ON THE LEFT OF THE VESSEL

The wavefunction is $\Psi(x) = (2/L)^{\frac{1}{2}} \sin(4\pi x/L)$

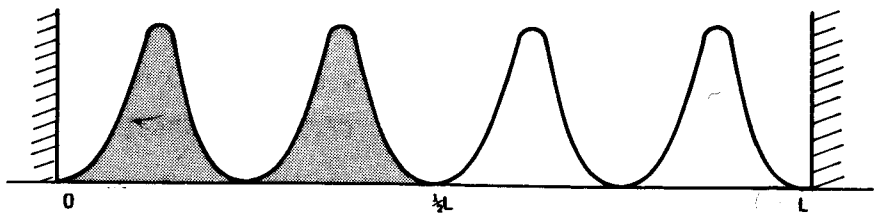


The probability density is

(A) $\Psi(x)^2 = (2/L) \sin^2(4\pi x/L)$



We require the total probability of finding the particle between x = 0 and x = ½L: this is the total area shaded:



The area is the integral

(B) $$\int_0^{\frac{1}{2}L} \Psi(x)^2 dx = (2/L)\int_0^{\frac{1}{2}L} \sin^2(4\pi x/L)dx$$

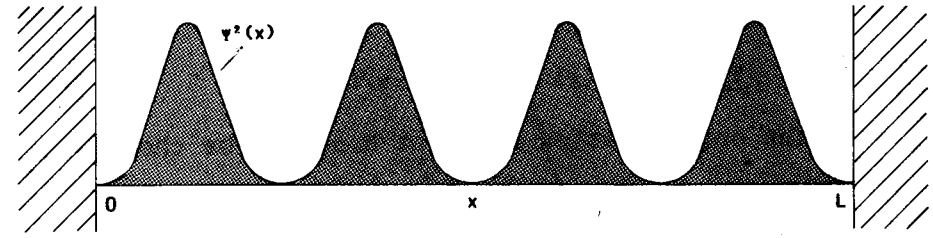
$$= (2/L)\times(L/4) = \tfrac{1}{2}$$

The total probability of the particle being found on the left is therefore

(C) $P_{left} = 0.5$

21 THE PROBABILITY OF FINDING THE PARTICLE ANYWHERE IN THE VESSEL

The probability is the total area shaded:



The area is the following integral:

(A) $$\int_0^L \Psi(x)^2 dx = (2/L)\int_0^L \sin^2(4\pi x/L) = (2/L)\times(L/2) = 1$$

The probability of finding the particle somewhere between x = 0 and x = L is therefore

(B) $P_{somewhere} = 1.$

In the case of the wavefunction

$$\Psi(x) = \boxed{(2/L)^{\frac{1}{2}}} \sin(4\pi x/L)$$

this is the normalization constant which guarantees that $P_{somewhere} = 1.$

22 AN EXAMPLE OF NORMALIZING A WAVEFUNCTION

Suppose $\Psi_{\text{unnormalized}}(x) = \sin(\pi x/L)$

and we know that the particle is certainly somewhere between $x = 0$ and $x = L$ (the walls of the container). Write

$$\Psi_{\text{normalized}}(x) = N \sin(\pi x/L).$$

Then the normalization constant N has to be chosen so that

$$\int \Psi^2_{\text{normalized}}\, dx = 1.$$

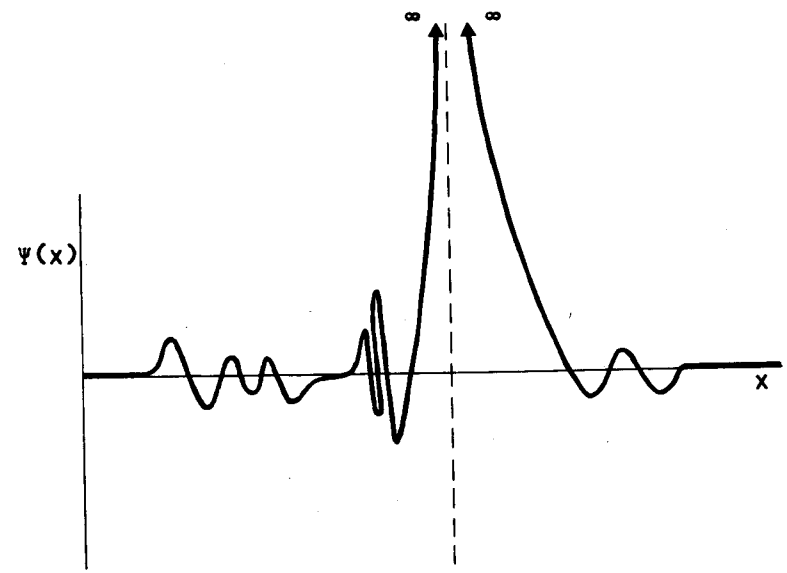
That is, we require

$$\begin{aligned} 1 &= N^2 \int_0^L \sin^2(\pi x/L)\,dx \\ &= N^2\{\tfrac{1}{2}x - (L/4\pi)\sin(2\pi x/L)\}\Big|_0^L \\ &= N^2\{[\tfrac{1}{2}L - (L/4\pi)\sin(2\pi)] - [0]\} \\ &= \tfrac{1}{2}LN^2. \end{aligned}$$

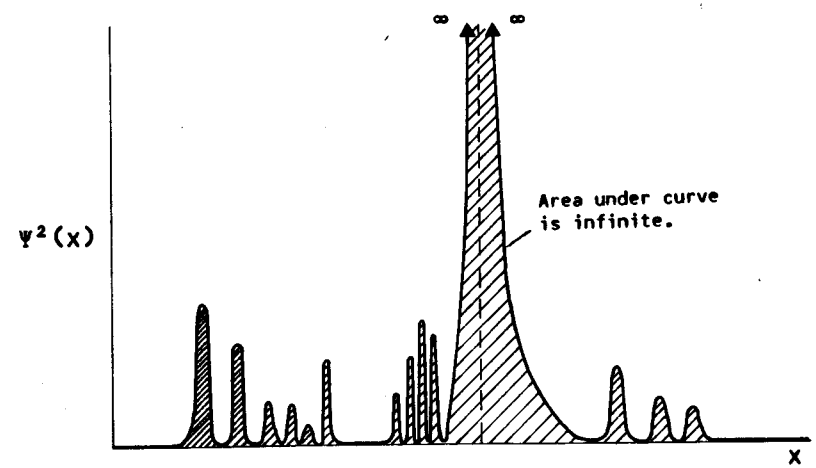
Therefore, we have to set $N = (2/L)^{\frac{1}{2}}$.

You should go on to show that for wavefunctions of the form $\sin(n\pi x/L)$, $n = 1, 2, 3, \ldots$, the normalization constant is always $(2/L)^{\frac{1}{2}}$ whatever the value of n.

23 AN UNACCEPTABLE WAVEFUNCTION

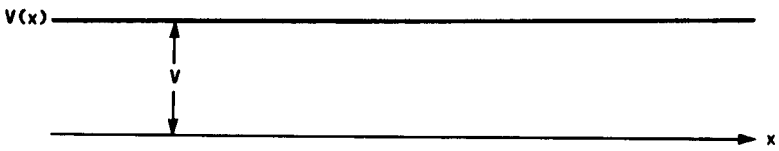


and its (unacceptable) probability density



24 THE RELATION BETWEEN KINETIC ENERGY AND CURVATURE

Consider a system in which the potential energy of the particle is independent of position:



The Schrödinger equation is

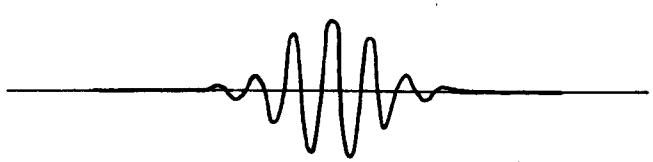
(A) $(-\hbar^2/2m)(d^2\Psi/dx^2) + V\Psi(x) = E\Psi(x)$

(B) $d^2\Psi/dx^2 = -(2m/\hbar^2)\underbrace{(E-V)}_{\boxed{\text{Kinetic energy}}}\Psi(x)$

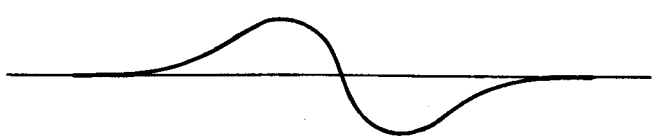
(C) $\underbrace{d^2\Psi/dx^2}_{\boxed{\text{Curvature}}} = -(2m/\hbar^2) \times (K.E.) \times \Psi(x)$

That is: **High curvature implies high kinetic energy.**

A particle with a wavefunction like this

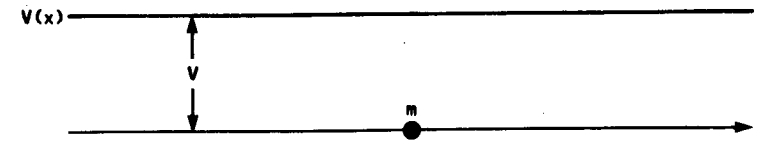


has a higher kinetic energy than one with a wavefunction like this:



25 THE QUANTUM MECHANICS OF FREE TRANSLATION

The potential energy is constant everywhere:



The Schrödinger equation is

(A) $(-\hbar^2/2m)(d^2\Psi/dx^2) + V\Psi(x) = E\Psi(x)$.

The general form of the solution is either

(B) $\Psi(x) = A \cos kx + B \sin kx$

or (B') $\Psi(x) = C\, e^{ikx} + D\, e^{-ikx}$

where $k = \sqrt{\{(2m/\hbar^2)(E-V)\}}$

and A, B and C, D are constants which have values determined by the boundary conditions we impose.

