

# Quantum Mechanics

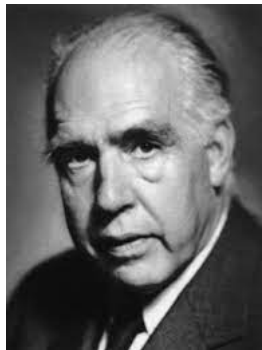
David Tew

University of Oxford

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“Anyone who is not shocked by quantum mechanics has not understood it”

– Niels Bohr



# Quantum Mechanics is a probabilistic theory

**Classical mechanics:** a particle has a definite position  $x$  and a definite momentum  $p$

**Quantum mechanics:** a particle is located at  $x$  with probability  $P_x(x)$  and has momentum  $p$  with probability  $P_p(p)$

We are used to thinking about particles on trajectories, experiencing forces. Now we have to think about how a probability distribution evolves with time. Moreover, the equations of quantum mechanics that govern the motion lead to unfamiliar phenomena such as *tunneling*, wave-like *interference* and *entanglement*.



Change in paradigm

# The language of probability

An experimental outcome  $x$  is observed with probability  $P(x)$ .  
 $P(x)$  is the *probability distribution*.

	Discrete	Continuous
Normalisation	$1 = \sum_i P_i$	$1 = \int P(x) dx$
Mean average	$\langle x \rangle = \sum_i x_i P_i$	$\langle x \rangle = \int x P(x) dx$
Variance	$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2$	
RMS deviation	$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$	

Special language is used for statistical measures arising from the probability distributions in quantum mechanics

Mean	$\longleftrightarrow$	Expectation value	$\langle x \rangle$
RMSD	$\longleftrightarrow$	Uncertainty	$\Delta x$

# The state of a system

For clarity, let's focus on the simple example of a single particle.

Classically, the *state* of a system is the position of the particle  $\mathbf{x}$  and its momentum  $\mathbf{p}$  – from this we can compute any property of interest.

e.g. the energy

$$E(\mathbf{x}, \mathbf{p}) = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x})$$

A *quantum* particle has

- a distribution of positions  $P_x(\mathbf{x})$ ,
- an associated distribution of momenta  $P_p(\mathbf{p})$ , and therefore
- an associated distribution of energies  $P_E(E)$ .

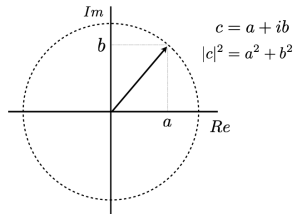
The properties of the system are computed from these probability distributions.

# The quantum state

Although the probability distributions are experimentally observable, the central objects in quantum mechanics are *probability amplitudes*:

- A complex number  $c$ , whose square modulus is a probability

$$P = |c|^2 = c^*c.$$



Notation:

$|\mathbf{x}\rangle$  is a state with definite position.  $|\mathbf{p}\rangle$  is a state with definite momentum

The quantum state  $|\Psi\rangle$  is a *linear superposition* states of definite position  
It is also a linear superposition of states of definite momentum

$$|\Psi\rangle = \sum_i |\mathbf{x}_i\rangle c_i^x = \sum_i |\mathbf{p}_i\rangle c_i^p$$

# The wavefunction

Probability amplitudes for position are particularly important in QM.

- We need to account for position being continuous, not discrete.
- The *coefficient*  $c_i^x$  becomes a *function* of  $\mathbf{x}$ : the *wavefunction*  $\Psi(\mathbf{x})$ .

$$\sum_i |\mathbf{x}_i\rangle c_i^x \longrightarrow \int |\mathbf{x}\rangle \Psi(\mathbf{x}) dV$$

The probability that the particle is within  $dV$  of position  $\mathbf{x}$  is  $|\Psi(\mathbf{x})|^2 dV$ .

