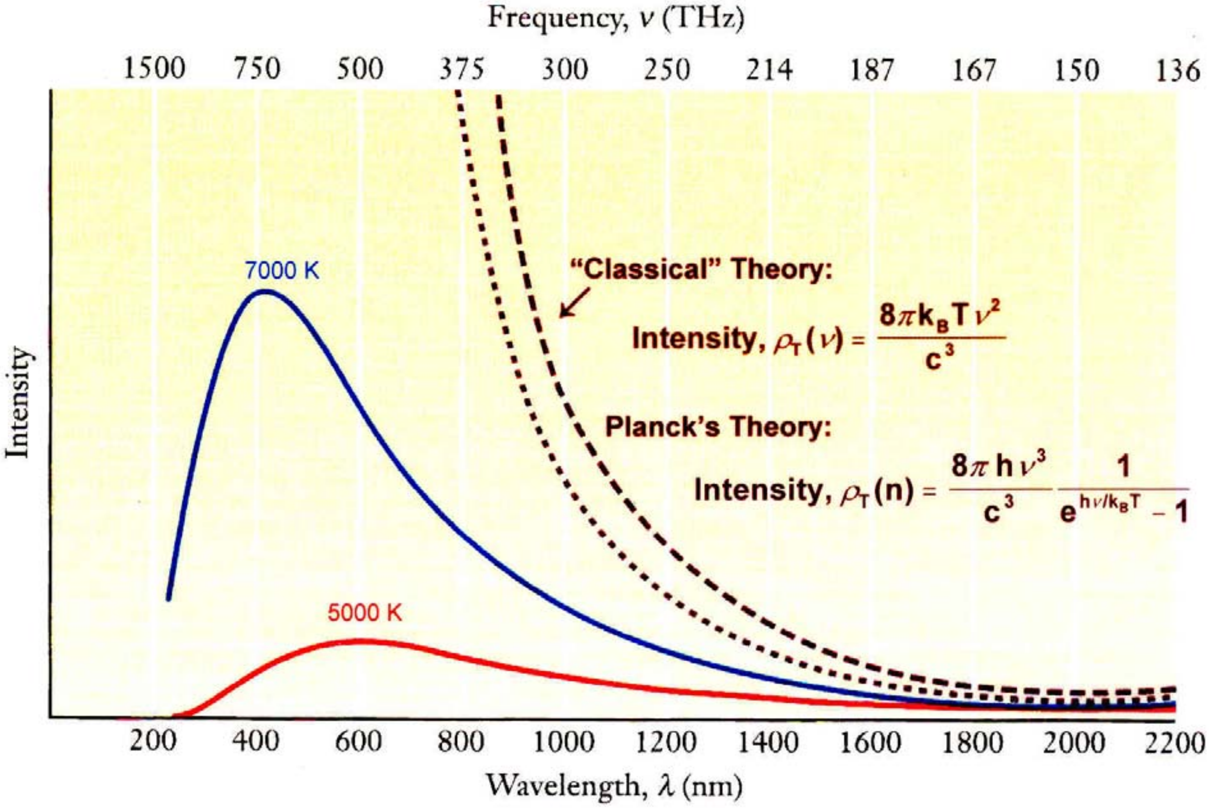
Topic 1B - Quantum Theory

Blackbody Radiation Intensity as a Function of Wavelength



Planck's Theory: $E = h\nu = \frac{hc}{\lambda}$ (h = Planck's Const. = 6.63×10^{-34} J-s)

The probability that a particular blackbody oscillator of frequency ν contains its minimum allowed energy ($h\nu$) is proportional to $\exp(-h\nu/k_BT)$.

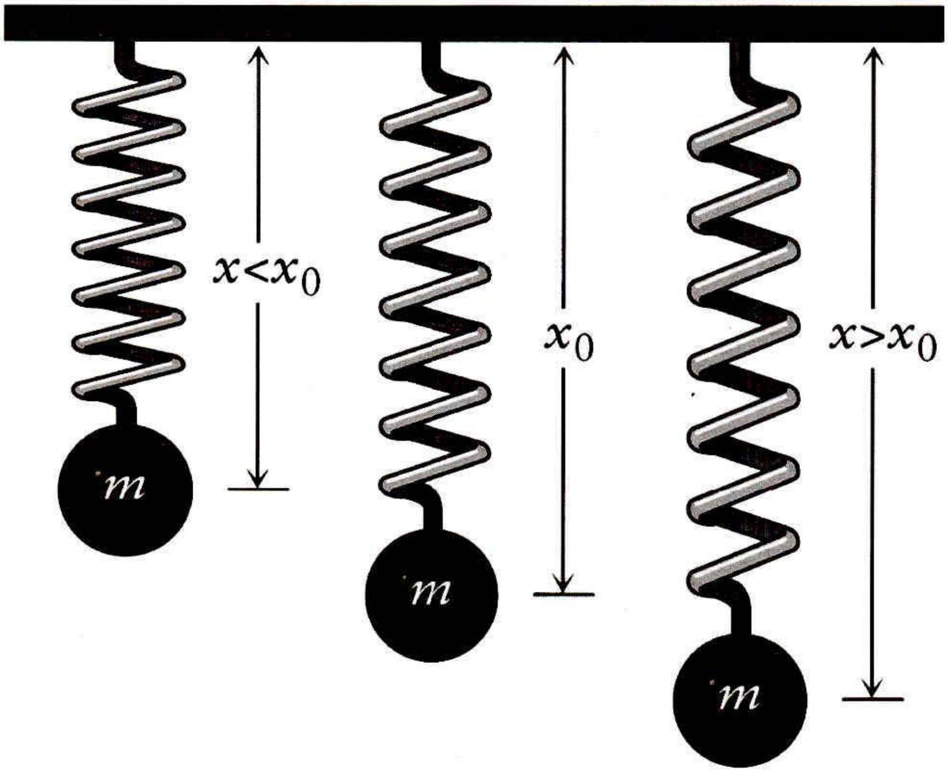
Thus, when $h\nu/k_BT$ for a particular oscillator is << 1 (*i.e.* at large wavelengths, low frequencies), the behavior of the oscillator conforms to the "classical" theory. However, when $h\nu/k_BT$ >> 1 (*i.e.*, at small wavelengths, large frequencies), there is virtually no contribution to blackbody radiation from that oscillator.

