Topic 1C - Wave Functions and Energy Levels

Origins of the Schrödinger Equation

We seek a wave equation that relates the second derivative of a function with respect to displacement **x** to the function itself. For a particle moving freely in <u>one</u> dimension, with classical momentum **p**, the deBroglie wavelength is $\lambda = h/p$. A wave function that describes such a wave is:

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

where A is a constant. From differential calculus, the first derivative (*i.e.*, slope) and second derivative of ψ(x) with respect to x are:

$$\frac{d\psi(x)}{dx} = A\frac{2\pi}{\lambda}\cos\frac{2\pi x}{\lambda} \qquad \text{and} \qquad \frac{d^2\psi(x)}{dx^2} = -A\left(\frac{2\pi}{\lambda}\right)^2\sin\frac{2\pi x}{\lambda}$$

The second equation above is just a constant, $(-2\pi/\lambda)^2$, multiplied by the original wave function ψ(x):

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

Now replace the wavelength λ with its equivalent (h/p) from the deBroglie equation:

$$\frac{d^2\psi(x)}{dx^2} = -\left(\frac{2\pi}{h}p\right)^2\psi(x) = -\frac{4\pi^2}{h^2}p^2\psi(x)$$

Multiplying both sides of this equation by $-h^2/8\pi^2 m$ gives

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = \frac{p^2}{2m}\psi(x) = \Im\,\psi(x)$$

where $\Im = p^2/2m$ is the kinetic energy of the particle. If external forces, such as a Coulombic interaction, are present, then a potential energy term, V(x), must be included. Representing the total energy as E (= $\Im$ + V(x)), then

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} + V(x) = E\,\psi(x)$$

which is the Schrödinger Equation in one dimension.

The Schrödinger wave equation can be written in the following form:

$$H\psi = E\psi$$

where H is the so-called Hamiltonian "operator" and E is the total energy.

By analogy with classical electromagnetic wave theory, just as the intensity of an electromagnetic wave is proportional to the square of the electric field amplitude,

$$\text{Intensity} \propto (E_{max})^2$$

so the probability of an electron being at a given position is proportional to the square of the wave function, $i.e.$, ψ^2.

For a particle that is free to move in one dimension (x), the Schrödinger Equation, as given above, is:

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} + V(x) = E\psi(x)$$

where m is the mass of the particle, V(x) is the potential energy, and E is the total energy. Thus, the Hamiltonian operator, H, in this case is:

$$H = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + V(x)$$
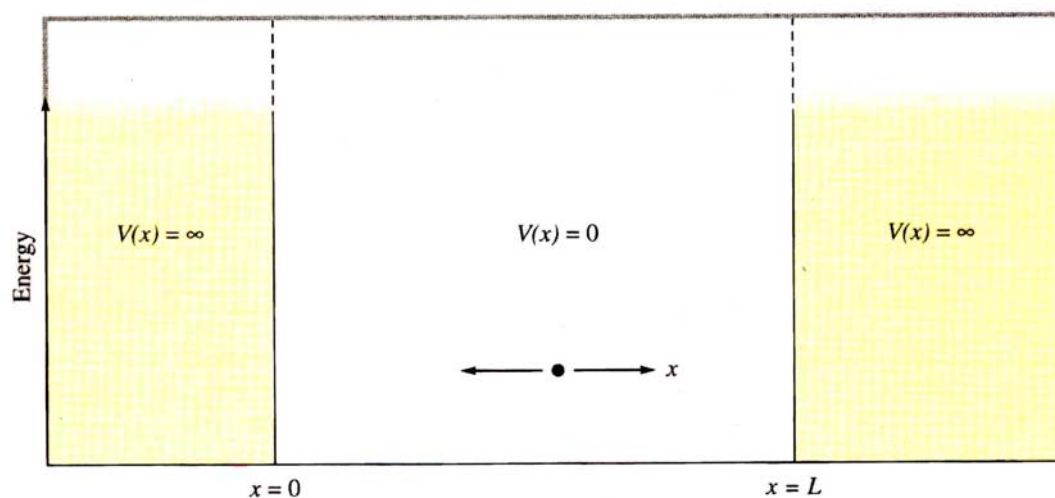
Schematic representation of a particle in a one-dimensional box with infinitely high potential walls.