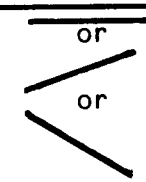
26 THE COMPUTER FOR UNFOLDING WAVEFUNCTIONS: THE BASIS

The Schrödinger equation can be written in the form

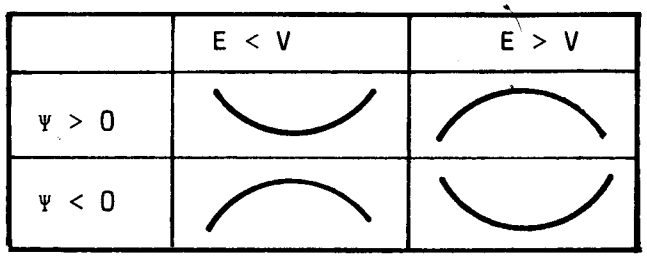
(A) $d^2\Psi/dx^2 = (2m/\hbar^2)(V-E)\Psi(x)$

(B) Sign of the curvature = Sign of V−E × Sign of Ψ

The sign of the curvature means the following:

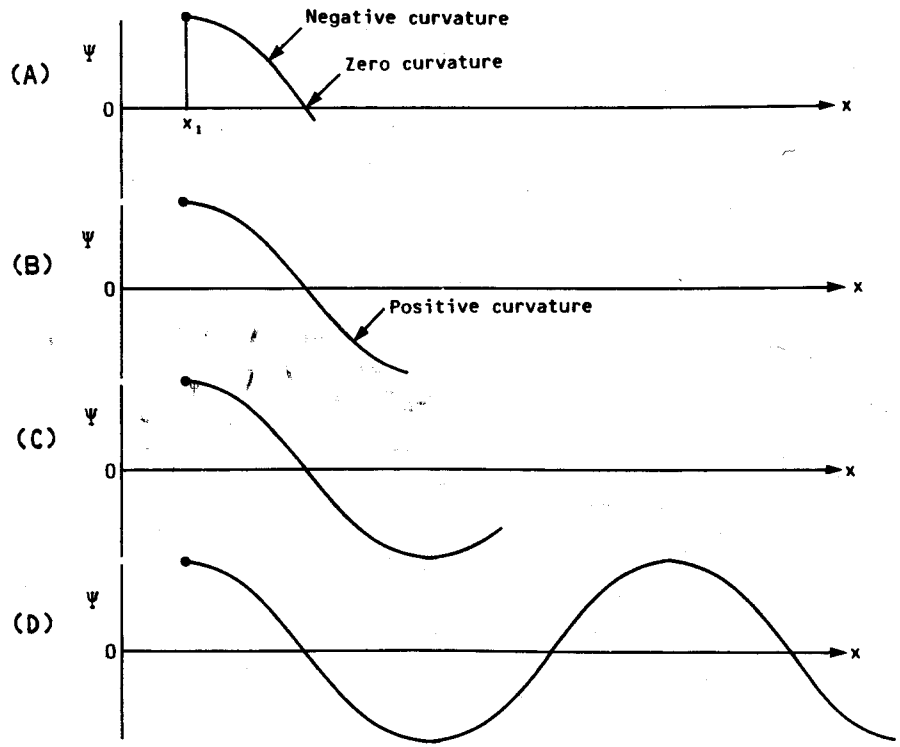
Negative	Zero	Positive
		

27 THE COMPUTER



You should note that the magnitude of the curvature depends on both the magnitude of E−V (i.e. the kinetic energy) and the amplitude of the wavefunction at the point of interest: see (A) in the last frame.

28 THE FIRST APPLICATION: THE FREE PARTICLE



29 THE WAVELENGTH OF THE WAVEFUNCTION OF A FREE PARTICLE

We already have the solution

(A) $\Psi(x) = A \cos kx + B \sin kx, \quad k = \sqrt{\{(2m/\hbar^2)(E-V)\}}$

Compare this to the expression for a wave of wavelength λ:

$(x) = A \cos(2\pi x/\lambda) + B \sin(2\pi x/\lambda)$

and conclude that the wavelength of the wavefunction is

(B) $\lambda = 2\pi/k = 2\pi/\sqrt{\{(2m/\hbar^2)(E-V)\}}$

$= h/\sqrt{\{2m(E-V)\}}.$

The kinetic energy E−V is related to the momentum p by

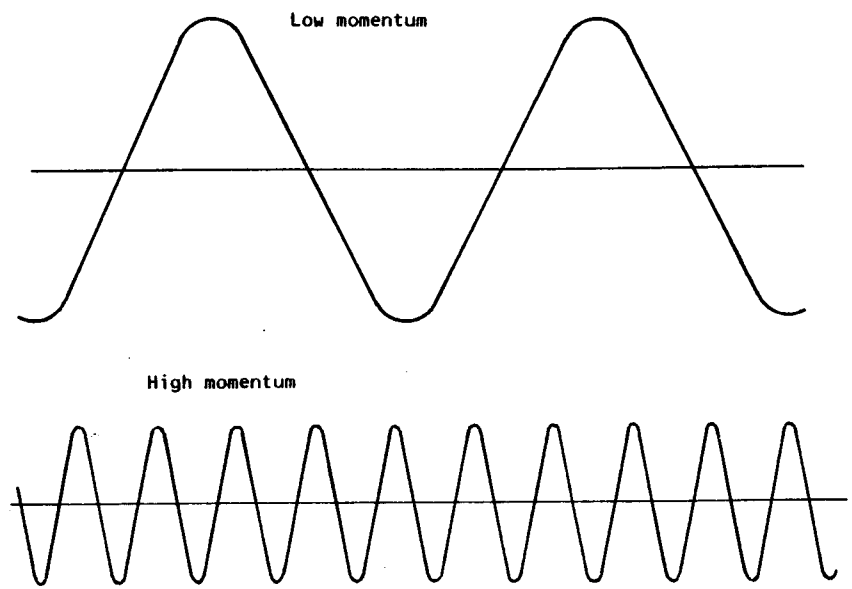
(C) $E-V = p^2/2m$

Therefore equation B can be written

(D) $\lambda = h/p$

which is de Broglie's relation.

30 WAVEFUNCTIONS FOR HIGH AND LOW MOMENTA



31 WAVEFUNCTIONS FOR STATES OF DEFINITE MOMENTUM

The basic solution is

(A) $\Psi(x) = A \cos kx + B \sin kx.$

The cosine and sine functions can be expressed as exponentials using the relations

(B) $\cos kx = \frac{1}{2}(e^{ikx} + e^{-ikx})$

$\sin kx = (1/2i)(e^{ikx} - e^{-ikx}).$

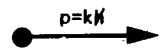
Therefore the wavefunction can also be written in the form

(C) $\Psi(x) = C\, e^{ikx} + D\, e^{-ikx}$

in which C is the combination $\frac{1}{2}(A-iB)$ and D is $\frac{1}{2}(A+iB)$.

The e^{ikx} wavefunction corresponds to linear momentum to the right while the other corresponds to momentum to the left:

32 WHERE IS THE PARTICLE WHEN IT IS IN A STATE OF DEFINITE MOMENTUM?

The wavefunction for the state of momentum 

is (A) $\Psi(x) = e^{ikx}$.

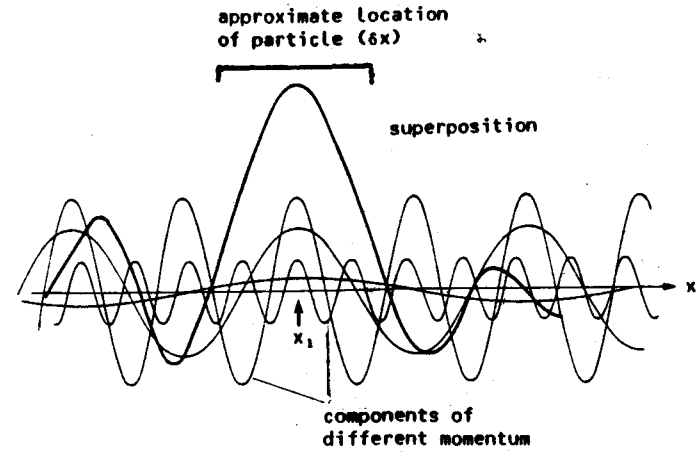
The probability density for finding the particle at x is

(B) $\Psi^*(x)\Psi(x) = (e^{ikx})^*(e^{ikx}) = (e^{-ikx})(e^{ikx}) = 1.$

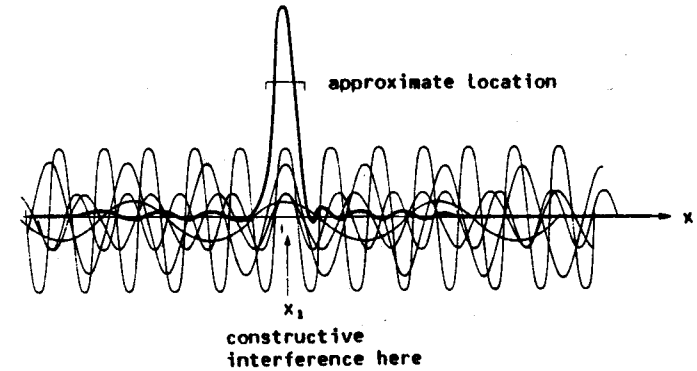
So, wherever we look, we stand the same chance of finding the particle! The location is totally unpredictable.

33 THE FORMATION OF A SUPERPOSITION OF WAVEFUNCTIONS: A WAVEPACKET

(A)



(B)



34 THE HEISENBERG UNCERTAINTY PRINCIPLE

Let δp be the spread of values of the momentum

δq be the spread of values of the location.

