Concepts of Wave Mechanics

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I. Wave Functions and Tunneling

A. Free-particle Wave Function

According to de Broglie's postulate, a particle with momentum p has a wavelength given by:

$$\lambda = h/p. \tag{1}$$

For non-relativistic particles, p = mv, so

$$\lambda = h/mv. \tag{2}$$

This can also be written in terms of the kinetic energy, $KE=1/2\ mv^2$, as

$$\lambda = \frac{h}{\sqrt{2mKE}} \tag{3}$$

The implication of de Broglie's postulate is that there is a wave function associated with the particle. For illustration, the wave function is sometimes taken to be a *sinusoidal plane wave*:

$$\psi(x,t) = A\sin(\frac{2\pi}{\lambda}x - 2\pi ft + \phi) \tag{4}$$

In this expression, ϕ is an arbitrary phase, A is the amplitude, to be discussed below, and f is the frequency, determined from the particle's total energy, E, from Einstein's postulate

$$E = hf. \tag{5}$$

For our immediate purposes, the time dependence is not important, so we will consider a time-independent wave function:

$$\psi(x) = A\sin(\frac{2\pi}{\lambda}x + \phi) \tag{6}$$

The significance of the wave function is that its square gives the particle's probability density :

$$\psi^2(x) = A^2 \sin^2\left(\frac{2\pi}{\lambda}x + \phi\right) \tag{7}$$

That is, $\psi^2(x)$ is the probability of finding the particle in an infinitesimal neighborhood around x. More generally, the probability of finding the particle between x_1 and x_2 is the area under the curve $\psi^2(x)$ between x_1 and x_2 as shown in Figure 1 below.

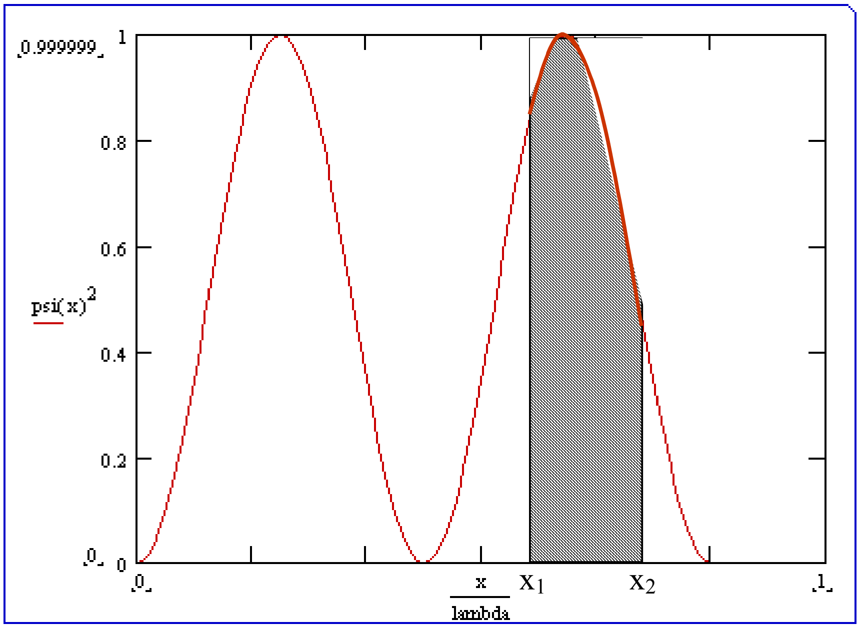

Figure 1: The probability of the particle's location being between x_1 and x_2 is equal to the area under the curve $\psi^2(x)$ between x_1 and x_2.

B. Confined Wave Functions

The idea of probability density brings up a difficulty with the wave function of equation (6). For a realistic wave function, the total area under the $\psi^2(x)$ curve must be equal to 1.0 – that is, the particle has to be somewhere, so the total probability over all space has to be unity. But the simple wave function given above oscillates infinitely in both directions, so the total area is infinite, unless A=0. Consequently, it is not a realistic wave function, although it is useful for conceptual calculations.

