

Part IB — Quantum Mechanics

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0 Introduction

Quantum Mechanics (QM) is a radical generalization of classical physics involving a new fundamental constant, *Planck's constant*:

$$\hbar = h/2\pi \approx 1.05 \times 10^{-34} \text{ Js},$$

with dimensions

$$\begin{aligned} [\hbar] &= ML^2T^{-1} = [\text{position}] \times [\text{momentum}] \\ &= [\text{energy}] \times [\text{time}] \end{aligned}$$

Profound new features of QM include:

- *Quantisation.* Physical quantities such as energy may be restricted to discrete sets of values, or may appear only in specific amounts, called *quanta*.
- *Wave-particle duality.* Classical concepts of a particle and a wave are merged; they become different aspects of a single entity that shows either particle-like or wave-like behaviour, depending on the circumstance.
- *Probability and uncertainty.* Predictions in QM involve probability in a fundamental way and there are limits to what can be asked about a physical system, even in principle¹. A famous example is the *Heisenberg uncertainty principle relation* for position and momentum.

Despite these radical changes, classical physics must be recovered in the limit $\hbar \rightarrow 0$ (which may require careful interpretation).

The following sections provide some physical background and summarise key experimental evidence for these novel features of QM.

0.1 Light Quanta

An electromagnetic (EM) wave, eg. light, consists of quanta called *photons*. Photons can be regarded as particles with energy, E , and momentum, p , related to frequency ν or ω , and² wavelength λ , or wavenumber k , according to

$$E = h\nu = \hbar\omega$$

$$p = h/\lambda = \hbar k$$

From the wave equation (satisfied by each EM field component)

$$c = \omega/k = vk \quad \text{or} \quad E = cp \text{ massless particle}$$

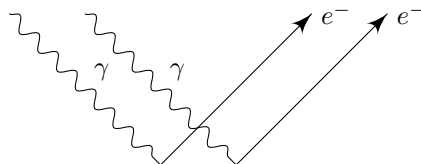
so the relations are consistent with photons being particles of rest mass zero, moving with the speed of light, c .

Compelling evidence for the existence of photons is provided by the *photoelectric effect*. Consider (Fig. 1) light of EM radiation (γ) of frequency ω

¹If we were able to keep track of every single particle we would know exactly what the system is doing. But in QM, we *still* can't know what the system is doing precisely.

² ν, ω both called frequency, and differ by a factor of 2π .

incident on a metal surface. For certain metals and suitable frequencies this results in the emission of electrons (e^-) and their maximum kinetic energy K can be measured.



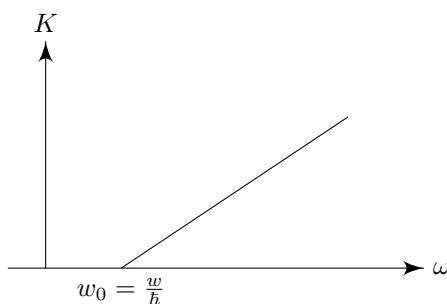
Experiments find that:

- (i) the rate at which electrons are emitted is proportional to the intensity of the radiation (the ‘brightness’ of the source);
- (ii) K depends linearly on ω but *not* on the intensity;
- (iii) for $\omega < \omega_0$, some critical value, *no* electrons are emitted, irrespective of the intensity.

The results are extremely hard to understand in terms of classical EM waves. However, they follow naturally from the assumption that the wave consists of photons, each with energy $E = \hbar\omega$, and with the intensity of the radiation proportional to the number of photons incident per unit time. Suppose that an electron is emitted as a result of absorbing a single photon with sufficiently high energy. If W is the minimum energy needed to liberate an electron from the metal then

$$K = \hbar\omega - W$$

is the maximum kinetic energy of an emitted electron if $\omega > \omega_0$, where $\omega_0 = W/\hbar$, and no emission is possible if $\omega < \omega_0$ (Fig 2). Furthermore, the rate at which electrons are emitted will be proportional to the rate at which incident photons arrive, and hence the intensity.

