PRINCIPLES OF QUANTUM MECHANICS

as Applied to Chemistry and Chemical Physics

DONALD D. FITTS

University of Pennsylvania

CAMBRIDGE
UNIVERSITY PRESS

PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS
The Edinburgh Building, Cambridge CB2 2RU, UK www.cup.cam.ac.uk
40 West 20th Street, New York, NY 10011-4211, USA www.cup.org
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

First published 1999

Printed in the United Kingdom at the University Press, Cambridge

Typeset in Times 11/14pt, in 3B2 [KT]

A catalogue record for this book is available from the British Library

Library of Congress Cataloguing in Publication data
Fitts, Donald D., 1932–
Principles of quantum mechanics: as applied to chemistry and
chemical physics / Donald D. Fitts.
p. cm.
Includes bibliographical references and index
ISBN 0 521 65124 7 (hc.). – ISBN 0 521 65841 1 (pbk.)
1. Quantum chemistry. I. Title.
QD462.F55 1999
541.2′8–dc21 98-39486 CIP

ISBN 0 521 65124 7 hardback
ISBN 0 521 65841 1 paperback

Contents

1

The wave function

Quantum mechanics is a theory to explain and predict the behavior of particles such as electrons, protons, neutrons, atomic nuclei, atoms, and molecules, as well as the photon–the particle associated with electromagnetic radiation or light. From quantum theory we obtain the laws of chemistry as well as explanations for the properties of materials, such as crystals, semiconductors, superconductors, and superfluids. Applications of quantum behavior give us transistors, computer chips, lasers, and masers. The relatively new field of molecular biology, which leads to our better understanding of biological structures and life processes, derives from quantum considerations. Thus, quantum behavior encompasses a large fraction of modern science and technology.

Quantum theory was developed during the first half of the twentieth century through the efforts of many scientists. In 1926, E. Schrödinger interjected wave mechanics into the array of ideas, equations, explanations, and theories that were prevalent at the time to explain the growing accumulation of observations of quantum phenomena. His theory introduced the wave function and the differential wave equation that it obeys. Schrödinger's wave mechanics is now the backbone of our current conceptional understanding and our mathematical procedures for the study of quantum phenomena.

Our presentation of the basic principles of quantum mechanics is contained in the first three chapters. Chapter 1 begins with a treatment of plane waves and wave packets, which serves as background material for the subsequent discussion of the wave function for a free particle. Several experiments, which lead to a physical interpretation of the wave function, are also described. In Chapter 2, the Schrödinger differential wave equation is introduced and the wave function concept is extended to include particles in an external potential field. The formal mathematical postulates of quantum theory are presented in Chapter 3.

1.1 Wave motion

Plane wave

A simple stationary harmonic wave can be represented by the equation

$$\psi(x) = \cos \frac{2\pi x}{\lambda}$$

and is illustrated by the solid curve in Figure 1.1. The distance λ between peaks (or between troughs) is called the *wavelength* of the harmonic wave. The value of $\psi(x)$ for any given value of x is called the *amplitude* of the wave at that point. In this case the amplitude ranges from $+1$ to -1. If the harmonic wave is $A\cos(2\pi x/\lambda)$, where A is a constant, then the amplitude ranges from $+A$ to $-A$. The values of x where the wave crosses the x-axis, i.e., where $\psi(x)$ equals zero, are the *nodes* of $\psi(x)$.

If the wave moves without distortion in the positive x-direction by an amount x_0, it becomes the dashed curve in Figure 1.1. Since the value of $\psi(x)$ at any point x on the new (dashed) curve corresponds to the value of $\psi(x)$ at point $x - x_0$ on the original (solid) curve, the equation for the new curve is

$$\psi(x) = \cos \frac{2\pi}{\lambda}(x - x_0)$$

If the harmonic wave moves in time at a constant velocity υ, then we have the relation $x_0 = \upsilon t$, where t is the elapsed time (in seconds), and $\psi(x)$ becomes

$$\psi(x, t) = \cos \frac{2\pi}{\lambda}(x - \upsilon t)$$

Suppose that in one second, ν cycles of the harmonic wave pass a fixed point on the x-axis. The quantity ν is called the *frequency* of the wave. The velocity

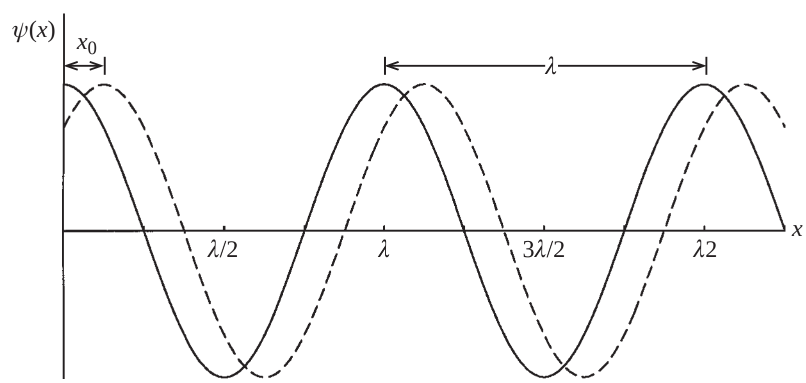

Figure 1.1 A stationary harmonic wave. The dashed curve shows the displacement of the harmonic wave by x_0.

υ of the wave is then the product of ν cycles per second and λ, the length of each cycle

$$\upsilon = \nu\lambda$$

and $\psi(x, t)$ may be written as

$$\psi(x, t) = \cos 2\pi\left(\frac{x}{\lambda} - \nu t\right)$$

It is convenient to introduce the *wave number* k, defined as

$$k \equiv \frac{2\pi}{\lambda} \tag{1.1}$$

and the *angular frequency* ω, defined as

$$\omega \equiv 2\pi\nu \tag{1.2}$$

Thus, the velocity υ becomes $\upsilon = \omega/k$ and the wave $\psi(x, t)$ takes the form

$$\psi(x, t) = \cos(kx - \omega t)$$

The harmonic wave may also be described by the sine function

$$\psi(x, t) = \sin(kx - \omega t)$$

The representation of $\psi(x, t)$ by the sine function is completely equivalent to the cosine-function representation; the only difference is a shift by $\lambda/4$ in the value of x when $t = 0$. Moreover, *any* linear combination of sine and cosine representations is also an equivalent description of the simple harmonic wave. The most general representation of the harmonic wave is the complex function

$$\psi(x, t) = \cos(kx - \omega t) + \mathrm{i}\sin(kx - \omega t) = \mathrm{e}^{\mathrm{i}(kx - \omega t)} \tag{1.3}$$

where i equals $\sqrt{-1}$ and equation (A.31) from Appendix A has been introduced. The real part, $\cos(kx - \omega t)$, and the imaginary part, $\sin(kx - \omega t)$, of the complex wave, (1.3), may be readily obtained by the relations

$$\mathrm{Re}\,[\mathrm{e}^{\mathrm{i}(kx - \omega t)}] = \cos(kx - \omega t) = \frac{1}{2}[\psi(x, t) + \psi^*(x, t)]$$

$$\mathrm{Im}\,[\mathrm{e}^{\mathrm{i}(kx - \omega t)}] = \sin(kx - \omega t) = \frac{1}{2\mathrm{i}}[\psi(x, t) - \psi^*(x, t)]$$

where $\psi^*(x, t)$ is the complex conjugate of $\psi(x, t)$

$$\psi^*(x, t) = \cos(kx - \omega t) - \mathrm{i}\sin(kx - \omega t) = \mathrm{e}^{-\mathrm{i}(kx - \omega t)}$$

The function $\psi^*(x, t)$ also represents a harmonic wave moving in the positive x-direction.

