

(1) Quantum Mechanics in 3–dimensions: Introduction.

In 3–D quantum mechanics the position and momentum vectors are:

$$\mathbf{r} = (x, y, z) = \{x_i, i = 1, 2, 3\} \quad (1)$$

$$\hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = \{\hat{\mathbf{p}}_i, i = 1, 2, 3\} \quad (2)$$

$$= -i\hbar\nabla \quad (3)$$

$$= \left(-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z} \right) \quad (4)$$

The Hamiltonian is the operator

$$\hat{H}(\mathbf{r}, \hat{\mathbf{p}}) = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(\mathbf{r}, t) \quad (5)$$

$$= -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t) \quad (6)$$

$$= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{r}, t) \quad (7)$$

The 3–D wave function is $\Psi(\mathbf{r}, t)$ which obeys the TDSE,

$$\hat{H}(\mathbf{r}, \mathbf{p}, t)\Psi(\mathbf{r}, t) = i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} \quad (8)$$

$$\text{i.e. } -\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} \quad (9)$$

$$\text{i.e. } -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(\mathbf{r}, t) + V(\mathbf{r}, t)\Psi(\mathbf{r}, t) = i\hbar\frac{\partial\Psi(\mathbf{r}, t)}{\partial t} \quad (10)$$

The Born Postulate in 3–D is that

$$|\Psi(\mathbf{r}, t)|^2 d^3x, \text{ where } d^3x \equiv dx dy dz \equiv dV,$$

is the **probability** that a **measurement** of the particle’s position at time t will yield a value lying in the volume element $dV = d^3x$ at position \mathbf{r} ,

and is therefore normalised to 1,

$$\int |\Psi(\mathbf{r}, t)|^2 d^3x = 1 \quad (11)$$

$$\text{i.e. } \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} |\Psi(\mathbf{r}, t)|^2 dx dy dz = 1 \text{ in cartesian coordinates,} \quad (12)$$

$$\text{i.e. } \int_{r=0}^{+\infty} \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} |\Psi(\mathbf{r}, t)|^2 r^2 dr \sin\theta d\theta d\varphi = 1 \text{ in spherical polar coordinates,} \quad (13)$$

The canonical commutation relations between position and momentum follow the same rules as in 1D, with x_i not commuting with its ‘fellow’ momentum \hat{p}_i because $\hat{p}_i = -i\hbar\partial/\partial x_i$ differentiates x_i ; however x_i *does* commute with any ‘alien’ $\hat{p}_j, j \neq i$ because here x_i just acts like a constant:

$$[x, \hat{p}_x] = i\hbar \quad (14)$$

$$[y, \hat{p}_y] = i\hbar \quad (15)$$

$$[z, \hat{p}_z] = i\hbar \quad (16)$$

$$\text{with all other commutators} = 0 \quad (17)$$

We can put this succinctly using the kronecker delta symbol,¹

$$[x_i, \hat{p}_j] = i\hbar\delta_{ij} \quad (18)$$

A consequence of non-commutation are the Heisenberg uncertainty relations:

$$\Delta x, \Delta p_x \geq \frac{\hbar}{2} \quad (19)$$

$$\Delta y, \Delta p_y \geq \frac{\hbar}{2} \quad (20)$$

$$\Delta z, \Delta p_z \geq \frac{\hbar}{2} \quad (21)$$

(2) The parallelepiped or 3–dimensional escape–proof rectangular box.

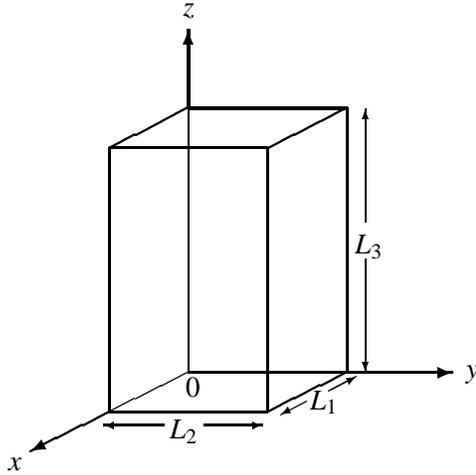


Figure 1. The parallelepiped or 3–D escape–proof rectangular box. The origin of coordinates is located at the lower vertex shown with a 0.