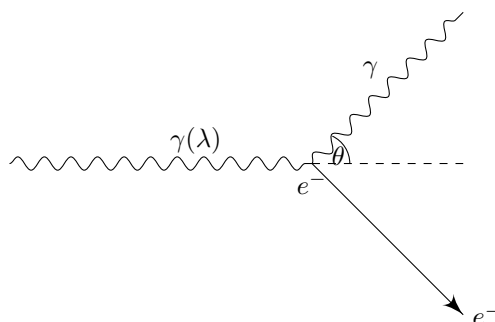


The energy-frequency relation for photons was introduced by Planck and used to derive the *black body spectrum*. This is the distribution of energy with frequency for EM radiation in thermal equilibrium, a fundamental result in thermodynamics of far-reaching importance (understanding the *cosmic microwave background*, for example). Einstein then applied the energy-frequency relation to explain the photoelectric effect. Further conclusive evidence for photons as particles,

including the momentum-wavelength relation, came from subsequent experiments involving *Compton scattering*.

Consider a photon of wavelength λ colliding with an electron that is stationary in the laboratory frame. Let λ' be the wavelength of the photon after the collision and θ the angle through which it is deflected. Treating the photon as a massless relativistic particle, conservation of four-momentum implies

$$\lambda' - \lambda = \frac{h}{m_e c} (1 - \cos\theta)$$



This dependence of the change in wavelength (or decrease in energy) can be verified experimentally (for X-rays, or γ -rays, for instance).

0.2 Bohr Model of the Atom

The *Rutherford model* of the atom was proposed to explain the results of scattering experiments (eg. alpha particles scattered by gold foil). The key assumption is that most of the mass of the atom is concentrated in a compact, positively-charged *nucleus* (subsequently understood to consist of protons and neutrons), with light, negatively charged electrons orbiting around it. The simplest case is the Hydrogen atom, in which a single electron with charge $-e$ and mass m_e orbits a nucleus consisting of a single proton with charge $+e$ and mass m_p . Since $m_p \gg m_e$ it is a good approximation to assume the proton is stationary, at the origin, say. The electron and proton interact via Coulomb's Law: the potential energy of the electron and the force it experiences are:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} \quad \mathbf{F}(\mathbf{r}) = -\nabla V = -\frac{e^2}{4\pi\epsilon_0} \hat{\mathbf{r}}$$

The classic equations of motion for the electron imply that its angular momentum, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, and its total energy,

$$E = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

are constant. The orbits are therefore planar and they can be determined exactly. For any value of $E < 0$ there is a closed orbit and the electron is *bound* to the proton to form a Hydrogen atom. For orbits with $E > 0$ the electron eventually escapes to infinity: it is not bound to the proton.

Despite its success in accounting for Rutherford scattering, this model has a number of problems. The treatment is identical, mathematically, to planetary

orbits governed by gravity (see Part IA Dynamics and Relativity, for example) but an important additional feature of electromagnetism has been left out. An accelerating charge radiates energy (carried away via EM fields) and this means that the electron would actually spiral inwards towards the proton: this is not a good model of a stable atom!

There is also experimental evidence for complex discrete structure within atoms. This comes from *line spectra*: bright emission lines (from a hot sample) or dark absorption lines (if radiation is passed through a cooler sample), both occurring at certain characteristic wavelengths or frequencies. This suggests that an atom can emit or absorb radiation only at these particular frequencies or wavelengths, which corresponds to photon with particular energies.

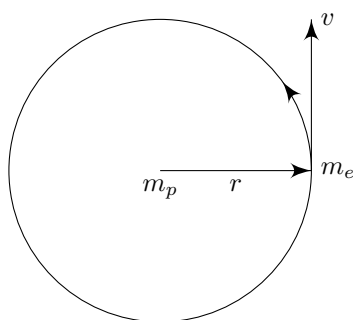
The *Bohr model* restricts the classical orbits of the Rutherford model by postulating that the angular momentum of the electron obeys the *Bohr quantisation condition*

$$L = n\hbar, \quad n = 1, 2, \dots,$$

with only these discrete values are allowed. This might seem to be an unsatisfactory way to address the issue of stability, but it proves to be remarkably successful in reproducing the complex experimental data relating to line spectra.