For  $|\Psi(\mathbf{x})|^2$  to be a valid probability distribution, the wavefunction must be

- continuous
- single valued
- normalisable



While Erwin Schrödinger formulated the wave equation, Max Born interpreted the wavefunction as a probability amplitude, a mathematical device from which physically observable probabilities can be derived.



## Normalisation

The inner product of a function  $f(\mathbf{x})$  is

$$\langle f|f \rangle = \int f(\mathbf{x})^* f(\mathbf{x}) dV \equiv \int |f(\mathbf{x})|^2 dV = N^2$$

This is the continuous analogue of the inner product a vector  $\mathbf{c}^* \cdot \mathbf{c}$   
 $N$  is the *norm* of the function. A wavefunction is *normalised* if

$$\langle \Psi|\Psi \rangle = \int |\Psi(\mathbf{x})|^2 dV = 1$$

If  $f(\mathbf{x})$  is single valued and continuous, but not normalised, the normalised wavefunction is

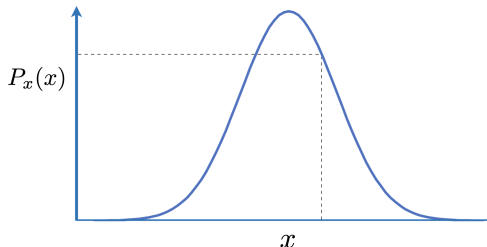
$$\Psi(\mathbf{x}) = \frac{1}{N} f(\mathbf{x})$$

# Measurement



The outcomes of measurements are probabilistic.

- If we measure the position of the particle, we will observe *one* of the allowed values of  $\mathbf{x}$  with probability  $P_{\mathbf{x}}(\mathbf{x}) = |\Psi(\mathbf{x})|^2$



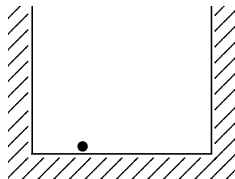
$$|\Psi\rangle = \int |\mathbf{x}\rangle \Psi(\mathbf{x}) dV$$

The average of many independent measurements is  $\langle x \rangle = \int \mathbf{x} |\Psi(\mathbf{x})|^2 dV$

## Example: particle in a box

Let's imagine a particle of mass  $m$  inside a large container and let's imagine that it has definite energy  $E$ , but is an equal superposition of definite momentum states  $|+p\rangle$  and  $|-p\rangle$ , with  $E = p^2/2m$

$$|\psi\rangle = |E\rangle = \frac{1}{\sqrt{2}}|+p\rangle + \frac{1}{\sqrt{2}}|-p\rangle$$

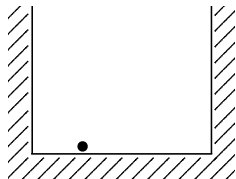


What are the expectation values  $\langle E \rangle$  and  $\langle p \rangle$ ?  
What are the uncertainties  $\Delta E$  and  $\Delta p$ ?

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$$|\Psi\rangle = |E\rangle = \frac{1}{\sqrt{2}}|+p\rangle + \frac{1}{\sqrt{2}}|-p\rangle$$



What are the expectation values  $\langle E \rangle$  and  $\langle p \rangle$ ?  
What are the uncertainties  $\Delta E$  and  $\Delta p$ ?

$$\langle E \rangle = E \qquad \Delta E = 0$$

$$\langle p \rangle = 0 \qquad \Delta p = p$$

# Dirac notation

Paul Dirac introduced compact bra-ket notation for QM

“bra”  $\langle \Psi |$       “ket”  $|\Psi\rangle$       where  $\langle \Psi | = (|\Psi\rangle)^\dagger$



