These worked examples follow “Rechenmethoden der Quantentheorie, Siegfried Flügge, Springer, Berlin, 1965”. Library of Congress Catalog Card Number 65-24546, title-nr. 7288

Hope I can help you with learning quantum mechanics.

We have a particle in a 3D-box. Within the box we have potential zero and infinity outside. Calculate the energy eigenvalues and the eigenfunctions.

We work with the Schrödinger equation:

$$\Delta u(r) + \frac{2mE}{\hbar^2} u(r) = 0$$

We abbreviate:

$$k^2 = \frac{2mE}{\hbar^2}$$

We write:

$$\Delta u + k^2 u = 0$$

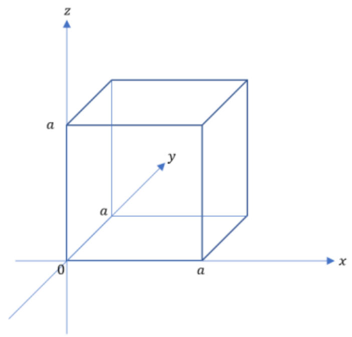
We have no potential in the box and can separate into x, y, z:

$$(\vec{r}|u) = X(x) \cdot Y(y) \cdot Z(z)$$

We get:

$$u(x,y,z) = A \cdot sin(k_x \cdot x + \delta_x) \cdot sin(k_y \cdot y + \delta_y) \cdot sin(k_z \cdot z + \delta_z)$$

Note: ${k_x}^2 + {k_y}^2 + {k_z}^2 = k^2$



From the potential we get the boundary conditions. On each plane we need $u = 0$.

Each plane is defined by:

$$x = 0, y = 0, z = 0, x = a, y = a, z = a$$

From the conditions $x = 0, y = 0, z = 0$ we get:

$$\delta_x = \delta_y = \delta_z = 0$$

From the conditions $x = a, y = a, z = a$ we get:

$$k_x = \frac{n_x \cdot \pi}{a}, k_y = \frac{n_y \cdot \pi}{a}, k_z = \frac{n_z \cdot \pi}{a}$$

Note: $n_x, n_y, n_z \in \mathbb{N}$

Note: these conditions determine the wave length for each direction.

We get the eigenfunctions:

$$u_{n_x,n_y,n_z}(x,y,z) = A \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)$$

We check the eigenfunctions.

We use the Schrödinger equation:

$$\Delta u(r) = -\frac{2mE}{\hbar^2} u(r)$$

$$\frac{\partial^2}{\partial x^2} u_{n_x,n_y,n_z}(x,y,z) + \frac{\partial^2}{\partial y^2} u_{n_x,n_y,n_z}(x,y,z) + \frac{\partial^2}{\partial z^2} u_{n_x,n_y,n_z}(x,y,z) =;$$

We do this step by step.

$$\frac{\partial}{\partial x} u_{n_x,n_y,n_z}(x,y,z) = A \cdot cos\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot \frac{n_x \cdot \pi}{a} \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)$$

$$\frac{\partial^2}{\partial x^2} u_{n_x,n_y,n_z}(x,y,z) = -A \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot \left(\frac{n_x \cdot \pi}{a}\right)^2 \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)$$

Similar:

$$\frac{\partial^2}{\partial y^2} u_{n_x,n_y,n_z}(x,y,z) = -A \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot \left(\frac{n_y \cdot \pi}{a}\right)^2 \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)$$

$$\frac{\partial^2}{\partial z^2} u_{n_x,n_y,n_z}(x,y,z) = -A \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right) \cdot \left(\frac{n_z \cdot \pi}{a}\right)^2 \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right)$$

We get:

$$\Delta u(r) = -A \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot \frac{n_x \cdot \pi}{a} \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right) - A \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot \frac{n_y \cdot \pi}{a} \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right) - A \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right) \cdot \frac{n_z \cdot \pi}{a} \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) =$$

$$-\left(A \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)\right) \cdot \left(\left(\frac{n_x \cdot \pi}{a}\right)^2 + \left(\frac{n_y \cdot \pi}{a}\right)^2 + \left(\frac{n_z \cdot \pi}{a}\right)^2\right) =$$

$$-\left(A \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)\right) \cdot \left(\frac{\pi}{a}\right)^2 \cdot \left({n_x}^2 + {n_y}^2 + {n_z}^2\right) =$$

$$-u(r) \cdot \left(\frac{\pi}{a}\right)^2 \cdot \left({n_x}^2 + {n_y}^2 + {n_z}^2\right)$$

From the Schrödinger equation we use the expression for the energy:

$$\frac{2mE}{\hbar^2} = \left(\frac{\pi}{a}\right)^2 \cdot \left({n_x}^2 + {n_y}^2 + {n_z}^2\right)$$

We get the energy E:

$$E = \frac{\hbar^2 \pi^2}{2ma^2} \left({n_x}^2 + {n_y}^2 + {n_z}^2\right)$$

We calculate the amplitude A by normalization:

$$\iiint_0^a \left|u_{n_x,n_y,n_z}(x,y,z)\right|^2 dxdydz = 1$$

Note: We solve the integral by successively integrating the x-dependent factor, the y-dependent factor and the z-dependent factor.

We integrate the $x - axis$:

$$\int_0^a \left|sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right)\right|^2 dx = \int_0^a sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right)^2 dx =$$

$$\left[\frac{x}{2} - \frac{a}{4n_x \cdot \pi} sin\left(\frac{2 \cdot n_x \cdot \pi}{a} \cdot x\right)\right]_0^a =$$

$$\frac{a}{2} - \frac{a}{4n_x \cdot \pi} sin(2 \cdot n_x \cdot \pi) - \frac{0}{2} + \frac{a}{4n_x \cdot \pi} sin(0) = \frac{a}{2}$$

Similar for the y, z axis:

$$\int_0^a \left|sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right)\right|^2 dy = \frac{a}{2}$$

$$\int_0^a \left|sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)\right|^2 dz = \frac{a}{2}$$

We get:

$$A^2 \iiint_0^a \left|sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)\right|^2 dxdydz =$$

$$A^2 \cdot \frac{a^3}{8}$$

We normalize:

$$A^2 \cdot \frac{a^3}{8} = 1 \rightarrow A = \sqrt{\frac{8}{a^3}}$$

Comment

For the motion of a macroscopic particle the wavelength is very small compared to the length a of the "box".

In this case the quantum numbers we get from $k_x = \frac{n_x \cdot \pi}{a}, k_y = \frac{n_y \cdot \pi}{a}, k_z = \frac{n_z \cdot \pi}{a}$ will be $\gg 1$.

The energy values $E = \frac{\hbar^2 \pi^2}{2ma^2}\left({n_x}^2 + {n_y}^2 + {n_z}^2\right)$ then are forming a quasi-continuum.

The quantity u^2:

$$\left(u_{n_x,n_y,n_z}(x, y, z)\right)^2 = \left(A \cdot sin\left(\frac{n_x \cdot \pi}{a} \cdot x\right) \cdot sin\left(\frac{n_y \cdot \pi}{a} \cdot y\right) \cdot sin\left(\frac{n_z \cdot \pi}{a} \cdot z\right)\right)^2$$

remains a rapidly oscillating function of the position.

For a macroscopic measurement, the error of the particle position is certainly large compared to a wavelength, so for macrophysics the expectation value of u^2 over several wavelengths is of interest. However, the expectation value of $u^2$is independent of the position within the permitted range.