CHAPTER 3

QUANTUM MECHANICS OF SOME SIMPLE SYSTEMS

The Free Particle

The simplest system in quantum mechanics has the potential energy V equal to zero everywhere. This is called a *free particle* since it has no forces acting on it. We consider the one-dimensional case, with motion only in the x-direction, giving the Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \tag{1}$$

Total derivatives can be used since there is but one independent variable. The equation simplifies to

$$\psi''(x) + k^2\,\psi(x) = 0 \tag{2}$$

with the definition
$$k^2 \equiv 2mE/\hbar^2 \tag{3}$$

Possible solutions of Eq (2) are

$$\psi(x) = \text{const} \begin{cases} \sin kx \\ \cos kx \\ e^{\pm ikx} \end{cases}$$

$$\tag{4}$$

There is no restriction on the value of k. Thus a free particle, even in quantum mechanics, can have any non-negative value of the energy

$$E = \frac{\hbar^2 k^2}{2m} \geq 0 \tag{5}$$

The energy levels in this case are *not* quantized and correspond to the same continuum of kinetic energy shown by a classical particle.

It is of interest also to consider the x-component of linear momentum for the free-particle solutions (4). According to Eq (2-32), the eigenvalue equation for momentum should read

$$\hat{p}_x \psi(x) = -i\hbar \frac{d\psi(x)}{dx} = p\,\psi(x) \tag{6}$$

where we have denoted the momentum eigenvalue as p. It is easily shown that neither of the functions $\sin kx$ or $\cos kx$ from (4) is an eigenfunction of $\hat{p}_x$. But $e^{\pm ikx}$ are both eigenfunctions with eigenvalues $p = \pm \hbar k$, respectively. Evidently the momentum p can take on any real value between $-\infty$ and $+\infty$. The kinetic energy, equal to $E = p^2/2m$, can correspondingly have any value between 0 and $+\infty$.

The functions $\sin kx$ and $\cos kx$, while not eigenfunctions of $\hat{p}_x$, are each *superpositions* of the two eigenfunctions $e^{\pm ikx}$, by virtue of the trigonometric identities

$$\cos kx = \frac{1}{2}(e^{ikx} + e^{-ikx}) \text{ and } \sin kx = \frac{1}{2i}(e^{ikx} - e^{-ikx}) \tag{7}$$

The eigenfunction e^{ikx} for $k > 0$ represents the particle moving from left to right on the x-axis, with momentum $p > 0$. Correspondingly, e^{-ikx} represents motion from right to left with $p < 0$. The functions $\sin kx$ and $\cos kx$ represent *standing waves*, obtained by superposition of opposing wave motions. Although these latter two are not eigenfunctions of $\hat{p}_x$ but *are* eigenfunctions of $\hat{p}_x^2$, hence of the Hamiltonian $\hat{H}$.

Particle in a Box

This is the simplest non-trivial application of the Schrödinger equation, but one which illustrates many of the fundamental concepts of quantum mechanics. For a particle moving in one dimension (again along the x-axis), the Schrödinger equation can be written

$$-\frac{\hbar^2}{2m}\psi''(x) + V(x)\psi(x) = E\,\psi(x) \tag{8}$$

Assume that the particle can move freely between two endpoints $x = 0$ and $x = a$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on x with

$$V(x) = \begin{cases} 0 & 0 \leq x \leq a \\ \infty & x < 0 \text{ and } x > a \end{cases} \tag{9}$$
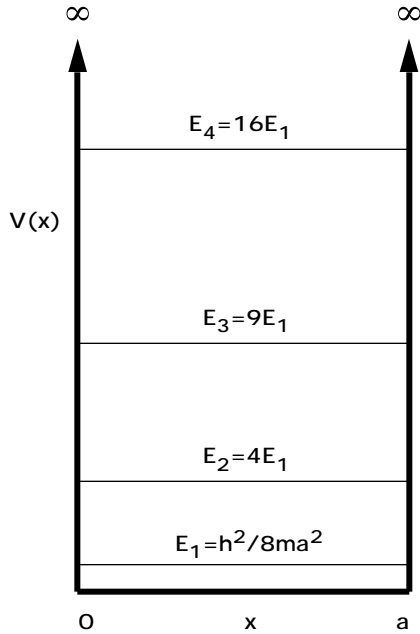
2

Figure 1. Potential well and lowest energy levels for particle in a box.