Then simultaneous determinations of the linear momentum along x and the location along the x coordinate are limited by

(A) $\delta p \delta q \geq \frac{1}{2}\hbar$.

(δp and δq are in fact the root mean square deviations of p and q from their mean values.)

These variables are complementary:

x and p_x, y and p_y, z and p_z,

J_x and J_y (angular momenta)

but these variables are not (and so can be determined simultaneously with arbitrary precision):

x and y, p_x and p_y, x and p_y, z and p_x,

$J^2 (= J_x^2 + J_y^2 + J_z^2)$ and J_z.

35 THE EFFECT OF A FORCE

The Schrödinger equation is

(A) $(-\hbar^2/2m)(d^2\Psi/dx^2) + V(x)\Psi(x) = E\Psi(x)$.

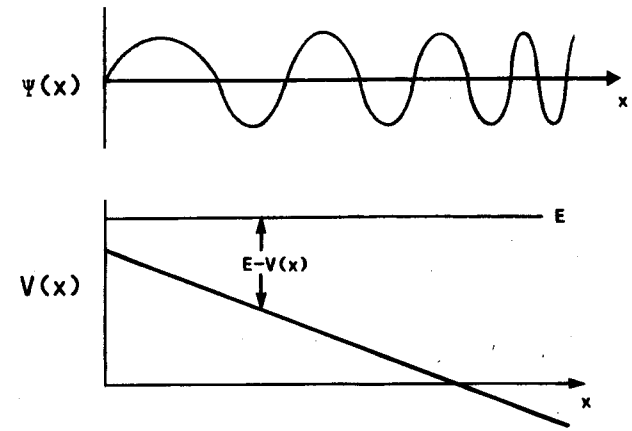
The potential energy of a particle subjected to a constant force f is

(B) $V(x) = -fx$.

The Schrödinger equation in this case is therefore

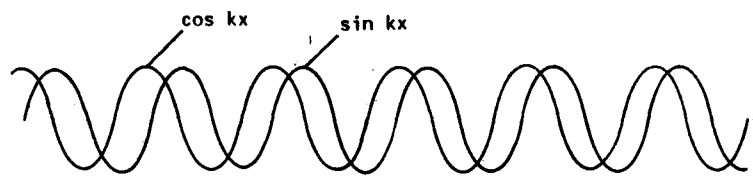
(C) $(-\hbar^2/2m)(d^2\Psi/dx^2) - fx\Psi(x) = E\Psi(x)$.

36 HOW A CONSTANT FORCE AFFECTS A WAVEFUNCTION

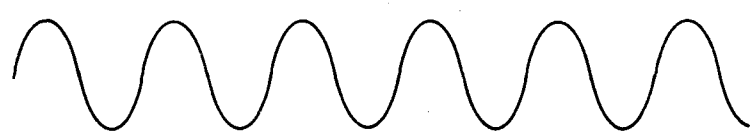


37 THE MOTION OF WAVEPACKETS - DEPICTING A WAVEFUNCTION FOR MOMENTUM

The wavefunction for a particle in a definite state of linear momentum is $\Psi(x) = e^{ikx} = \cos kx + i \sin kx$. This complex function could be drawn as follows:

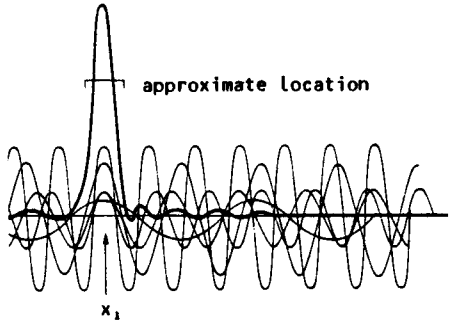


But thinking about the two components simultaneously is too troublesome, and so from now on we shall draw only the real component. The wavefunction for this state of momentum will therefore be drawn as follows:

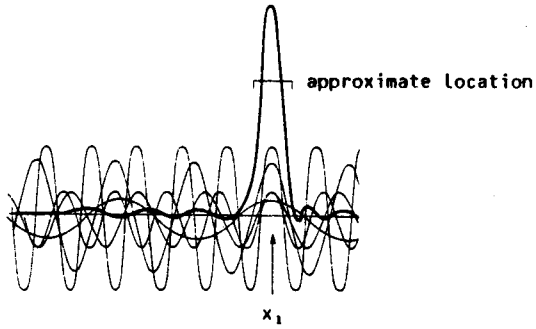


38 THE MOTION OF A WAVEPACKET

Initially the wavepacket looks like this:

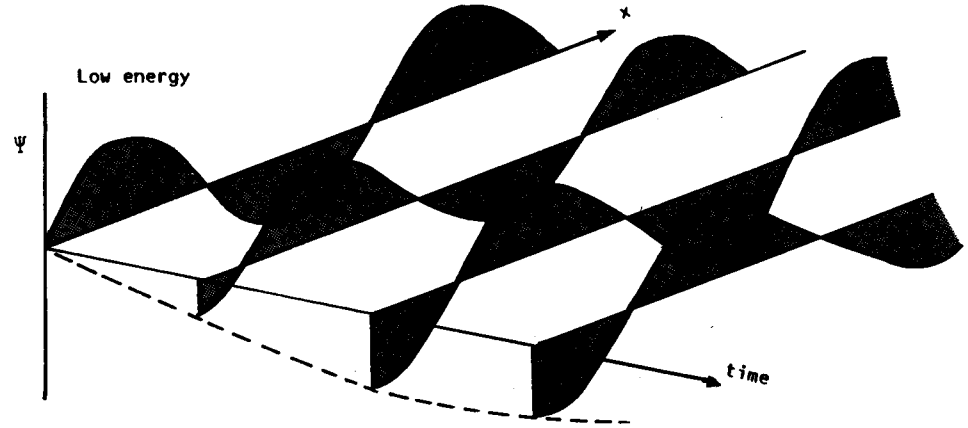


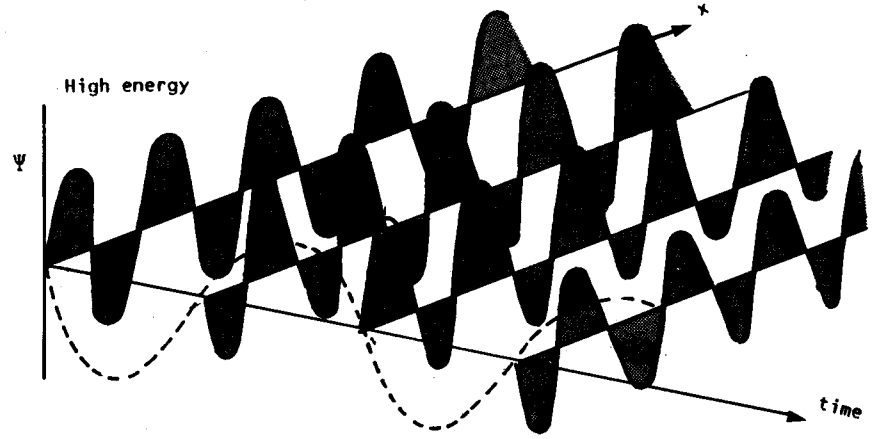
Later, the position of constructive interference has moved:



39 THE MOTION OF WAVEPACKETS: THE TIME-DEPENDENCE OF THE COMPONENTS

Wavefunctions oscillate in time: the greater their energy the faster they oscillate. We can illustrate this for a low energy and a high energy wavefunction as follows:

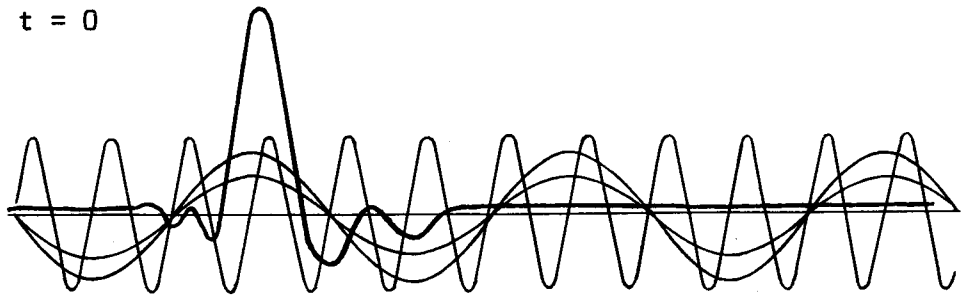




40 THE MOTION OF A WAVEPACKET IN THE PRESENCE OF A FORCE

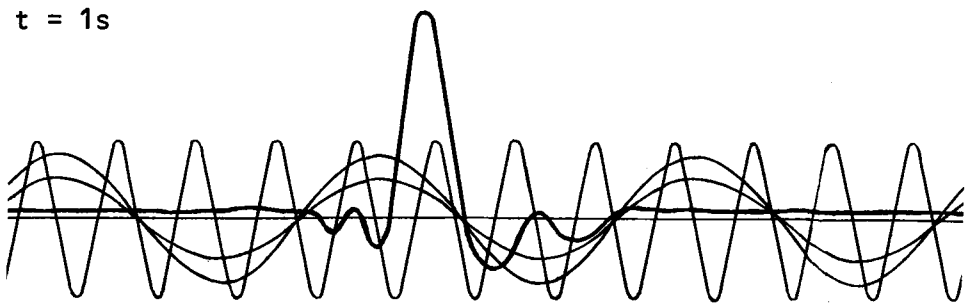
Initially the wavepacket looks like this:

t = 0



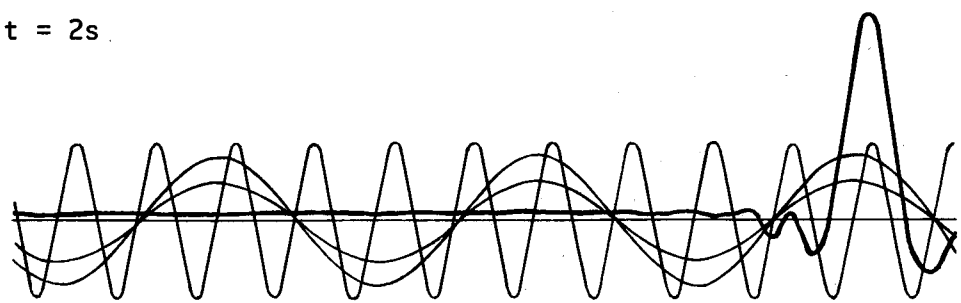
Later, the position of constructive interference has moved:

t = 1s

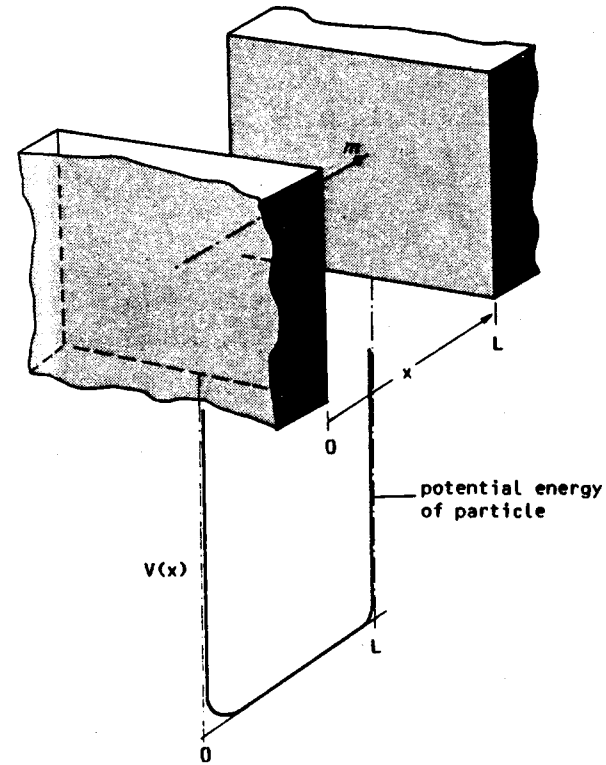


Later still, it is moving faster:

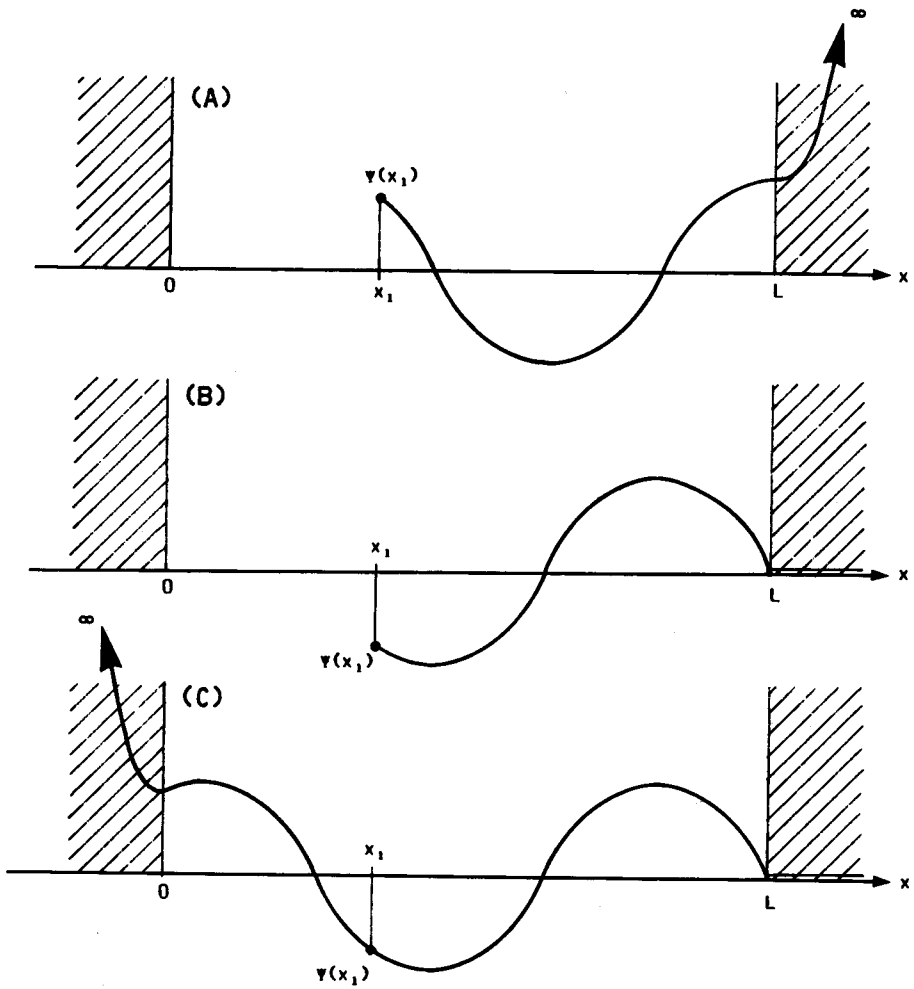
t = 2s



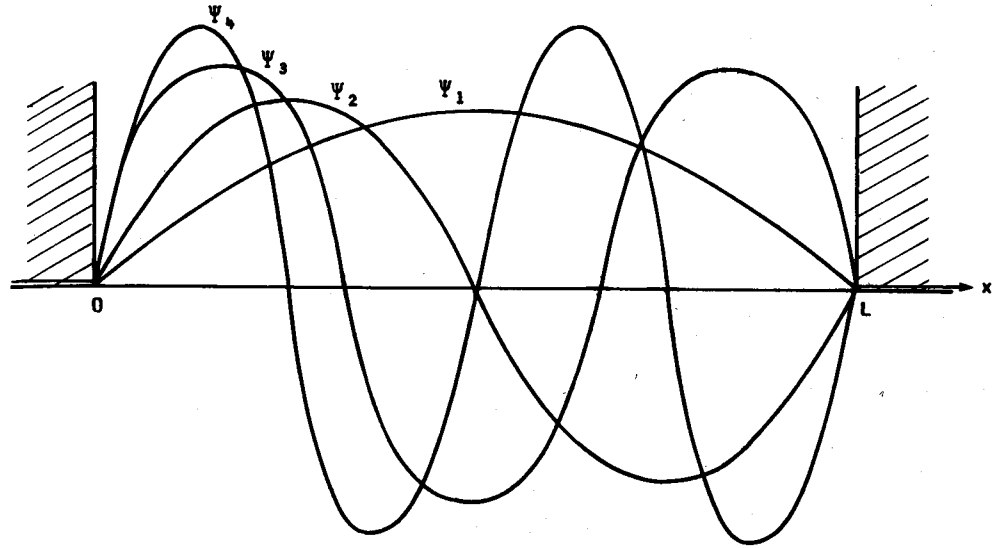
41 THE WAVEFUNCTIONS FOR A PARTICLE IN A 1-DIMENSIONAL BOX. (1) THE SYSTEM



42 THE WAVEFUNCTIONS FOR A PARTICLE IN A 1-DIMENSIONAL BOX: (2) THEIR CONSTRUCTION



43 THE WAVEFUNCTIONS FOR A PARTICLE IN A 1-DIMENSIONAL BOX. (3) THE ACCEPTABLE ONES



44 THE PERMITTED ENERGIES OF A PARTICLE CONFINED IN A BOX

The kinetic energy and the momentum are related by

(A) $E = p^2/2m$.

The momentum is related to the wavelength by

(B) $p = h/\lambda$.

The wavelengths are confined to the values (see the last frame)

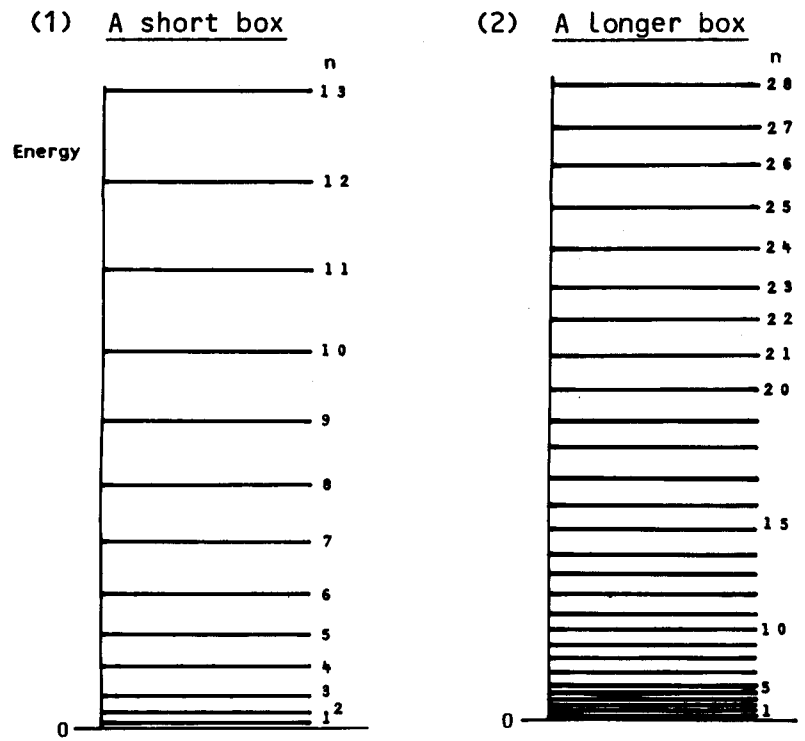
(C) $\lambda = 2L, L, 2L/3, 2L/4, 2L/5, \ldots$