A more realistic – although still idealized – case is that of a "particle in a box." That is, we suppose that the particle is confined within an infinitely deep potential well, so that the wave function is zero at the boundaries. The wave function of equation (6) is applicable within the box, with A, ϕ and λ determined by the "boundary conditions" – that is, the fact that $\psi(x)$ must equal zero at the edges.

If the origin is chosen to coincide with the left-hand wall of the box, then $\phi = 0$. The allowed values of λ are determined by the requirement $\psi(L)=0$ – just as with the normal modes of vibration of a stretched string, an integer number of half-wavelengths must fit within the box. Consequently,

$$\frac{n\lambda_n}{2} = L, \quad n = 1,2,3,... \tag{8}$$

or

$$\lambda_n = \frac{2L}{n}, \quad n = 1,2,3,... \tag{9}$$

The particle's energy can be determined from the wavelength from equation (3) (inside the box the potential energy is zero, the the kinetic energy and total energy are identical):

$$E_n = \frac{h^2}{2m\lambda_n^2} = \frac{h^2 n^2}{8mL^2}, \quad n = 1,2,3,... \tag{10}$$

An important conclusion of this analysis is that a bound particle never has zero energy – there is a minimum, or *ground state* energy.

The probability densities for the first few values of n are illustrated in Figure 2. Notice that the wave functions have "nodes" – points where there is zero probability of finding the particle. Higher-energy (higher-n) states have a larger number of nodes. The constant A in equation (6) is determined by the requirement that the total area under the curve be equal to 1. The result is $A^2=2/L$.

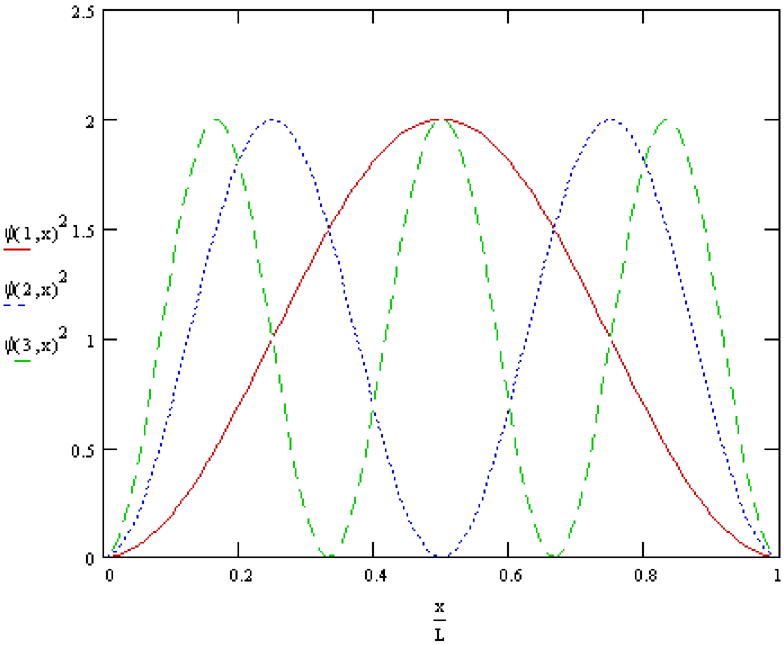

Figure 2: Probability density for the first 3 particle-in-a-box wave functions. Since the barriers that form the "walls" of the box are assumed to be infinitely high, the wave function must be exactly zero at the boundaries.