Particle in a Box

Because the potential energy is zero everywhere inside the one-dimensional box, then $V(x) = 0$ and all of the particle's energy must be kinetic. Thus, the Schrödinger Equation for this system is:

$$-\frac{h^2}{8\pi^2 m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad \text{or} \qquad \frac{d^2\psi(x)}{dx^2} = -\frac{8\pi^2 mE}{h^2}\psi(x)$$

This differential equation is solved by determining functions, $\psi(x)$, that satisfy it. One such function is $\psi(x) = A\sin(kx)$, where A and k are constants, since

$$\frac{d^2\psi(x)}{dx^2} = A\frac{d}{dx}\left(\frac{d[\sin(kx)]}{dx}\right) = A\frac{d}{dx}[k\cos(kx)]$$

$$= kA\left(\frac{d[\cos(kx)]}{dx}\right) = -k\sin(kx)$$

$$= -k^2 A\sin(kx) = -k^2\psi$$

Thus, $\qquad k^2 = \dfrac{8\pi^2 mE}{h^2} \quad \text{and} \quad E = \dfrac{h^2 k^2}{8\pi^2 m}$

The constants A and k can be determined by applying the "boundary conditions" of the system:

1.) The particle is bound inside the box, *i.e.*, $0 \le x \le L$

2.) The total probability of finding the particle somewhere inside the box must be 1.

3.) The wave function must be continuous.

The first and third of these boundary conditions require that

$$\psi(0) = 0 \quad \text{and} \quad \psi(L) = 0$$

or

$$A \sin(k \times 0) = 0 \quad \text{and} \quad A \sin(k \times L) = 0$$

But sin x = 0 only when x = nπ radians, where n = 0, 1, 2, ...
Thus,

$$\psi(x) = A \sin\left(\frac{n\pi}{L}x\right) \quad \Rightarrow \quad k = \frac{n\pi}{L}$$

The constant A is determined by invoking the second of the above boundary conditions. The probability of finding the particle on an infinitesimal length, dx, of the x-axis is $\psi^2(x)dx$. Thus, summing over the entire length of the x-axis (0 to L) gives the total probability of finding the particle in the box:

$$\int_0^L \psi^2(x)\,dx = 1$$

Substituting the value of ψ(x):

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

or

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

This definite integral evaluates to L/2. Thus,

$$\frac{L}{2} = \frac{1}{A^2} \quad \text{and} \quad A = \sqrt{\frac{2}{L}}$$

Substituting the values of k and A into the wave function ψ(x):

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

Substituting the value of k (= nπ/L) into the expression for the total energy, E, gives:

$$E_n \;=\; \frac{h^2 k^2}{8\pi^2 m} \;=\; \frac{h^2 (n\pi/L)^2}{8\pi^2 m} \;=\; \frac{n^2 h^2}{8mL^2}$$

where n = 1, 2, 3, ...

The <u>difference</u> in energy between two adjacent energy levels (n, n+1) is:

$$E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} \;=\; \frac{(2n+1)h^2}{8mL^2}$$

Thus, as L <u>increases</u>, the allowed energy levels <u>decrease</u> and become <u>more closely spaced</u>. At very large L (*i.e.*, macroscopic size), the allowed energy levels are so closely spaced that they are essentially continuous.

Particle in a One-Dimensional "Box"

$$\psi(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi}{L}x\right)$$

$$E_n = \frac{n^2h^2}{8mL^2}$$
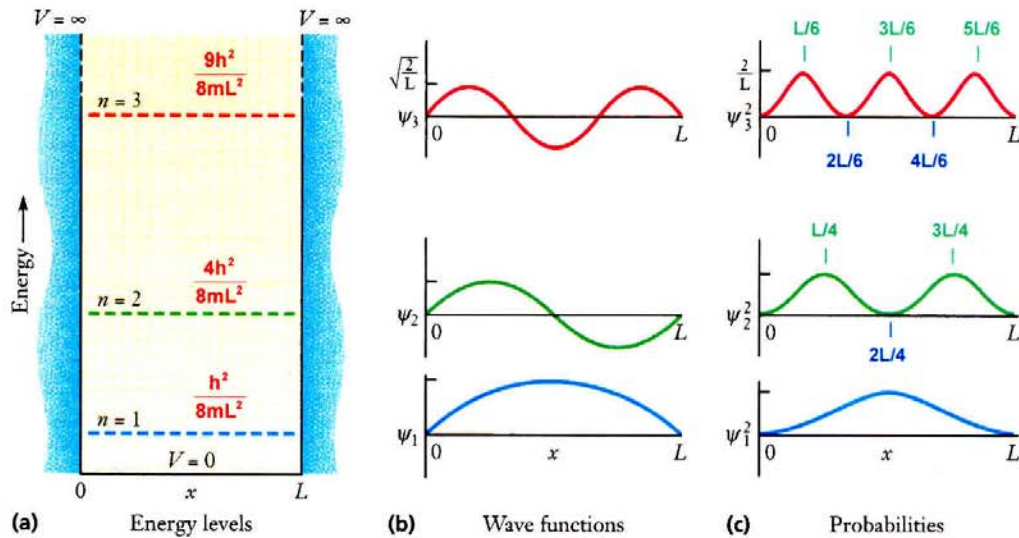
FIGURE 15.25 (a) The potential energy for a particle in a box of length L, with the first three energy levels marked. (b) Wave functions, showing the ground state ψ_1 and the first two excited states. The more numerous the nodes, the higher the energy of the state. (c) The squares of the wave functions from part b, equal to the probability density for finding the particle at a particular point in the box.

