2.23 DEGENERACY

In the case of particle in a one-dimensional box, the state of the particle could be specified by specifying energy of the system. All of the energies and eigen functions are different. For the general 3-D particle in a box, because the total energy depends on not only the quantum numbers n_x, n_y and n_z but also the individual dimensions of the box, a, b, and c, one can imagine that in some cases the quantum numbers and the lengths might be such that different sets of quantum numbers (n_x, n_y and n_z) would yield the same energy of the two different wave functions.

An interesting situation arises if the box is cubical i.e., $a = b = c$, then the wave functions and energies are represented as:

$$\Psi_{(x,y,z)} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) \tag{2.80}$$

$$E = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{2.81}$$

The energy depends on a set of constants and the sum of the squares of the quantum numbers. If a set of three quantum numbers adds up to the same total as another set of three quantum numbers, or if the quantum numbers themselves exchange values, the energies would be exactly the same even though the wave functions are different. This condition is called *degeneracy*. Different, linearly independent wave functions that have the same energy are called *degenerate*. A specific level of degeneracy is indicated by the number of different wave functions that have the exact same energy. If these are two the energy level is two-fold (doubly) degenerate; if there are three different wave functions, it is three-fold (triply) degenerate and so on.

Let

n_x	n_y	n_z	
1	2	1	$E_{121} = 6 \cdot \frac{h^2}{8ma^2}$
2	1	1	$E_{211} = 6 \cdot \frac{h^2}{8ma^2}$
1	1	2	$E_{112} = 6 \cdot \frac{h^2}{8ma^2}$

E_{121}, E_{211} and E_{112} have same energy, even through each energy observable corresponds to a different wave function. This value of energy is three-fold degenerate. There are three different wave functions that have the same energy. Degenerate wave functions may have different eigen values of other observable.

This example of degeneracy is a consequence of a wave function in three dimensional space where each dimension is independent but equivalent. This might be considered degeneracy by symmetry. One can also find examples of accidental degeneracy. For example, a cubical box has wave functions with the sets of quantum numbers (3, 3, 3) and (5, 1, 1) and energies are

$$E_{333} = \frac{h^2}{8ma^2}(9 + 9 + 9) = 27 \cdot \frac{h^2}{8ma^2}$$

$$E_{511} = \frac{h^2}{8ma^2}(25 + 1 + 1) = 27 \cdot \frac{h^2}{8ma^2}$$

This is an example of *accidental degeneracy*. The corresponding wave functions have no common quantum number; but their energy eigenvalues are exactly the same. If we recognize that E_{151} and E_{115} also have the same energy, the level of degeneracy in this example becomes four-fold. The number of different quantum states belonging to the same energy level is known as *degree of degeneracy*. Degeneracy depends upon the symmetry of the atoms and molecules. If symmetry increases, its degeneracy also increases and vice versa. A diagram of the energy levels of the 3-D particle in a box is shown in Fig.2.17. For a particle in three-dimensional box, this degree of degeneracy can be removed by a slight distortion of the system, or by using a box of different dimensions.

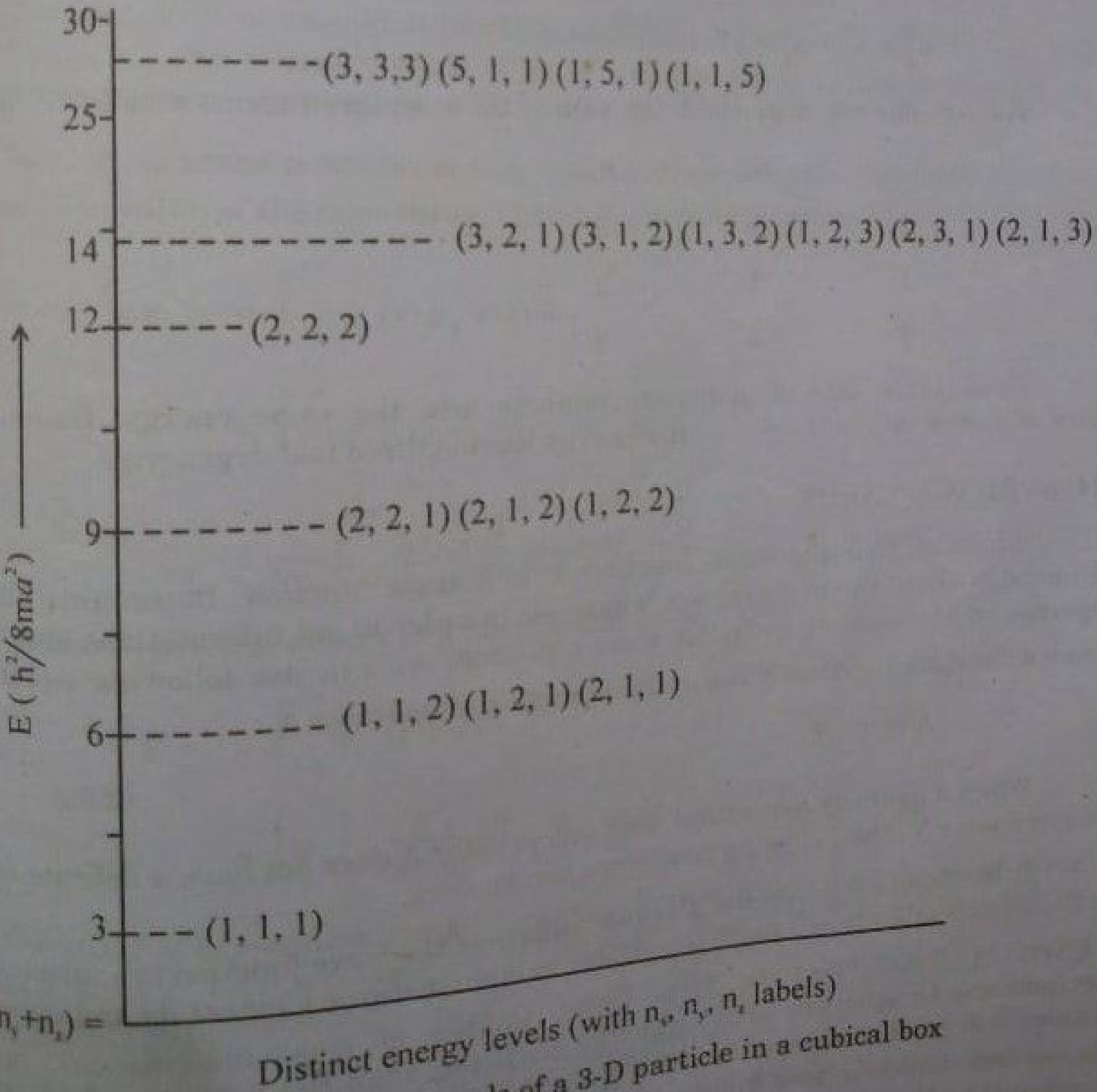

Fig.2.17 The energy levels of a 3-D particle in a cubical box