Let's see how to use it to compute the norm of a wavefunction

$$\langle \Psi | = c_1^* \langle p_1 | + c_2^* \langle p_2 | \quad \text{“bra”}$$

$$|\Psi\rangle = |p_1\rangle c_1 + |p_2\rangle c_2 \quad \text{“ket”}$$

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The inner product is

$$\begin{aligned} \langle \Psi | \Psi \rangle &= c_1^* \langle p_1 | p_1 \rangle c_1 + c_1^* \langle p_1 | p_2 \rangle c_2 + c_2^* \langle p_2 | p_1 \rangle c_1 + c_2^* \langle p_2 | p_2 \rangle c_2 \\ &= c_1^* \quad 1 \quad c_1 + c_1^* \quad 0 \quad c_2 + c_2^* \quad 0 \quad c_1 + c_2^* \quad 1 \quad c_2 \\ &= |c_1|^2 + |c_2|^2 \end{aligned}$$

Note: states of definite momentum are orthonormal

$$\langle p_i | p_j \rangle = \delta_{ij}$$

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$$|\Psi\rangle = |p_1\rangle c_1 + |p_2\rangle c_2 \quad \text{“ket”}$$

Dirac notation is often combined with matrix notation

$$\begin{aligned} \langle \Psi | \Psi \rangle &= (c_1^* \quad c_2^*) \begin{pmatrix} \langle p_1 | p_1 \rangle & \langle p_1 | p_2 \rangle \\ \langle p_2 | p_1 \rangle & \langle p_2 | p_2 \rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\ &= (c_1^* \quad c_2^*) \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = (c_1^* \quad c_2^*) \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = |c_1|^2 + |c_2|^2 \end{aligned}$$

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“bra”  $\langle \Psi |$       “ket”  $|\Psi\rangle$       where  $\langle \Psi | = (|\Psi\rangle)^\dagger$



Dirac's notation is equally applicable to the continuous case

$$\langle \Psi | = \int \Psi(\mathbf{x})^* \langle \mathbf{x} | dV \qquad | \Psi \rangle = \int | \mathbf{x} \rangle \Psi(\mathbf{x}) dV$$

The inner product is

$$\begin{aligned} \langle \Psi | \Psi \rangle &= \int \int \Psi(\mathbf{x})^* \langle \mathbf{x} | \mathbf{x}' \rangle \Psi(\mathbf{x}') dV dV' \\ &= \int \int \Psi(\mathbf{x})^* \delta(\mathbf{x} - \mathbf{x}') \Psi(\mathbf{x}') dV dV' = \int \Psi(\mathbf{x})^* \Psi(\mathbf{x}) dV \end{aligned}$$

Note: states of definite position are orthonormal

$$\langle \mathbf{x} | \mathbf{x}' \rangle = \delta(\mathbf{x} - \mathbf{x}')$$

## Summary so far

- Quantum particles are in a linear superposition of allowed positions

$$|\Psi\rangle = \int |\mathbf{x}\rangle \Psi(\mathbf{x}) dV$$

- The wavefunction  $\Psi(\mathbf{x})$  is single valued, continuous and normalised

$$\langle \Psi | \Psi \rangle = \int |\Psi(\mathbf{x})|^2 dV = 1$$

- Measuring position returns one value of  $\mathbf{x}$  with probability  $|\Psi(\mathbf{x})|^2$
- The average of many independent measurements is the expectation value

$$\langle \mathbf{x} \rangle = \int \mathbf{x} P_x(\mathbf{x}) dV = \int \mathbf{x} |\Psi(\mathbf{x})|^2 dV$$

## Physical observables have a quantum operator

We have introduced the idea of states of definite position, energy and momentum and have asserted that the quantum state is a linear superposition of them.

$$|\Psi\rangle = \int |\mathbf{x}_i\rangle \Psi(\mathbf{x}) dV = \sum_i |E_i\rangle c_i^E \quad \text{etc}$$

We need to be explicit about what they are.