The functions $\exp[\mathrm{i}(kx + \omega t)]$ and $\exp[-\mathrm{i}(kx + \omega t)]$ represent harmonic waves moving in the negative x-direction. The quantity $(kx + \omega t)$ is equal to $k(x + \upsilon t)$ or $k(x + x_0)$. After an elapsed time t, the value of the shifted harmonic wave at any point x corresponds to the value at the point $x + x_0$ at time $t = 0$. Thus, the harmonic wave has moved in the negative x-direction.

The moving harmonic wave $\psi(x, t)$ in equation (1.3) is also known as a *plane wave*. The quantity $(kx - \omega t)$ is called the *phase*. The velocity ω/k is known as the *phase velocity* and henceforth is designated by v_{ph}, so that

$$v_{\text{ph}} = \frac{\omega}{k} \tag{1.4}$$

Composite wave

A composite wave is obtained by the addition or superposition of any number of plane waves

$$\Psi(x, t) = \sum_{j=1}^{n} A_j e^{i(k_j x - \omega_j t)} \tag{1.5}$$

where A_j are constants. Equation (1.5) is a Fourier series representation of $\Psi(x, t)$. Fourier series are discussed in Appendix B. The composite wave $\Psi(x, t)$ is not a moving harmonic wave, but rather a superposition of n plane waves with different wavelengths and frequencies and with different amplitudes A_j. Each plane wave travels with its own phase velocity $v_{\text{ph},j}$, such that

$$v_{\text{ph},j} = \frac{\omega_j}{k_j}$$

As a consequence, the profile of this composite wave changes with time. The wave numbers k_j may be positive or negative, but we will restrict the angular frequencies ω_j to positive values. A plane wave with a negative value of k has a negative value for its phase velocity and corresponds to a harmonic wave moving in the negative x-direction. In general, the angular frequency ω depends on the wave number k. The dependence of $\omega(k)$ is known as the *law of dispersion* for the composite wave.

In the special case where the ratio $\omega(k)/k$ is the same for each of the component plane waves, so that

$$\frac{\omega_1}{k_1} = \frac{\omega_2}{k_2} = \cdots = \frac{\omega_n}{k_n}$$

then each plane wave moves with the same velocity. Thus, the profile of the composite wave does not change with time even though the angular frequencies and the wave numbers differ. For this *undispersed wave motion*, the angular frequency $\omega(k)$ is proportional to $|k|$

$$\omega(k) = c|k| \tag{1.6}$$

where c is a constant and, according to equation (1.4), is the phase velocity of each plane wave in the composite wave. Examples of undispersed wave motion are a beam of light of mixed frequencies traveling in a vacuum and the undamped vibrations of a stretched string.

For *dispersive wave motion*, the angular frequency $\omega(k)$ is not proportional to $|k|$, so that the phase velocity v_{ph} varies from one component plane wave to another. Since the phase velocity in this situation depends on k, the shape of the composite wave changes with time. An example of dispersive wave motion is a beam of light of mixed frequencies traveling in a dense medium such as glass. Because the phase velocity of each monochromatic plane wave depends on its wavelength, the beam of light is dispersed, or separated onto its component waves, when passed through a glass prism. The wave on the surface of water caused by dropping a stone into the water is another example of dispersive wave motion.

Addition of two plane waves

As a specific and yet simple example of composite-wave construction and behavior, we now consider in detail the properties of the composite wave $\Psi(x, t)$ obtained by the addition or superposition of the two plane waves $\exp[\mathrm{i}(k_1 x - \omega_1 t)]$ and $\exp[\mathrm{i}(k_2 x - \omega_2 t)]$

$$\Psi(x,\ t) = \mathrm{e}^{\mathrm{i}(k_1 x - \omega_1 t)} + \mathrm{e}^{\mathrm{i}(k_2 x - \omega_2 t)} \tag{1.7}$$

We define the average values $\overline{k}$ and $\overline{\omega}$ and the differences Δk and $\Delta\omega$ for the two plane waves in equation (1.7) by the relations

$$\overline{k} = \frac{k_1 + k_2}{2} \qquad \overline{\omega} = \frac{\omega_1 + \omega_2}{2}$$
$$\Delta k = k_1 - k_2 \qquad \Delta\omega = \omega_1 - \omega_2$$

so that

$$k_1 = \overline{k} + \frac{\Delta k}{2}, \qquad k_2 = \overline{k} - \frac{\Delta k}{2}$$
$$\omega_1 = \overline{\omega} + \frac{\Delta\omega}{2}, \qquad \omega_2 = \overline{\omega} - \frac{\Delta\omega}{2}$$

Using equation (A.32) from Appendix A, we may now write equation (1.7) in the form

$$\begin{aligned}\Psi(x,\ t) &= \mathrm{e}^{\mathrm{i}(\overline{k}x - \overline{\omega}t)}[\mathrm{e}^{\mathrm{i}(\Delta kx - \Delta\omega t)/2} + \mathrm{e}^{-\mathrm{i}(\Delta kx - \Delta\omega t)/2}] \\ &= 2\cos\left(\frac{\Delta kx - \Delta\omega t}{2}\right)\mathrm{e}^{\mathrm{i}(\overline{k}x - \overline{\omega}t)}\end{aligned} \tag{1.8}$$

Equation (1.8) represents a plane wave $\exp[\mathrm{i}(\overline{k}x - \overline{\omega}t)]$ with wave number $\overline{k}$, angular frequency $\overline{\omega}$, and phase velocity $\overline{\omega}/\overline{k}$, but with its amplitude modulated by the function $2\cos[(\Delta kx - \Delta\omega t)/2]$. The real part of the wave (1.8) at some fixed time t_0 is shown in Figure 1.2(a). The solid curve is the plane wave with wavelength $\lambda = 2\pi/\overline{k}$ and the dashed curve shows the profile of the amplitude of the plane wave. The profile is also a harmonic wave with wavelength

