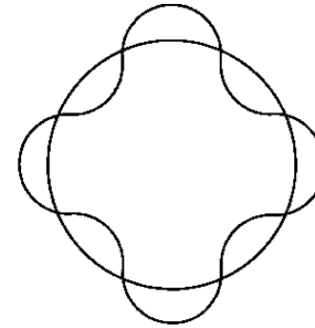
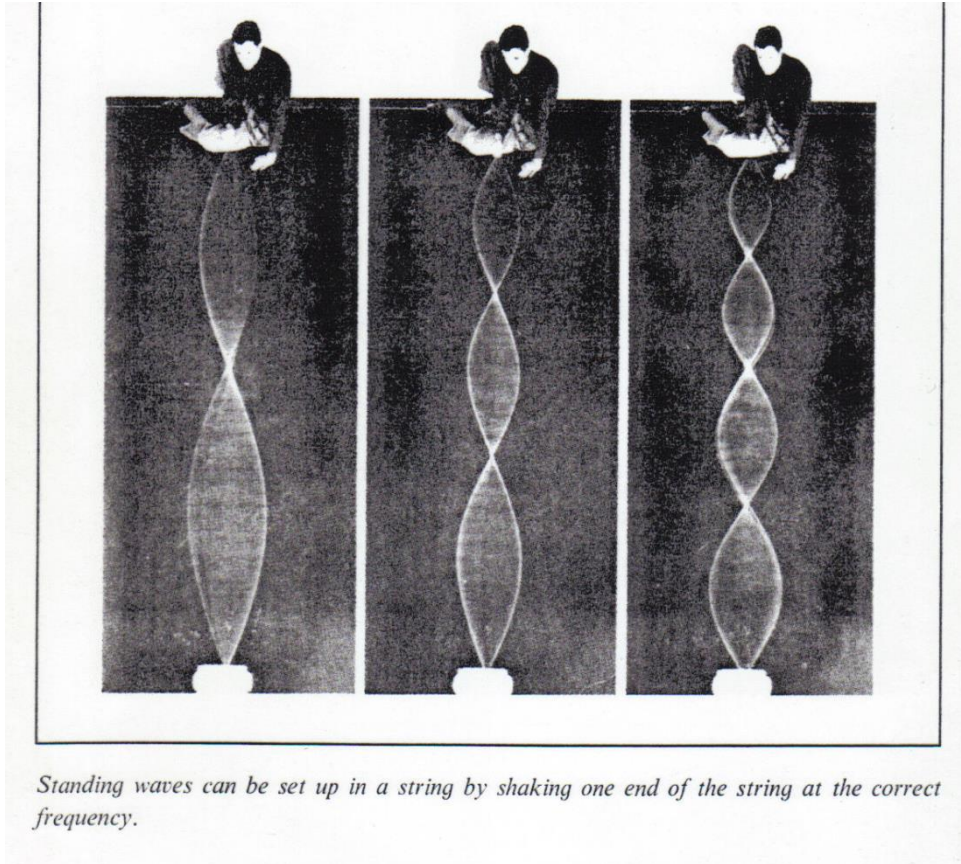
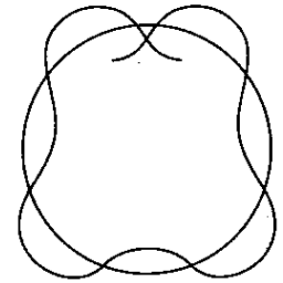


Partícula na Caixa



(a)



(b)

An illustration of matching and mismatching de Broglie waves travelling in Bohr orbits.

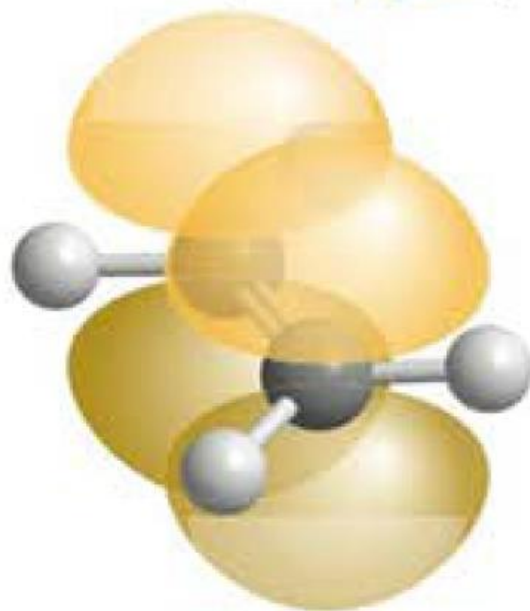
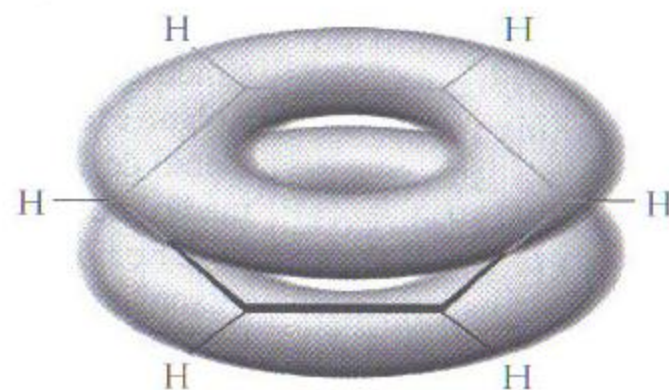
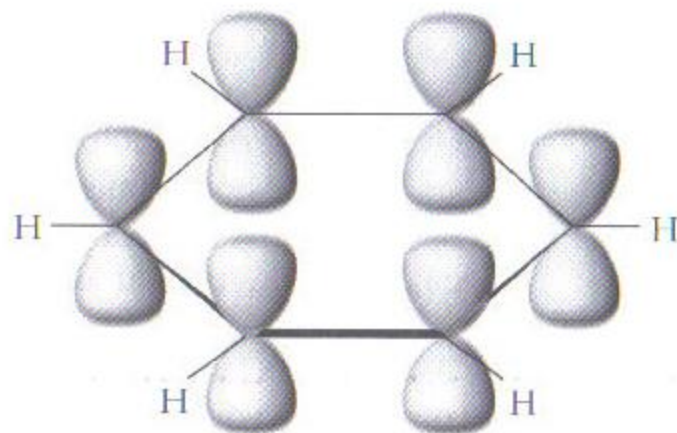
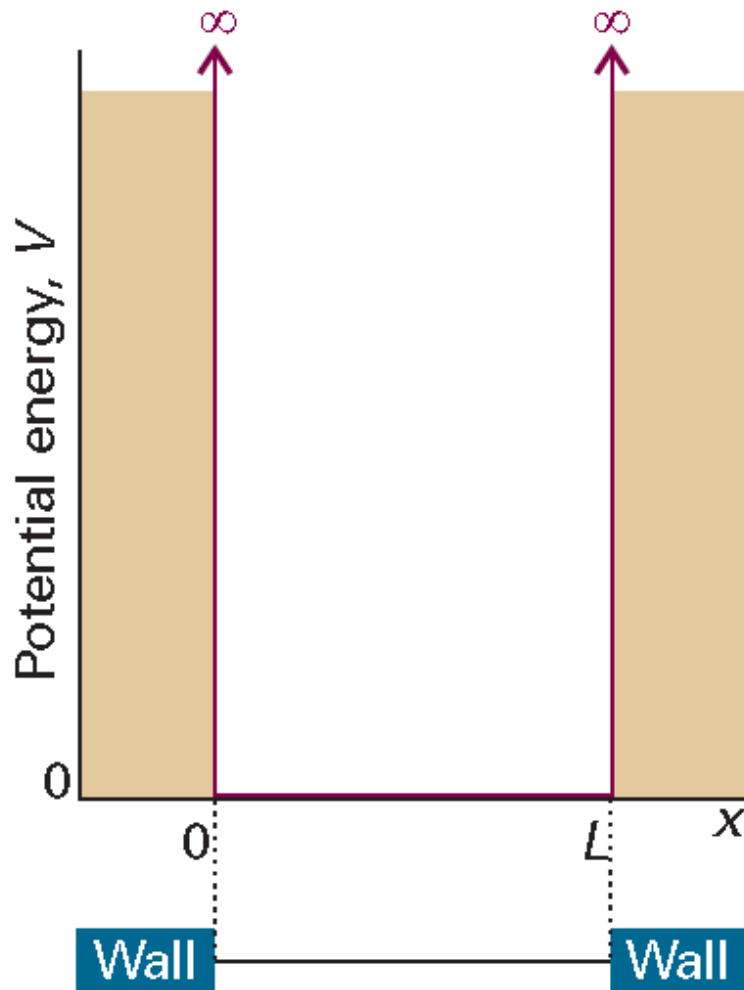