Specializing to circular orbits (Fig. 4) for simplicity, we have

$$F = m_e v^2 / r \quad \text{and} \quad L = m_e r v$$



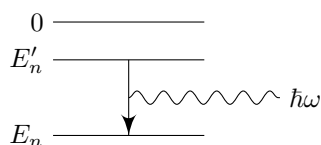
It is then straightforward to check that the quantisation condition leads to the following set of *Bohr orbits*

$$r_n = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} n^2, \quad v_n = \frac{e^2}{4\pi\epsilon_0\hbar} \frac{1}{n}, \quad E_n = -\frac{1}{2} m_e \left(\frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \frac{1}{n^2}, \quad n = 1, 2, \dots$$

Note that the allowed energy levels are now discrete.

Suppose that an electron makes a transition between levels n and n' (with $n' > n$, say) accompanied by emission or absorption of a photon of frequency ω (Fig 5). Then

$$\hbar\omega = E_{n'} - E_n = \frac{1}{2} m_e \left(\frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 \left(\frac{1}{n^2} - \frac{1}{n'^2} \right)$$



This formula accounts for a vast amount of experimental data on spectral lines for Hydrogen. The Bohr model also provides an estimate for the *size* of the Hydrogen atom $r_1 \approx 5.29 \times 10^{-11} \text{m}$, the *Bohr radius*. Despite these considerable successes, the origin of the Bohr quantisation condition seems obscure. A better explanation is needed.

0.3 Matter Waves

The relations used to associate particle properties (E and p) to waves can also be used to associate wave properties (v or ω and λ or k) to particles. This applies not just to relativistic photons but also to non-relativistic particles, electrons for example, and λ is called the *de Broglie wavelength* of the particle. A strong hint that this might be important for a better understanding of the Bohr quantisation condition comes from observing that for a circular orbit

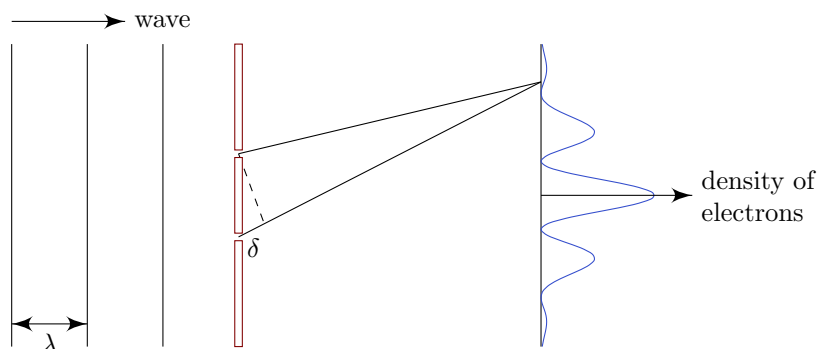
$$L = pr = n\hbar \quad \Longleftrightarrow \quad n\lambda = 2\pi r$$

The Bohr condition therefore says that the circumference of each orbit is exactly an integral number of de Broglie wavelengths.

[Fig 6]

It can also be verified experimentally that electrons do indeed exhibit wave-like behaviour, and a helpful idealisation is the *double slit experiment*. Consider a source which emits a beam of electrons, a barrier with two slits that can be open or closed, and a screen on which the electrons are detected.

Suppose that first one slit is open and the other is closed. We cannot say with certainty where any particular electron will be detected, but after many electrons have been emitted, the number detected varies with transverse position. If *both* slits are open, however, then the electrons produce (perhaps unexpectedly) an interference pattern.



This matches the interference pattern obtained for waves of length λ incident on a barrier. Consider a point P at some fixed perpendicular distance from the barrier, and let δ be the difference of the distances to P from each of the slits.

Constructive interference occurs for $\delta = n\lambda$ while destructive interference occurs for $\delta = (n + 1/2)\lambda$. The result is that the (amplitude)² of the superposed waves varies as P varies.

In diffraction experiments with electrons, we cannot predict what will happen to any *single* particle; the most that can be said is that it will be detected at a given position with a certain *probability*. The diffraction pattern is conclusive evidence of interference and so confirms the existence of matter waves, and diffraction experiments allow an experimental determination of the de Broglie wavelength. The results also suggest that the probability distribution for particles can be expressed as the (amplitude)² of a wave.

1 Wave functions and Operators

In first few chapters we consider a quantum particle in one dimension, introduce some key ideas and three postulates for how to extract physical information from mathematical framework. Later (Chapter 6) we will state general axioms from which these follow.