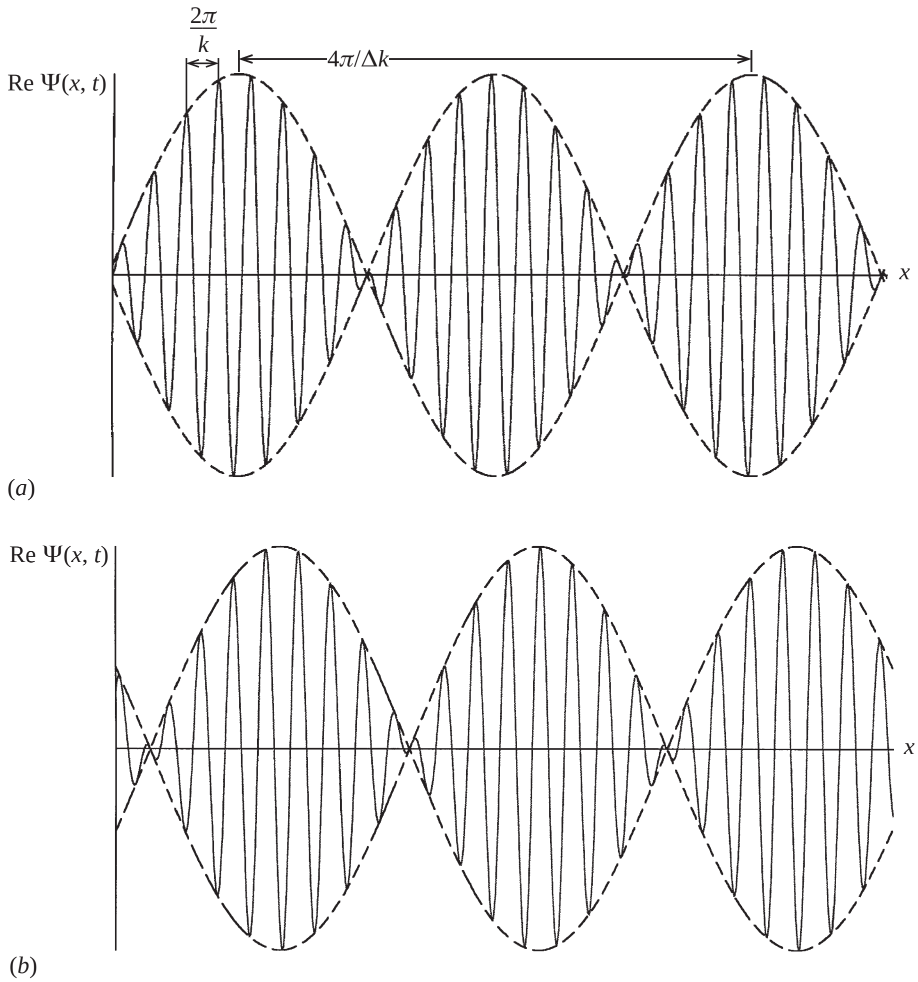

Figure 1.2 (*a*) The real part of the superposition of two plane waves is shown by the solid curve. The profile of the amplitude is shown by the dashed curve. (*b*) The positions of the curves in Figure 1.2(*a*) after a short time interval.

$4\pi/\Delta k$. At the points of maximum amplitude, the two original plane waves interfere constructively. At the nodes in Figure 1.2(*a*), the two original plane waves interfere destructively and cancel each other out.

As time increases, the plane wave $\exp[\mathrm{i}(\overline{k}x - \overline{\omega}t)]$ moves with velocity $\overline{\omega}/\overline{k}$. If we consider a fixed point x_1 and watch the plane wave as it passes that point, we observe not only the periodic rise and fall of the amplitude of the unmodified plane wave $\exp[\mathrm{i}(\overline{k}x - \overline{\omega}t)]$, but also the overlapping rise and fall of the amplitude due to the modulating function $2\cos[(\Delta kx - \Delta\omega t)/2]$. Without the modulating function, the plane wave would reach the same maximum and the same minimum amplitude with the passage of each cycle. The modulating function causes the maximum (or minimum) amplitude for each cycle of the plane wave to oscillate with frequency $\Delta\omega/2$.

The pattern in Figure 1.2(*a*) propagates along the x-axis as time progresses. After a short period of time Δt, the wave (1.8) moves to a position shown in Figure 1.2(*b*). Thus, the position of maximum amplitude has moved in the positive x-direction by an amount $v_g \Delta t$, where v_g is the *group velocity* of the composite wave, and is given by

$$v_g = \frac{\Delta\omega}{\Delta k} \tag{1.9}$$

The expression (1.9) for the group velocity of a composite of two plane waves is exact.

In the special case when k_2 equals $-k_1$ and ω_2 equals ω_1 in equation (1.7), the superposition of the two plane waves becomes

$$\Psi(x, t) = e^{i(kx - \omega t)} + e^{-i(kx + \omega t)} \tag{1.10}$$

where

$$k = k_1 = -k_2$$
$$\omega = \omega_1 = \omega_2$$

The two component plane waves in equation (1.10) travel with equal phase velocities ω/k, but in opposite directions. Using equations (A.31) and (A.32), we can express equation (1.10) in the form

$$\begin{aligned}\Psi(x, t) &= (e^{ikx} + e^{-ikx})e^{-i\omega t}\\ &= 2\cos kx\, e^{-i\omega t}\\ &= 2\cos kx\,(\cos\omega t - i\sin\omega t)\end{aligned}$$

We see that for this special case the composite wave is the product of two functions: one only of the distance x and the other only of the time t. The composite wave $\Psi(x, t)$ vanishes whenever $\cos kx$ is zero, i.e., when $kx = \pi/2$, $3\pi/2$, $5\pi/2$, $\ldots$, regardless of the value of t. Therefore, the nodes of $\Psi(x, t)$ are independent of time. However, the amplitude or profile of the composite wave changes with time. The real part of $\Psi(x, t)$ is shown in Figure 1.3. The solid curve represents the wave when $\cos\omega t$ is a maximum, the dotted curve when $\cos\omega t$ is a minimum, and the dashed curve when $\cos\omega t$ has an intermediate value. Thus, the wave does not travel, but pulsates, increasing and decreasing in amplitude with frequency ω. The imaginary part of $\Psi(x, t)$ behaves in the same way. A composite wave with this behavior is known as a *standing wave*.

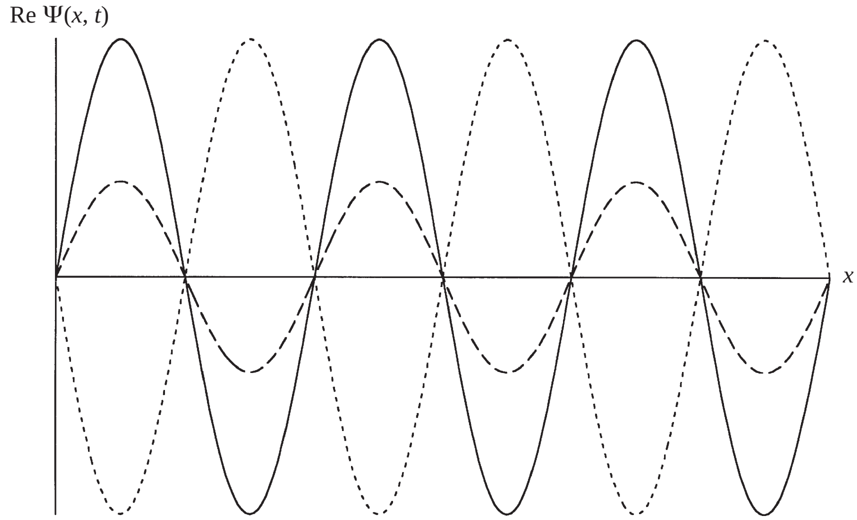

Figure 1.3 A standing harmonic wave at various times.