FIGURA 18.7 A ligação π (representada pelas nuvens eletrônicas amarelas) em uma molécula de alqueno torna a molécula resistente à torção da ligação dupla. Em consequência, os seis átomos (os dois átomos de C que formam a ligação e os quatro átomos a eles ligados) estão no mesmo plano.



Partícula na Caixa



$$V(x) = \begin{cases} 0, & 0 \leq x \leq L \\ \infty, & x < 0, x > L \end{cases}$$

condições de contorno:

$$\psi(x) = 0 \text{ em } \begin{cases} x = 0 \\ x = L \end{cases}$$

Fig. 9.1 A particle in a one-dimensional region with impenetrable walls. Its potential energy is zero between $x = 0$ and $x = L$, and rises abruptly to infinity as soon as it touches the walls.

equação de Schrödinger:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + \hat{V} \psi(x) = E \psi(x)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} = E \psi \quad \text{solução proposta: } \psi(x) = A \sin(kx)$$

$$\psi(x) = 0 \text{ em } \begin{cases} x = 0 \\ x = L \end{cases} \Rightarrow kL = n\pi, \quad n = 1, 2, 3, \dots$$

$$k = \frac{n\pi}{L}$$

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right), \quad n = 1, 2, 3, \dots$$

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

$$\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)$$

$$\frac{d^2\psi}{dx^2} = -\left(\frac{n\pi}{L}\right)^2 \psi$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L}\right)^2 \psi$$

↓
 E_n

$$E_n = \frac{n^2 h^2}{8mL^2}, \quad n = 1, 2, 3, \dots$$

Normalização da função de onda

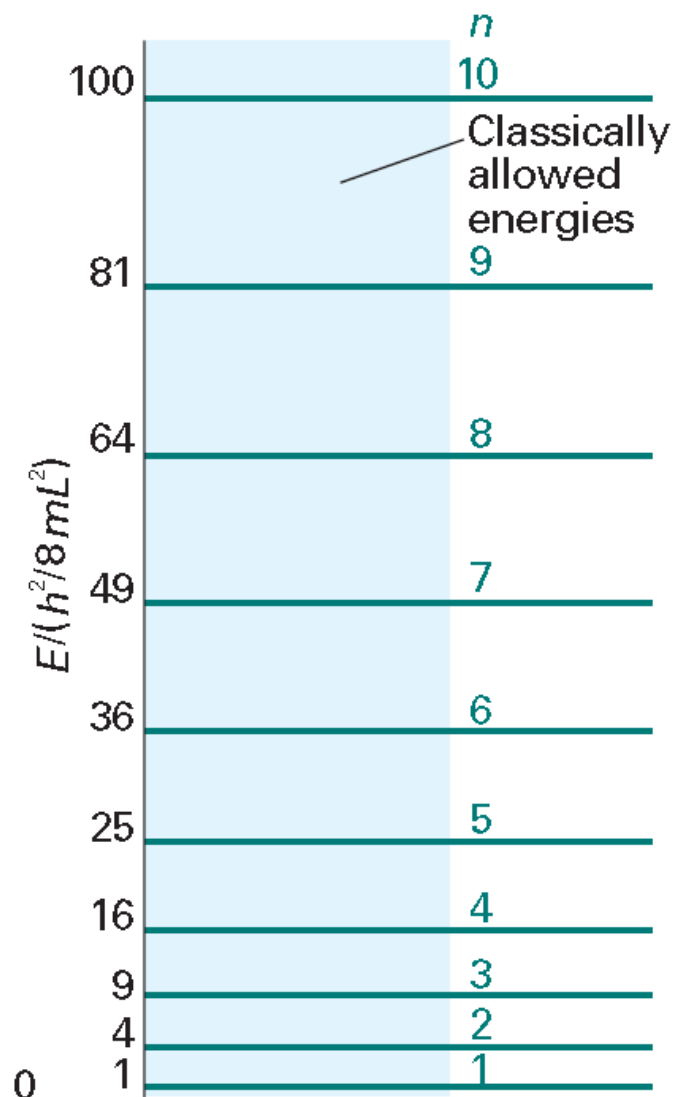
$$\int \psi^* \psi d\tau = 1$$

$$A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1 \quad \Rightarrow \quad A^2 \frac{L}{2} = 1, \quad A = \sqrt{\frac{2}{L}}$$

$$\int \sin^2(ax) dx = \frac{x}{2} - \frac{\sin(2ax)}{4a} \quad \int_0^L \sin^2(ax) dx = \frac{x}{2} \Big|_0^L - \frac{\sin(2ax)}{4a} \Big|_0^L = \frac{L}{2}$$

$0, a = \frac{n\pi}{L}$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad E_n = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, \dots$$



Energia do ponto zero:
a energia do estado fundamental
não é zero, $E_{n=1} \neq 0$

Fig. 9.2 The allowed energy levels for a particle in a box. Note that the energy levels increase as n^2 , and that their separation increases as the quantum number increases.