1.1 Wave functions and States

A classical point particle in one-dimension has a position x at each time. In QM a particle has a *state* at each time given by a complex-valued,³ wavefunction

$$\psi(x)$$

Postulate(P1): A measurement of position gives a result with probability density $|\psi(x)|^2$. ie. $|\psi(x)|^2 dx$ prob particle is found between x and $x + dx$, or

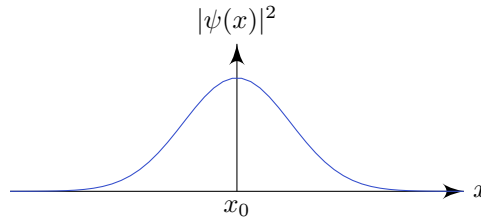
$$\int_a^b |\psi(x)|^2 dx$$

is the probability the particle is found in the interval $a \leq x \leq b$. This requires $\psi(x)$ is *normalised*.

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1 \quad \text{single particle - total probability 1}$$

Example. (Gaussian wavefunction)

$$\psi(x) = C e^{-(x-x_0)^2/2\alpha} \quad \text{real } \alpha > 0$$



$$\begin{aligned} \int_{-\infty}^{\infty} |\psi(x)|^2 dx &= |C|^2 \int_{-\infty}^{\infty} e^{-(x-x_0)^2/\alpha} dx \\ &= |C|^2 (\alpha\pi)^{\frac{1}{2}} = 1 \end{aligned}$$

So⁴ ψ normalised if $C = (\frac{1}{\alpha\pi})^{\frac{1}{4}}$. α small \Rightarrow sharp peak around $x = x_0$, \Rightarrow “particle-like”. α large \Rightarrow more spread out (diffuse)

³non-zero

⁴Recall $\int_{-\infty}^{\infty} e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx = \sqrt{2\pi\sigma^2}$

It is convenient to deal more generally with *normalisable* wavefunctions

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx < \infty \quad \text{finite/convergent}$$

Then $\psi(x)$ and $\phi(x) = \lambda\psi(x)$ are physically equivalent and represent same state for any $\lambda \neq 0$. Provided ψ normalisable, we can choose λ so that ϕ normalised. But if ψ normalised already, then $\phi(x) = e^{i\alpha}\psi(x)$ (for any real α) gives same probability distribution.

$$|\phi(x)|^2 = |\psi(x)|^2$$

So quantum state is strictly an equivalence class of non-zero wave functions but in practice we often refer to $\psi(x)$ as “the state”.

Any non-zero normalisable wave function $\phi(x)$ represents a physical state. For our purposes we can assume, *unless* we say otherwise, $\psi(x)$ is smooth (can be differentiated any number of times), and $\psi(x) \rightarrow 0$ as $|x| \rightarrow \infty$

If $\psi_1(x)$ and $\psi_2(x)$ are normalisable then so is

$$\psi = \lambda_1\psi_1 + \lambda_2\psi_2$$

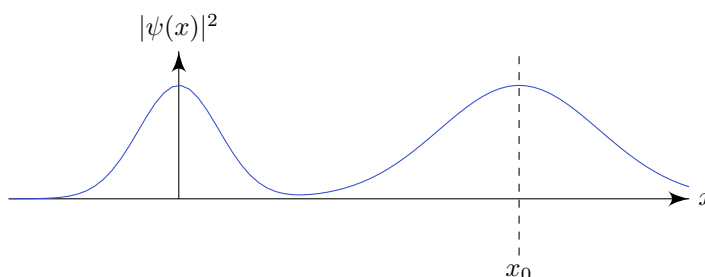
for any complex λ_1, λ_2 .

Physically: principle of super position Mathematically: structure of complex vector space.

Example. (Superposition of Gaussians)

$$\psi(x) = B(e^{\frac{-x^2}{2\alpha}} + e^{-(x-x_0)^2/2\beta})$$

Can choose B so that ψ is normalised



1.2 Operators and Observables

A quantum state contains information about other physical quantities or *observables* (momentum, energy) not just position. In QM each observable is represented by an *operator* (denoted by a hat when necessary) acting on wave functions

position	$\hat{x} = x$	$\hat{x}\psi = x\psi(x)$
momentum	$\hat{p} = -i\hbar \frac{\partial}{\partial x}$	$\hat{p}\psi = -i\hbar\psi'(x)$
energy	$H = \frac{\hat{p}^2}{2m} + V(\hat{x})$	$H\psi = -\hbar^2 \frac{\partial^2}{\partial x^2}\psi + V(x)\psi(x)$

for a particle of mass m in a potential $V(x)$.