1.2 Wave packet

We now consider the formation of a composite wave as the superposition of a continuous spectrum of plane waves with wave numbers k confined to a narrow band of values. Such a composite wave $\Psi(x, t)$ is known as a *wave packet* and may be expressed as

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) \mathrm{e}^{\mathrm{i}(kx - \omega t)} \mathrm{d}k \tag{1.11}$$

The weighting factor $A(k)$ for each plane wave of wave number k is negligible except when k lies within a small interval Δk. For mathematical convenience we have included a factor $(2\pi)^{-1/2}$ on the right-hand side of equation (1.11). This factor merely changes the value of $A(k)$ and has no other effect.

We note that the wave packet $\Psi(x, t)$ is the inverse Fourier transform of $A(k)$. The mathematical development and properties of Fourier transforms are presented in Appendix B. Equation (1.11) has the form of equation (B.19). According to equation (B.20), the Fourier transform $A(k)$ is related to $\Psi(x, t)$ by

$$A(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x, t) \mathrm{e}^{-\mathrm{i}(kx - \omega t)} \, \mathrm{d}x \tag{1.12}$$

It is because of the Fourier relationships between $\Psi(x, t)$ and $A(k)$ that the factor $(2\pi)^{-1/2}$ is included in equation (1.11). Although the time t appears in the integral on the right-hand side of (1.12), the function $A(k)$ does not depend on t; the time dependence of $\Psi(x, t)$ cancels the factor $\mathrm{e}^{\mathrm{i}\omega t}$. We consider below two specific examples for the functional form of $A(k)$. However, in order to evaluate the integral over k in equation (1.11), we also need to know the dependence of the angular frequency ω on the wave number k.

In general, the angular frequency $\omega(k)$ is a function of k, so that the angular frequencies in the composite wave $\Psi(x, t)$, as well as the wave numbers, vary from one plane wave to another. If $\omega(k)$ is a slowly varying function of k and the values of k are confined to a small range Δk, then $\omega(k)$ may be expanded in a Taylor series in k about some point k_0 within the interval Δk

$$\omega(k) = \omega_0 + \left(\frac{\mathrm{d}\omega}{\mathrm{d}k}\right)_0 (k - k_0) + \frac{1}{2}\left(\frac{\mathrm{d}^2\omega}{\mathrm{d}k^2}\right)_0 (k - k_0)^2 + \cdots \tag{1.13}$$

where ω_0 is the value of $\omega(k)$ at k_0 and the derivatives are also evaluated at k_0. We may neglect the quadratic and higher-order terms in the Taylor expansion (1.13) because the interval Δk and, consequently, $k - k_0$ are small. Substitution of equation (1.13) into the phase for each plane wave in (1.11) then gives

$$\begin{aligned} kx - \omega t &\approx (k - k_0 + k_0)x - \omega_0 t - \left(\frac{\mathrm{d}\omega}{\mathrm{d}k}\right)_0 (k - k_0)t \\ &= k_0 x - \omega_0 t + \left[x - \left(\frac{\mathrm{d}\omega}{\mathrm{d}k}\right)_0 t\right](k - k_0) \end{aligned}$$

so that equation (1.11) becomes

$$\Psi(x, t) = B(x, t)\mathrm{e}^{\mathrm{i}(k_0 x - \omega_0 t)} \tag{1.14}$$

where

$$B(x, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} A(k)\mathrm{e}^{\mathrm{i}[x - (\mathrm{d}\omega/\mathrm{d}k)_0 t](k - k_0)}\,\mathrm{d}k \tag{1.15}$$

Thus, the wave packet $\Psi(x, t)$ represents a plane wave of wave number k_0 and angular frequency ω_0 with its amplitude modulated by the factor $B(x, t)$. This modulating function $B(x, t)$ depends on x and t through the relationship $[x - (\mathrm{d}\omega/\mathrm{d}k)_0 t]$. This situation is analogous to the case of two plane waves as expressed in equations (1.7) and (1.8). The modulating function $B(x, t)$ moves in the positive x-direction with group velocity v_g given by

$$v_\mathrm{g} = \left(\frac{d\omega}{\mathrm{d}k}\right)_0 \tag{1.16}$$

In contrast to the group velocity for the two-wave case, as expressed in equation (1.9), the group velocity in (1.16) for the wave packet is not uniquely defined. The point k_0 is chosen arbitrarily and, therefore, the value at k_0 of the derivative $\mathrm{d}\omega/\mathrm{d}k$ varies according to that choice. However, the range of k is narrow and $\omega(k)$ changes slowly with k, so that the variation in v_g is small. Combining equations (1.15) and (1.16), we have

$$B(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(k) \mathrm{e}^{\mathrm{i}(x - v_g t)(k - k_0)} \, \mathrm{d}k \tag{1.17}$$

Since the function $A(k)$ is the Fourier transform of $\Psi(x, t)$, the two functions obey Parseval's theorem as given by equation (B.28) in Appendix B

$$\int_{-\infty}^{\infty} |\Psi(x, t)|^2 \mathrm{d}x = \int_{-\infty}^{\infty} |B(x, t)|^2 \, \mathrm{d}x = \int_{-\infty}^{\infty} |A(k)|^2 \, \mathrm{d}k \tag{1.18}$$

Gaussian wave number distribution

In order to obtain a specific mathematical expression for the wave packet, we need to select some form for the function $A(k)$. In our first example we choose $A(k)$ to be the gaussian function

$$A(k) = \frac{1}{\sqrt{2\pi\alpha}} \mathrm{e}^{-(k - k_0)^2/2\alpha^2} \tag{1.19}$$

This function $A(k)$ is a maximum at wave number k_0, which is also the average value for k for this distribution of wave numbers. Substitution of equation (1.19) into (1.17) gives

$$|\Psi(x, t)| = B(x, t) = \frac{1}{\sqrt{2\pi}} \mathrm{e}^{-\alpha^2 (x - v_g t)^2/2} \tag{1.20}$$

where equation (A.8) has been used. The resulting modulating factor $B(x, t)$ is also a gaussian function–following the general result that the Fourier transform of a gaussian function is itself gaussian. We have also noted in equation (1.20) that $B(x, t)$ is always positive and is therefore equal to the absolute value $|\Psi(x, t)|$ of the wave packet. The functions $A(k)$ and $|\Psi(x, t)|$ are shown in Figure 1.4.

