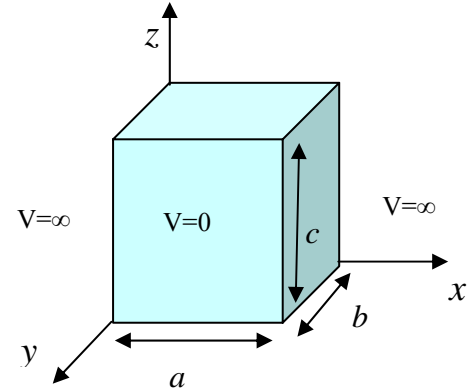# Schrödinger Equation
## in
## Three Dimensional Square Well

In the figure, consider a 3d rectangular "infinite square well" with the dimensions ($a$, $b$, $c$) and the potential boundary conditions:

$$V(x,y,z) = \begin{cases} 0, & 0\langle x \langle a, 0\langle y \langle b, 0\langle z \langle c \\ \\ \infty, & \text{otherwise} \end{cases}$$



As we have the "boundary" condition that $\psi$ be zero in the infinitely disallowed region outside the box. Inside the box, where the potential is zero, we have the Schrödinger's equation:

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

Since the Hamiltonian is the sum of three terms with totally separate variables, we try a product wavefunction:

$$\psi(x,y,z)=X(x)Y(y)Z(z)$$

As usual with separation of variables, the Schrödinger's equation separates into three terms, one only in $x$, the next only in $y$, the last only in $z$:

$$\frac{d^2X(x)}{dx^2}+k_x^2X(x)=0, \quad k_x^2=\frac{2mE_x}{\hbar^2},$$

$$\frac{d^2Y(y)}{dy^2}+k_y^2Y(y)=0, \quad k_y^2=\frac{2mE_y}{\hbar^2},$$

$$\frac{d^2Z(z)}{dz^2}+k_z^2Z(z)=0, \quad k_z^2=\frac{2mE_z}{\hbar^2}.$$

where

$$E=E_x+E_y+E_z$$

These familiar differential equations have the usual solution:

$$X(x) = A_x \sin(k_x x) + B_x \cos(k_x x)$$

$$Y(y) = A_y \sin(k_y y) + B_y \cos(k_y y)$$

$$Z(z) = A_z \sin(k_z z) + B_z \cos(k_z z)$$

Now we apply our boundary conditions

$$\psi(0,y,z)=\psi(a,y,z)=0 \quad \text{for all } y, \text{ and } z$$
$$\psi(x,0,z)=\psi(x,b,z)=0 \quad \text{for all } x, \text{ and } z$$
$$\psi(x,y,0)=\psi(x,y,c)=0 \quad \text{for all } x, \text{ and } y$$

Which implies:

$$X(x) = \sqrt{\frac{2}{a}} \sin k_x x, \quad k_x = \frac{n_x \pi}{a}, \quad n_x = 1, 2, \cdots$$

$$Y(y) = \sqrt{\frac{2}{b}} \sin k_y y, \quad k_y = \frac{n_y \pi}{b}, \quad n_y = 1, 2, \cdots$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin k_z Z \quad k_z = \frac{n_z \pi}{c}, \quad n_z = 1, 2, \cdots$$

The resulting normalized wavefunctions are:

$$\psi(x,y,z) = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{a} y\right) \sin\left(\frac{n_z \pi}{a} z\right), \quad \begin{array}{l} n_x = 1, 2, \cdots \\ n_y = 1, 2, \cdots \\ n_z = 1, 2, \cdots \end{array}$$