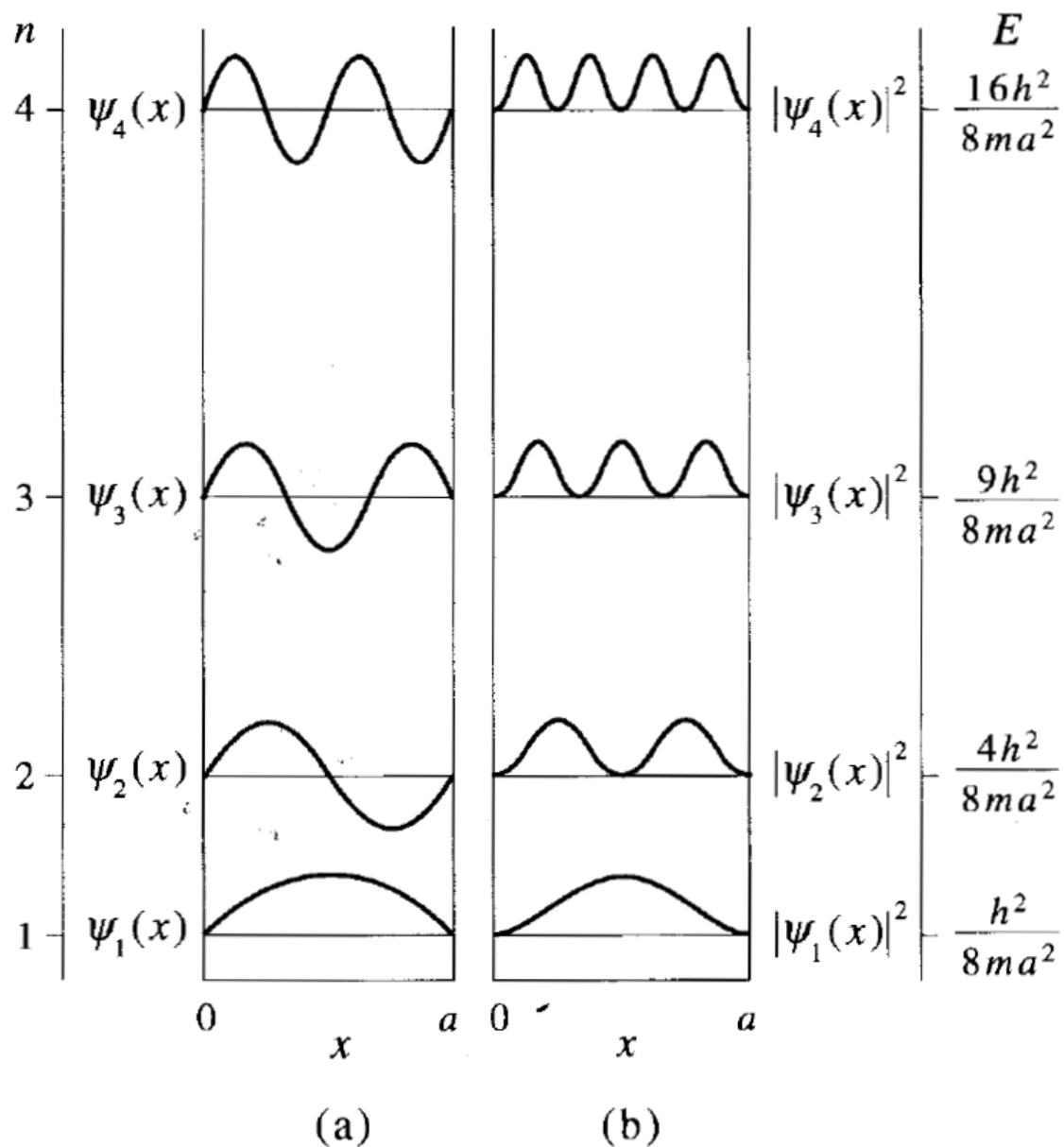


FIGURE 3.2

The energy levels, wave functions (a), and probability densities (b) for the particle in a box

Exemplo de cálculo de média: $\langle x \rangle$

$$\langle a \rangle = \int \psi^* \hat{A} \psi d\tau$$

$$\langle x \rangle = \frac{2}{L} \int_0^L \sin\left(\frac{n\pi x}{L}\right) x \sin\left(\frac{n\pi x}{L}\right) dx$$

$$\int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx = \frac{L^2}{4}$$

$$\langle x \rangle = \frac{L}{2}$$

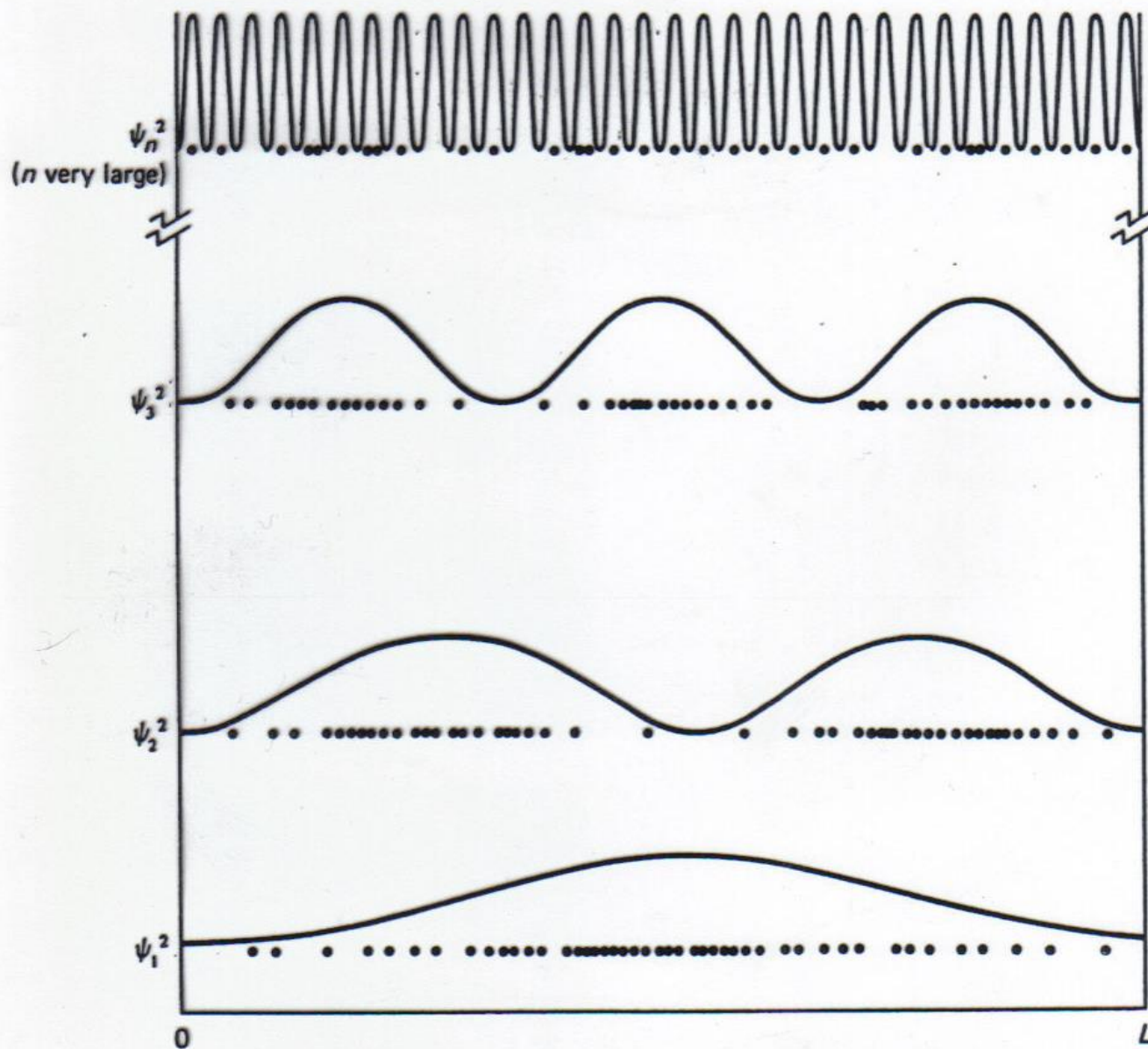
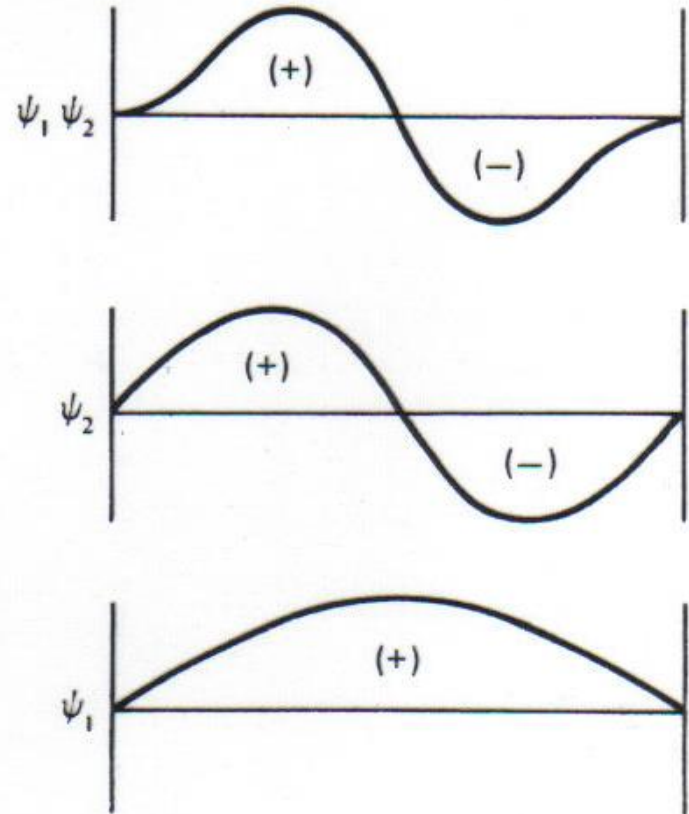