This potential is represented by the dark lines in Fig. 1. Infinite potential energy constitute an impenetrable barrier. The particle is thus bound to a *potential well*. Since the particle cannot penetrate beyond $x = 0$ or $x = a$,

$$\psi(x) = 0 \quad \text{for} \quad x < 0 \quad \text{and} \quad x > a \tag{10}$$

By the requirement that the wavefunction be continuous, it must be true as well that

$$\psi(0) = 0 \quad \text{and} \quad \psi(a) = 0 \tag{11}$$

which constitutes a pair of boundary conditions on the wavefunction *within* the box. Inside the box, $V(x) = 0$, so the Schrödinger equation reduces to the free-particle form (1)

$$-\frac{\hbar^2}{2m} \psi''(x) = E \, \psi(x), \qquad 0 \leq x \leq a \tag{12}$$

We again have the differential equation

$$\psi''(x) + k^2 \, \psi(x) = 0 \qquad \text{with} \qquad k^2 = 2mE/\hbar^2 \tag{13}$$

The general solution can be written

$$\psi(x) = A \sin kx + B \cos kx \tag{14}$$

3

where A and B are constants to be determined by the boundary conditions (11). By the first condition, we find

$$\psi(0) = A\sin 0 + B\cos 0 = B = 0 \tag{15}$$

The second boundary condition at $x = a$ then implies

$$\psi(a) = A\sin ka = 0 \tag{16}$$

It is assumed that $A \neq 0$, for otherwise $\psi(x)$ would be zero everywhere and the particle would disappear. The condition that $\sin kx = 0$ implies that

$$ka = n\pi \tag{17}$$

where n is a integer, positive, negative or zero. The case $n = 0$ must be excluded, for then $k = 0$ and again $\psi(x)$ would vanish everywhere. Eliminating k between (13) and (17), we obtain

$$E_n = \frac{\hbar^2\pi^2}{2ma^2}n^2 = \frac{h^2}{8ma^2}n^2 \qquad n = 1, 2, 3\ldots \tag{18}$$

These are the only values of the energy which allow solution of the Schrödinger equation (12) consistent with the boundary conditions (11). The integer n, called a *quantum number*, is appended as a subscript on E to label the allowed energy levels. Negative values of n add nothing new because the energies in Eq (18) depends on n^2. Fig. 1 shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space. For the free particle, the absence of confinement allowed an energy continuum. Note that, in both cases, the number of energy levels is infinite—denumerably infinite for the particle in a box but nondenumerably infinite for the free particle.

The particle in a box assumes its lowest possible energy when $n = 1$, namely

$$E_1 = \frac{h^2}{8ma^2} \tag{19}$$

The state of lowest energy for a quantum system is termed its *ground state.* An interesting point is that $E_1 > 0$, whereas the corresponding classical

system would have a minimum energy of zero. This is a recurrent phenomenon in quantum mechanics. The residual energy of the ground state, that is, the energy in excess of the classical minimum, is known as *zero point energy*. In effect, the kinetic energy, hence the momentum, of a bound particle cannot be reduced to zero. The minimum value of momentum is found by equating E_1 to $p^2/2m$, giving $p_{\min} = \pm h/2a$. This can be expressed as an *uncertainty* in momentum given by $\Delta p \approx h/a$. Coupling this with the uncertainty in position, $\Delta x \approx a$, from the size of the box, we can write

$$\Delta x \, \Delta p \approx h \tag{20}$$

This is in accord with the *Heisenberg uncertainty principle*, which we will discuss in greater detail later.