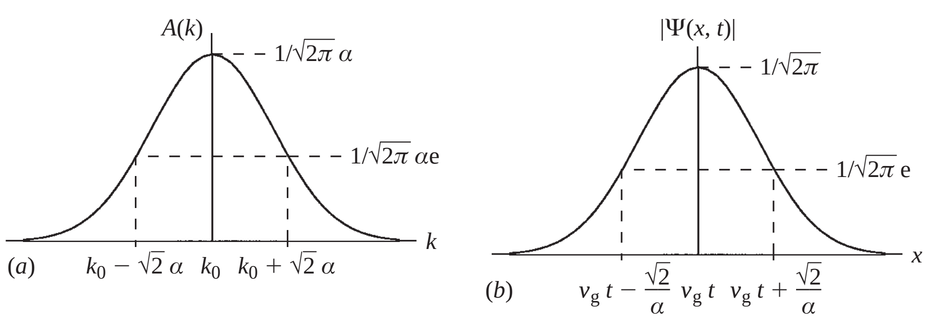

Figure 1.4 (a) A gaussian wave number distribution. (b) The modulating function corresponding to the wave number distribution in Figure 1.4(a).

Figure 1.5 shows the real part of the plane wave $\exp[i(k_0 x - \omega_0 t)]$ with its amplitude modulated by $B(x, t)$ of equation (1.20). The plane wave moves in the positive x-direction with phase velocity v_{ph} equal to ω_0/k_0. The maximum amplitude occurs at $x = v_g t$ and propagates in the positive x-direction with group velocity v_g equal to $(d\omega/dk)_0$.

The value of the function $A(k)$ falls from its maximum value of $(\sqrt{2\pi}\alpha)^{-1}$ at k_0 to $1/e$ of its maximum value when $|k - k_0|$ equals $\sqrt{2}\alpha$. Most of the area under the curve (actually 84.3%) comes from the range

$$-\sqrt{2}\alpha < (k - k_0) < \sqrt{2}\alpha$$

Thus, the distance $\sqrt{2}\alpha$ may be regarded as a measure of the width of the distribution $A(k)$ and is called the *half width*. The half width may be defined using $1/2$ or some other fraction instead of $1/e$. The reason for using $1/e$ is that the value of k at that point is easily obtained without consulting a table of numerical values. These various possible definitions give different numerical values for the half width, but all these values are of the same order of magnitude. Since the value of $|\Psi(x, t)|$ falls from its maximum value of $(2\pi)^{-1/2}$ to $1/e$ of that value when $|x - v_g t|$ equals $\sqrt{2}/\alpha$, the distance $\sqrt{2}/\alpha$ may be considered the half width of the wave packet.

When the parameter α is small, the maximum of the function $A(k)$ is high and the function drops off in value rapidly on each side of k_0, giving a small value for the half width. The half width of the wave packet, however, is large because it is proportional to $1/\alpha$. On the other hand, when the parameter α is large, the maximum of $A(k)$ is low and the function drops off slowly, giving a large half width. In this case, the half width of the wave packet becomes small.

If we regard the uncertainty Δk in the value of k as the half width of the distribution $A(k)$ and the uncertainty Δx in the position of the wave packet as its half width, then the product of these two uncertainties is

$$\Delta x \Delta k = 2$$

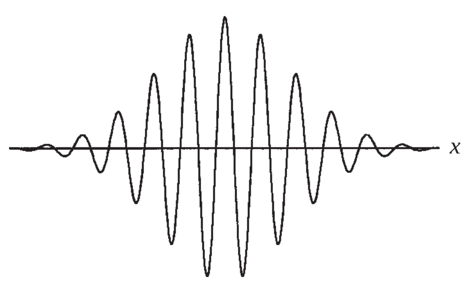

Figure 1.5 The real part of a wave packet for a gaussian wave number distribution.

Thus, the product of these two uncertainties Δx and Δk is a constant of order unity, independent of the parameter α.

Square pulse wave number distribution

As a second example, we choose $A(k)$ to have a constant value of unity for k between k_1 and k_2 and to vanish elsewhere, so that

$$\begin{aligned} A(k) &= 1, \qquad k_1 \leqslant k \leqslant k_2 \\ &= 0, \qquad k < k_1,\ k > k_2 \end{aligned} \tag{1.21}$$

as illustrated in Figure 1.6(a). With this choice for $A(k)$, the modulating function $B(x,\ t)$ in equation (1.17) becomes

$$\begin{aligned} B(x,\ t) &= \frac{1}{\sqrt{2\pi}} \int_{k_1}^{k_2} \mathrm{e}^{\mathrm{i}(x - v_\mathrm{g} t)(k - k_0)}\, \mathrm{d}k \\ &= \frac{1}{\sqrt{2\pi}\mathrm{i}(x - v_\mathrm{g} t)} [\mathrm{e}^{\mathrm{i}(x - v_\mathrm{g} t)(k_2 - k_0)} - \mathrm{e}^{\mathrm{i}(x - v_\mathrm{g} t)(k_1 - k_0)}] \\ &= \frac{1}{\sqrt{2\pi}\mathrm{i}(x - v_\mathrm{g} t)} [\mathrm{e}^{\mathrm{i}(x - v_\mathrm{g} t)\Delta k/2} - \mathrm{e}^{-\mathrm{i}(x - v_\mathrm{g} t)\Delta k/2}] \\ &= \sqrt{\frac{2}{\pi}} \frac{\sin[(x - v_\mathrm{g} t)\Delta k/2]}{x - v_\mathrm{g} t} \end{aligned} \tag{1.22}$$

where k_0 is chosen to be $(k_1 + k_2)/2$, Δk is defined as $(k_2 - k_1)$, and equation (A.33) has been used. The function $B(x,\ t)$ is shown in Figure 1.6(b).

The real part of the wave packet $\Psi(x,\ t)$ obtained from combining equations (1.14) and (1.22) is shown in Figure 1.7. The amplitude of the plane wave $\exp[\mathrm{i}(k_0 x - \omega_0 t)]$ is modulated by the function $B(x,\ t)$ of equation (1.22), which has a maximum when $(x - v_\mathrm{g} t)$ equals zero, i.e., when $x = v_\mathrm{g} t$. The nodes of $B(x,\ t)$ nearest to the maximum occur when $(x - v_\mathrm{g} t)\Delta k/2$ equals $\pm\pi$, i.e., when x is $\pm(2\pi/\Delta k)$ from the point of maximum amplitude. If we consider the half width of the wave packet between these two nodes as a measure of the uncertainty Δx in the location of the wave packet and the width $(k_2 - k_1)$ of the square pulse $A(k)$ as a measure of the uncertainty Δk in the value of k, then the product of these two uncertainties is

$$\Delta x \Delta k = 2\pi$$

Uncertainty relation

We have shown in the two examples above that the uncertainty Δx in the position of a wave packet is inversely related to the uncertainty Δk in the wave numbers of the constituent plane waves. This relationship is generally valid and