FIG. 2-5 ψ^2 and observed particle distribution for the three lowest-energy and one high-energy state of the particle in a one-dimensional box.

ψ_1 is symmetric, ψ_2 is antisymmetric, and $\psi_1\psi_2$ is antisymmetric. The total signed area bounded by the odd functions is zero since complete cancellation of positive and negative components occurs.



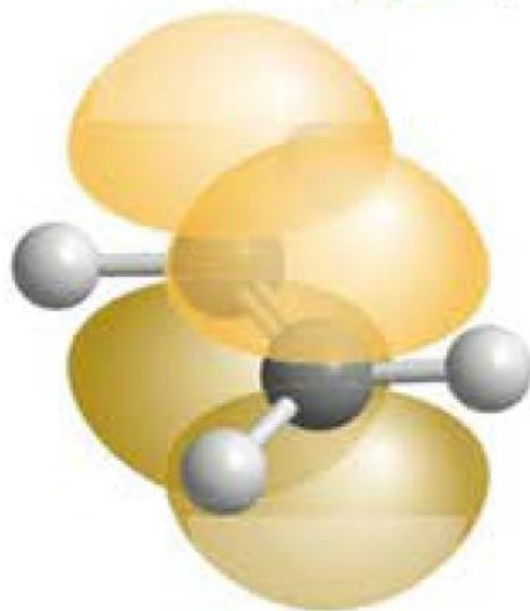
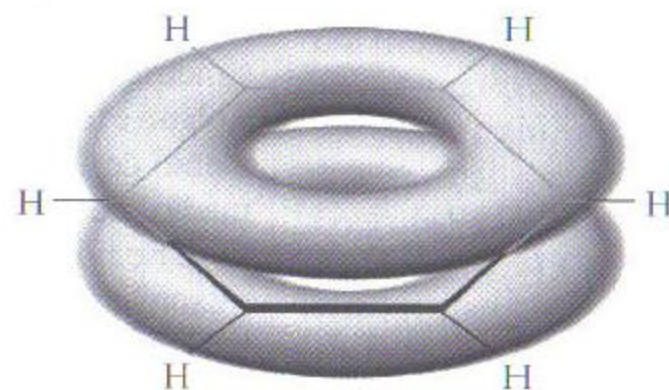
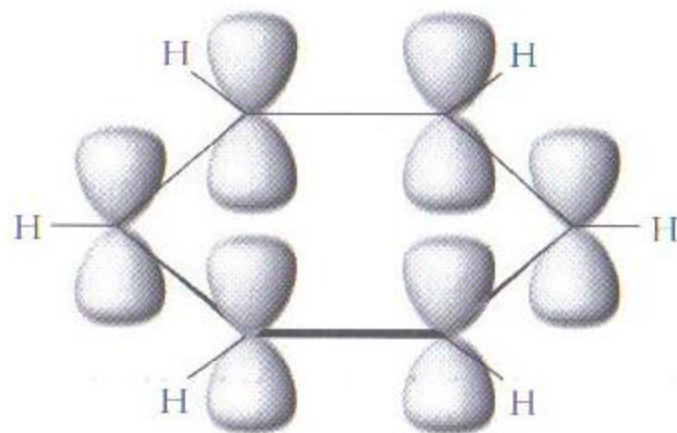
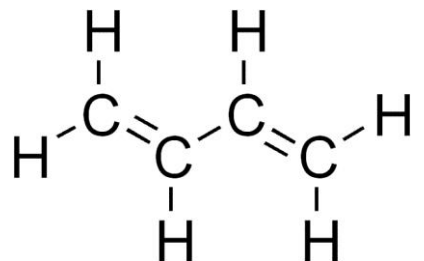


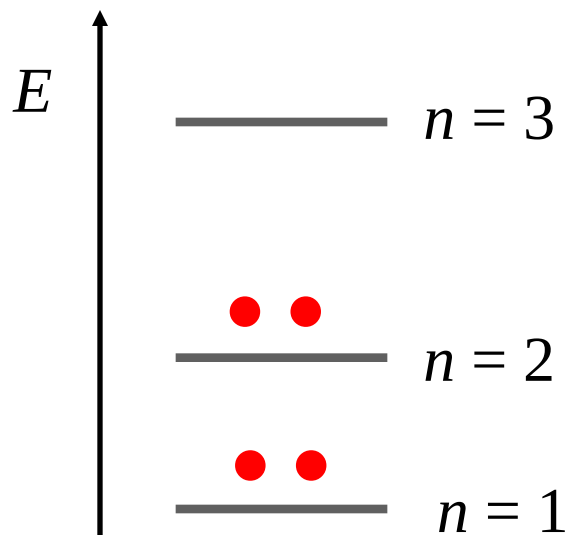
FIGURA 18.7 A ligação π (representada pelas nuvens eletrônicas amarelas) em uma molécula de alqueno torna a molécula resistente à torção da ligação dupla. Em consequência, os seis átomos (os dois átomos de C que formam a ligação e os quatro átomos a eles ligados) estão no mesmo plano.