The particle-in-a-box eigenfunctions are given by Eq (14), with $B = 0$ and $k = n\pi/a$, in accordance with (17):

$$\psi_n(x) = A \sin \frac{n\pi x}{a}, \qquad n = 1, 2, 3 \dots \tag{21}$$

These, like the energies, can be labelled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition (2-39) is, in this case,

$$\int_0^a [\psi_n(x)]^2 \, dx = 1 \tag{22}$$

the integration running over the domain of the particle, $0 \le x \le a$. Substituting (21) into (22),

$$A^2 \int_0^a \sin^2 \frac{n\pi x}{a} \, dx = A^2 \frac{a}{n\pi} \int_0^{n\pi} \sin^2 \theta \, d\theta = A^2 \frac{a}{2} = 1 \tag{23}$$

We have made the substitution $\theta = n\pi x/a$ and used the fact that the average value of $\sin^2 \theta$ over an integral number of half wavelenths equals $1/2$. (Alternatively, one could refer to standard integral tables.) From (23), we can identify the normalization constant $A = (2/a)^{1/2}$, for all values of n. Finally we can write the normalized eigenfunctions:

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a}, \qquad n = 1, 2, 3 \dots \tag{24}$$

The first few eigenfunctions and the corresponding probability distributions are plotted in Fig. 2. There is a close analogy between the states of this quantum system and the modes of vibration of a violin string. The patterns of standing waves on the string are, in fact, identical in form with the wavefunctions (24).
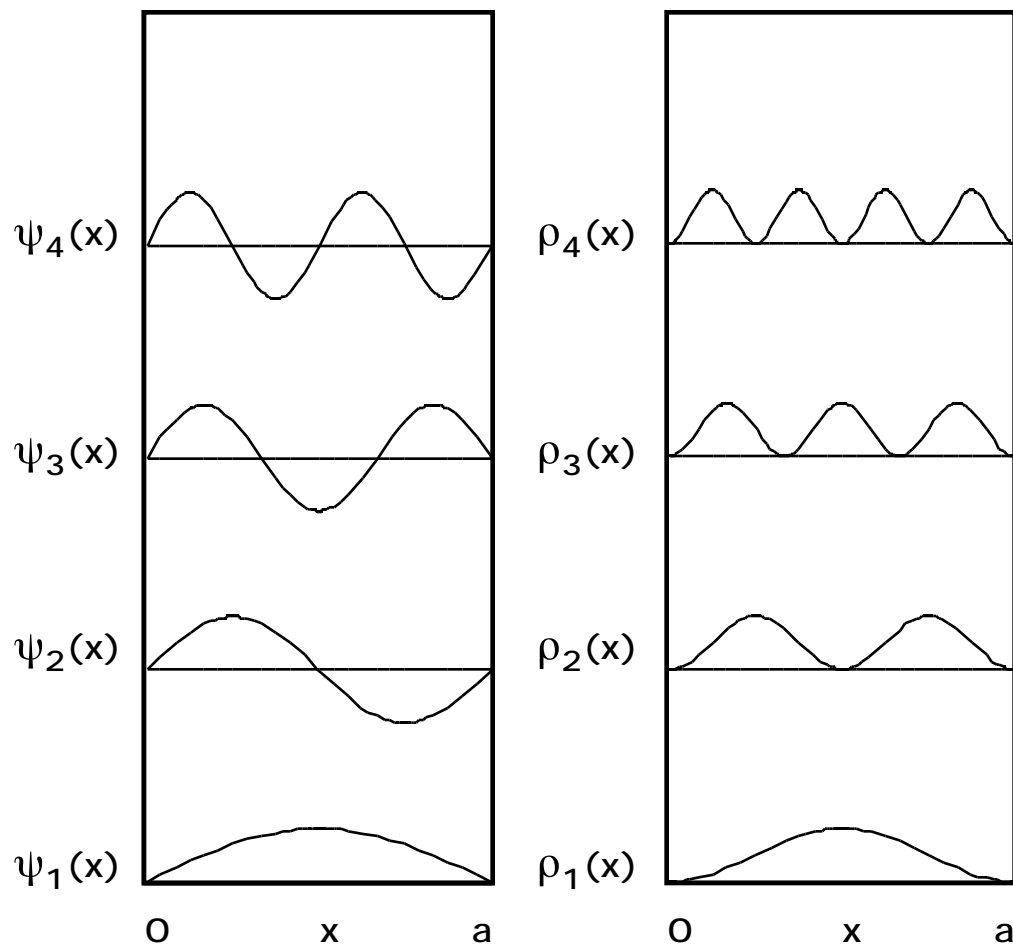