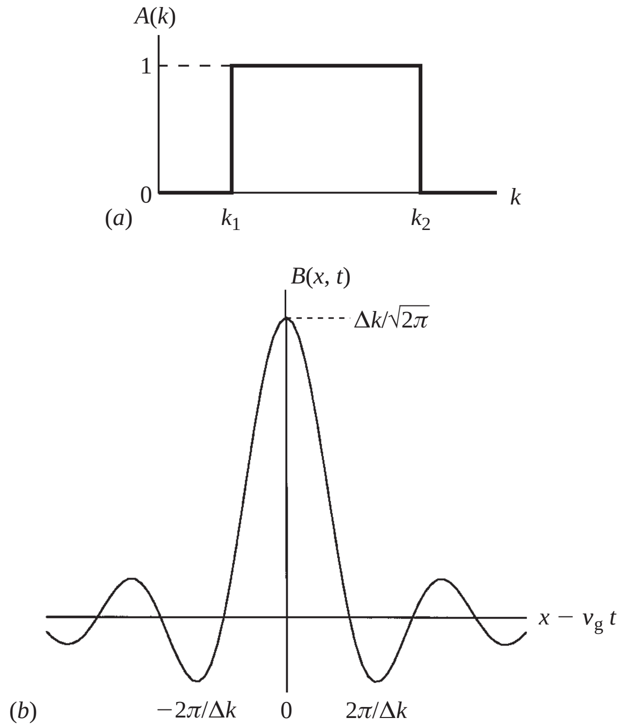

Figure 1.6 (*a*) A square pulse wave number distribution. (*b*) The modulating function corresponding to the wave number distribution in Figure 1.6(*a*).

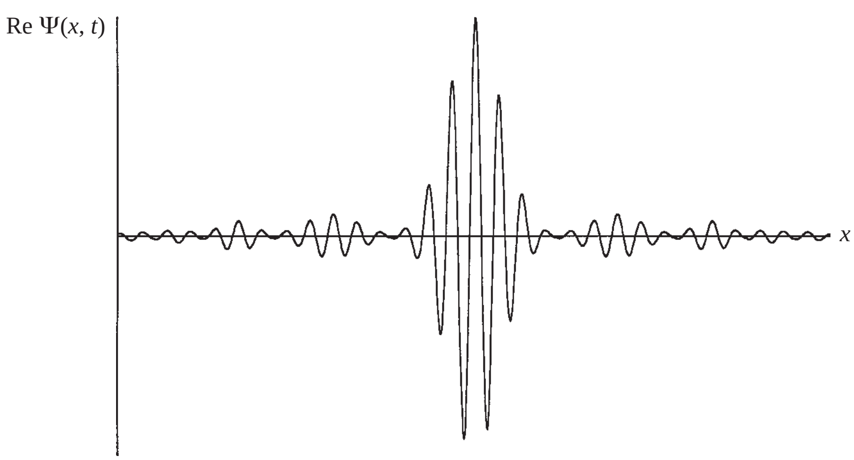

Figure 1.7 The real part of a wave packet for a square pulse wave number distribution.

is a property of Fourier transforms. In order to localize a wave packet so that the uncertainty Δx is very small, it is necessary to employ a broad spectrum of plane waves in equations (1.11) or (1.17). The function $A(k)$ must have a wide distribution of wave numbers, giving a large uncertainty Δk. If the distribution $A(k)$ is very narrow, so that the uncertainty Δk is small, then the wave packet becomes broad and the uncertainty Δx is large.

Thus, for all wave packets the product of the two uncertainties has a lower bound of order unity

$$\Delta x \Delta k \geqslant 1 \tag{1.23}$$

The lower bound applies when the narrowest possible range Δk of values for k is used in the construction of the wave packet, so that the quadratic and higher-order terms in equation (1.13) can be neglected. If a broader range of k is allowed, then the product $\Delta x \Delta k$ can be made arbitrarily large, making the right-hand side of equation (1.23) a lower bound. The actual value of the lower bound depends on how the uncertainties are defined. Equation (1.23) is known as the *uncertainty relation*.

A similar uncertainty relation applies to the variables t and ω. To show this relation, we write the wave packet (1.11) in the form of equation (B.21)

$$\Psi(x,\ t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} G(\omega) \mathrm{e}^{\mathrm{i}(kx-\omega t)}\, \mathrm{d}\omega \tag{1.24}$$

where the weighting factor $G(\omega)$ has the form of equation (B.22)

$$G(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,\ t) \mathrm{e}^{-\mathrm{i}(kx-\omega t)}\, \mathrm{d}t$$

In the evaluation of the integral in equation (1.24), the wave number k is regarded as a function of the angular frequency ω, so that in place of (1.13) we have

$$k(\omega) = k_0 + \left(\frac{\mathrm{d}k}{\mathrm{d}\omega}\right)_0 (\omega - \omega_0) + \cdots$$

If we neglect the quadratic and higher-order terms in this expansion, then equation (1.24) becomes

$$\Psi(x,\ t) = C(x,\ t)\mathrm{e}^{\mathrm{i}(k_0 x - \omega_0 t)}$$

where

$$C(x,\ t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(\omega) \mathrm{e}^{-\mathrm{i}[t-(\mathrm{d}k/\mathrm{d}\omega)_0 x](\omega-\omega_0)}\, \mathrm{d}\omega$$

As before, the wave packet is a plane wave of wave number k_0 and angular frequency ω_0 with its amplitude modulated by a factor that moves in the positive x-direction with group velocity v_g, given by equation (1.16). Following the previous analysis, if we select a specific form for the modulating function $G(\omega)$ such as a gaussian or a square pulse distribution, we can show that the product of the uncertainty Δt in the time variable and the uncertainty $\Delta\omega$ in the angular frequency of the wave packet has a lower bound of order unity, i.e.

$$\Delta t \Delta\omega \geqslant 1 \tag{1.25}$$

This uncertainty relation is also a property of Fourier transforms and is valid for all wave packets.

1.3 Dispersion of a wave packet

In this section we investigate the change in contour of a wave packet as it propagates with time.

The general expression for a wave packet $\Psi(x, t)$ is given by equation (1.11). The weighting factor $A(k)$ in (1.11) is the inverse Fourier transform of $\Psi(x, t)$ and is given by (1.12). Since the function $A(k)$ is independent of time, we may set t equal to any arbitrary value in the integral on the right-hand side of equation (1.12). If we let t equal zero in (1.12), then that equation becomes

$$A(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \Psi(\xi, 0)\mathrm{e}^{-\mathrm{i}k\xi}\,\mathrm{d}\xi \tag{1.26}$$

where we have also replaced the dummy variable of integration by ξ. Substitution of equation (1.26) into (1.11) yields

$$\Psi(x, t) = \frac{1}{2\pi}\iint_{-\infty}^{\infty} \Psi(\xi, 0)\mathrm{e}^{\mathrm{i}[k(x-\xi)-\omega t]}\,\mathrm{d}k\,\mathrm{d}\xi \tag{1.27}$$

Since the limits of integration do not depend on the variables ξ and k, the order of integration over these variables may be interchanged.

Equation (1.27) relates the wave packet $\Psi(x, t)$ at time t to the wave packet $\Psi(x, 0)$ at time $t = 0$. However, the angular frequency $\omega(k)$ is dependent on k and the functional form must be known before we can evaluate the integral over k.