The 3–D version of the 1–D infinite square well is the escape–proof parallelepiped illustrated here with sides of length L_1, L_2, L_3 . The corresponding potential is

$$V(\mathbf{r}) = 0 \quad \text{inside, i.e. for } 0 < (x, y, z) < (L_1, L_2, L_3) \quad (22)$$

$$= \infty \quad \text{on the faces, i.e. for } (x, y, z) = 0 \text{ and } (x, y, z) = (L_1, L_2, L_3) \quad (23)$$

Since a particle inside the box cannot escape, the probability of finding it outside is zero, hence the wave function vanishes there

$$\psi(\mathbf{r}) = 0 \quad \text{outside the box.} \quad (24)$$

Inside the box the potential vanishes, with the wave function given by the TISE:

$$\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) &= E\psi(\mathbf{r}) \\ \text{i.e. } \nabla^2\psi(\mathbf{r}) &= -k^2\psi(\mathbf{r}) \end{aligned} \quad (25)$$

where the real constant k depends on the energy eigenvalue,

$$k = \sqrt{\frac{2mE}{\hbar^2}} \quad (26)$$

¹Note that ‘alien’ components of position and momentum may both be measured with 100% precision, *provided* their *respective* momentum and position are not measured at all, i.e. remain 100% uncertain. Thus we can in principle measure x and p_y with 100% accuracy, $\Delta x = 0$ and $\Delta p_y = 0$, *provided* we avoid measuring p_x and y .

A cartesian coordinate system is clearly the most convenient one for applying the boundary conditions. In cartesians we can separate this TISE into three independent infinite square well problems by looking for solutions of separable form:

$$\Psi(\mathbf{r}) = X(x)Y(y)Z(z), \quad (27)$$

where each factor is a function of only one of the indicated independent coordinates. Substituting into the TISE and dividing the equation by $-X(x)Y(y)Z(z)$, yields a suggestive form of the equation:

$$-\frac{1}{X(x)} \frac{d^2X(x)}{dx^2} - \frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} - \frac{1}{Z(z)} \frac{d^2Z(z)}{dz^2} = k^2 \quad (28)$$

Since each term on the left can be changed independently of the others by varying only its independent variable, they can only conspire to sum up to the constant k^2 if they are each constant:

$$-\frac{1}{X(x)} \frac{d^2X(x)}{dx^2} = k_1^2 \quad (29)$$

$$-\frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} = k_2^2 \quad (30)$$

$$-\frac{1}{Z(z)} \frac{d^2Z(z)}{dz^2} = k_3^2 \quad (31)$$

$$\text{with } k_1^2 + k_2^2 + k_3^2 = k^2 = \frac{2mE}{\hbar^2} \quad (32)$$

Each of these equations is identical to that for a 1-D infinite square well. Imposing boundary conditions yields independent energy quantization in each dimension:

$$X(x) = N_1 \sin\left(\frac{n_1\pi}{L_1}x\right), \quad n_1 = 1, 2, 3, \dots \quad \text{and} \quad k_1 = \frac{n_1\pi}{L_1} \quad (33)$$

$$Y(y) = N_2 \sin\left(\frac{n_2\pi}{L_2}y\right), \quad n_2 = 1, 2, 3, \dots \quad \text{and} \quad k_2 = \frac{n_2\pi}{L_2} \quad (34)$$

$$Z(z) = N_3 \sin\left(\frac{n_3\pi}{L_3}z\right), \quad n_3 = 1, 2, 3, \dots \quad \text{and} \quad k_3 = \frac{n_3\pi}{L_3} \quad (35)$$

Since our solution vanishes outside the box the normalization condition, $\int_{-\infty}^{+\infty} |\Psi(\mathbf{r})|^2 d^3x = 1$ translates into

$$(N_1N_2N_3) \int_0^{L_1} \sin^2\left(\frac{n_1\pi}{L_1}x\right) dx \int_0^{L_2} \sin^2\left(\frac{n_2\pi}{L_2}y\right) dy \int_0^{L_3} \sin^2\left(\frac{n_3\pi}{L_3}z\right) dz = 1$$

$$(N_1N_2N_3) \frac{L_1}{2} \frac{L_2}{2} \frac{L_3}{2} = 1$$

yielding the neat result,

$$(N_1N_2N_3) = \sqrt{\frac{8}{L_1L_2L_3}} = \sqrt{\frac{8}{V}} \quad \text{where } V = \text{Volume of the box} \quad (36)$$

The normalised energy eigenstates are labelled by the three quantum numbers

$$\Psi_{n_1n_2n_3}(\mathbf{r}) = \sqrt{\frac{8}{L_1L_2L_3}} \sin\left(\frac{n_1\pi}{L_1}x\right) \sin\left(\frac{n_2\pi}{L_2}y\right) \sin\left(\frac{n_3\pi}{L_3}z\right) \quad (37)$$

with their energy eigenvalues given by the sum of three *independent* terms,

$$E_{n_1n_2n_3} = \frac{\hbar^2\pi^2}{2m} \left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \quad (38)$$

Corresponding wavenumbers, expressed in momentum units for later use, are

$$p_i = \hbar k_i = \frac{\hbar \pi}{L_i} n_i \quad (39)$$

(3) Energy Levels, Symmetry and Degeneracy.