For a two-dimensional box:

$$E_{n_x n_y} = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]$$
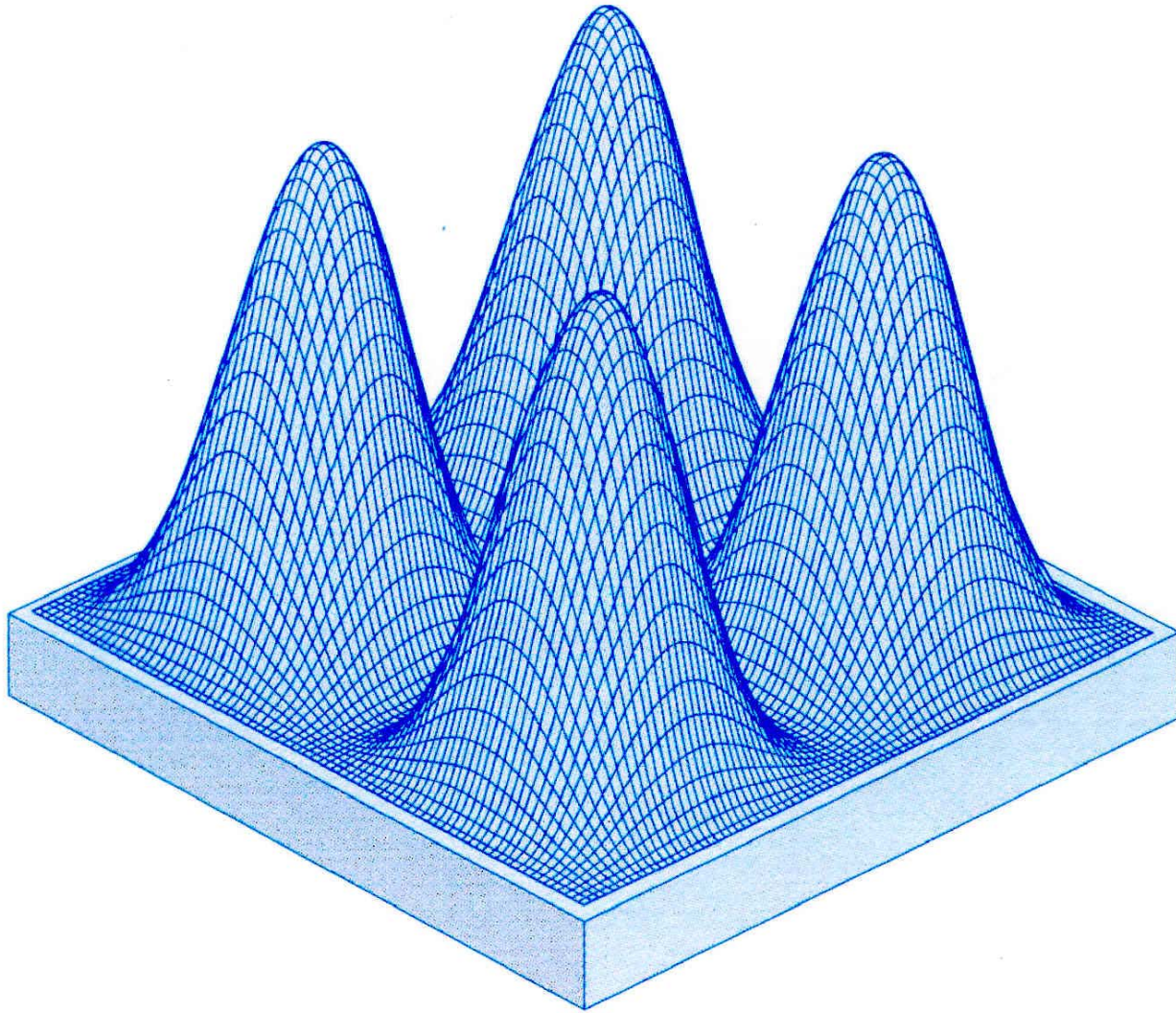
where n_x and n_y, are quantum numbers.