Planck's theory reduces to classical theory at low frequencies:

$$\rho_T(n) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/k_BT} - 1} \approx \frac{8\pi h\nu^3}{c^3}\frac{1}{([1 + h\nu/k_BT] - 1)} = \frac{8\pi k_B T\nu^2}{c^3}$$

Harmonic oscillator model applied to blackbody problem

Atoms in blackbody modeled as oscillating bodies:



According to classical mechanics, the restoring force, F, for a given displacement $(x - x_0)$ of the particle m from its equilibrium position, x_0 is given by Hooke's Law:

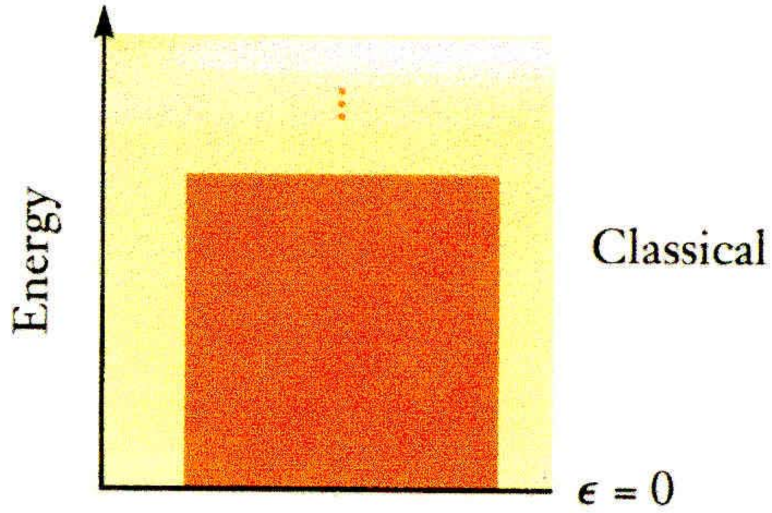
$$F = -k(x - x_0)$$

The displacement $(x - x_0)$ of the particle oscillates about the equilibrium position, x_0, at a periodic frequency:

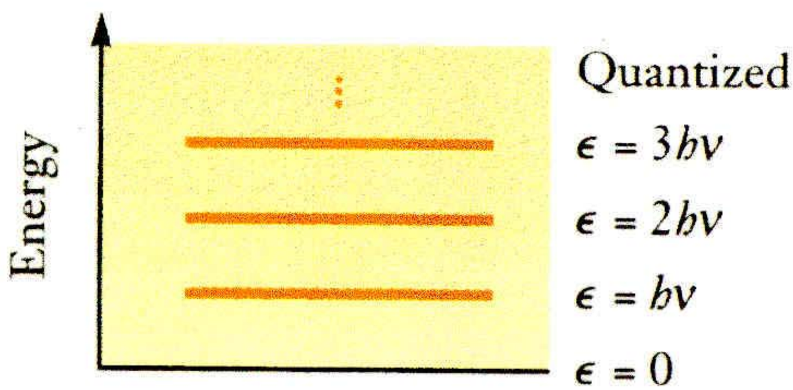
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

The potential energy of the particle is given by:

$$V(x) = -\int_{x_0}^{x} F dx = k\int_{x_0}^{x} (x - x_0) dx = \frac{1}{2} k(x - x_0)^2$$

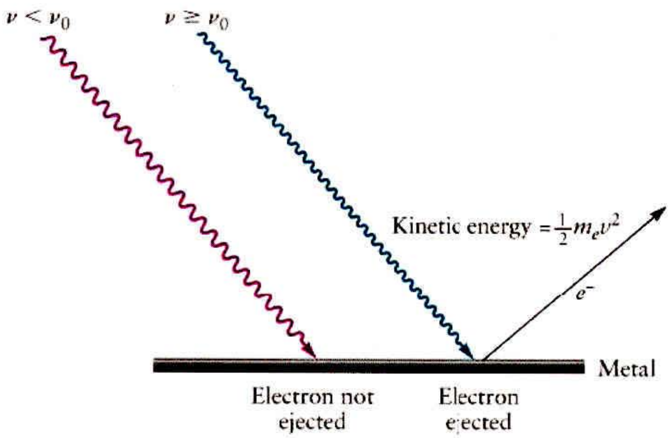


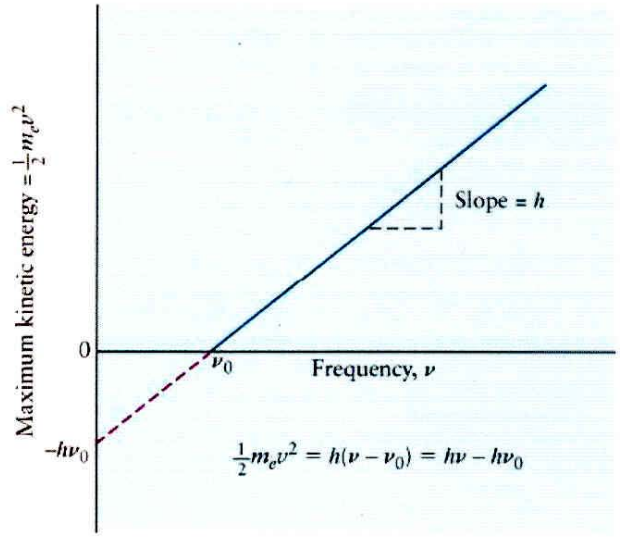
An oscillator obeying classical mechanics has continuous values of energy and can gain or lose energy in arbitrary amounts.