When all the dimensions of the box are different the energy levels are usually all distinct; this is depicted in Figure 2 (with the choice $L_1 < L_2 < L_3$ and with energies expressed in units of $\hbar^2 \pi^2 / 2m$). When there is no coincidence of different energy levels corresponding to different quantum numbers, we say that the energy levels are **non-degenerate**. The lowest energy level always has $(n_1, n_2, n_3) = (1, 1, 1)$ denoted E_{111} – recall that no n can be zero, otherwise the wave function would be identically zero. Given our chosen ordering of L -values, the next highest energy is obtained by incrementing n_3 by one because the third term in the energy is the smallest: hence the next level corresponds to $(n_1, n_2, n_3) = (1, 1, 2)$ denoted E_{112} . The next highest level depends on how different the L -values are. Assume they don't differ very much. In that case the next highest level comes from increasing n_2 by one unit, giving a slightly higher increment from the ground state than would increasing n_3 ; thus the next highest level corresponds to $(n_1, n_2, n_3) = (1, 2, 1)$ denoted E_{121} . The next level corresponds to $(n_1, n_2, n_3) = (2, 1, 1)$ denoted E_{211} . These are illustrated in Figure 2. The ordering of subsequent levels depends somewhat more on the details of the L -values; indeed there can be so-called **accidental degeneracies** when the squared lengths are in certain rational ratios. For example, when the ratio $(L_2/L_3)^2 = 8/9$, then $E_{n_1 15} = E_{n_1 34}$ for all n_1 .

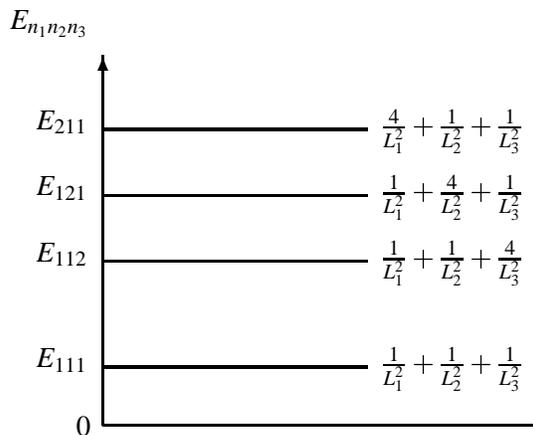


Figure 2.

Energy-level diagram (not drawn to scale) for a particle in an escape-proof 3-D box. Shown on the right is the dependence on the n_i and L_i for $L_1 < L_2 < L_3$.

So far we have discussed the case of a box with different width, breadth and height, i.e. different dimensions L_i . Here the box has the least possible *symmetry* where we find no degeneracies, i.e. no coinciding energy levels, as illustrated in Figure 2. What happens as we allow the box to become more and more symmetrical?

Suppose the faces parallel to the $x - y$ plane go from rectangular to square, $L_1 = L_2 < L_3$. The result is a symmetry between the quantum numbers n_1 and n_2 : interchanging them does not change the energy. Of the four lowest levels two become degenerate: $E_{121} = E_{211}$. Quantum states are **degenerate** when their energies are equal, but their quantum numbers are different. We notice that introduction of greater symmetry in the geometry of the system or potential – a square base of the box rather than a rectangular base – gives rise to degeneracy. Conversely, when we go the other way and break the square symmetry of the base, turning it into a rectangle, we **lift the degeneracy** of the energy levels and they separate. These phenomena are widespread in nature and the concept is used throughout quantum physics, especially in the theory of elementary particles. We shall see several important examples in this course including the two-well model for the H_2^+ molecular ion, the maser and atoms and molecules in magnetic fields (Zeeman effect, etc.).

If we increase the symmetry even further by turning our parallelepiped into a cube with all 6 square faces identical, $L_1 = L_2 = L_3$, then the symmetry between the quantum numbers n_1 and n_2 extends to n_3 also: interchanging any pair leaves the energy unchanged, with three energy levels now degenerate, $E_{121} = E_{211} = E_{112}$. These properties are illustrated in the following Figure.