With:

$$E = E_x + E_y + E_z = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$
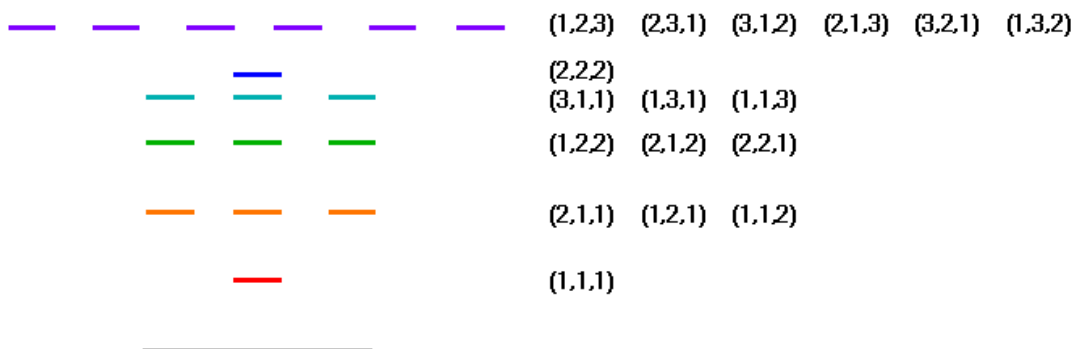
**H.W.:** Check the normalization:

$$\int_{-\infty}^{\infty} |\psi|^2 dxdydz = \int_0^a |X(x)|^2 dx \int_0^b |Y(y)|^2 dy \int_0^c |Z(z)|^2 dz = 1$$

It is often convenient to describe wavefunctions in terms of "*k*-space" or "*n*-space", that is we label wavefunctions by **k**=($k_x$,$k_y$,$k_x$) vector or by **n**=($n_x$,$n_y$,$n_z$). In either case there is a lattice of points in the plane each one of which represents a possible wavefunctions. In the case of *n*-space, the lattice consists of those points with whole number *x,y,z* values. In the case of *k*-space, the lattice points are spaced by $\pi/a$, $\pi/b$, $\pi/c$. (*k*-space goes by many different names. The momentum $p = \hbar k$ is closely related to *k*, hence "momentum space". *k* is also closed related to "reciprocal lattice space". Since $k = 2\pi/\lambda$, *k* is often called a "wave number". The main idea for us is that $E \propto k^2$

Here is an energy level diagram showing the relationship between **n**=($n_x$,$n_y$,$n_z$) and the energy for a cube $(a = b = c = L)$ square well.

$$E = E_x + E_y + E_z = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) = E_1\left(n_x^2 + n_y^2 + n_z^2\right)$$



| | |
|---|---|
| —  —  —  —  —  — | (1,2,3)  (2,3,1)  (3,1,2)  (2,1,3)  (3,2,1)  (1,3,2) |
| — | (2,2,2) |
| —  —  — | (3,1,1)  (1,3,1)  (1,1,3) |
| —  —  — | (1,2,2)  (2,1,2)  (2,2,1) |
| —  —  — | (2,1,1)  (1,2,1)  (1,1,2) |
| — | (1,1,1) |

| $\psi_{n_x,n_y,n_z}$ | $n_x$ | $n_y$ | $n_z$ | $n^2$ | degeneracy |
|---|---|---|---|---|---|
| $\psi_{1,1,1}$ | 1 | 1 | 1 | 3 | 1 |
| $\psi_{1,1,2}$ | 1 | 1 | 2 | 6 | |
| $\psi_{1,2,1}$ | 1 | 2 | 1 | 6 | 3 |
| $\psi_{2,1,1}$ | 2 | 1 | 1 | 6 | |
| $\psi_{1,2,2}$ | 1 | 2 | 2 | 9 | |
| $\psi_{2,1,2}$ | 2 | 1 | 2 | 9 | 3 |
| $\psi_{2,2,1}$ | 2 | 2 | 1 | 9 | |
| $\psi_{1,1,3}$ | 1 | 1 | 3 | 11 | |
| $\psi_{1,3,1}$ | 1 | 3 | 1 | 11 | 3 |
| $\psi_{3,1,1}$ | 3 | 1 | 1 | 11 | |
| $\psi_{2,2,2}$ | 2 | 2 | 2 | 12 | 1 |

**Example:** Discuss the number of energy levels in a small energy range *dE* for a particle in a very large potential box.