Figure 2. Eigenfunctions and probability densities for particle in a box.

A significant feature of the particle-in-a-box quantum states is the occurrence of *nodes*. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of finding the particle. The nth quantum state has, in fact, $n-1$ nodes. It is generally true that the number of nodes increases with the energy of a quantum state, which can

be rationalized by the following qualitative argument. As the number of nodes increases, so does the number and steepness of the 'wiggles' in the wavefunction. It's like skiing down a slalom course. Accordingly, the average curvature, given by the second derivative, must increase. But the second derivative is proportional to the kinetic energy operator. Therefore, the more nodes, the higher the energy. This will prove to be an invaluable guide in more complex quantum systems.

Another important property of the eigenfunctions (24) applies to the integral over a product of two *different* eigenfunctions. It is easy to see from Fig. 3 that the integral
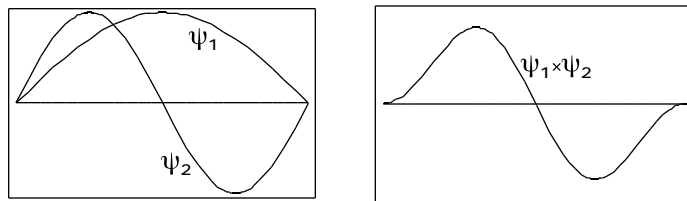
$$\int_0^a \psi_2(x)\,\psi_1(x)\,dx = 0$$

Figure 3. Product of n=1 and n=2 eigenfunctions.

To prove this result in general, use the trigonometric identity

$$\sin\alpha\,\sin\beta = \frac{1}{2}[\cos(\alpha-\beta) - \cos(\alpha+\beta)]$$

to show that

$$\int_0^a \psi_m(x)\,\psi_n(x)\,dx = 0 \quad \text{if} \quad m \neq n \tag{25}$$

This property is called *orthogonality*. We will show in the Chap. 4 that this is a general result for quantum-mechanical eigenfunctions. The normalization (22) together with the orthogonality (25) can be combined into a single relationship

$$\int_0^a \psi_m(x)\,\psi_n(x)\,dx = \delta_{mn} \tag{26}$$

in terms of the *Kronecker delta*

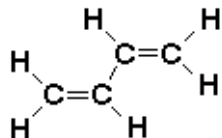$$\delta_{mn} \equiv \begin{cases} 1 \text{ if } m = n \\ 0 \text{ if } m \neq n \end{cases}$$

A set of functions $\{\psi_n\}$ which obeys (26) is called *orthonormal.*

Free-Electron Model

The simple quantum-mechanical problem we have just solved can provide an instructive application to chemistry: the *free-electron model* (FEM) for delocalized π-electrons. The simplest case is the 1,3-butadiene molecule