For a three-dimensional box:

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right]$$

where n_x, n_y, and n_z are quantum numbers.
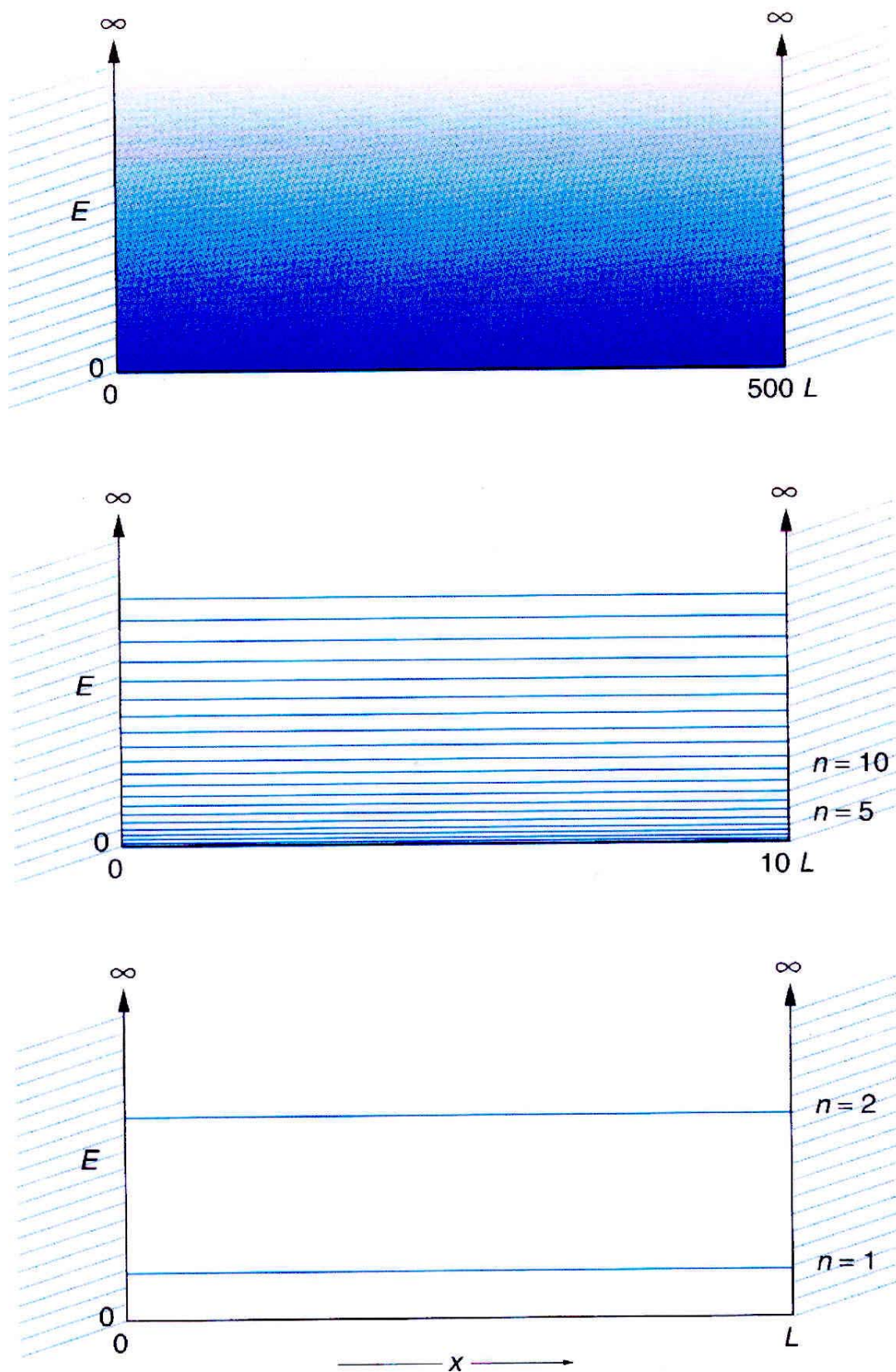
Figure 4.4. The effect of decreasing box size on the spacing of quantized levels for a translating particle.