**Solution:** For simplicity we shall consider a cubical potential box of side *a*. Then, as we saw in the previous problem, the energy levels of a particle in the box are given by

$$E = \left( \frac{\hbar^2 \pi^2}{2mL^2} \right)\left( n_1^2 + n_2^2 + n_3^2 \right) = E_1 \left( n_1^2 + n_2^2 + n_3^2 \right)$$

where $n_1$, $n_2$, and $n_3$ are integers. We note that for a small box (i.e., small value of $L$ ) the energy levels are spaced widely, as shown in Fig.1(a). But for a very large box, as is the case for molecules of a gas in a container or for electrons in a metal, successive levels are so close that they practically form a continuous spectrum, as shown in Fig. 1(b).

**TABLE 1   Energy Levels and Degeneracies in a**
**Cubical Box** $\left(E_1 = \hbar^2 \pi^2 / 2mL^2\right)$

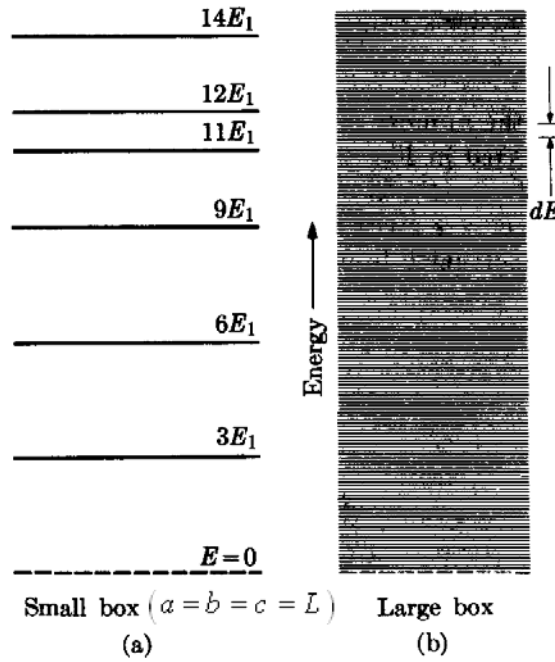| Energy | Combinations of $n_1, n_2, n_3$ | Degeneracy, $g$ |
|---|---|---|
| $3E_1$ | (1, 1, 1) | 1 |
| $6E_1$ | (2, 1, 1)(1, 2, 1)(1, 1, 2) | 3 |
| $9E_1$ | (2, 2, 1)(2, 1, 2)(1, 2, 2) | 3 |
| $11E_1$ | (3, 1, 1)(1, 3, 1)(1, 1, 3) | 3 |
| $12E_1$ | (2, 2, 2) | 1 |
| $14E_1$ | (1, 2, 3)(3, 2, 1)(2, 3, 1)<br>(1, 3, 2)(2, 1, 3)(3, 1, 2) | 6 |

Fig. 1. Energy levels for (a) a small potential box, (b) a large potential box.

Our problem is to find how many energy levels there are in a small energy range $dE$ when the potential box is very large. This problem is very similar to that of finding the modes of oscillations of waves trapped in a cavity whose dimensions are much larger than the wavelength.

Let us introduce the coordinates $\xi, \eta, \zeta$ in a certain representative space (Fig. 2—11); each point, of coordinates $\xi = n_1, \eta = n_2, \zeta = n_3$, represents an energy level, and to each point there corresponds a cell of unit volume in this representative space. Let us define $k^2 = \xi^2 + \eta^2 + \zeta^2$, and say that the number of points having positive integral coordinates and lying on the surface of a sphere of radius $k$ give the different states associated with the energy

$$E = \frac{\pi^2 \hbar^2}{2mL^2} k^2 \quad \Rightarrow \quad k = \frac{L}{\pi \hbar} \sqrt{2m} \, E^{1/2}$$
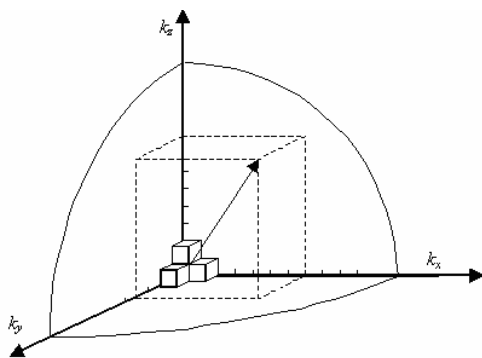