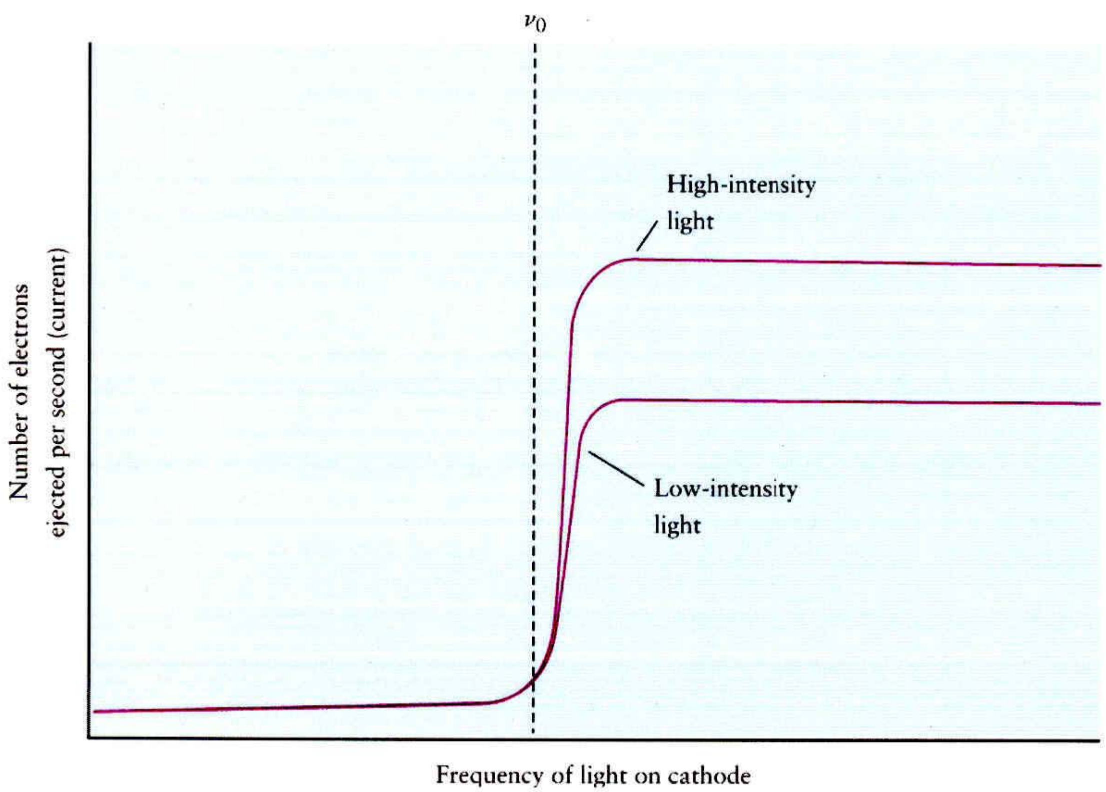


An oscillator described by Planck's postulate has discrete energy levels. It can gain or lose energy only in amounts that correspond to the difference between two energy levels.

The Photoelectric Effect:


$\nu < \nu_0$
$\nu \geq \nu_0$
Kinetic energy $= \frac{1}{2}m_e v^2$
e^-
Metal
Electron not ejected
Electron ejected


Maximum kinetic energy $= \frac{1}{2}m_e v^2$
Slope = h
0
ν_0
Frequency, ν
$-h\nu_0$
$\frac{1}{2}m_e v^2 = h(\nu - \nu_0) = h\nu - h\nu_0$


ν_0
High-intensity light
Low-intensity light
Number of electrons ejected per second (current)
Frequency of light on cathode

Bohr Model of the Atom

The total energy, kinetic plus potential, of the electron in a one-electron atom is given by:

$$E = \frac{1}{2} m_e v^2 - \frac{Ze^2}{4\pi \varepsilon_0 r} \quad (1)$$

The Coulombic attractive force between the electron and the proton(s) in the nucleus is the negative derivative of the potential energy, with respect to r:

$$F_{coul} = -\frac{Ze^2}{4\pi \varepsilon_0 r^2} \quad (2)$$

Since according to Newton's Second Law, F = ma, and because the acceleration of the electron in uniform circular motion is v^2/r, then the *absolute magnitude* of the Coulombic force is:

$$F_{coul} = m_e a = \frac{Ze^2}{4\pi \varepsilon_0 r^2} = m_e \frac{v^2}{r} \quad (3)$$

In order to explain the observed experimental spectroscopy results, Bohr postulated that, unlike in classical mechanics, the angular momentum of the circulating electron is quantized and occurs only as integral multiples of h/2π:

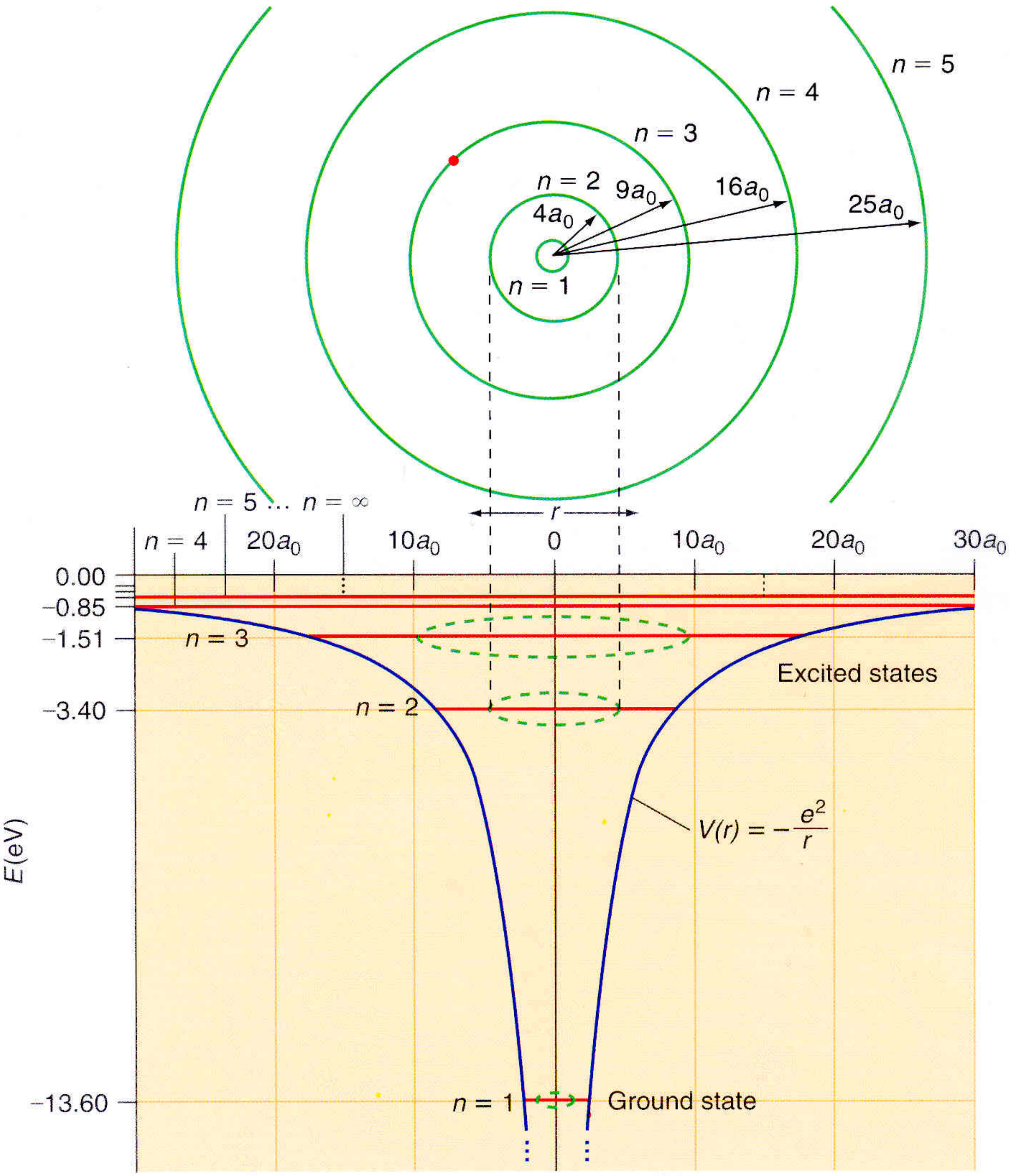
$$L = m_e v r = n\frac{h}{2\pi} = n\hbar \qquad n = 1,2,3,\ldots \quad (4)$$

Combining equations (1), (3), and (4), the radii of the allowed electron "orbits" are given by:

$$r_n = \frac{\varepsilon_0 n^2 h^2}{\pi Z e^2 m_e} = \frac{n^2}{Z} a_0 \quad (5)$$

where a_0 is called the Bohr radius and has the numerical value 5.29×10^{-11} m = 0.529 Å, which corresponds to the radius for an electron having the lowest allowed energy (n = 1) in a hydrogen atom (Z = 1).

Figure 2.12: Bohr Orbits and Energy Levels



The velocities of electrons in the allowed "orbits" are then given by (substitute r_n from Eq. 5 into Eq. 4):

$$v_n = \frac{nh}{2\pi m_e r_n} = \frac{Ze^2}{2\varepsilon_0 nh} \qquad (6)$$

The energies of electrons in the allowed "orbits" can be obtained by substituting values for r_n and v_n into equation (1):

$$\begin{aligned} E_n &= -\frac{Z^2 e^4 m_e}{8\varepsilon_0 n^2 h^2} = -(2.18\times 10^{-18}\ \text{J})\frac{Z^2}{n^2} \\ &= -(13.60\ \text{eV})\frac{Z^2}{n^2} \qquad n = 1,2,3,\ldots \end{aligned} \qquad (7)$$

where the quantity 2.18×10^{-18} J is referred to as a rydberg.

When an electron in a one-electron atom undergoes a transition from one allowed energy state to another ($n_i \rightarrow n_f$), light of an appropriate wavelength, as given by Planck's Equation, is either absorbed ($n_f > n_i$) or emitted ($n_f < n_i$):

$$\Delta E = h\nu = \frac{Z^2 e^4 m_e}{8\varepsilon_0{}^2 h^2}\left[\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right] \qquad (8)$$

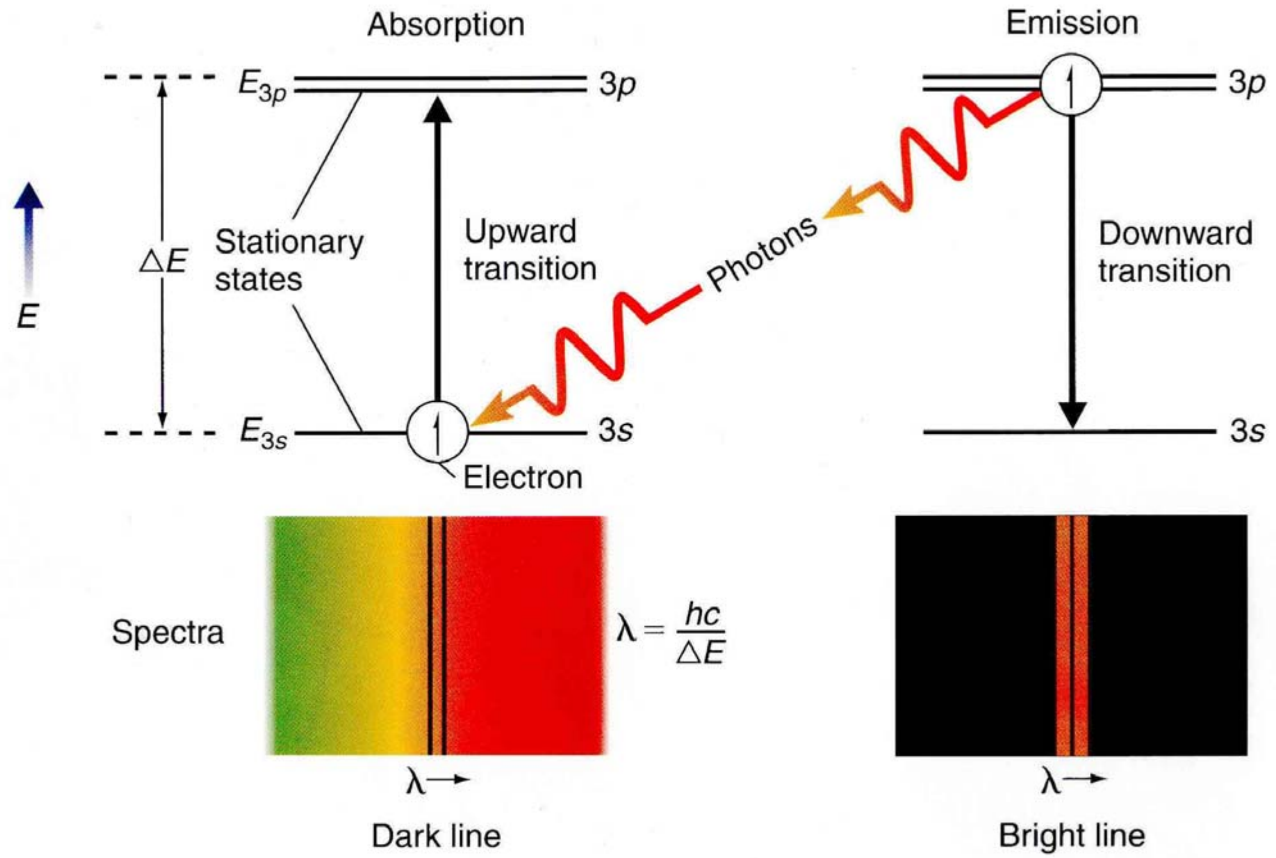
from which the frequencies of light that are emitted during the transitions are then given by