Therefore the energies are confined to the values

(D) $E = h^2/2m\lambda^2 = h^2/8mL^2, 4h^2/8mL^2, 9h^2/8mL^2, \ldots$

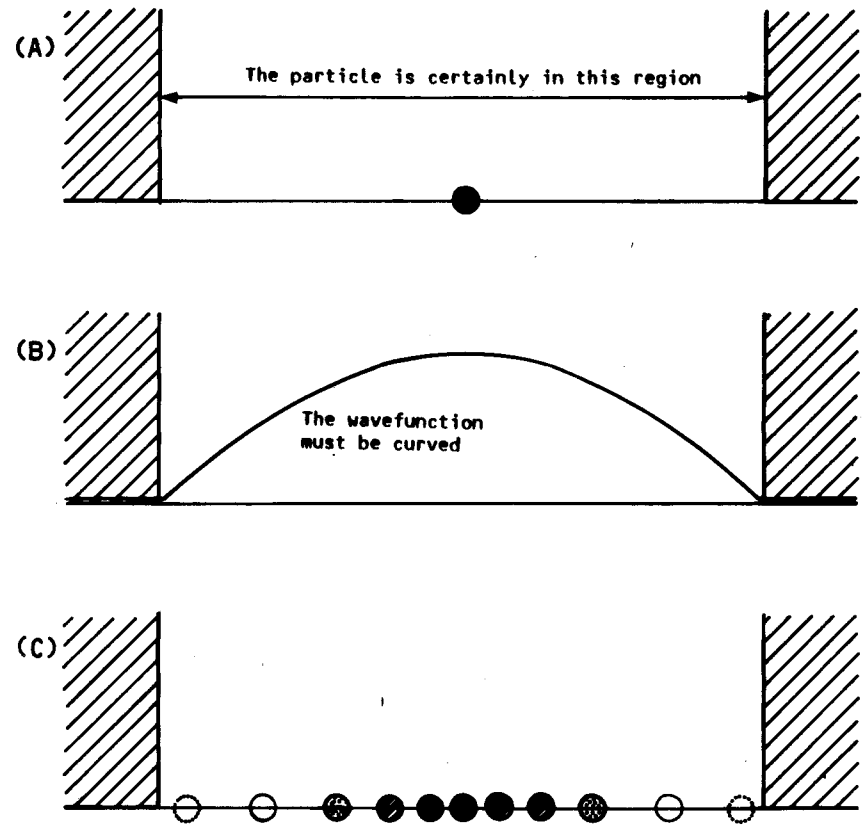
$= n^2(h^2/8mL^2), n = 1, 2, 3, \ldots$

45 THE SPECTRUM OF ENERGY LEVELS FOR A PARTICLE IN A BOX



46 THE ZERO POINT ENERGY

The lowest possible energy is $E = h^2/8mL^2$.



47 SUMMARY OF THE QUANTUM MECHANICS OF TRANSLATIONAL MOTION

(1) The translational energy is not quantized when the particle is able to move in an unbounded region of space.

(2) The wavelength of a free particle's wavefunction is related to its momentum by the de Broglie relation, $\lambda = h/p$.

(3) When a particle is confined between two walls its wavefunction is a sine function, and the only acceptable states are those in which an integral number of half-wavelengths can fit into the container.

(4) As a consequence of the boundaries, the translational energies of a confined particle are quantized, with only the energies $n^2(h^2/8mL^2)$ being allowed.

(5) There is an irremovable zero point energy of magnitude $h^2/8mL^2$.

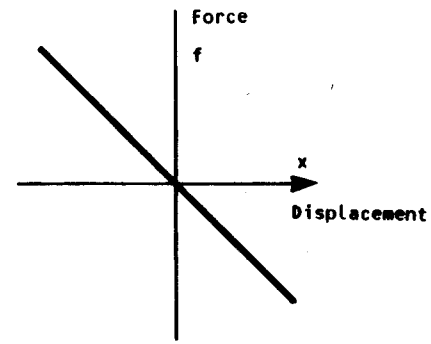
48 THE QUANTUM MECHANICS OF VIBRATION: THE SIMPLE HARMONIC OSCILLATOR

A particle undergoes simple harmonic motion when it is subjected to a restoring force that is proportional to its displacement:

Restoring force $\propto$ Displacement

(A) $f = -kx$

the force constant.

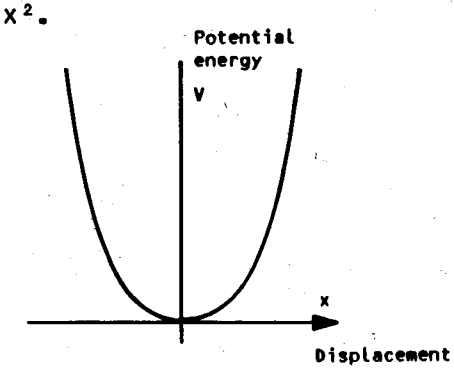


The force is the negative slope of the potential energy:

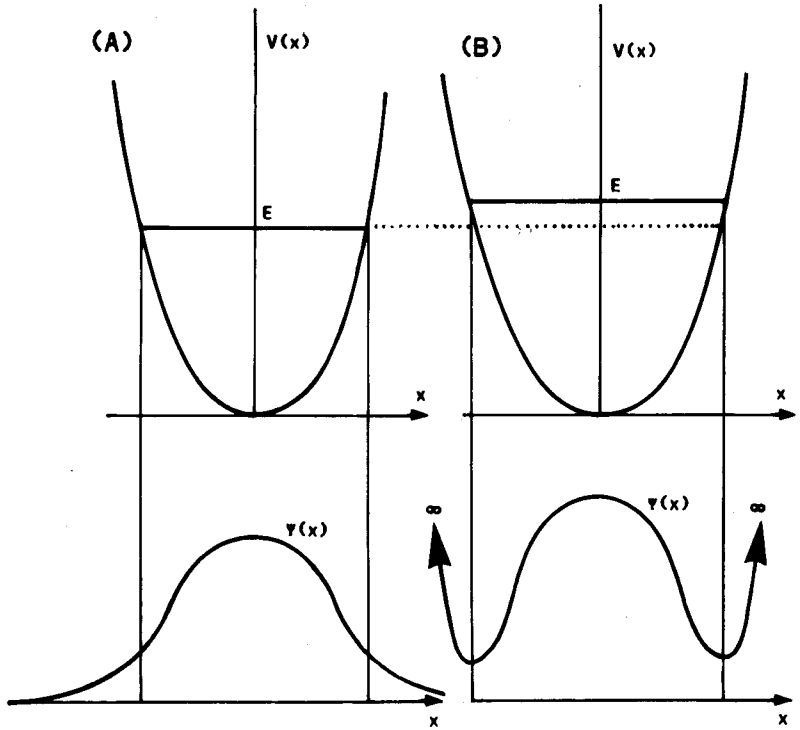
(B) $f = -dV/dx$.

Therefore, in the case of a harmonic oscillator, the potential energy at a displacement x is

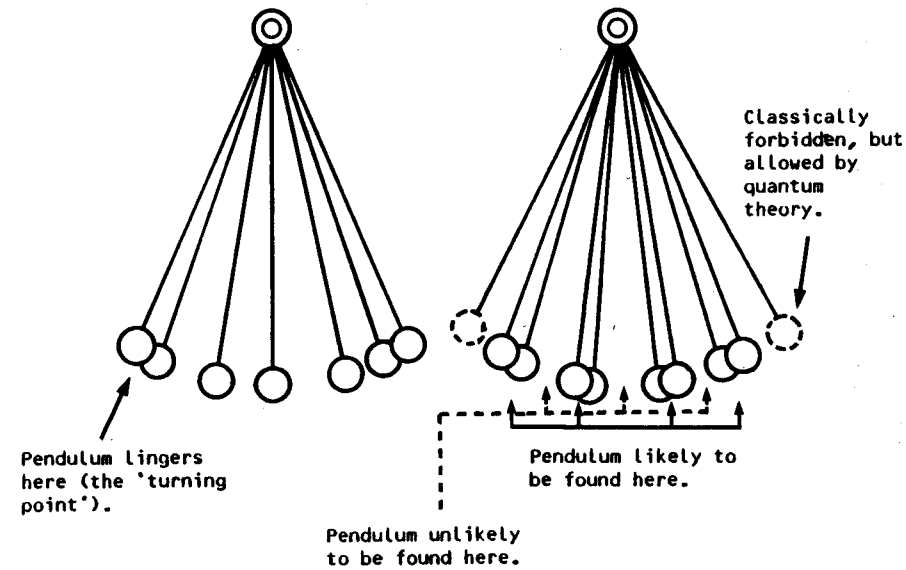
(C) $V(x) = \frac{1}{2}kx^2$.