Every physical observable  $A$  has an associated operator  $\hat{A}$ . A state with a definite value of  $A = a_i$  is an *eigenfunction* of  $\hat{A}$  with *eigenvalue*  $a_i$

$$\hat{A}|a_i\rangle = a_i|a_i\rangle$$

All operators  $\hat{A}$  in quantum mechanics are *linear* and *hermitian*

# Linearity and Hermiticity

An operator is *linear* if the action of  $\hat{A}$  on a function satisfies two criteria:

$$\hat{A}(f + g) = \hat{A}f + \hat{A}g \quad \text{additivity}$$

$$\hat{A}(cf) = c\hat{A}f \quad \text{multiplicativity}$$

where  $f$  and  $g$  are functions and  $c$  is a constant.

These two conditions can be combined into one

$$\hat{A}(cf + dg) = c\hat{A}f + d\hat{A}g$$

An operator is *hermitian* if

$$\left( \int f(\mathbf{x})^* \hat{A}g(\mathbf{x}) dV \right)^* = \int g(\mathbf{x})^* \hat{A}f(\mathbf{x}) dV$$

## Position

The effect of the position operator on a state of definite position is to multiply it by its value of  $\mathbf{x}$ .

$$\hat{\mathbf{x}}|\mathbf{x}\rangle = \mathbf{x}|\mathbf{x}\rangle \quad \longrightarrow \quad \hat{\mathbf{x}}\Psi(\mathbf{x}) = \mathbf{x}\Psi(\mathbf{x})$$

Aside: the eigenfunctions are Dirac delta functions  $\Psi(\mathbf{x}) = \delta(\mathbf{x})$

$$\begin{aligned}\langle \mathbf{x} \rangle &= \langle \Psi | \hat{\mathbf{x}} | \Psi \rangle = \int \int \Psi(\mathbf{x})^* \langle \mathbf{x} | \hat{\mathbf{x}} | \mathbf{x}' \rangle \Psi(\mathbf{x}') dV dV' \\ &= \int \int \Psi(\mathbf{x})^* \mathbf{x}' \delta(\mathbf{x} - \mathbf{x}') \Psi(\mathbf{x}') dV dV' \\ &= \int \Psi(\mathbf{x})^* \mathbf{x} \Psi(\mathbf{x}) dV \\ &= \int \mathbf{x} P_{\mathbf{x}}(\mathbf{x}) dV\end{aligned}$$

Example: 1-d Gaussian distribution  $\Psi(x) = \pi^{-1/4} \exp(x^2/2)$

# Momentum

The effect of the momentum operator on a state of definite momentum is to multiply it by its value of  $\mathbf{p}$ .

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle$$

Example: the effect of the momentum operator on  $|\Psi\rangle = |p_1\rangle c_1 + |p_2\rangle c_2$

$$\begin{aligned}\hat{\mathbf{p}}|\Psi\rangle &= \hat{\mathbf{p}}|p_1\rangle c_1 + \hat{\mathbf{p}}|p_2\rangle c_2 \\ &= |p_1\rangle p_1 c_1 + |p_2\rangle p_2 c_2\end{aligned}$$

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Taking the inner product with the bra state gives the expectation value

$$\begin{aligned}\langle\Psi|\hat{\mathbf{p}}|\Psi\rangle &= c_1^* \langle p_1|p_1\rangle p_1 c_1 + c_1^* \langle p_1|p_2\rangle p_2 c_2 + c_2^* \langle p_2|p_1\rangle p_1 c_1 + c_2^* \langle p_2|p_2\rangle p_2 c_2 \\ &= p_1 |c_1|^2 + p_2 |c_2|^2 \\ &= \sum_i p_i P_p(p_i)\end{aligned}$$

# Momentum

The effect of the momentum operator on a state of definite momentum is to multiply it by its value of  $\mathbf{p}$ .