Figure 4.11. The particle in a two-dimensional square box for $n_1 = n_2 = 2$. The values of $|\psi|^2$ are shown in order to visualize the probability of finding the particle at various locations in the box.

The wave function for a particle in a cubic box of length L on each side, and with one corner of the box located at the origin of Cartesian coordinates, is:

$$y_{n_x n_y n_z}(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi x}{L}\right) \sin\left(\frac{n_z \pi x}{L}\right)$$

FIGURE 4.29 Isosurfaces for $\tilde{\Psi}_{123}(\tilde{x}, \tilde{y}, \tilde{z})$ for a particle in a cubic box. (a) Isosurfaces for wave function value $\tilde{\Psi}_{123} = \pm 0.8$. (b) Isosurfaces for wave function value $\tilde{\Psi}_{123} = \pm 0.2$. Each isosurface is shown in the same color as the corresponding contour in Figure 4.28.
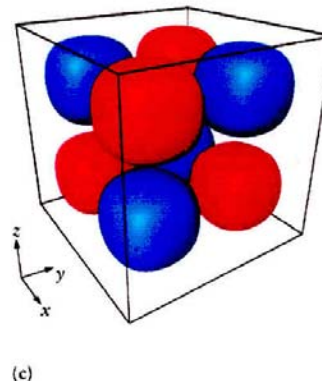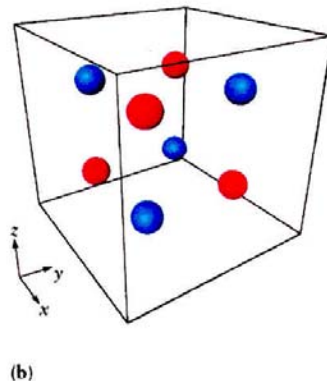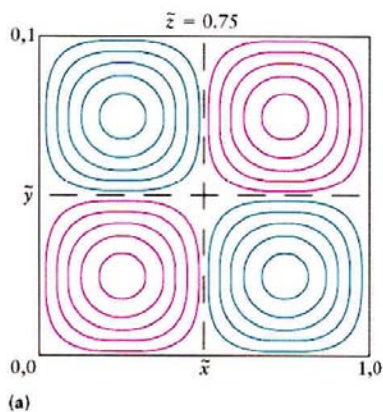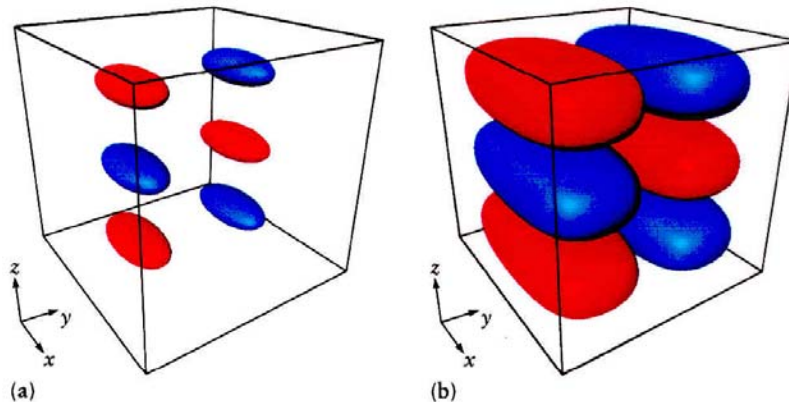
FIGURE 4.30 Representations of $\tilde{\Psi}_{222}(\tilde{x}, \tilde{y}, \tilde{z})$ for a particle in a cubic box. (a) Contour plots for a cut taken at $\tilde{z} = 0.75$. (b) Isosurfaces for wave function value $\tilde{\Psi}_{222} = \pm 0.9$. (c) Isosurfaces for wave function value $\tilde{\Psi}_{222} = \pm 0.3$. Each isosurface is shown in the same color as the corresponding contour in (a).