Partícula na caixa: modelo para o elétron confinado numa molécula



$L \approx 580 \text{ pm}$



absorção experimental: $\lambda = 217 \text{ nm}$

$$\Delta E = E_3 - E_2 = \frac{h^2}{8mL^2} (3^2 - 2^2)$$

$$\Delta E = \frac{(6,6262 \times 10^{-34} \text{ Js})^2}{8,9,109 \times 10^{-31} \text{ kg} (580 \times 10^{-12} \text{ m})^2} (3^2 - 2^2)$$

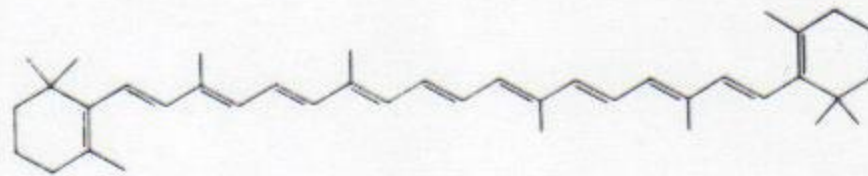
$$\Delta E = 9,02 \times 10^{-19} \text{ J}$$

$$h\nu = h \frac{c}{\lambda} \quad \text{energia da radiação}$$

absorção calculada: $\lambda = 220 \text{ nm}$

hexatrieno, $\lambda = 260 \text{ nm}$

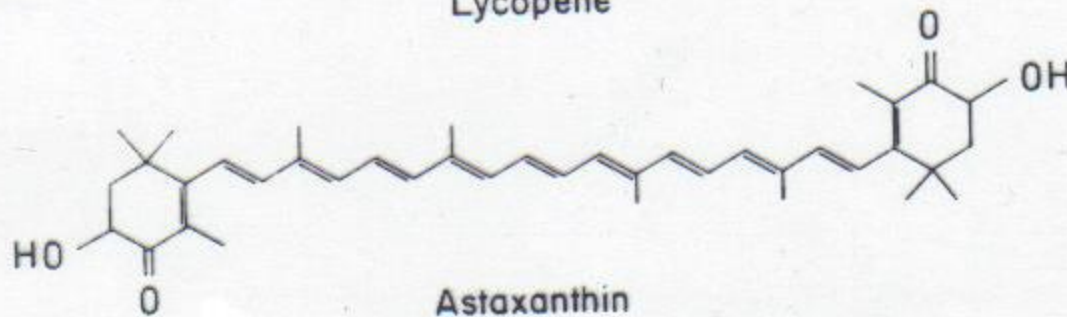
octatetraeno, $\lambda = 302 \text{ nm}$



β - Carotene

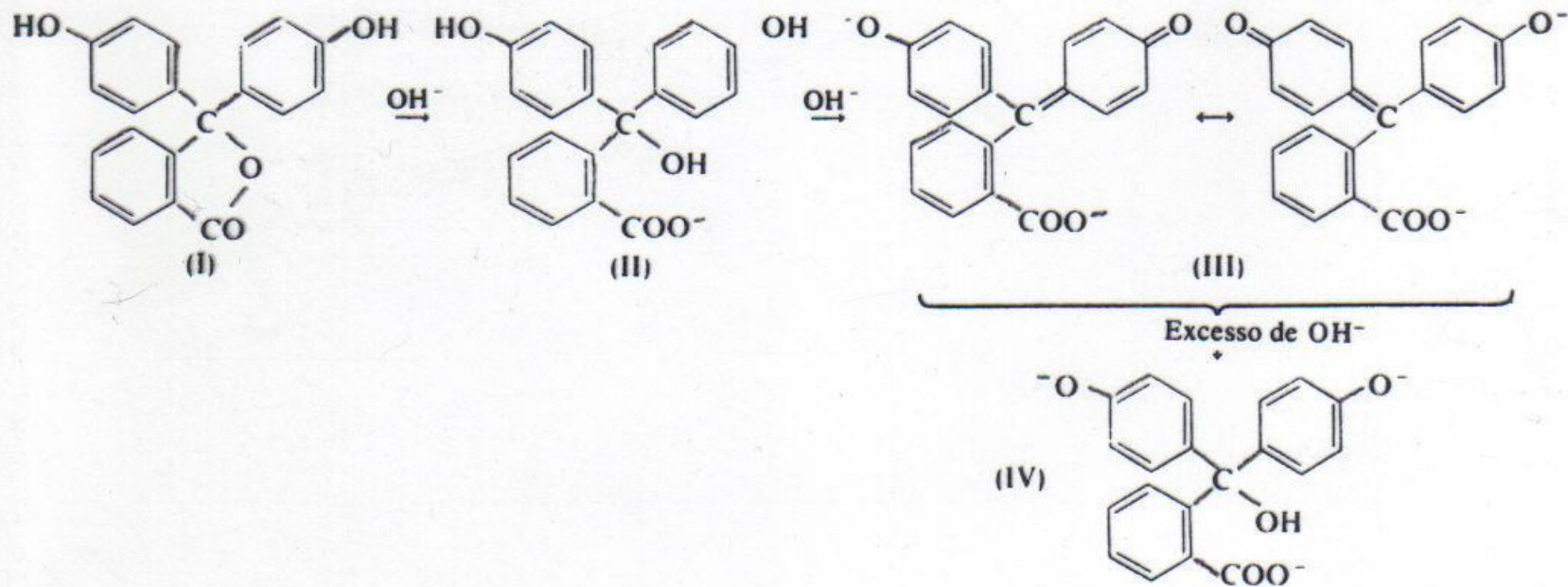


Lycopene

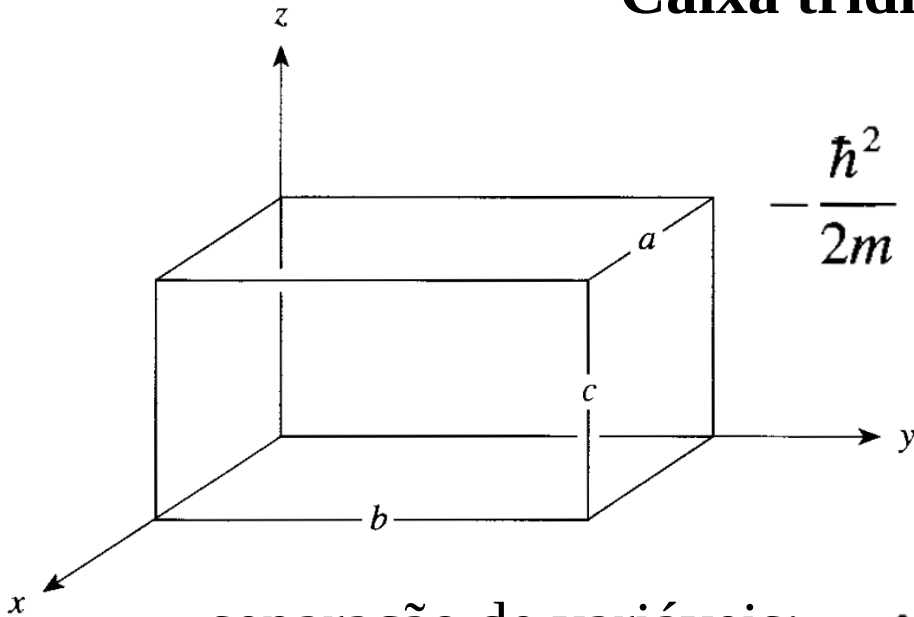


Astaxanthin

Structures of three carotenoids.