$$\nu = \frac{Z^2 e^4 m_e}{8\varepsilon_0{}^2 h^3}\left[\frac{1}{n\ {}^2} - \frac{1}{n_i{}^2}\right] = (3.29\times 10^{15}\ \text{s}^{-1})Z^2\left[\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right] \qquad (9)$$

where $n_i > n_f$. When $n_f > n_i$ (light absorption), the corresponding frequencies are:

$$\nu = \frac{Z^2 e^4 m_e}{8\varepsilon_0{}^2 h^3}\left[\frac{1}{n\ {}^2} - \frac{1}{n_i{}^2}\right] = (3.29\times 10^{15}\ \text{s}^{-1})Z^2\left[\frac{1}{n_i{}^2} - \frac{1}{n_f{}^2}\right] \qquad (10)$$

Figure 2.8: Bohr's Stationary State Hypothesis



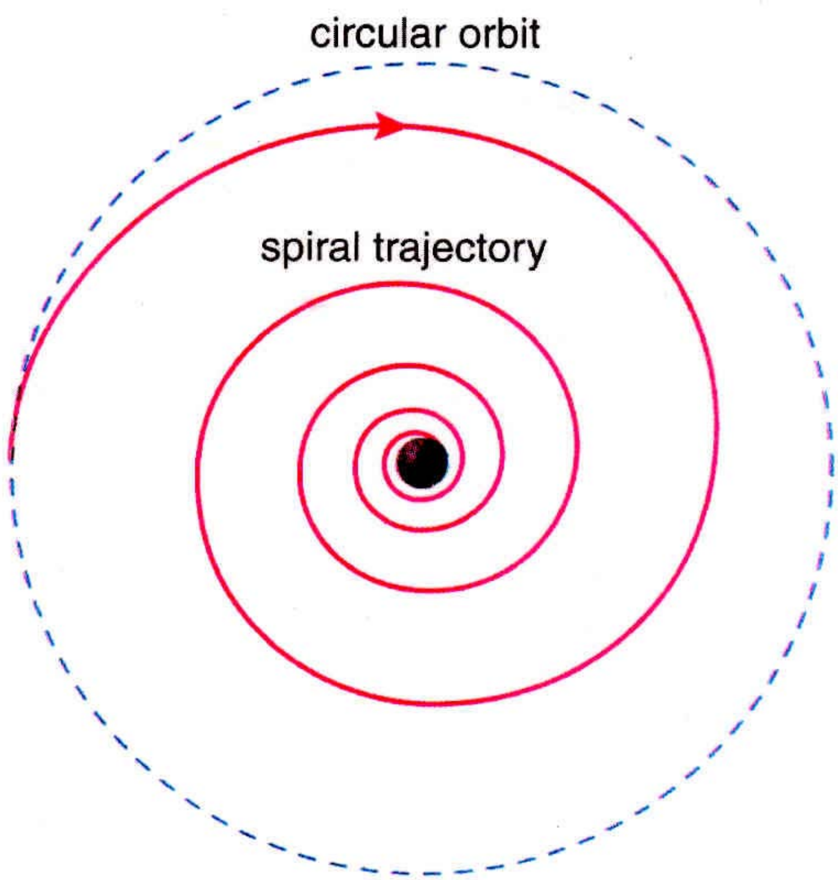
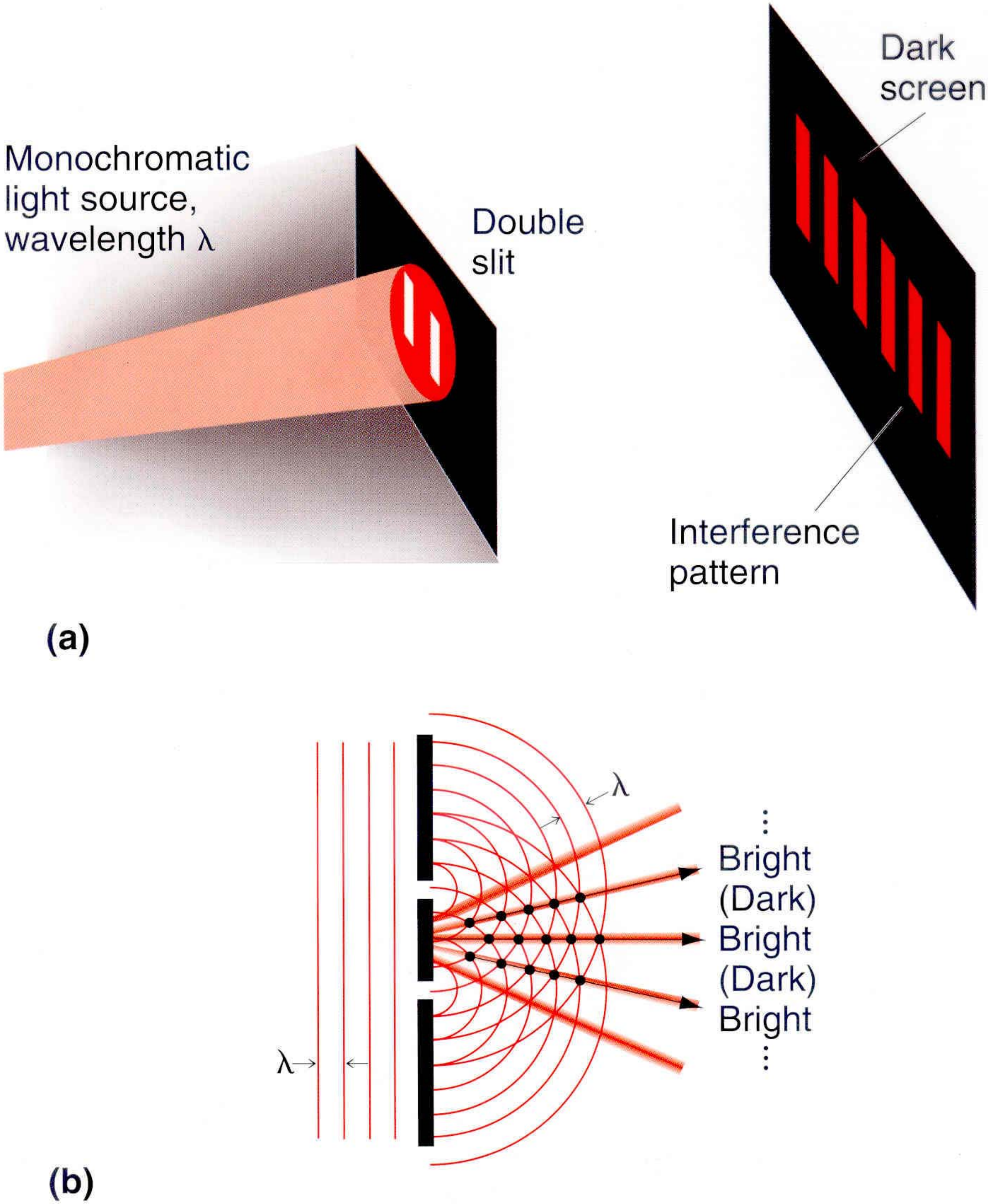