49 HARMONIC OSCILLATOR WAVEFUNCTIONS: UNFOLDING THE SOLUTIONS



50 THE NON-CLASSICAL BEHAVIOUR OF A QUANTUM HARMONIC OSCILLATOR



51 THE ENERGY LEVELS OF A HARMONIC OSCILLATOR

The energies permitted are

(A) $E_n = (n+\frac{1}{2})\hbar\omega, \quad n = 0, 1, 2, \ldots$

$\omega = \sqrt{(k/m)}$

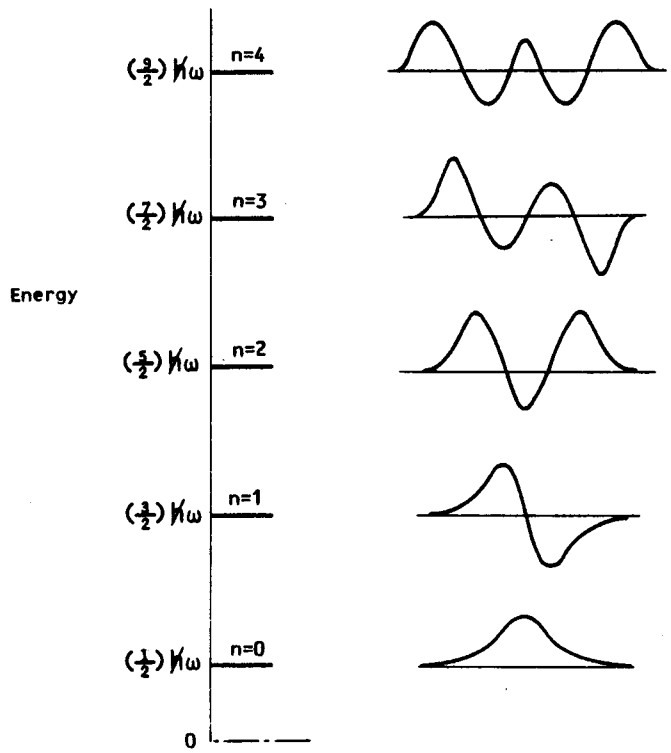
Note that the frequency of the oscillator is

(B) $\nu = \omega/2\pi = (1/2\pi)\sqrt{(k/m)}.$

There is a zero point energy

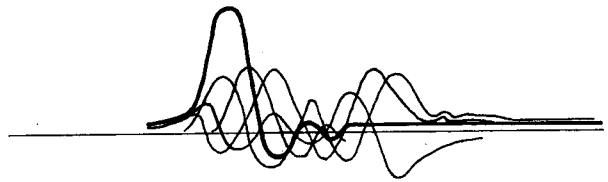
(C) $E_0 = \frac{1}{2}\hbar\omega = \frac{1}{2}h\nu.$

52 THE WAVEFUNCTIONS AND ENERGY LEVELS OF A HARMONIC OSCILLATOR

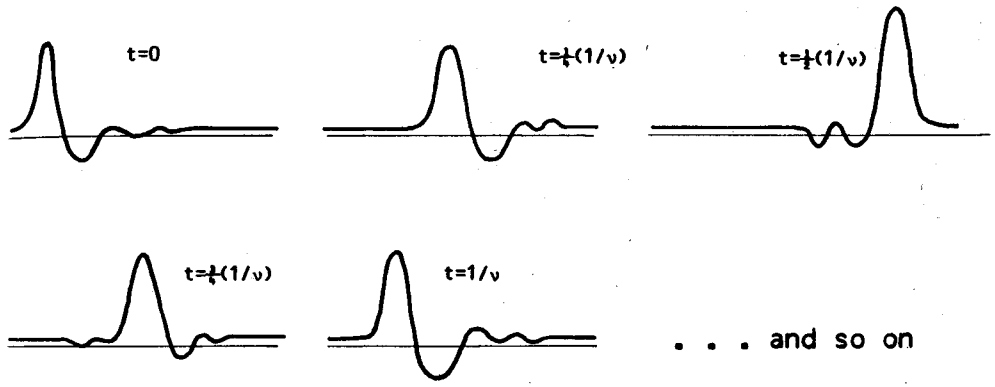


53 A HARMONIC OSCILLATOR WAVEPACKET

A wavepacket constructed like this:

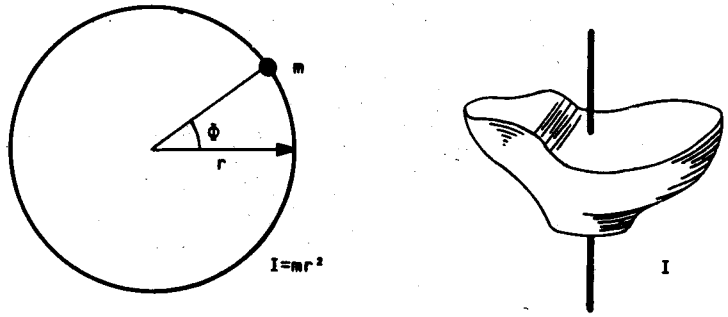


evolves in time like this:

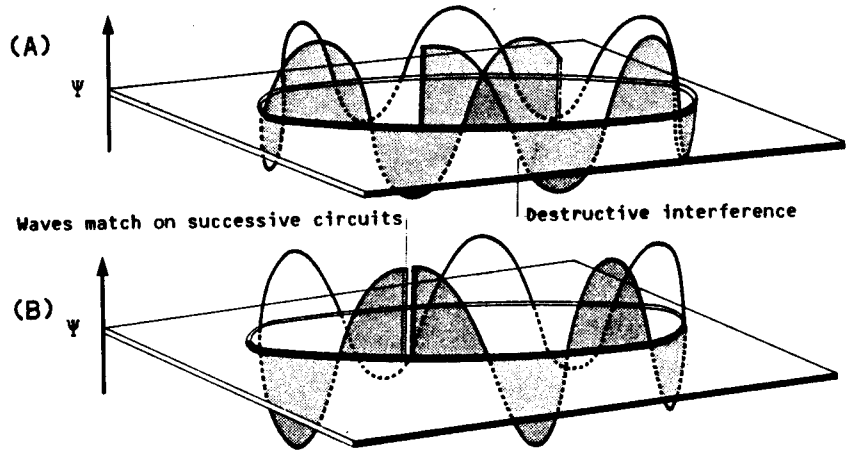


. . . and so on

54 THE PARTICLE ON A RING



55 ACCEPTABLE AND UNACCEPTABLE WAVEFUNCTIONS FOR A PARTICLE ON A RING



56 THE ENERGY LEVELS OF A PARTICLE ON A RING: (1) THE SIMPLE APPROACH

The energy of the particle is its kinetic energy,

(A) $E = p^2/2m$.

The de Broglie relation $p = h/\lambda$ lets this be written in terms of the wavelength of the particle's wavefunction as

(B) $E = h^2/2m\lambda^2$.

The only wavefunctions admissible are the ones with wavelengths

(C) $\lambda = \infty,\ 2\pi r,\ (2\pi r)/2,\ (2\pi r)/3,\ \ldots$

$= 2\pi r/m_\ell,\quad m_\ell$ an integer.

It follows that the energies are

(D) $E = \{(h^2/2(2\pi r)^2 m\}m_\ell^2 = (\hbar^2/2mr^2)m_\ell^2$

$= (\hbar^2/2I)m_\ell^2,\quad m_\ell$ an integer.

I is the moment of inertia of the system ($I = mr^2$). You will see from the work in the next frame that the permitted values of the quantum number m_ℓ are

$$m_\ell = 0,\ \pm1,\ \pm2,\ \ldots$$

57 THE ENERGY LEVELS OF A PARTICLE ON A RING: (2) A MORE FORMAL SOLUTION

The Schrödinger equation for the problem should be written in terms of the x, y coordinates of the particle because the motion is in two dimensions. But it is obviously more sensible to work in polar coordinates. As the radius is constant it turns out that the kinetic energy curvature term, $\partial^2/\partial x^2 + \partial^2/\partial y^2$ is simply $(1/r^2)(\partial^2/\partial\varphi^2)$. Therefore the equation is

$$(-\hbar^2/2m)(1/r^2)(d^2\Psi/d\varphi^2) = E\Psi(\varphi).$$

The solutions are

$$\Psi(\varphi) = (1/2\pi)^{\frac{1}{2}}\, e^{im_\ell\varphi},\quad E = (\hbar^2/2I)m_\ell^2$$

with $I = mr^2$. The factor $(1/2\pi)^{\frac{1}{2}}$ normalizes the wavefunctions to unity. Since Ψ must match at points separated by a complete revolution we require the condition $\Psi_{m_\ell}(\varphi) = \Psi_{m_\ell}(\varphi+2\pi)$ to be satisfied. But

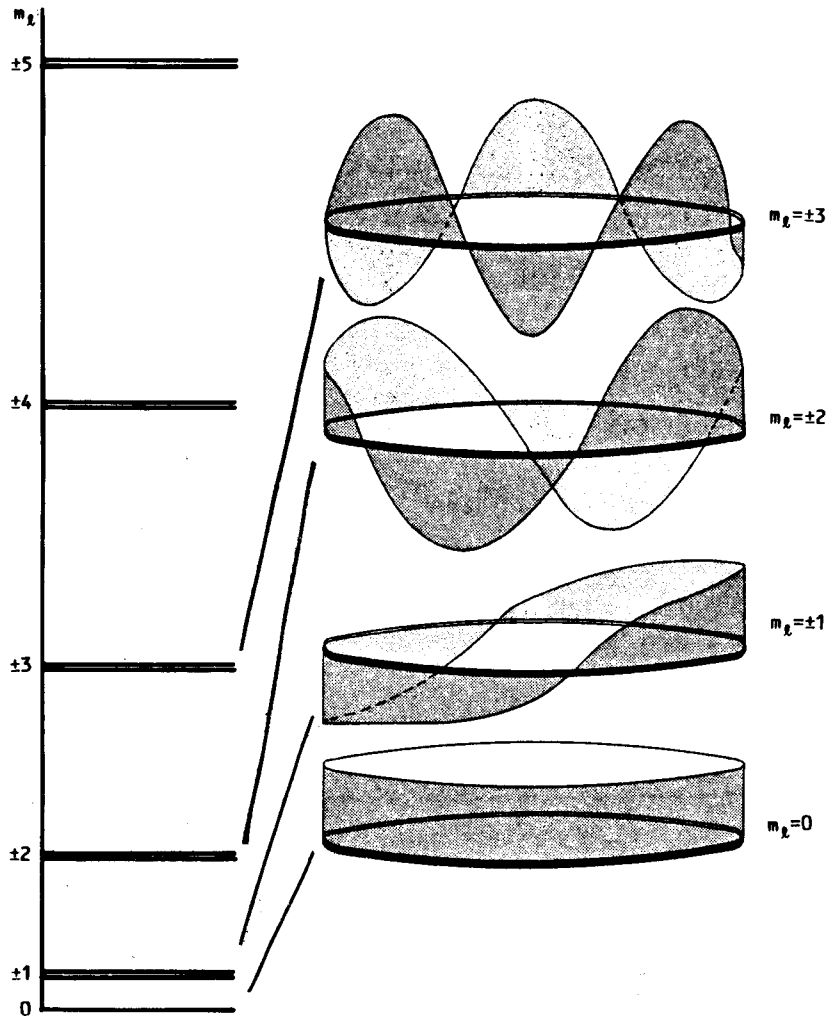
$$\Psi_{m_\ell}(\varphi+2\pi) = (1/2\pi)^{\frac{1}{2}}e^{im_\ell\varphi}e^{2\pi i m_\ell} = (e^{2\pi i m_\ell})\Psi_{m_\ell}(\varphi).$$