Caixa tridimensional



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

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi$$

separação de variáveis: $\psi(x, y, z) = X(x)Y(y)Z(z)$

$$-\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{d^2 X}{dx^2} = E_x$$

$$-\frac{\hbar^2}{2m} \frac{1}{Y(y)} \frac{d^2 Y}{dy^2} = E_y$$

$$-\frac{\hbar^2}{2m} \frac{1}{Z(z)} \frac{d^2 Z}{dz^2} = E_z$$

$$E_x + E_y + E_z = E$$

Caixa tridimensional

$$E_{n_x n_y n_z} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad \begin{array}{l} n_x = 1, 2, 3, \dots \\ n_y = 1, 2, 3, \dots \\ n_z = 1, 2, 3, \dots \end{array}$$

Se a caixa for um cubo: $a = b = c$

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

Estados degenerados são estados com a mesma energia.

Por exemplo, $E_{211} = E_{121} = E_{112} = \frac{6h^2}{8ma^2}$

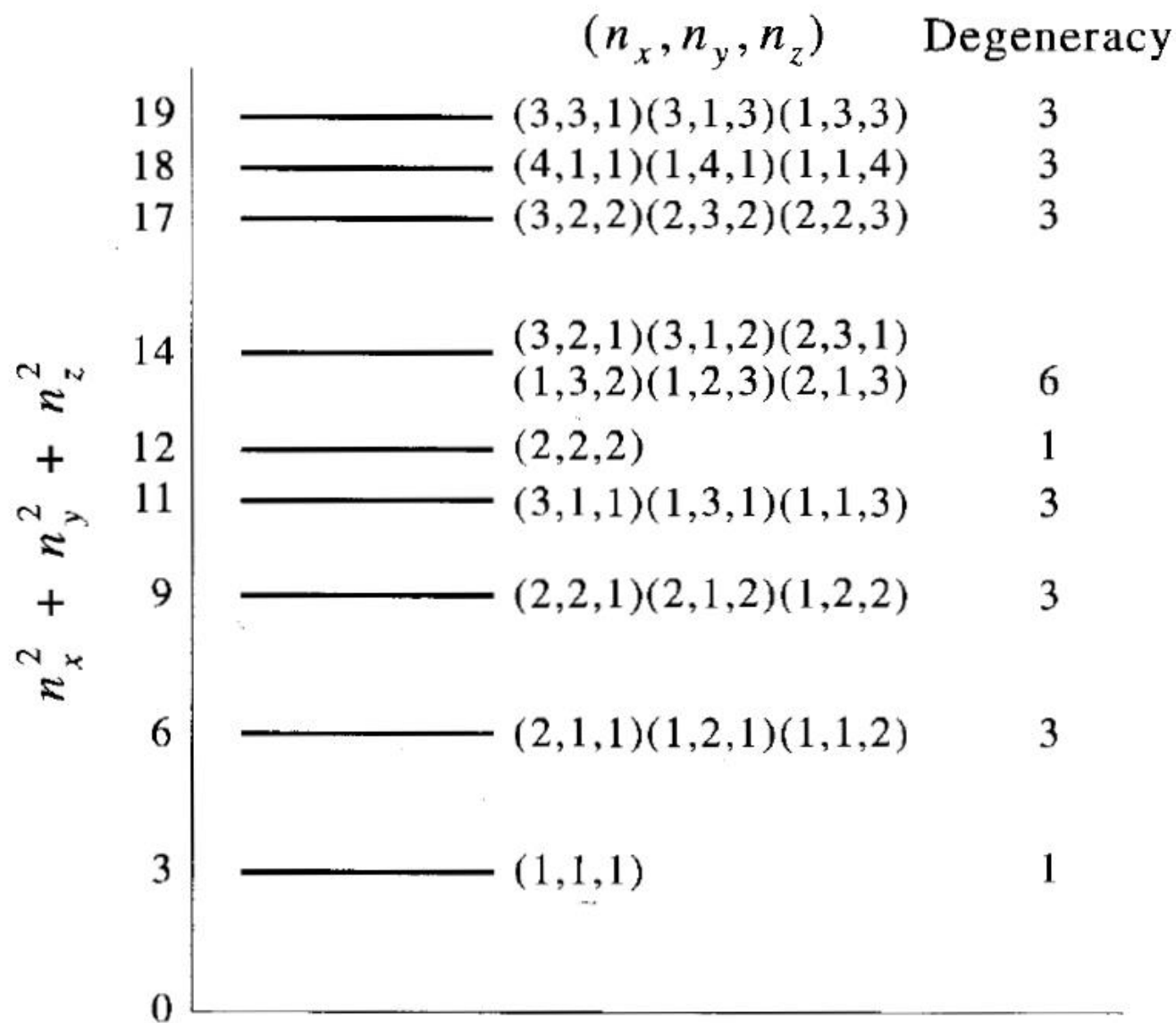
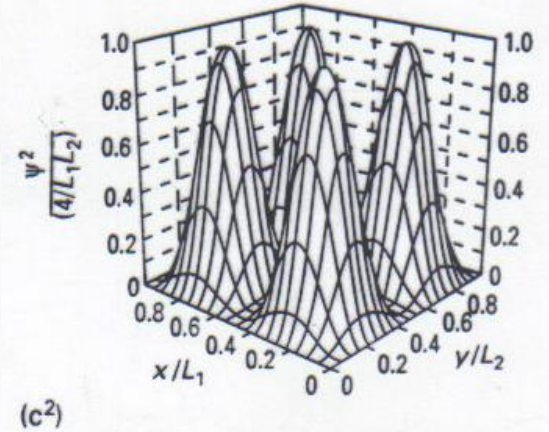
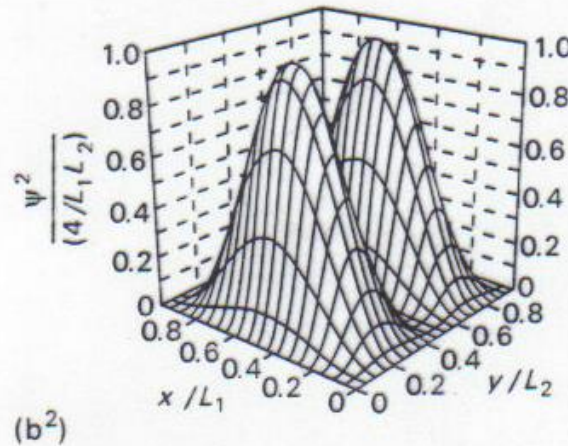
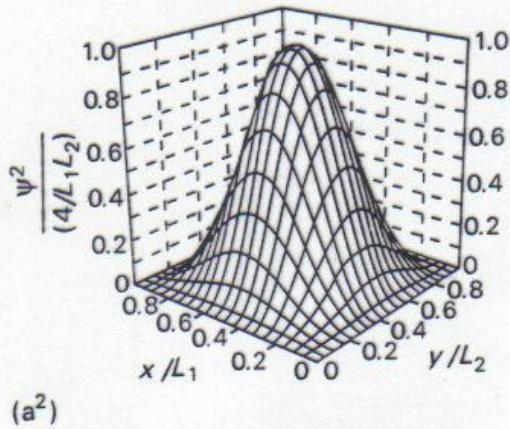
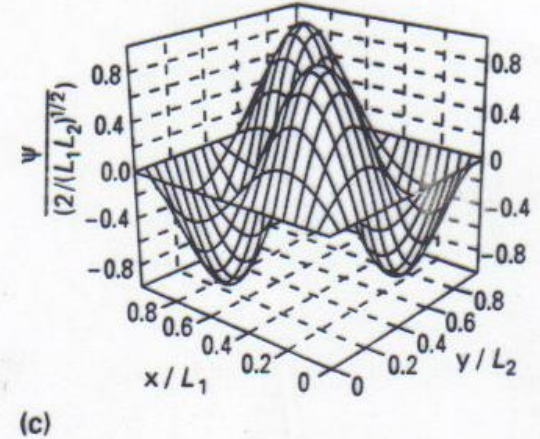
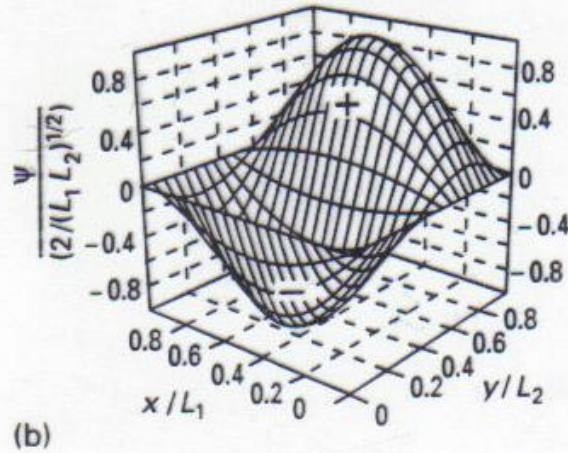
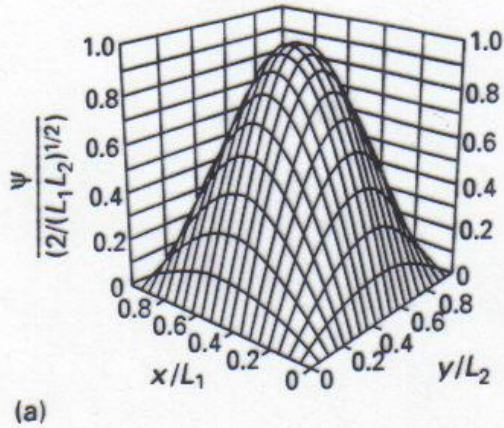