FIGURE 12.11

Classical particle-based physics predicts that an electron in a circular orbit will lose energy by radiation and spiral into the nucleus.

Figure 2.2: Diffraction Interface of Light Waves



DeBroglie's Wave-Particle Duality

The allowed wavelengths for <u>standing</u> waves over a length, L, are:

$$n\frac{\lambda}{2} = L \qquad n = 1, 2, 3, \ldots$$

The allowed wavelengths for standing <u>circular</u> waves for a radius, r, are:

$$n\lambda = 2\pi r \qquad n = 1, 2, 3, \ldots$$

From Bohr's quantization of angular momentum:

$$m_e v r = n\frac{h}{2\pi} \quad \text{or} \quad 2\pi r = n\left(\frac{h}{m_e v}\right)$$

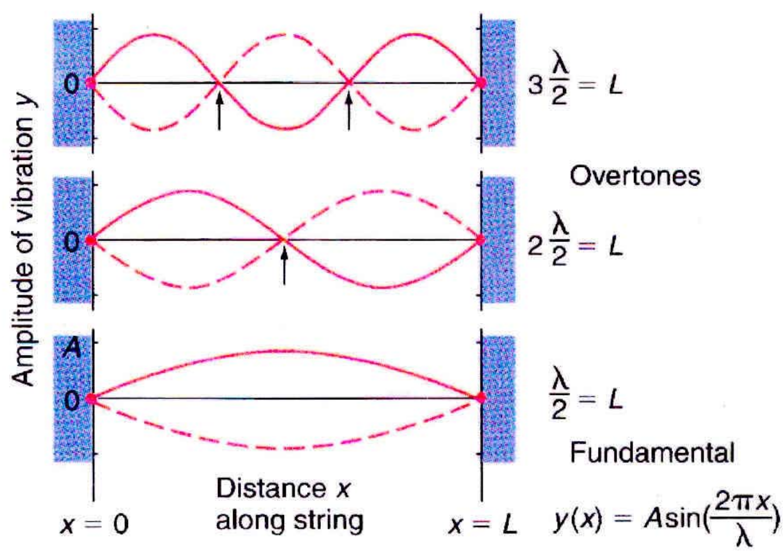
Combining the two above expressions for $2\pi r$:

$$\lambda = \frac{h}{m_e v} = \frac{h}{p}$$

DeBroglie's generalization is that <u>any</u> particle moving with linear momentum, p, has wave-like properties and a wavelength $\lambda = h/p$ associated with it.

This principle applies both to particles having a mass (*e.g.*, electrons) and to massless particles (*e.g.*, photons).

Figure 2.9
The three simplest allowed standing wave vibrations of a plucked string of length L. Each waveform obeys the equation $n(\lambda/2) = L$, with $n = 1, 2, 3, \ldots$, and λ the wavelength of the vibration. The arrows indicate the nodes of the waves, places where the waves change sign. The constraint on λ results from tying down the ends of the string.