As $e^{i\pi} = -1$ it follows that m_ℓ must be a positive or negative integer in order to satisfy the repetition condition. Hence we conclude that $m_\ell = 0,\ \pm1,\ \pm2,\ \ldots$

The wavefunctions are

$$\Psi_{m_\ell}(\varphi) = (1/2\pi)^{\frac{1}{2}}e^{im_\ell\varphi} = (1/2\pi)^{\frac{1}{2}}(\cos m_\ell\varphi + i\sin m_\ell\varphi).$$

58 SOME OF THE ENERGY LEVELS AND WAVEFUNCTIONS FOR A PARTICLE ON A RING



59 THE QUANTIZATION OF ANGULAR MOMENTUM

The magnitude of the angular momentum in classical mechanics is

(A) $J = mvr.$

The kinetic energy of a particle of mass m and speed v is

(B) $E = \frac{1}{2}mv^2 = \frac{1}{2}(mvr)^2/mr^2 = \frac{1}{2}J^2/mr^2.$

Since the moment of inertia is $I = mr^2$ this may be written

(C) $E = J^2/2I.$

Compare this with the quantum expression

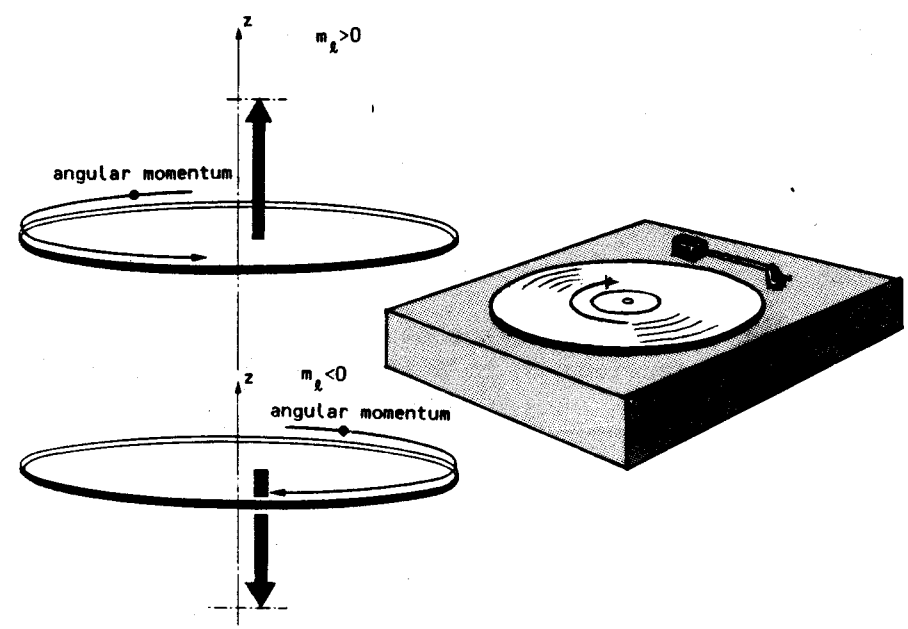
(D) $E = m_\ell^2(\hbar^2/2I)$

and conclude that

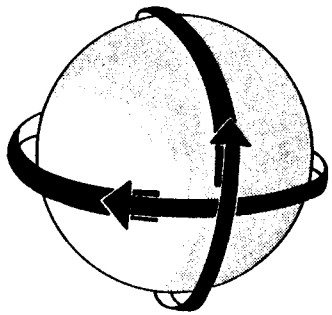
(E) $J = m_\ell\hbar,$

which implies that the angular momentum (about the z-axis) is quantized and limited to the values $0, \pm\hbar, \pm2\hbar, \ldots$

60 THE SIGNIFICANCE OF THE SIGN OF m_ℓ



61 MOTION IN THREE DIMENSIONS: THE PARTICLE CAN MIGRATE OVER THE SURFACE OF A SPHERE



62 THE QUANTUM MECHANICS OF THREE-DIMENSIONAL ROTATION

(1) The energy of a rotating body (of moment of inertia inertia I) is quantized and limited to the values

(A) $E_\ell = \ell(\ell+1)(\hbar^2/2I), \quad \ell = 0, 1, 2, \ldots$

(2) The magnitude of the angular momentum is quantized and is confined to the values

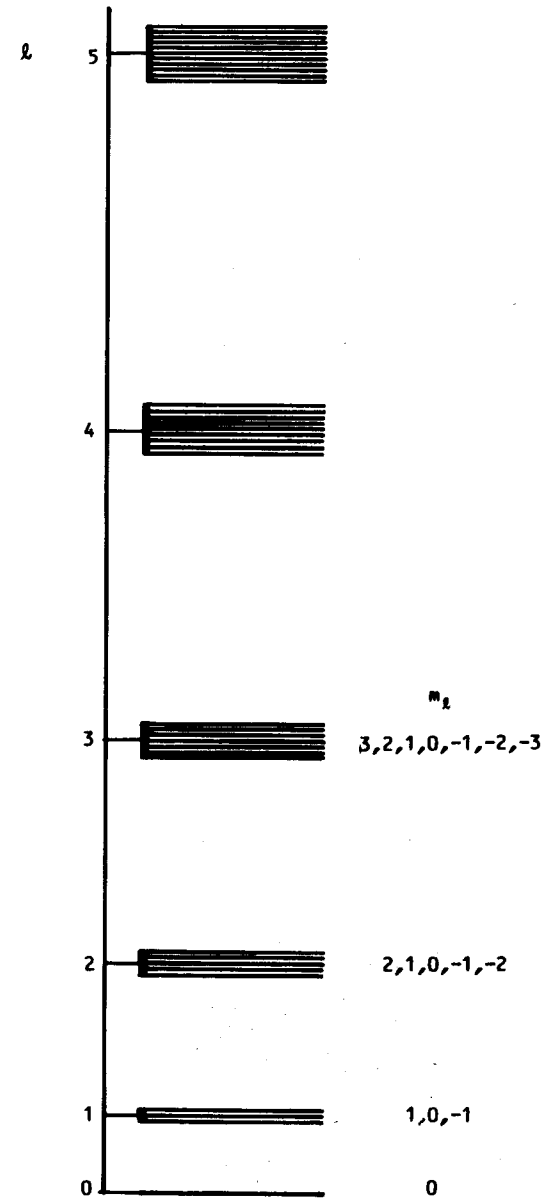
(B) $J = \sqrt{\ell(\ell+1)}\,\hbar, \quad \ell = 0, 1, 2, \ldots$

(3) The projection of the angular momentum on an axis is also quantized and limited to the values

(C) $J_z = m_\ell\hbar, \quad m_\ell = 0, \pm1, \pm2, \ldots,$.

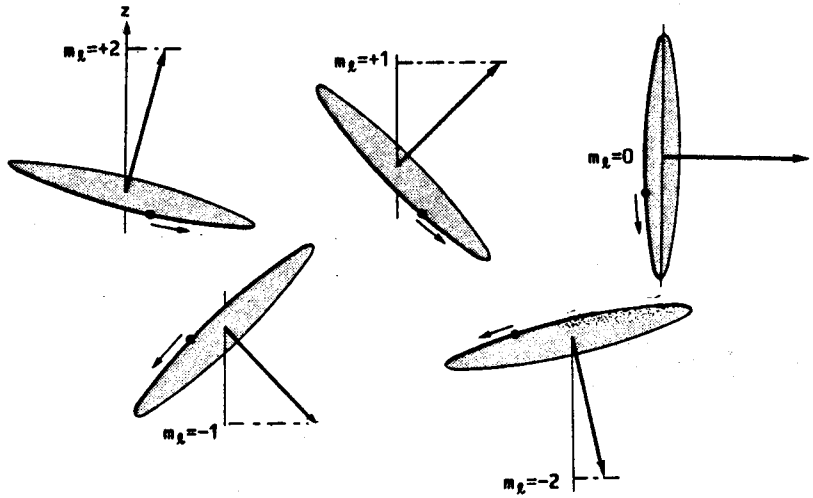
(Note that for a given value of ℓ there are $2\ell+1$ permitted projections on to a selected axis.)