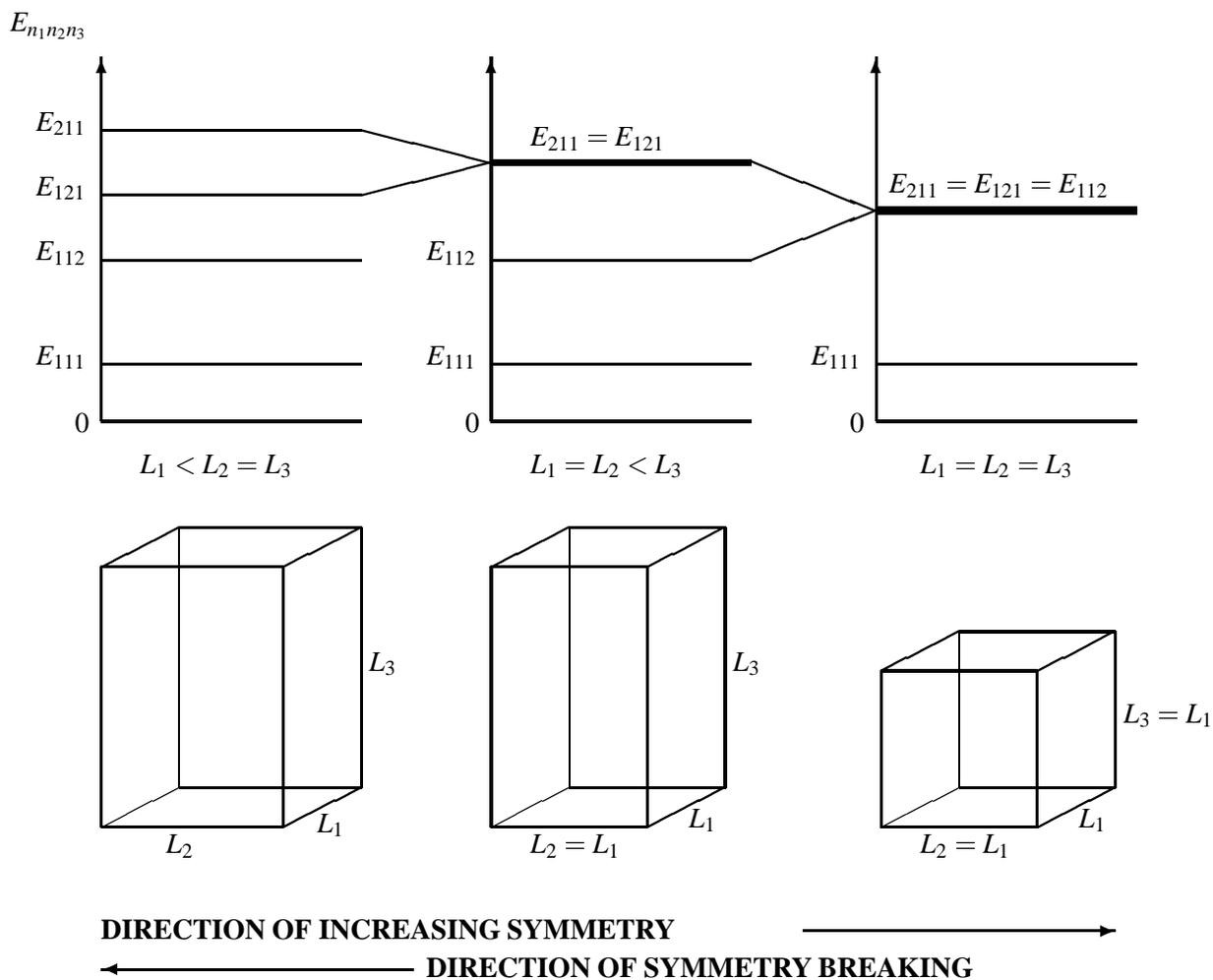


Figure 3. Lifting degeneracy by symmetry breaking.

Here we have depicted the process of **degeneracy lifting by symmetry breaking**: starting with a cube, the parallelepiped with maximum symmetry and the system with the largest amount of degeneracy, we remove the degeneracy by **breaking the symmetry** of the cube by creating more unequal faces. In the Zeeman effect degeneracy is lifted by applying a magnetic field; this breaks the symmetry of space, making one direction of space distinguishable from any other.

(3) Counting Quantum States in a 3-D Box: the Density of States.