The four π-electrons are assumed to move freely over the four-carbon framework of single bonds. We neglect the zig-zagging of the C–C bonds and assume a one-dimensional box. We also overlook the reality that π-electrons actually have a node in the plane of the molecule. Since the electron wavefunction extends beyond the terminal carbons, we add approximately one-half bond length at each end. This conveniently gives a box of length equal to the number of carbon atoms times the C–C bond length, for butadiene, approximately 4×1.40 Å. Recall that 1 Å$=10^{-10}$m, Now, in the lowest energy state of butadiene, the 4 delocalized electrons will fill the two lowest FEM "molecular orbitals." The total π-electron density will be given (as shown in Fig. 4) by
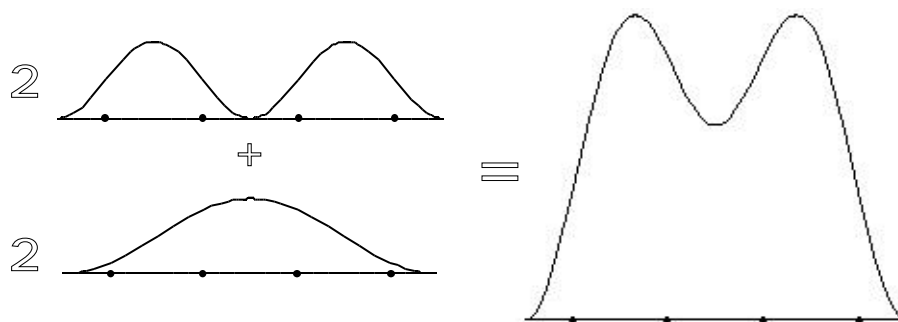
$$\rho = 2\psi_1^2 + 2\psi_2^2 \qquad (28)$$

Figure 4. Pi-electron density in butadiene.

A chemical interpretation of this picture might be that, since the π-electron density is concentrated between carbon atoms 1 and 2, and between 3 and 4, the predominant structure of butadiene has double bonds between these two pairs of atoms. Each double bond consists of a π- bond, in addition

to the underlying σ-bond. However, this is not the complete story, because we must also take account of the residual π-electron density between carbons 2 and 3. In the terminology of valence-bond theory, butadiene would be described as a *resonance hybrid* with the contributing structures $CH_2=CH\text{-}CH=CH_2$ (the predominant structure) and $°CH_2\text{-}CH=CH\text{-}CH_2°$ (a secondary contribution). The reality of the latter structure is suggested by the ability of butadiene to undergo 1,4-addition reactions.

The free-electron model can also be applied to the electronic spectrum of butadiene and other linear polyenes. The lowest unoccupied molecular orbital (LUMO) in butadiene corresponds to the $n = 3$ particle-in-a-box state. Neglecting electron-electron interaction, the longest-wavelength (lowest-energy) electronic transition should occur from $n = 2$, the highest occupied molecular orbital (HOMO).
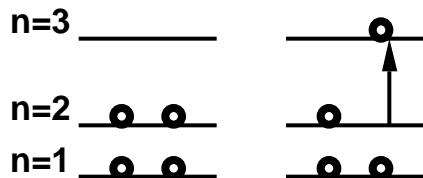
The energy difference is given by

$$\Delta E = E_3 - E_2 = (3^2 - 2^2)\frac{h^2}{8mL^2} \tag{29}$$

Here m represents the mass of an electron (not a butadiene molecule!), 9.1×10^{-31} Kg, and L is the effective length of the box, $4 \times 1.40 \times 10^{-10}$ m. By the Bohr frequency condition

$$\Delta E = h\nu = \frac{hc}{\lambda} \tag{30}$$

The wavelength is predicted to be 207 nm. This compares well with the experimental maximum of the first electronic absorption band, $\lambda_{\max} \approx 210$ nm, in the ultraviolet region.

We might therefore be emboldened to apply the model to predict absorption spectra in higher polyenes $CH_2=(CH\text{-}CH=)_{n-1}CH_2$. For the molecule with $2n$ carbon atoms (n double bonds), the HOMO $\to$ LUMO transition corresponds to $n \to n + 1$, thus

$$\frac{hc}{\lambda} \approx [(n+1)^2 - n^2]\frac{h^2}{8m(2nL_{\text{CC}})^2} \tag{31}$$