If $\omega(k)$ is proportional to $|k|$ as expressed in equation (1.6), then (1.27) gives

$$\Psi(x, t) = \frac{1}{2\pi}\iint_{-\infty}^{\infty} \Psi(\xi, 0)\mathrm{e}^{\mathrm{i}k(x-ct-\xi)}\,\mathrm{d}k\,\mathrm{d}\xi$$

The integral over k may be expressed in terms of the Dirac delta function through equation (C.6) in Appendix C, so that we have

$$\Psi(x,\ t) = \int_{-\infty}^{\infty} \Psi(\xi,\ 0)\delta(x - ct - \xi)\,\mathrm{d}\xi = \Psi(x - ct,\ 0)$$

Thus, the wave packet $\Psi(x,\ t)$ has the same value at point x and time t that it had at point $x - ct$ at time $t = 0$. The wave packet has traveled with velocity c without a change in its contour, i.e., it has traveled without dispersion. Since the phase velocity v_{ph} is given by $\omega_0/k_0 = c$ and the group velocity v_{g} is given by $(\mathrm{d}\omega/\mathrm{d}k)_0 = c$, the two velocities are the same for an undispersed wave packet.

We next consider the more general situation where the angular frequency $\omega(k)$ is not proportional to $|k|$, but is instead expanded in the Taylor series (1.13) about $(k - k_0)$. Now, however, we retain the quadratic term, but still neglect the terms higher than quadratic, so that

$$\omega(k) \approx \omega_0 + v_{\mathrm{g}}(k - k_0) + \gamma(k - k_0)^2$$

where equation (1.16) has been substituted for the first-order derivative and γ is an abbreviation for the second-order derivative

$$\gamma \equiv \frac{1}{2}\left(\frac{\mathrm{d}^2\omega}{\mathrm{d}k^2}\right)_0$$

The phase in equation (1.27) then becomes

$$\begin{aligned} k(x - \xi) - \omega t &= (k - k_0)(x - \xi) + k_0(x - \xi) - \omega_0 t \\ &\quad - v_{\mathrm{g}} t(k - k_0) - \gamma t(k - k_0)^2 \\ &= k_0 x - \omega_0 t - k_0\xi + (x - v_{\mathrm{g}} t - \xi)(k - k_0) - \gamma t(k - k_0)^2 \end{aligned}$$

so that the wave packet (1.27) takes the form

$$\Psi_\gamma(x,\ t) = \frac{\mathrm{e}^{\mathrm{i}(k_0 x - \omega_0 t)}}{2\pi} \iint_{-\infty}^{\infty} \Psi(\xi,\ 0)\mathrm{e}^{-\mathrm{i}k_0\xi}\mathrm{e}^{\mathrm{i}(x - v_{\mathrm{g}} t - \xi)(k - k_0) - \mathrm{i}\gamma t(k - k_0)^2}\,\mathrm{d}k\,\mathrm{d}\xi$$

The subscript γ has been included in the notation $\Psi_\gamma(x,\ t)$ in order to distinguish that wave packet from the one in equations (1.14) and (1.15), where the quadratic term in $\omega(k)$ is omitted. The integral over k may be evaluated using equation (A.8), giving the result

$$\Psi_\gamma(x,\ t) = \frac{\mathrm{e}^{\mathrm{i}(k_0 x - \omega_0 t)}}{2\sqrt{\mathrm{i}\pi\gamma t}} \iint_{-\infty}^{\infty} \Psi(\xi,\ 0)\mathrm{e}^{-\mathrm{i}k_0\xi}\mathrm{e}^{-(x - v_{\mathrm{g}} t - \xi)^2/4\mathrm{i}\gamma t}\,\mathrm{d}\xi \tag{1.28}$$

Equation (1.28) relates the wave packet at time t to the wave packet at time $t = 0$ if the k-dependence of the angular frequency includes terms up to k^2. The profile of the wave packet $\Psi_\gamma(x,\ t)$ changes as time progresses because of the factor $t^{-1/2}$ before the integral and the t in the exponent within the integral. If we select a specific form for the wave packet at time $t = 0$, the nature of this time dependence becomes more evident.

Gaussian wave packet

Let us suppose that $\Psi(x,\ 0)$ has the gaussian distribution (1.20) as its profile, so that equation (1.14) at time $t = 0$ is

$$\Psi(\xi,\ 0) = \mathrm{e}^{\mathrm{i}k_0\xi}B(\xi,\ 0) = \frac{1}{\sqrt{2\pi}}\mathrm{e}^{\mathrm{i}k_0\xi}\mathrm{e}^{-\alpha^2\xi^2/2} \tag{1.29}$$

Substitution of equation (1.29) into (1.28) gives

$$\Psi_\gamma(x,\ t) = \frac{\mathrm{e}^{\mathrm{i}(k_0x-\omega_0t)}}{2\pi\sqrt{2\mathrm{i}\gamma t}}\int_{-\infty}^{\infty}\mathrm{e}^{-\alpha^2\xi^2/2}\mathrm{e}^{-(x-v_\mathrm{g}t-\xi)^2/4\mathrm{i}\gamma t}\,\mathrm{d}\xi$$

The integral may be evaluated using equation (A.8) accompanied with some tedious, but straightforward algebraic manipulations, yielding

$$\Psi_\gamma(x,\ t) = \frac{\mathrm{e}^{\mathrm{i}(k_0x-\omega_0t)}}{\sqrt{2\pi(1+2\mathrm{i}\alpha^2\gamma t)}}\mathrm{e}^{-\alpha^2(x-v_\mathrm{g}t)^2/2(1+2\mathrm{i}\alpha^2\gamma t)} \tag{1.30}$$

The wave packet, then, consists of the plane wave $\exp\mathrm{i}[k_0x - \omega_0t]$ with its amplitude modulated by

$$\frac{1}{\sqrt{2\pi(1+2\mathrm{i}\alpha^2\gamma t)}}\mathrm{e}^{-\alpha^2(x-v_\mathrm{g}t)^2/2(1+2\mathrm{i}\alpha^2\gamma t)}$$

which is a complex function that depends on the time t. When γ equals zero so that the quadratic term in $\omega(k)$ is neglected, this complex modulating function reduces to $B(x,\ t)$ in equation (1.20). The absolute value $|\Psi_\gamma(x,\ t)|$ of the wave packet (1.30) is given by

$$|\Psi_\gamma(x,\ t)| = \frac{1}{(2\pi)^{1/2}(1+4\alpha^4\gamma^2t^2)^{1/4}}\mathrm{e}^{-\alpha^2(x-v_\mathrm{g}t)^2/2(1+4\alpha^4\gamma^2t^2)} \tag{1.31}$$

We now contrast the behavior of the wave packet in equation (1.31) with that of the wave packet in (1.20). At any time t, the maximum amplitudes of both occur at $x = v_\mathrm{g}t$ and travel in the positive x-direction with the same group velocity v_g. However, at that time t, the value of $|\Psi_\gamma(x,\ t)|$ is $1/e$ of its maximum value when the exponent in equation (1.31) is unity, so that the half width or uncertainty Δx for $|\Psi_\gamma(x,\ t)|$ is given by

$$\Delta x = |x - v_\mathrm{g}t| = \frac{\sqrt{2}}{\alpha}\sqrt{1+4\alpha^4\gamma^2t^2}$$