If we measure one of these quantities, what answers can we get and what are the probabilities? Partial answers provided by (P2) and (P3)

1.2.1 Expectation Values

For any (normalisable) $\psi(x)$ and $\phi(x)$, define

$$(\psi, \phi) := \int_{-\infty}^{\infty} \psi(x)^* \phi(x) \, dx$$

Note that this is the complex inner product on vector space,

For $\psi(x)$ normalised, define the *expectation value* of an observable Q in this state, to be

$$\begin{aligned} \langle Q \rangle_{\psi} &:= (\psi, Q\psi) \\ &= \int_{-\infty}^{\infty} \psi^*(Q\psi) \, dx \end{aligned}$$

Note

$$\begin{aligned} \langle \hat{x} \rangle &= (\psi, \hat{x}\psi) \\ &= \int_{-\infty}^{\infty} x |\psi(x)|^2 \, dx \end{aligned}$$

standard expression for mean, or expected value of x , given (P1)

Postulate (P2): For any observable, $\langle Q \rangle_{\psi}$ is the mean result (expected value) if Q is measured many times (N times and then $N \rightarrow \infty$) with the particle in state ψ before each measurement.

Consider wave functions:

$$\phi(x) = \psi(x)e^{ikx} \quad \text{with } k \text{ real constant}$$

Clearly

$$|\phi(x)|^2 = |\psi(x)|^2$$

and so

$$\langle \hat{x} \rangle_{\phi} = \langle \hat{x} \rangle_{\psi}$$

But

$$\begin{aligned} \langle \hat{p} \rangle_{\phi} &= \int_{-\infty}^{\infty} \phi^* (-i\hbar \phi') \, dx \\ &= \int_{-\infty}^{\infty} \psi^* (-i\hbar \psi') \, dx + \hbar k \int_{-\infty}^{\infty} \psi^* \psi \, dx \\ &= \langle \hat{p} \rangle_{\psi} + \hbar k \end{aligned}$$

where $\hat{p} = -i\hbar \frac{d}{dx}$

Example.

$$\psi(x) = Ce^{-x^2/2\alpha}$$

as in 1.1 with $x_0 = 0$

$$\Rightarrow \langle \hat{p} \rangle_\psi = 0$$

and

$$\phi(x) = Ce^{-x^2/2\alpha} e^{ikx}$$

$$\Rightarrow \langle \hat{p} \rangle_\psi = \hbar k$$

If we accept (P2) then this result accounts for the choice of momentum operator $\hat{p} = -i\hbar \frac{d}{dx}$

1.2.2 Eigenstates and Eigenvalues

A state ψ ($\neq 0$) is an *eigenstate* or *eigenfunction* of an operator or observable Q with eigenvalue q if

$$Q\psi = q\psi$$

Postulate (P3): If Q is measured when the particle is an eigenstate ψ , as above, then the result is the eigenvalue q with probability 1.

Example. (i) $Q = \hat{x}$ no (continuous) eigenfunctions since

$$\hat{x}\psi(x) = x\psi(x) = q\psi(x) \Rightarrow \psi(x) = 0 \text{ for } x \neq q$$

(ii) $Q = \hat{p} = -i\hbar \frac{d}{dx}$ eigenfunctions obey

$$-i\hbar\psi' = q\psi$$

$$\Rightarrow \psi(x) = Ce^{ikx} \quad \text{with } q = \hbar k$$

But not normalisable since $|\psi(x)|^2 = |C|^2$, so can't interpret this directly as wave function for a single particle on $-\infty < x < \infty$.

Could normalise on interval of length l by choosing $C = \frac{1}{\sqrt{l}}$, but then need to look carefully at boundary conditions on interval

(iii) $Q = H$ Hamiltonian (energy) with particular choice of potential $V(x) = \frac{1}{2}Kx^2$ with $K > 0$.