In many applications of quantum mechanics to fields as diverse as Statistical Mechanics, Solid State Physics, Nuclear and Elementary Particle Physics, Astrophysics and Astronomy, it is important to know the **number of distinct quantum states**, $dN(p)$ in the momentum interval $\mathbf{p} \rightarrow \mathbf{p} + d\mathbf{p}$. From eq. (39), using $\hbar\pi = h/2$, the only allowed quantum states in a cube of side L have momenta,

$$p_x = \frac{h}{2L}n_1, \quad n_1 = 1, 2, 3, \dots \quad (40)$$

$$p_y = \frac{h}{2L}n_2, \quad n_2 = 1, 2, 3, \dots \quad (41)$$

$$p_z = \frac{h}{2L}n_3, \quad n_3 = 1, 2, 3, \dots \quad (42)$$

$$(43)$$

Each state can be depicted as discrete points in 3-D **momentum space** with coordinates,

$$\mathbf{p} = \frac{h}{2L}(n_1, n_2, n_3) \quad (44)$$

These mark out a cubic lattice of points with tiny lattice spacing, $h/2L$ as depicted in Figure 4a.

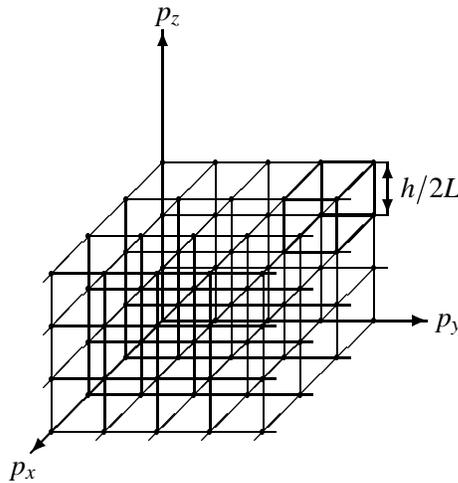


Figure 4a: Allowed quantum states are points at the vertices of a cubic lattice in momentum space.

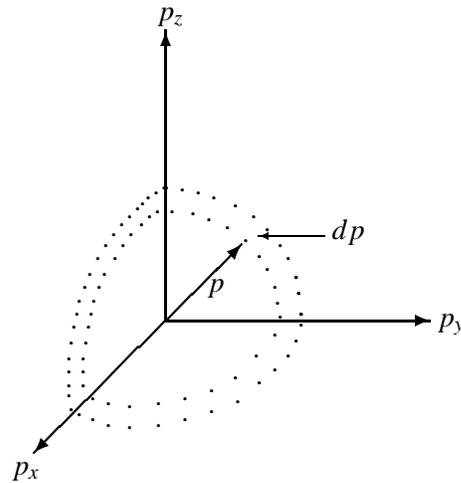


Figure 4b: Spherical shell in momentum space with radius p and thickness dp .

For a macroscopic container a typical size might be $L \sim 10^{-1}\text{m}$, so that points in momentum space representing the allowed quantum states are separated by $h/2L \sim 10^{-33}\text{Jsm}^{-1}$. This is extremely small on any relevant scale of momenta: a H atom at 300K has an average momentum around 10^{-24}Jsm^{-1} . We conclude that the points are so close together that we may treat them as very nearly continuously distributed in the positive quadrant of momentum space.²

From Figure 4a we observe that each point at the vertex of a cube is shared between 8 cubes, but each

²Positive because the quantum numbers n_i are positive numbers.

cube has 8 vertices; therefore there is 1 state per cube, or 1 quantum state in volume $(h/2L)^3$ of momentum space. Thus, **there are $(2L/h)^3$ states per unit volume of momentum space.**

Now consider the thin spherical shell in Figure 4b occupying the positive quadrant. With thickness dp and radius p , its total volume is $4\pi p^2 dp/8$, and so it contains a number of states,

$$dN(p) = \frac{1}{8} 4\pi p^2 \left(\frac{2L}{h} \right)^3 \quad (45)$$

where the last factor is the number of states per unit volume of momentum space. Recognizing $\bar{E} = V$ as the volume of the box containing the particle, we obtain the final result:

Number of quantum states available to a particle with momentum in the range $p \rightarrow p + dp$ in a box of volume V is

$$dN(p) = \frac{V 4\pi p^2 dp}{h^3} \quad (46)$$

This very fundamental result has a simple interpretation: if we call ‘**phase space**’ the 6–dimensional space made up of ‘**configuration space**’(ordinary space), with coordinates (x, y, z) , and ‘**momentum space**’, with coordinates (p_x, p_y, p_z) , then

$$\begin{aligned} V &= \text{configuration space volume} \\ 4\pi p^2 dp &= \text{momentum space volume} \end{aligned}$$

$$\text{and } dN(p) = \frac{(\text{Phase Space Volume})}{h^3}$$

i.e. there is one allowed quantum state for every volume h^3 of 6–D phase space.

Notice that in the classical limit $h \rightarrow 0$, there are infinitely many allowed states in any finite volume of phase space: in this case the energy levels are continuous and not quantized.