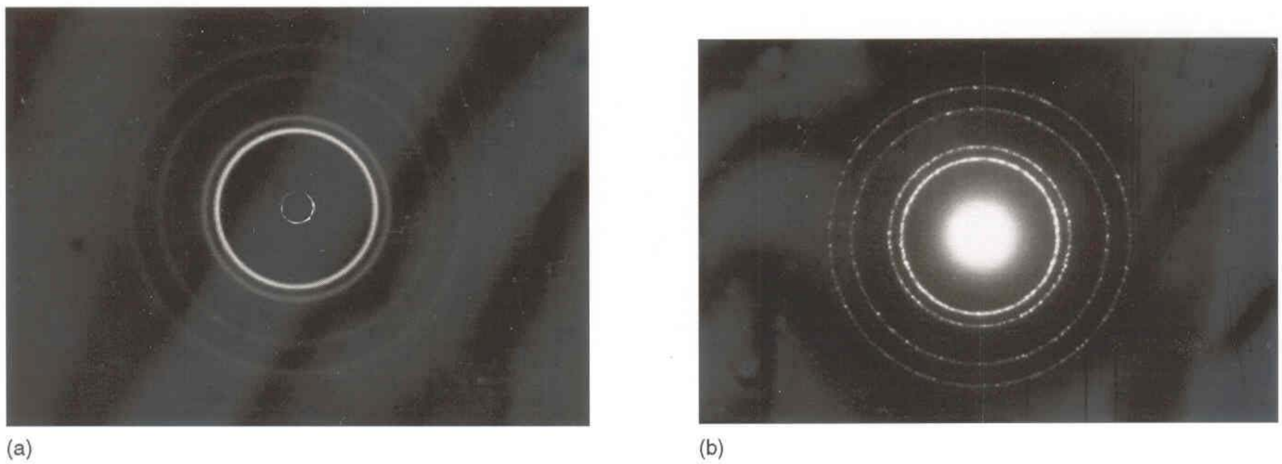


Figure 2.10
Comparison of the scattering of (**a**) X-rays and (**b**) electrons by aluminum foil. The striking similarity of the photographs, whose bright rings can be explained using a wave model, is persuasive evidence of the correctness of de Broglie's postulate of matter waves.

For an electron traveling at 10% of the speed of light (c):

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.62 \times 10^{-34}\,\mathrm{J \cdot s}}{9.11 \times 10^{-31}\,\mathrm{kg} \times 0.1 \times 3 \times 10^{8}\,\mathrm{m/s}}$$

$$= 7.3 \times 10^{-11}\,\mathrm{m}$$

$$= 0.73\ \mathrm{A}^{\circ} \quad (0.073\ \mathrm{nm})$$

Table 2.1: De Broglie Wavelengths

TABLE 2.1

de Broglie wavelengths for various moving objects

Object	Mass (g)	Wavelength (Å)
1-Volt electron	9.11×10^{-28}	12.3
10-Volt electron	9.11×10^{-28}	3.88
100-Volt electron	9.11×10^{-28}	1.23
Helium atom at room temperature	6.65×10^{-24}	0.73
α particle from radium	6.65×10^{-24}	0.000066
Average protein molecule	6.64×10^{-20}	0.0073
Floating chalk dust	$\sim 10^{-6}$	$\sim 6.6 \times 10^{-13}$
Driven golf ball	45	4.9×10^{-24}
Pitched baseball	140	1.9×10^{-24}
Chemistry professor, pacing	8×10^{4}	8.3×10^{-26}
Car at 30 mph	9×10^{5}	5.5×10^{-28}
Earth in orbit around sun	6×10^{27}	3.7×10^{-53}

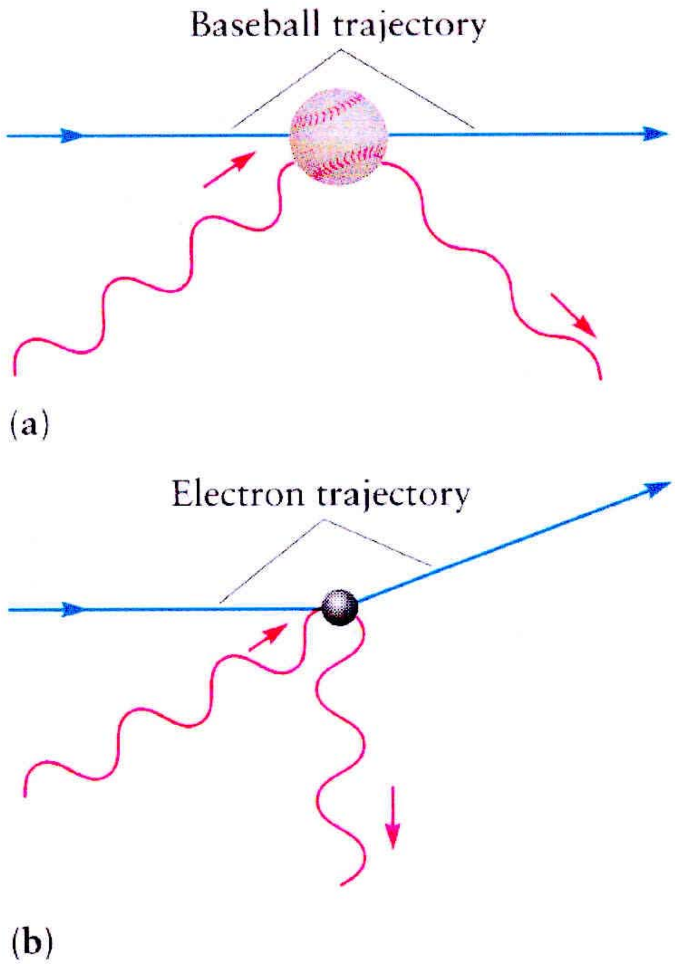


FIGURE 4.23 A photon, which has a negligible effect on the trajectory of a baseball (a), significantly perturbs the trajectory of the far less massive electron (b).

To accurately locate the position of an object using electromagnetic radiation (*i.e.*, light), it is necessary to use a wavelength that is ≤ the size of the object. For an object as small as an electron in an atom, the required wavelength is thus ~ 0.1 nm. However, photons having this wavelength (x-rays) have such large momenta that their interaction with the electron unavoidably disturbs its position, thus decreasing the certainty of the measurement.

Heisenberg Uncertainty Principle

$$\Delta \mathbf{x} \cdot \Delta \mathbf{p} \geq \frac{\hbar}{2} \quad \left(\geq \frac{\mathbf{h}}{4\pi} \right)$$

where Δx and Δp are the uncertainties in position and momentum, respectively, and h = Planck's constant (6.63×10^{-34} J-s).