C. Evanescent Wave Function – Barrier Penetration

In classical mechanics, a particle cannot surmount a potential barrier that exceeds the energy of the particle. One of the novel features of quantum mechanics is that a particle can penetrate a barrier that exceeds the particle's energy. Consider a particle with total energy E that faces a barrier of potential energy U, as in Figure 3 below. The particle's kinetic energy should be its total energy minus the potential energy:

$$\mathrm{KE(x)} = \begin{cases} \mathrm{E}, & \mathrm{x} < 0 \\ \mathrm{E} - \mathrm{U}, & \mathrm{x} > 0 \end{cases} \tag{11}$$

If E>U, the wave function on the right side of the barrier will have the same form as that on the left side, but with a longer wavelength corresponding to the reduced kinetic energy.

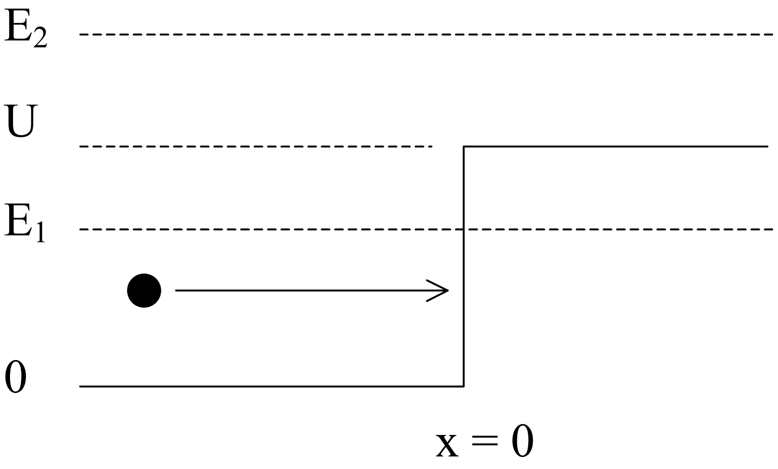

Figure 3: A particle of total energy E strikes a potential barrier of height U. In classical mechanics, a particle with energy E_2 will pass over the barrier, but a particle with energy E_1 does not have sufficient energy to surmount the barrier and is forbidden to enter the region x>0.

The more interesting case is when E<U. In that case it would seem that the kinetic energy must be negative for x>0, which leads to an imaginary wavelength. In classical mechanics this state of affairs is not possible, but in quantum mechanics it leads to an *evanescent wave* – a wave function that decreases exponentially. The form of this wave function is:

$$\psi(x) = Be^{-\alpha x} \tag{12}$$

were α is the decay constant, given by:

$$\alpha = \frac{2\pi\sqrt{2m(U-E)}}{h} \tag{13}$$

Except for the factor of 2π, this is the reciprocal of the expression for the wavelength of the free particle wave function, with U-E substituted for KE.

Figure 4 shows how a sinusoidal wave function merges into an evanescent wave function at a barrier with U>E. The greater the potential barrier relative to the particle energy, the faster the wave function decays. If the barrier height is only slightly greater that the particle energy, the particle's wave function can penetrate significantly into the classically forbidden region.