Calculation of the number of states with wavenumber less than $k$.
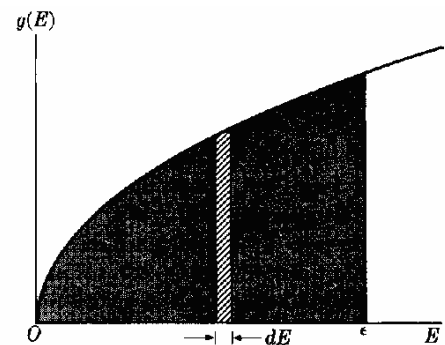


Density of energy levels
in a large cubical potential box.

To find the number of states $N(E)$ with energy between zero and $E$, we must find the volume of an octant ($\frac{1}{8}$) of a sphere of radius $k$, since only positive values of $n_1$, $n_2$, and $n_3$ are allowed. Thus, remembering that $\hbar = h/2\pi$, we obtain

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$$N(E) = \frac{1}{8}\left(\frac{4}{3}\pi k^3\right) = \frac{\pi}{6}V\left(\frac{8m}{h^2}\right)^{3/2} E^{3/2},$$

where $V = L^3$ is the volume of the potential box. The number of states with energy between E and E + dE is obtained by differentiating the above expression. This yields

$$dN(E) = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}dE.$$

It is convenient to write $dN(E) = g(E)dE$, so that

$$g(E) = \frac{dN(E)}{dE} = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}$$

is the number of states per unit energy interval at the energy E. The function $g(E)$ is plotted in Fig. 2—12. The area of a strip of width $dE$ gives the corresponding number $dN(E) = g(E)dE$ of states in such an energy range. The area under the curve from $E = 0$ to $E = \varepsilon$ gives the total number of states in that energy interval. The last equation has been used extensively in different fields of physics, such as: solid state, statistical mechanics, quantum mechanics etc.

In some instances it is more convenient to use the number of states within the momentum interval dp between p and p + dp. Recalling that the particle within the box acts as a free particle, we have E = p²/2m. Defining g(p) so that $dN(E) = g(p)dp = g(E)dE$, we have

$$g(p) = g(E)\frac{dE}{dp} = \frac{V}{h^3}4\pi p^2$$

This expression applies as well for the number of modes of longitudinal waves trapped in a cavity of volume V. In such cases it is more convenient to use the frequency $v$. We recall that $p = \hbar/\lambda$ and $v = c/\lambda$, where $c$ is the phase velocity of the waves. Therefore, defining $g(v)$ so that $g(v)dv = g(p)dp$, we have

$$g(v) = g(p)\frac{dp}{dv} = \frac{V}{c^3}4\pi v^2$$

which is a very useful relation. Also, using $E = \hbar\omega$, one can has $g(\omega) = \frac{V}{(2\pi)^3 c^3}\omega^2$.

The following is another simple way to calculate the density of state of cubic box with length *L*:

$$k_x L = 2\pi n_x \quad \Rightarrow \quad dn_x = \frac{L}{2\pi}dk_x,$$

$$k_y L = 2\pi n_y \quad \Rightarrow \quad dn_y = \frac{L}{2\pi}dk_y,$$

$$k_z L = 2\pi n_z \quad \Rightarrow \quad dn_z = \frac{L}{2\pi}dk_z$$

$$d^3n = dn_x dn_y dn_z = \frac{L^3}{(2\pi)^3}d^3k$$

$$= \frac{V}{(2\pi)^3}d^3k = \frac{V}{(2\pi\hbar)^3}d^3p, \qquad\qquad d^3p = 4\pi p^2 dp$$

Note that: $p = \hbar k, \quad \hbar = h/2\pi$