FIGURE 3.6

The energy levels for a particle in a cube. The degeneracy of each level is also indicated.

Caixa bidimensional



$$n_x = 1, n_y = 1$$

$$n_x = 1, n_y = 2$$

$$n_x = 2, n_y = 2$$

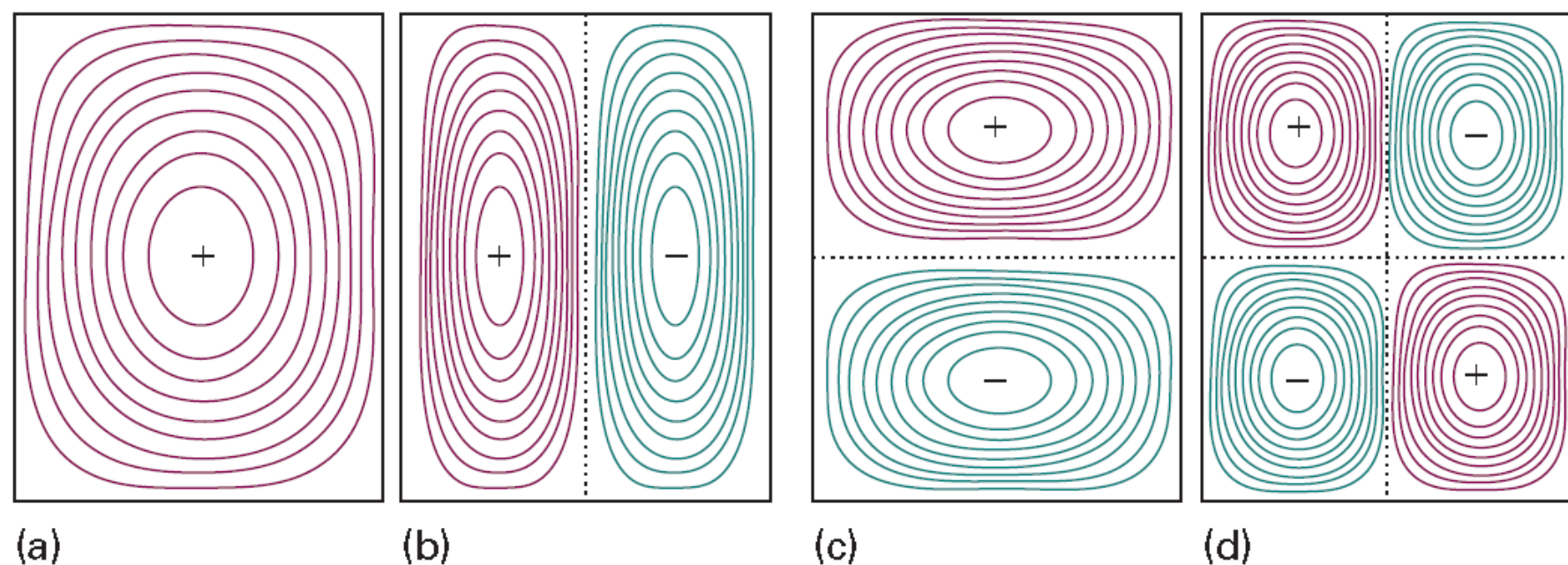
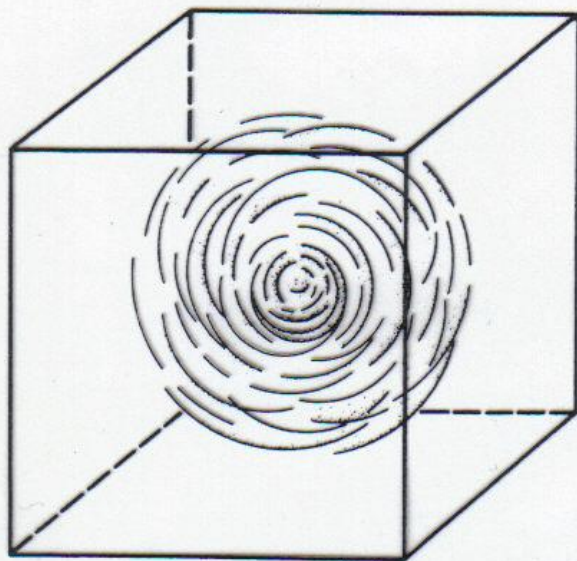
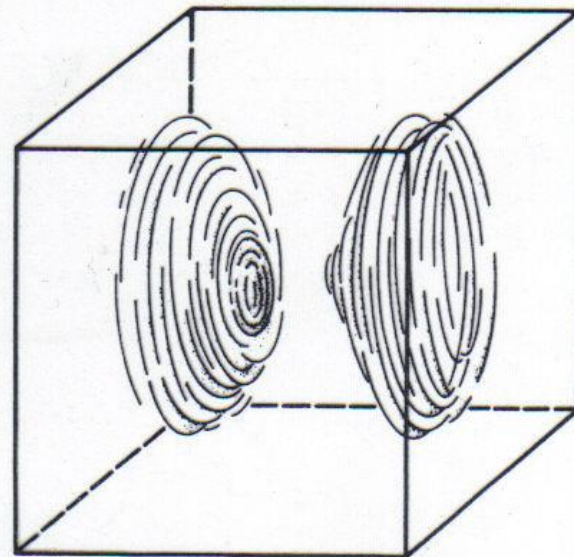


