Particle in a 3D box – Jonathan Lam PH214C Final Pset

Potential function:

$$V(\vec{r}) = V(x,y,z) = \begin{cases} 0 & 0<x<L_x, 0<y<L_y, 0<z<L_z \\ \infty & \text{otherwise} \end{cases}$$

The time-independent Schrödinger equation is given by:

$$\lim_{V\to\infty}\left[-\frac{\hbar^2}{2m}\nabla^2 U + V(\vec{r})U = EU\right]$$

Dividing each term by V leads to the boundary conditions $U(\vec{r} \text{ on boundary}) = 0$. Since $V=0$ in the box, we have:

$$-\frac{\hbar^2}{2m}\nabla^2 U + 0 = EU \Rightarrow \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)U = EU$$

To solve this, assume U is separable, i.e., $U(\vec{r}) = U_1(x)U_2(y)U_3(z)$. Thus:

$$-\frac{\hbar^2}{2m}\left(U_2U_3\frac{d^2U_1}{dx^2}+U_1U_3\frac{d^2U_2}{dy^2}+U_1U_2\frac{d^2U_3}{dz^2}\right) = EU \Rightarrow \frac{\hbar^2}{2m}\left(\frac{1}{U_1}\frac{d^2U_1}{dx^2}+\frac{1}{U_2}\frac{d^2U_2}{dy^2}+\frac{1}{U_3}\frac{d^2U_3}{dz^3}\right) = -E \qquad (1)$$

This is always be true in the box, in particular when $d^2U_2/dy^2 = d^2U_3/dz^2 = 0$ (on a line parallel to the x-axis). In this case, let the energy eigenvalue be E_1:

$$\frac{\hbar^2}{2m}\left(\frac{1}{U_1}\frac{d^2U_1}{dx^2}+0+0\right) = \frac{\hbar^2}{2m}\frac{d^2U_1}{dx^2} = -E_1U_1 \qquad (U_1(0) = U_1(L_x) = 0)$$

This is exactly the one-dimensional particle-in-a-box setup and differential equation (including boundary conditions), so the solution to U_1 should be the same as the 1D case.

$$U_1(x) = A_x\sin k_1x,\ k_1 = \frac{\sqrt{2mE_1}}{\hbar} = \frac{\pi n_1}{L_x},\ E_1 = \frac{\pi^2\hbar^2n_1^2}{2mL_x^2} \qquad (n_1\in\{1,2,3,\dots\})$$

The analogous result is true for U_2, U_3. Using (1), we obtain the discrete set of total energy eigenvalues for U (which unsurprisingly is the sum of the component energies, each of which is a discrete set):

$$\frac{1}{U_1}\frac{d^2U_1}{dx^2} = \frac{1}{A_1\sin k_1x}(-A_1k_1^2\sin k_1x) = -k_1^2 = -\frac{2mE_1}{\hbar^2} \qquad \text{(analogous results for } U_2,\ U_3)$$

$$E = -\frac{\hbar^2}{2m}\left(\frac{1}{U_1}\frac{d^2U_1}{dx^2}+\frac{1}{U_2}\frac{d^2U_2}{dy^2}+\frac{d^2U_3}{dz^2}\right) = -\frac{\hbar^2}{2m}\left(-\frac{2mE_1}{\hbar^2}-\frac{2mE_2}{\hbar^2}-\frac{2mE_3}{\hbar^2}\right) = E_1+E_2+E_3$$

By our assumption of separability, we have an explicit set of solutions for U (purely real) and ψ and can normalize:

$$U = U_1U_2U_3 = A\sin(k_1x)\sin(k_2y)\sin(k_3z) \Rightarrow \psi(\vec{r},t) = U(\vec{r})\exp(-iEt/\hbar)$$

$$1 = \int_V dV\,\psi^*\psi = \int_0^{L_x}dx\int_0^{L_y}dy\int_0^{L_z}dz\ [U\exp(iEt/\hbar)]\,[U\exp(-iEt/\hbar)] = \int_0^{L_x}dx\int_0^{L_y}dy\int_0^{L_z}dz\,U^2$$

$$= A^2\int_0^{L_x}dx\sin^2k_1x\int_0^{L_y}dy\sin^2k_2y\int_0^{L_z}dz\sin^2k_3z$$

$$\left[\text{example integral: }\int_0^{L_x}dx\sin^2k_1x = \int_0^{L_x}dx\left(\frac{1}{2}-\frac{\cos 2k_1x}{4k_1}\right) = \frac{L_x}{2}-\frac{1}{4k_1}\sin(2k_1L_x(=2\pi))\Big|_0^{L_x} = \frac{L_x}{2}\right]$$

$$= \frac{1}{8}A^2L_xL_yL_z \Rightarrow A = \sqrt{\frac{8}{L_xL_yL_z}}$$

In summary:

$$\psi(\vec{r},t) = \sqrt{\frac{8}{L_xL_yL_z}}\sin\left(\frac{\pi n_1x}{L_x}\right)\sin\left(\frac{\pi n_2y}{L_y}\right)\sin\left(\frac{\pi n_3z}{L_z}\right)\exp(-iEt/\hbar)$$

$$E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{L_x^2}+\frac{n_2^2}{L_y^2}+\frac{n_3^2}{L_z^2}\right) \quad (n_1,n_2,n_3\in\{1,2,3,\dots\})$$

In the case where $L_x = L_y = L_z = L$ (a cube):

$$\psi(\vec{r},t) = \sqrt{\frac{8}{L^3}}\sin\left(\frac{\pi n_1x}{L}\right)\sin\left(\frac{\pi n_2x}{L}\right)\sin\left(\frac{\pi n_3x}{L}\right)\exp\left(-\frac{iEt}{\hbar}\right),\ E = \frac{\pi^2\hbar^2}{2mL^2}(n_1^2+n_2^2+n_3^2)$$

$$(n_1,n_2,n_3\in\{1,2,3,\dots\})$$