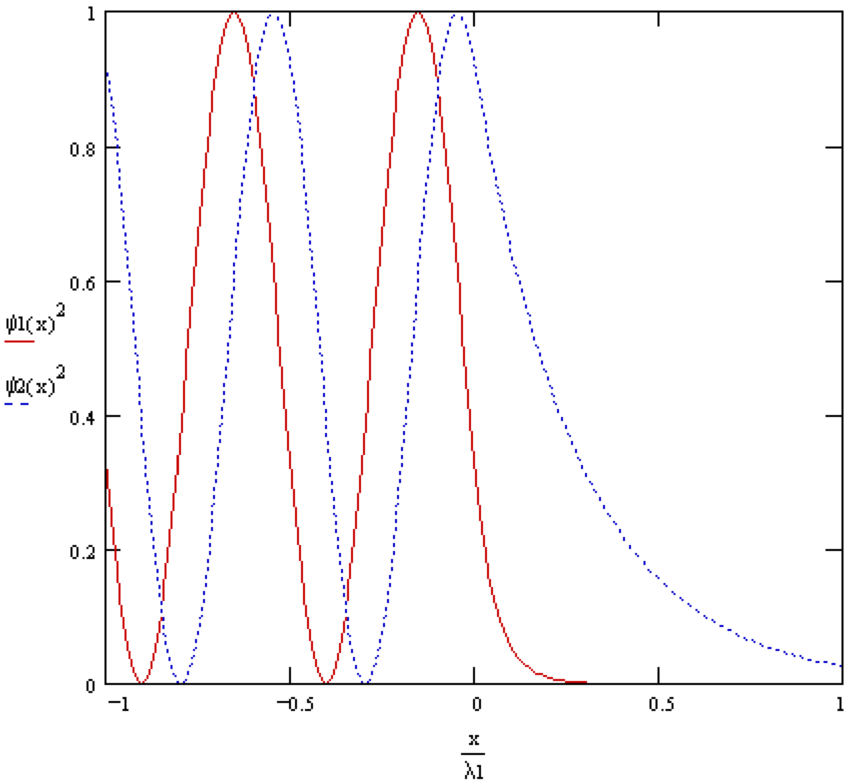

Figure 4: Probability density for a particle incident on a step potential barrier. For the case that the potential is much greater than the particle's energy (solid line, U=1.5 E) the evanescent wave penetrates only a small distance past the barrier. For a step height only slightly greater than the particle energy (dashed line, U= 1.05 E) the evanescent wave penetrates more deeply past the barrier.

If the barrier is of finite width, the wave function may extend completely through the barrier region and merge into another oscillating wave function on the far side. Thus there is a finite probability that the particle will pass through the barrier, even though the barrier height is greater than the particle energy. This phenomenon, which is illustrated in Figure 5, is called *tunneling*.

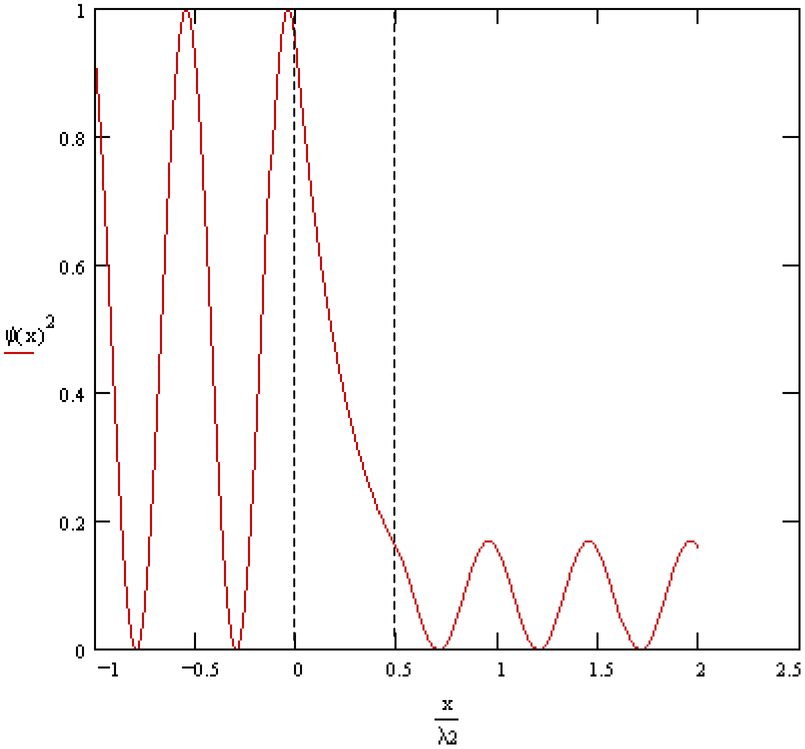

Figure 5: Tunneling of a particle of energy E through a finite-width barrier of height 1.02 E. The barrier extends between the two dashed lines.