63 THE ROTATIONAL ENERGY LEVELS OF AN OBJECT OF MOMENT OF INERTIA I

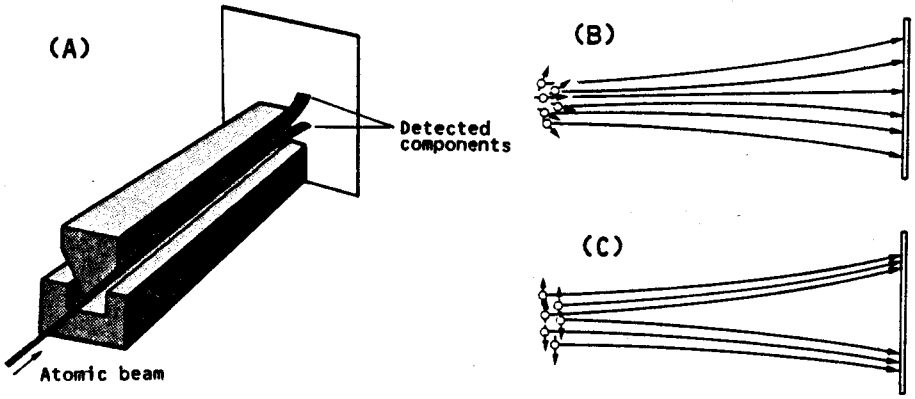


64 SPACE QUANTIZATION

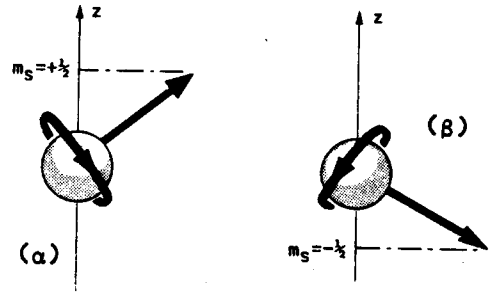
Take, for instance, $\ell = 2$: then the magnitude of the angular momentum is $\sqrt{2(2+1)}\,\hbar = \sqrt{6}\,\hbar$ and the permitted projections are $0, \pm\hbar, \pm 2\hbar$.



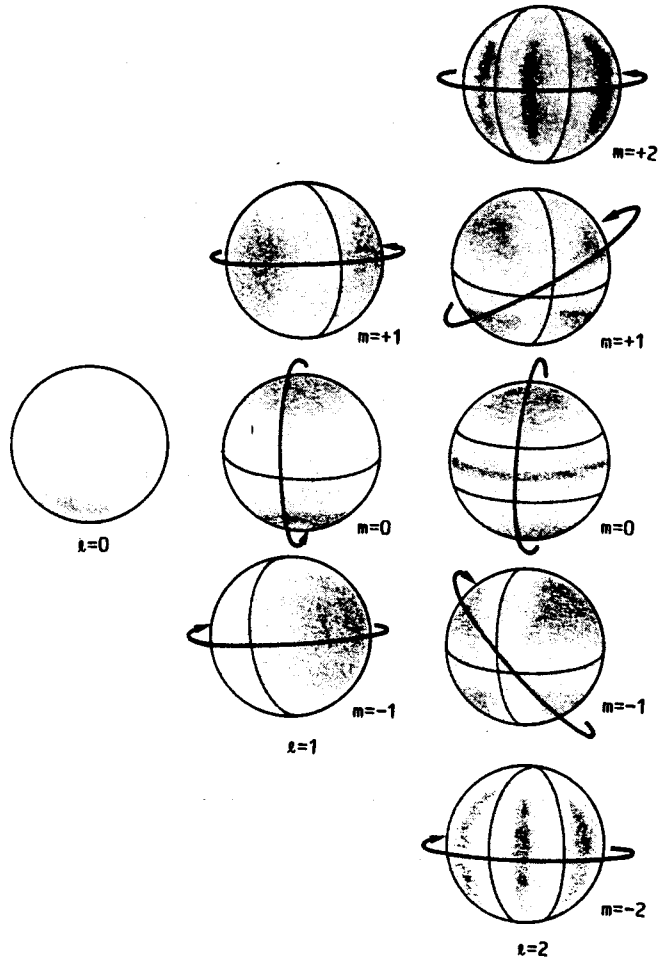
65 THE STERN-GERLACH EXPERIMENT



66 THE TWO PERMITTED PROJECTIONS OF AN ELECTRON SPIN

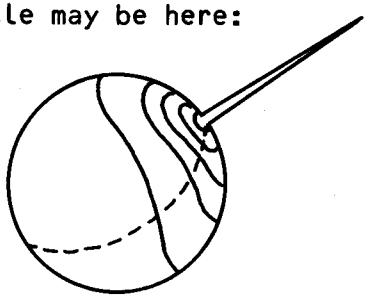


67 THE WAVEFUNCTIONS FOR ROTATIONAL MOTION

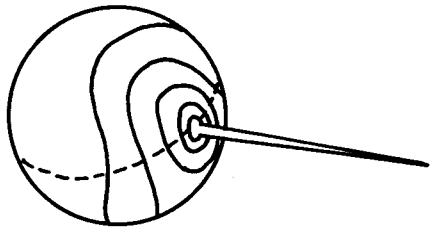


68 THE MOTION OF A WAVEPACKET FOR A ROTATING SYSTEM

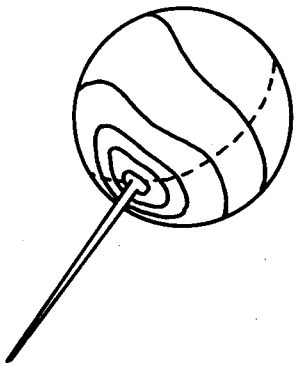
Initially the particle may be here:



but later it will be found here:



and later still here:



FURTHER READING

If you would like to extend further your understanding of the topics that have been discussed in this Chemistry Cassette the following books will prove useful.

Basic ideas about quantum theory are described in a non-mathematical way, and arranged like an encyclopedia, in
QUANTA: A HANDBOOK OF CONCEPTS
by P W ATKINS, Oxford University Press, 1974.

The background to the tape is more fully discussed, but in a similar style in
PHYSICAL CHEMISTRY
by P W ATKINS, Oxford University Press and W H Freeman & Company, 1978.
(Many of the illustrations were drawn from Chapter 13 of this book.)

A more detailed account of the material, with chemical applications, is given in
MOLECULAR QUANTUM MECHANICS
by P W ATKINS, Oxford University Press, 1970.

Good material is to be found in
THE STRANGE STORY OF THE QUANTUM
by B HOFFMAN, Dover Books, 1959

THE CONCEPTUAL DEVELOPMENT OF QUANTUM MECHANICS
by B JAMMER, McGraw-Hill, 1965

BLACK-BODY THEORY AND THE QUANTUM DISCONTINUITY, 1894 1894 - 1912
by T S KUHN, Oxford University Press, 1978.

Careful accounts of the physical interpretation of quantum phenomena will be found in
THE PHYSICAL PRINCIPLES OF THE QUANTUM THEORY
by W HEISENBERG, Dover Books, 1930

LECTURES IN PHYSICS
by R P FEYNMAN, R B LEIGHTON and M SANDS, Freeman, 1963

QUANTUM THEORY
by D BOHM, Prentice Hall, 1951.

7. One wavefunction of a particle in a box of length L has the form $(2/L)^{\frac{1}{2}} \sin(\pi x/L)$. Let the box be 10 nm long. What is the probability of finding the particle

(a) between x = 4.95 nm and 5.05 nm;
(b) between x = 1.95 nm and 2.05 nm;
(c) between x = 9.90 nm and 10.00 nm;
(d) the right half of the box;
(e) the central third of the box?

8. The wavefunction for the lowest state of a harmonic oscillator has the form $\exp(-gx^2)$, where x is the displacement from equilibrium. Show that this function satisfies the Schrödinger equation for the oscillator, and find g in terms of the force constant and the mass. What is the energy of the oscillator in this state? What is its minimum excitation energy?

9. What are the minimum excitation energies of the following oscillators:

(a) a pendulum of length 1 m on the earth's surface;
(b) the 33 kHz quartz crystal of a watch;
(c) the bond between two oxygen atoms ($k = 1177\ N\ m^{-1}$)?

10. The following molecules absorb radiation at the wavenumbers listed:

HCl	2989.74 cm^{-1}
HBr	2649.72 cm^{-1}
HI	2309.53 cm^{-1}
CO	2170.21 cm^{-1}
NO	1904.03 cm^{-1}.

The transition is ascribable to vibrational excitations of the molecules. On the basis that wavenumber, σ, is inverse wavelength, and that the relevant mass is reduced mass

$$\mu = m_1 m_2/(m_1 + m_2)$$

m_1 and m_2 being the masses of the two atoms, find the force constants of the bonds and arrange the bonds in order of increasing stiffness.

11. The rotation of an HI molecule can be visualised as the orbiting of the hydrogen atom at a distance of 160 pm from the virtually stationary iodine atom. Suppose the molecule rotates in only one plane. How much energy (in cm^{-1} and in kJ mol^{-1}) is needed to excite the stationary molecule into rotation?

12. Calculate the energies of the first four rotational levels of HI, allowing it to rotate in three dimensions about its centre of mass. Express your answer in cm^{-1} and kJ mol^{-1}. What are the degeneracies of the energy levels?

13. One wavefunction, $\Psi_{J,M}$, for full three-dimensional rotation is

$$\Psi_{3,3} = -\frac{1}{8}\,(35/\pi)^{\frac{1}{2}} \sin^2\vartheta \exp(3i\varphi).$$

Confirm that it is normalised to unity (take the integration over the surface of a sphere). To what energy does the state correspond? Sketch the real and imaginary components of the function.

14. In the vector model of angular momentum, a state with quantum numbers ℓ, m_ℓ (or s, m_s) is represented by a vector of length $\sqrt{\{\ell(\ell+1)\}}$ units and a z-component of m units. Draw scale diagrams for the state of an electron with

(a) $s = \frac{1}{2}$, $m_s = \frac{1}{2}$
(b) $\ell = 1$, $m_\ell = +1$
(c) $\ell = 2$, $m_\ell = 0$.

What is the half-angle of the cone of precession in terms of the quantum numbers ℓ and m_ℓ? Show that the minimum possible angle approaches zero as ℓ approaches infinity (so that only then can the angular momentum lie exactly along z).

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