A useful constant in this computation is the Compton wavelength $h/mc = 2.426 \times 10^{-12}$m. For $n = 3$, hexatriene, the predicted wavelength is 332 nm, while experiment gives $\lambda_{\text{max}} \approx 250$ nm. For $n = 4$, octatetraene, FEM predicts 460 nm, while $\lambda_{\text{max}} \approx 300$ nm. Clearly the model has been pushed beyond it range of quantitative validity, although the trend of increasing absorption band wavelength with increasing n is correctly predicted. Incidentally, a compound should be colored if its absorption includes any part of the visible range 400–700 nm. Retinol (vitamin A), which contains a polyene chain with $n = 5$, has a pale yellow color. This is its structure:
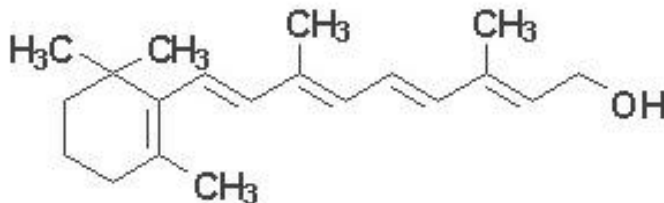
Particle in a Three-Dimensional Box

A *real* box has three dimensions. Consider a particle which can move freely with in rectangular box of dimensions $a \times b \times c$ with impenetrable walls. In terms of potential energy, we can write

$$V(x, y, z) = \begin{cases} 0 & \text{inside box} \\ \infty & \text{outside box} \end{cases}$$

$$(32)$$

Again, the wavefunction must vanish everywhere outside the box. By the continuity requirement, the wavefunction must also valish in the six surfaces of the box. Orienting the box so its edges are parallel to the cartesian axes, with one corner at (0,0,0), the following boundary conditions must be satisfied:

$$\psi(x, y, z) = 0 \text{ when } x = 0, x = a, y = 0, y = b, z = 0 \text{ or } z = c \qquad (33)$$

Inside the box, where the potential energy is everywhere zero, the Hamiltonian is simply the three-dimensional kinetic energy operator and the Schrödinger equation reads

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x, y, z) = E \, \psi(x, y, z) \qquad (34)$$

subject to the boundary conditions (33). This second-order partial diffential equation is separable in cartesian coordinates, with a solution of the form

$$\psi(x, y, z) = X(x)\, Y(y)\, Z(z) \tag{35}$$

subject to the boundary conditions

$$X(0) = X(a) = 0, \qquad Y(0) = Y(b) = 0, \qquad Z(0) = Z(c) = 0 \tag{36}$$

Substituting (35) into (34) and dividing through by (35), we obtain

$$\frac{X''(x)}{X(x)} + \frac{Y''(y)}{Y(y)} + \frac{Z''(z)}{Z(z)} + \frac{2mE}{\hbar^2} = 0 \tag{37}$$

Each of the first three terms in (37) depends on one variable only, independent of the other two. This is possible only if each term separately equals a constant, say, $-\alpha^2$, $-\beta^2$ and $-\gamma^2$, respectively. These constants must be negative in order that $E > 0$. Eq (37) is thereby transformed into three ordinary differential equations

$$X'' + \alpha^2 X = 0, \qquad Y'' + \beta^2 Y = 0, \qquad Z'' + \gamma^2 Z = 0 \tag{38}$$

subject to the boundary conditions (36). The constants are related by

$$\frac{2mE}{\hbar^2} = \alpha^2 + \beta^2 + \gamma^2 \tag{39}$$

Each of the equations (38), with its associated boundary conditions in (36) is equivalent to the one-dimensional problem (13) with boundary conditions (11). The normalized solutions $X(x)$, $Y(y)$, $Z(z)$ can therefore be written down in complete analogy with (24):

$$X_{n_1}(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n_1 \pi x}{a}, \qquad n_1 = 1, 2 \ldots$$

$$Y_{n_2}(y) = \left(\frac{2}{b}\right)^{1/2} \sin\frac{n_2 \pi y}{b}, \qquad n_2 = 1, 2 \ldots$$

$$Z_{n_3}(x) = \left(\frac{2}{c}\right)^{1/2} \sin\frac{n_3\pi z}{c}, \qquad n_3 = 1, 2\ldots \tag{40}$$