II. Wave Packets and the Uncertainty Principle

A. Position-Momentum Uncertainty

As mentioned above, the simple sinusoidal wave function of equation (6) is not realistic, because it extends to plus and minus infinity. However, if many wave functions of that form but with different wavelengths are added together – the technical term is *superposition* - the resulting function has a more limited spatial extent. A wave function that is formed by summing a number of sinusoidal functions is called a wave packet. Some examples are given in Figure 6. Notice that as a larger number of terms are added, the wave packet becomes more localized.[1]

This fact illustrates the *uncertainty principle* : the more variation there is in a particle's wavelength (or momentum) the less uncertainty there is in the particle's position. The

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[1] Actually we are cheating a little, since by adding discrete wavelengths we produce a function that repeats periodically, and we are looking only at one period. A more correct method is to add a continuum of wavelengths, but this approach requires calculus.

sinusoidal wave function represents an extreme case – its wavelength is known exactly, so its position is completely unknown. A more rigorous analysis shows that the relationship between the position and momentum uncertainty is:

$$\Delta p \Delta x \geq \hbar \qquad (14)$$

where $\hbar$ is Planck's constant, h, divided by 2π.

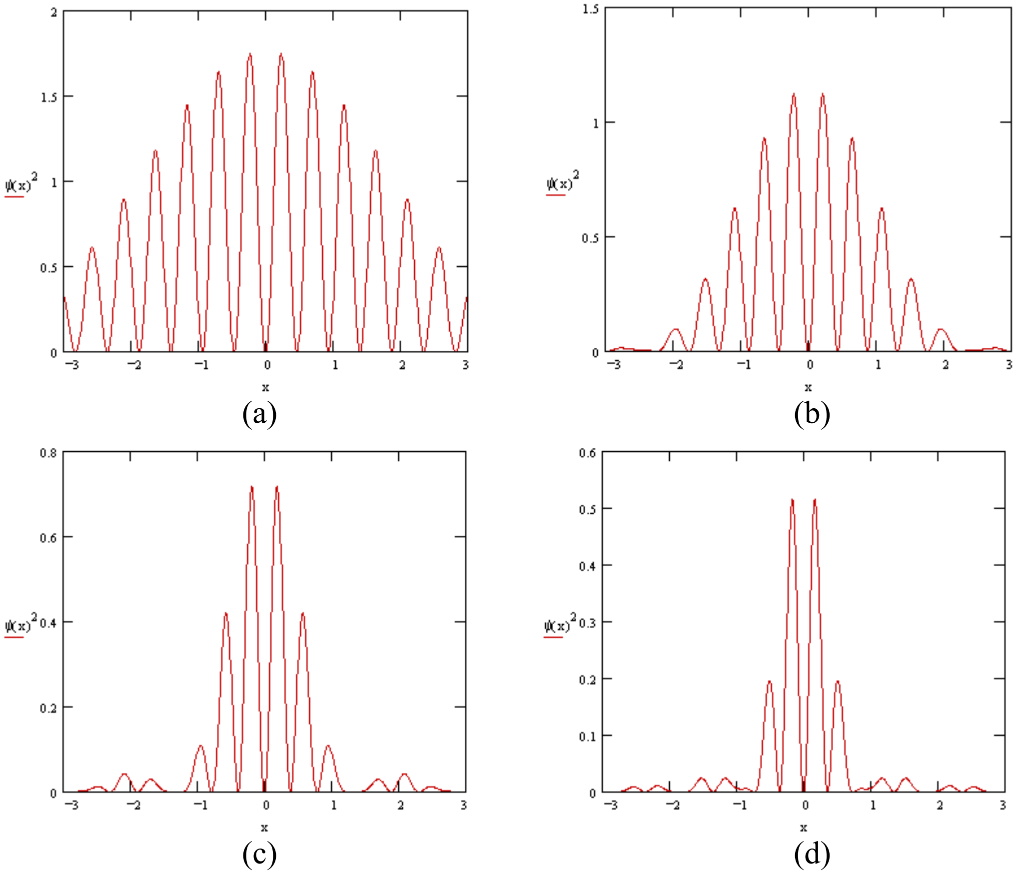


Figure 6: Wave packets formed by adding several sinusoidal waves (equation 6) with different wavelengths. (a) 5 terms (b) 10 terms (c) 20 terms (d) 30 terms.