So

$$H = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}K\hat{x}^2$$

and

$$H\psi = -\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}Kx^2\psi = E\psi$$

This is satisfied for

$$\psi(x) = Ce^{-x^2/2\alpha}$$

if we choose $\alpha^2 = \hbar^2/Km$ and then

$$E = \frac{\hbar}{2}\sqrt{\frac{K}{m}}$$

is energy eigenvalue.

Note classically for fixed E have $|x| \leq (2E/K)^{\frac{1}{2}}$ but wave function above gives non-zero probability density along entire x -axis

In general, the energy eigenvalue equation

$$H\psi = E\psi$$

or

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

for a particle of mass m in potential determines states of definite energy and allowed energy values.

This is the *time-independent Schrödinger Equation*

Solving this for H -atom is our eventual aim.

1.2.3 Comments

- (i) Defined $\langle Q \rangle_\psi = (\psi, Q\psi)$ used in (P2) for ψ normalised: if ψ is not normalised,

$$\langle Q \rangle_\psi = \frac{(\psi, Q\psi)}{\psi, \psi}$$

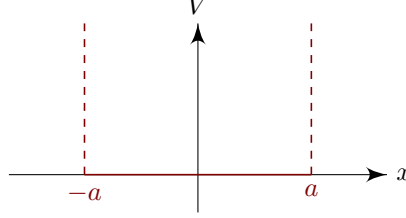
- (ii) Definition for $Q = \hat{x}$ reproduce standard defn of mean. For \hat{p} and H can check explicitly (taking complex conjugates and integrating by parts) that $\langle \hat{p} \rangle_\psi$ and $\langle H \rangle_\psi$ are real
- (iii) (P3) is consistent with (P2) - consider energy, for example.

$$\begin{aligned} H\psi = E\psi &\Rightarrow (\psi, H\psi) = \langle H \rangle_\psi \\ &= (\psi, E\psi) = E \text{ if } \psi \text{ normalised} \end{aligned}$$

ie. measurement of energy gives result E with prob = 1 \Rightarrow mean result is E .

- (iv) From (ii) and (iii) we deduce that any eigenvalue of H is real.

1.3 Infinite Potential Well or Particle in a Box



$$V(x) = \begin{cases} 0 & \text{if } |x| \leq a \\ U & \text{if } |x| > a \end{cases}$$

in the limit $U \rightarrow \infty$.

Time indep SE:

$$\begin{aligned} \frac{-\hbar^2}{2m}\psi'' &= E\psi & |x| \leq a \\ \frac{-\hbar^2}{2m}\psi'' + U\psi &= E\psi & |x| > a \end{aligned}$$

Taking the limit as $U \rightarrow \infty$, 2nd equation suggests we must take $\psi = 0$ for $|x| > a$.

This will be justified shortly. In this case the appropriate boundary conditions are $\psi = 0$ for $|x| > a$ and ψ continuous at $x = \pm a$. So we are left to solve

$$-\frac{\hbar^2}{2m}\psi'' = E\psi \quad \text{on } -a \leq x \leq a \text{ with } \psi(\pm a) = 0$$

For $E > 0$ set

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{with } k > 0$$

and we get

$$\psi'' + k^2\psi = 0$$

$$\Rightarrow \psi = A \cos kx + B \sin kx$$

and boundary conditions imply $A \cos ka \pm B \sin ka = 0$ ie. $A \cos ka = B \sin ka = 0$. Since $\sin ka$ and $\cos ka$ cannot both be zero simultaneously, we have:

- (i) $B = 0$ and $ka = n\pi/2$ for $n = 1, 3, \dots$ or
- (ii) $A = 0$ and $ka = n\pi/2$ for $n = 2, 4, \dots$

Hence

$$E_n = \frac{\hbar^2 \pi^2}{8ma^2} n^2 \quad \text{for } n = 1, 2, 3, 4, \dots$$

discrete set of allowed energies, with normalised wave functions

$$\psi_n(x) = \left(\frac{1}{a}\right)^{\frac{1}{2}} \begin{cases} \cos \frac{n\pi x}{2a} & n \text{ odd} \\ \sin \frac{n\pi x}{2a} & n \text{ even} \end{cases}.$$