For an uncertainty in the position of an electron of 1% of 0.05 nm,

$$\Delta x = (0.01)(0.05) \times 10^{-9} \text{ m/nm} = 5 \times 10^{-13} \text{ m}$$

Thus, the uncertainty in momentum (p) is

$$\Delta \mathbf{p} = \frac{\mathbf{h}}{4\pi \Delta \mathbf{x}} = \frac{6.63 \times 10^{-34} \mathbf{kg} \cdot \mathbf{m}^2 / \mathbf{s}}{4(3.14)(5 \times 10^{-13} \mathbf{m})} = 1.05 \times 10^{-22} \frac{\mathbf{kg} \cdot \mathbf{m}}{\mathbf{s}}$$

Since p = mv, then Δp = mΔv, and

$$\Delta \mathbf{v} = \frac{\Delta \mathbf{p}}{\mathbf{m}} = \frac{1.05 \times 10^{-22} \mathbf{kg} \cdot \mathbf{m} / \mathbf{s}}{9.11 \times 10^{-31} \mathbf{kg}} \approx 1 \times 10^{8} \mathbf{m} / \mathbf{s}$$

Because this uncertainty in electron velocity is close to the speed of light (3×10^{8} m/s), the electron's velocity is essentially unknown.

For an uncertainty in the position of a 145 g baseball of 1% of 0.05 m,

$$\Delta \mathbf{v} = \frac{\Delta \mathbf{p}}{\mathbf{m}} = \frac{\mathbf{h}}{\Delta \mathbf{x} \cdot \mathbf{m} \cdot 4\pi} = \frac{6.63 \times 10^{-34} \mathbf{kg} \cdot \mathbf{m}^2 / \mathbf{s}}{(5 \times 10^{-4} \mathbf{m})(0.145 \mathbf{kg})(4)(3.14)} = 7.3 \times 10^{-31} \mathbf{m} / \mathbf{s}$$

This uncertainty in velocity is negligibly small, and a baseball's velocity can, in principle, be known with great accuracy.

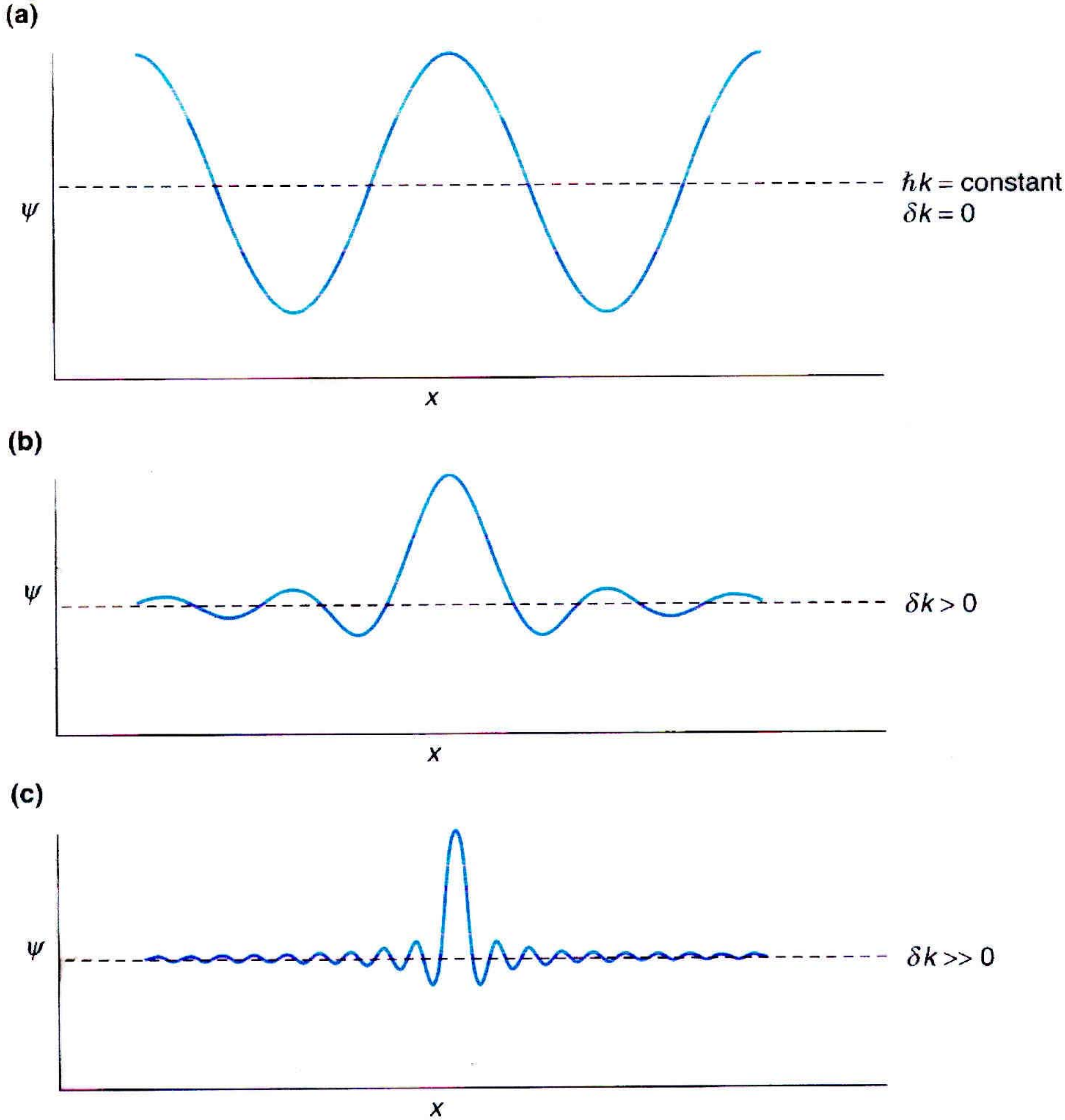


Figure 3.10. A particle becoming more and more well defined in position, while becoming less and less defined in momentum from (a) to (c). For $\delta k \gg 0$ many values of momenta, $\hbar k$, are summed together.