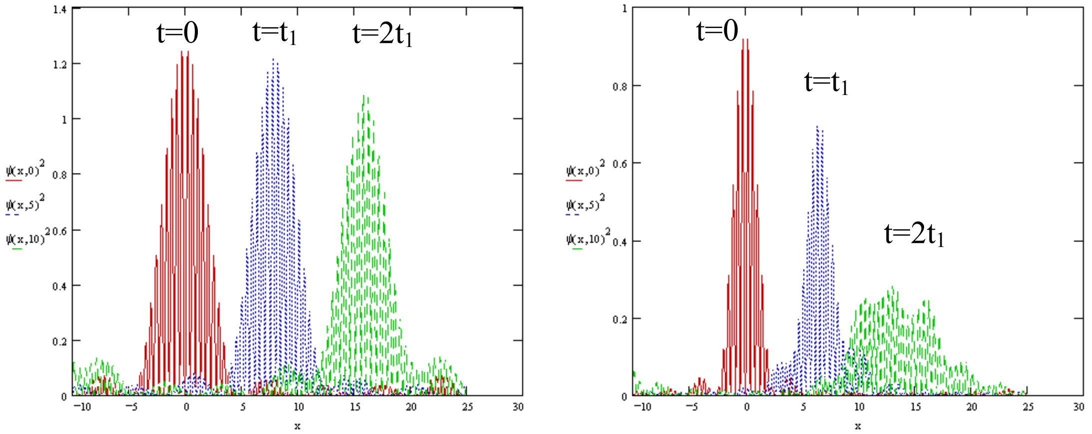
B. Time Evolution and Energy-Time Uncertainty

Until now we have ignored the time dependence of wave functions – that is, we set t = 0 in equation (4), but important conclusions can be drawn from examining the time dependence of wave packets as well. The frequency is related to the kinetic energy by equation (3). In a region of zero potential the kinetic energy and the total energy are identical, so equation (4) becomes:

$$\psi(x,t) = A\sin(\frac{2\pi}{\lambda}x - \frac{\pi h}{m\lambda^2}t + \phi) . \tag{17}$$

If several terms of the form (17) are added, the different components will propagate with different speeds, causing the wave packet to spread out. This phenomenon is well known in electromagnetic wave propagation, particularly optics, and is called *dispersion*. The time evolution of wave packets (a) and (b) from Figure 6 is shown in Figure 7. In (a), the wave packet consists of a small number of terms, 5. In that case, the width of the wave packet spreads out only slightly over the time scale of the graph. [The time scale is arbitrary, but it is the same in (a) and (b).] In (b), where the wave packet consists of a larger number of terms, 10, it spreads out much faster. In other words, the greater the uncertainty in energy, the shorter the time over which the packet will hold its shape. This illustrates the energy-time uncertainty relation, which has the same form as the position-momentum relation discussed above:

$$\Delta E \Delta t \geq \hbar . \tag{18}$$



(a) (b)

Figure 7: Time evolution of wave packets formed by adding several sinusoidal waves (equation 17) with different wavelengths and energies. (a) 5 terms (b) 10 terms. The particle is propagating from left to right.

An important application of the energy-time uncertainty relation is the connection between excited-state lifetimes and the inherent width of atomic spectral lines. According to the simple Bohr model, for example, an energy-level transition has a precise energy that corresponds to a precise frequency of the absorbed or emitted photon. But in reality, there is an inherent spread in energies, and therefore a finite width to the spectral line. This line width is related to the *lifetime* of the excited state – that is, how long on average it takes for an electron in that state to return to its ground state. The longer the lifetime of the state, the narrower the spectral line. The precise relationship between the line width in units of energy and the excited-state lifetime is given by (18).