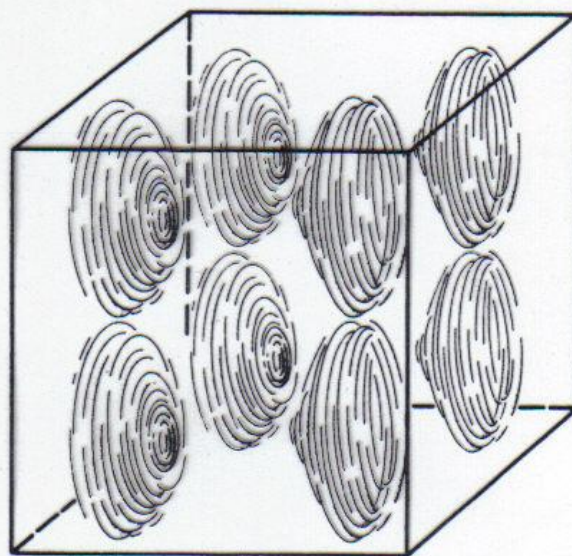
Fig. 9.7 The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude. (a) $n_1 = 1$, $n_2 = 1$, the state of lowest energy, (b) $n_1 = 1$, $n_2 = 2$, (c) $n_1 = 2$, $n_2 = 1$, and (d) $n_1 = 2$, $n_2 = 2$.



(a)



(b)



(c)

Sketches of particle probability distributions for a particle in a cubical box. (a) $n_x = n_y = n_z = 1$. (b) $n_x = 2, n_y = n_z = 1$. (c) $n_x = n_y = n_z = 2$.

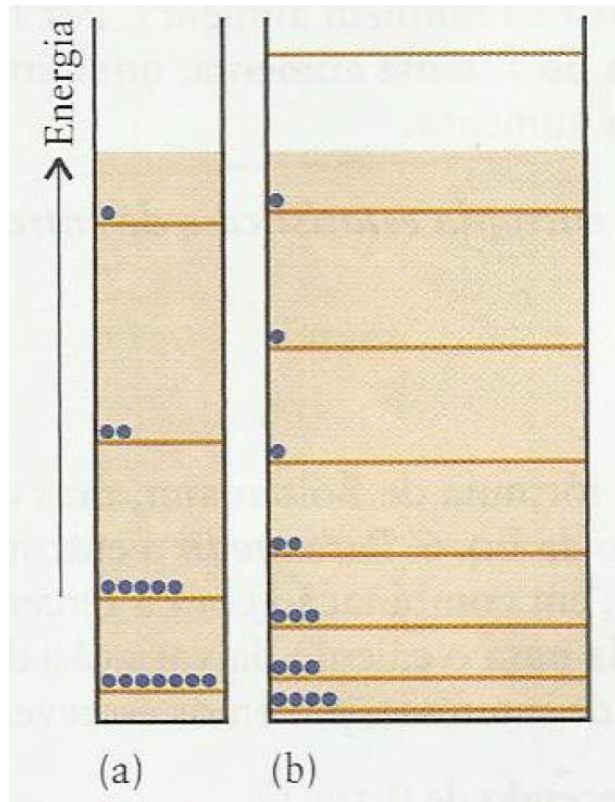


FIGURA 7.7 Os níveis de energia da partícula em uma caixa tornam-se mais próximos à medida que o comprimento da caixa aumenta. Como resultado, o número de níveis acessíveis à partícula aumenta e a entropia do sistema cresce. O intervalo de níveis termicamente acessíveis é ilustrado pela faixa colorida. A mudança de (a) para (b) é um modelo da expansão isotérmica de um gás ideal. A energia total das partículas é a mesma em cada caso.

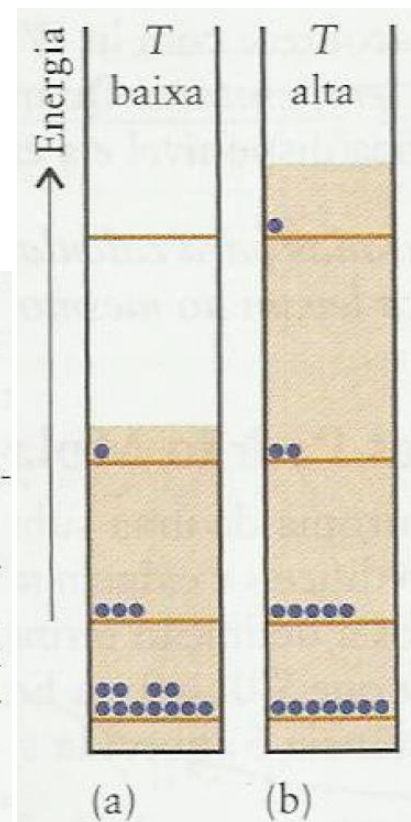


FIGURA 7.8 Mais níveis de energia tornam-se acessíveis em uma caixa de comprimento fixo à medida que a temperatura aumenta. A mudança de (a) para (b) é um modelo do efeito do aquecimento de um gás ideal, em volume constante. Os níveis termicamente acessíveis são ilustrados pela faixa colorida. A energia média das moléculas também aumenta com o aumento da temperatura, isto é, a energia interna e a entropia aumentam com a temperatura.

Richard P. Feynman, “*Lectures on Physics*”, Vol. I, Cap. 46 (1963).

“It is the change from an ordered arrangement to a disordered arrangement which is the source of the irreversibility.

...

It is not a question of pleasant order or unpleasant disorder.

...

We measure “disorder” by the number of ways to arrange...”.

Ludwig Boltzmann, 1877

$$S = k \ln W$$

In a reversible adiabatic work process, the distribution of molecules over a system's energy levels remains unchanged; in any other reversible process, the heat transferred across the system boundary is related to the change in the distribution of molecules over energy levels.

In an irreversible process, there is in general a change in the molecular distribution whether heat is transferred or not, since the work performed differs from that in the corresponding reversible process.

Berry, Rice, and Ross, *Physical Chemistry*, cap. 13.8, pg. 382