The constants in Eq (39) are given by

$$\alpha = \frac{n_1\pi}{a}, \qquad \beta = \frac{n_2\pi}{b}, \qquad \gamma = \frac{n_3\pi}{c} \tag{41}$$

and the allowed energy levels are therefore

$$E_{n_1,n_2,n_3} = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right), \qquad n_1, n_2, n_3 = 1, 2\ldots \tag{42}$$

Three quantum numbers are required to specify the state of this three-dimensional system. The corresponding eigenfunctions are

$$\psi_{n_1,n_2,n_3}(x, y, z) = \left(\frac{8}{V}\right)^{1/2} \sin\frac{n_1\pi x}{a}\,\sin\frac{n_2\pi y}{b}\,\sin\frac{n_3\pi z}{c} \tag{43}$$

where $V = abc$, the volume of the box. These eigenfunctions form an orthonormal set [cf. Eq (26)] such that

$$\int_0^a \int_0^b \int_0^c \psi_{n_1',n_2',n_3'}(x, y, z)\,\psi_{n_1,n_2,n_3}(x, y, z)\,dx\,dy\,dz$$
$$= \delta_{n_1',n_1}\,\delta_{n_2',n_2}\,\delta_{n_3',n_3} \tag{44}$$

Note that two eigenfunctions will be orthogonal unless *all three* quantum numbers match. The three-dimensonal matter waves represented by (43) are comparable with the modes of vibration of a solid block. The nodal surfaces are planes parallel to the sides, as shown here:
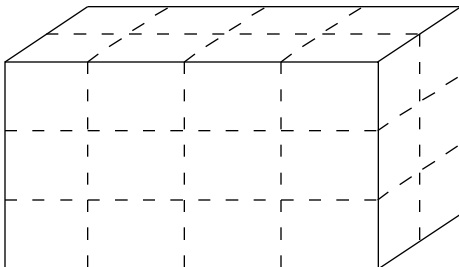

Figure 5. Nodal planes for particle in a box, for $n_1 = 4, n_2 = 2, n_3 = 3$.

When the box has the symmetry of a cube, with $a = b = c$, the energy formula (42) simplifies to

$$E_{n_1,n_2,n_3} = \frac{h^2}{8ma^2}(n_1^2 + n_2^2 + n_3^2), \quad n_1, n_2, n_3 = 1, 2 \ldots \qquad (45)$$

Quantum systems with symmetry generally exhibit *degeneracy* in their energy levels. This means that there can exist distinct eigenfunctions which share the same eigenvalue. An eigenvalue which corresponds to a unique eigenfunction is termed *nondegenerate* while one which belongs to n different eigenfunctions is termed *n-fold degenerate*. As an example, we enumerate the first few levels for a cubic box, with E_{n_1,n_2,n_3} expressed in units of $h^2/8ma^2$:

$E_{1,1,1} = 3$ (nondegenerate)

$E_{1,1,2} = E_{1,2,1} = E_{2,1,1} = 6$ (3-fold degenerate)

$E_{1,2,2} = E_{2,1,2} = E_{2,2,1} = 9$ (3-fold degenerate)

$E_{1,1,3} = E_{1,3,1} = E_{3,1,1} = 11$ (3-fold degenerate)

$E_{2,2,2} = 12$ (nondegenerate)

$E_{1,2,3} = E_{1,3,2} = E_{2,1,3} = E_{2,3,1} = E_{3,1,2} = E_{3,2,1} = 14$ (6-fold degenerate)

The particle in a box is applied in statistical thermodynamics to model the perfect gas. Each molecule is assumed to move freely within the box *without* interacting with the other molecules. The total energy of N molecules, in any distribution among the energy levels (45), is proportional to $1/a^2$, thus

$$E = \text{const}\, V^{-2/3}$$

From the differential of work $dw = -p\, dV$, we can identify

$$p = -\frac{dE}{dV} = \frac{2}{3}\frac{E}{V}$$

But the energy of a perfect monatomic gas is known to equal $\frac{3}{2}nRT$, which leads to the perfect gas law

$$pV = nRT$$