Moreover, the maximum amplitude for $|\Psi_\gamma(x,\ t)|$ at time t is given by

$$(2\pi)^{-1/2}(1+4\alpha^4\gamma^2t^2)^{-1/4}$$

As time increases from $-\infty$ to 0, the half width of the wave packet $|\Psi_\gamma(x, t)|$ continuously decreases and the maximum amplitude continuously increases. At $t = 0$ the half width attains its lowest value of $\sqrt{2}/\alpha$ and the maximum amplitude attains its highest value of $1/\sqrt{2\pi}$, and both values are in agreement with the wave packet in equation (1.20). As time increases from 0 to ∞, the half width continuously increases and the maximum amplitude continuously decreases. Thus, as t^2 increases, the wave packet $|\Psi_\gamma(x, t)|$ remains gaussian in shape, but broadens and flattens out in such a way that the area under the square $|\Psi_\gamma(x, t)|^2$ of the wave packet remains constant over time at a value of $(2\sqrt{\pi}\alpha)^{-1}$, in agreement with Parseval's theorem (1.18).

The product $\Delta x \Delta k$ for this spreading wave packet $\Psi_\gamma(x, t)$ is

$$\Delta x \Delta k = 2\sqrt{1 + 4\alpha^4\gamma^2 t^2}$$

and increases as $|t|$ increases. Thus, the value of the right-hand side when $t = 0$ is the lower bound for the product $\Delta x \Delta k$ and is in agreement with the uncertainty relation (1.23).

1.4 Particles and waves

To explain the photoelectric effect, Einstein (1905) postulated that light, or electromagnetic radiation, consists of a beam of particles, each of which travels at the same velocity c (the speed of light), where c has the value

$$c = 2.997\,92 \times 10^8 \text{ m s}^{-1}$$

Each particle, later named a *photon*, has a characteristic frequency ν and an energy $h\nu$, where h is Planck's constant with the value

$$h = 6.626\,08 \times 10^{-34} \text{ J s}$$

The constant h and the hypothesis that energy is quantized in integral multiples of $h\nu$ had previously been introduced by M. Planck (1900) in his study of blackbody radiation.[1] In terms of the angular frequency ω defined in equation (1.2), the energy E of a photon is

$$E = \hbar\omega \tag{1.32}$$

where $\hbar$ is defined by

$$\hbar \equiv \frac{h}{2\pi} = 1.054\,57 \times 10^{-34} \text{ J s}$$

Because the photon travels with velocity c, its motion is governed by relativity

[1] The history of the development of quantum concepts to explain observed physical phenomena, which occurred mainly in the first three decades of the twentieth century, is discussed in introductory texts on physical chemistry and on atomic physics. A much more detailed account is given in M. Jammer (1966) *The Conceptual Development of Quantum Mechanics* (McGraw-Hill, New York).

theory, which requires that its rest mass be zero. The magnitude of the momentum p for a particle with zero rest mass is related to the relativistic energy E by $p = E/c$, so that

$$p = \frac{E}{c} = \frac{h\nu}{c} = \frac{\hbar\omega}{c}$$

Since the velocity c equals ω/k, the momentum is related to the wave number k for a photon by

$$p = \hbar k \tag{1.33}$$

Einstein's postulate was later confirmed experimentally by A. Compton (1924).

Noting that it had been fruitful to regard light as having a corpuscular nature, L. de Broglie (1924) suggested that it might be useful to associate wave-like behavior with the motion of a particle. He postulated that a particle with linear momentum p be associated with a wave whose wavelength λ is given by

$$\lambda = \frac{2\pi}{k} = \frac{h}{p} \tag{1.34}$$

and that expressions (1.32) and (1.33) also apply to particles. The hypothesis of wave properties for particles and the de Broglie relation (equation (1.34)) have been confirmed experimentally for electrons by G. P. Thomson (1927) and by Davisson and Germer (1927), for neutrons by E. Fermi and L. Marshall (1947), and by W. H. Zinn (1947), and for helium atoms and hydrogen molecules by I. Estermann, R. Frisch, and O. Stern (1931).

The classical, non-relativistic energy E for a free particle, i.e., a particle in the absence of an external force, is expressed as the sum of the kinetic and potential energies and is given by

$$E = \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V \tag{1.35}$$

where m is the mass and v the velocity of the particle, the linear momentum p is

$$p = mv$$

and V is a constant potential energy. The force F acting on the particle is given by

$$F = -\frac{\mathrm{d}V}{\mathrm{d}x} = 0$$

and vanishes because V is constant. In classical mechanics the choice of the zero-level of the potential energy is arbitrary. Since the potential energy for the free particle is a constant, we may, without loss of generality, take that constant value to be zero, so that equation (1.35) becomes

$$E = \frac{p^2}{2m} \tag{1.36}$$

Following the theoretical scheme of Schrödinger, we associate a wave packet $\Psi(x, t)$ with the motion in the x-direction of this free particle. This wave packet is readily constructed from equation (1.11) by substituting (1.32) and (1.33) for ω and k, respectively

$$\Psi(x, t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} A(p) e^{i(px-Et)/\hbar} \, dp \tag{1.37}$$

where, for the sake of symmetry between $\Psi(x, t)$ and $A(p)$, a factor $\hbar^{-1/2}$ has been absorbed into $A(p)$. The function $A(k)$ in equation (1.12) is now $\hbar^{1/2} A(p)$, so that

$$A(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x, t) e^{-i(px-Et)/\hbar} \, dx \tag{1.38}$$

The law of dispersion for this wave packet may be obtained by combining equations (1.32), (1.33), and (1.36) to give

$$\omega(k) = \frac{E}{\hbar} = \frac{p^2}{2m\hbar} = \frac{\hbar k^2}{2m} \tag{1.39}$$

This dispersion law with ω proportional to k^2 is different from that for undispersed light waves, where ω is proportional to k.

If $\omega(k)$ in equation (1.39) is expressed as a power series in $k - k_0$, we obtain

$$\omega(k) = \frac{\hbar k_0^2}{2m} + \frac{\hbar k_0}{m}(k - k_0) + \frac{\hbar}{2m}(k - k_0)^2 \tag{1.40}$$

This expansion is exact; there are no terms of higher order than quadratic. From equation (1.40) we see that the phase velocity v_{ph} of the wave packet is given by

$$v_{\text{ph}} = \frac{\omega_0}{k_0} = \frac{\hbar k_0}{2m} \tag{1.41}$$

and the group velocity v_g is

$$v_g = \left(\frac{d\omega}{dk}\right)_0 = \frac{\hbar k_0}{m} \tag{1.42}$$

while the parameter γ of equations (1.28), (1.30), and (1.31) is

$$\gamma = \frac{1}{2}\left(\frac{d^2\omega}{dk^2}\right)_0 = \frac{\hbar}{2m} \tag{1.43}$$

If we take the derivative of $\omega(k)$ in equation (1.39) with respect to k and use equation (1.33), we obtain

$$\frac{d\omega}{dk} = \frac{\hbar k}{m} = \frac{p}{m} = v$$