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle$$

Example: the expected momentum for  $|\Psi\rangle = |p_1\rangle c_1 + |p_2\rangle c_2$

$$\begin{aligned}\langle\Psi|\hat{p}|\Psi\rangle &= (c_1^* \ c_2^*) \begin{pmatrix} \langle p_1|\hat{p}|p_1\rangle & \langle p_1|\hat{p}|p_2\rangle \\ \langle p_2|\hat{p}|p_1\rangle & \langle p_2|\hat{p}|p_2\rangle \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\ &= (c_1^* \ c_2^*) \begin{pmatrix} p_1 & 0 \\ 0 & p_2 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\ &= p_1|c_1|^2 + p_2|c_2|^2\end{aligned}$$

# Momentum

But what if we only have the wavefunction  $\Psi(\mathbf{x})$  and not  $c_i^p$ ?  
We need the effect of  $\hat{\mathbf{p}}$  on the coordinates.

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle \quad \longrightarrow \quad \hat{\mathbf{p}}\Psi(\mathbf{x}) = -i\hbar\nabla\Psi(\mathbf{x})$$

Aside:

$$\begin{aligned}\langle\Psi|\hat{\mathbf{p}}|\Psi\rangle &= \int\int\Psi(\mathbf{x})^*\langle\mathbf{x}|\hat{\mathbf{p}}|\mathbf{x}'\rangle\Psi(\mathbf{x}')dVdV' \\ &= -i\hbar\int\int\Psi(\mathbf{x})^*\nabla\delta(\mathbf{x}-\mathbf{x}')\Psi(\mathbf{x}')dVdV' \\ &= -i\hbar\int\Psi(\mathbf{x})^*\nabla\Psi(\mathbf{x})dV\end{aligned}$$

Example: 1-d Gaussian distribution  $\Psi(x) = \pi^{-1/4}\exp(x^2/2)$

# States of definite momentum are plane waves

What do states of definite momentum look like in the coordinate representation?

- Solve the 1-d eigenvalue equation  $\hat{p}_x |p_x\rangle = p_x |p_x\rangle$

$$-i\hbar \frac{\partial}{\partial x} \Psi_p(x) = p_x \Psi_p(x)$$

The solution is a plane wave

$$\Psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \exp(i \frac{p_x}{\hbar} x)$$



The wavelength  $\lambda_x$  of the plane wave is the value of  $x$  where  $p_x x / \hbar = 2\pi$ .

Direct connection to the De Broglie relation of wave-particle duality.

$$\lambda = \frac{h}{p}$$

# Heisenberg's uncertainty principle

Can a quantum state have definite values of more than one observable?

Werner Heisenberg's uncertainty principle:

$$\Delta A \Delta B \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle|$$

*Def.* The commutator between  $\hat{A}$  and  $\hat{B}$  is

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

If  $\hat{A}$  and  $\hat{B}$  commute, then it *is* possible for there to be a quantum state that has definite values of  $A$  and  $B$  at the same time.

Examples:  $[\hat{p}_y, \hat{x}]$  and  $[\hat{p}_x, \hat{x}]$



## Summary so far

- Quantum states are linear superpositions  $|\Psi\rangle = \int |\mathbf{x}\rangle \Psi(\mathbf{x}) dV$
- $|\Psi(\mathbf{x})|^2$  is the probability distribution of positions
- States of definite  $\mathbf{x}$  ( $\mathbf{p}$ ) are eigenfunctions of  $\hat{\mathbf{x}}$  ( $\hat{\mathbf{p}}$ )

$$\hat{\mathbf{x}}|\mathbf{x}\rangle = \mathbf{x}|\mathbf{x}\rangle$$

$$\hat{\mathbf{x}}\Psi(\mathbf{x}) = \mathbf{x}\Psi(\mathbf{x})$$

$$\hat{\mathbf{p}}|\mathbf{p}\rangle = \mathbf{p}|\mathbf{p}\rangle$$

$$\hat{\mathbf{p}}\Psi(\mathbf{x}) = -i\hbar\nabla\Psi(\mathbf{x})$$

- States of definite momentum are plane waves
- The expectation value for observable  $A$  is given by the formula

$$\langle\Psi|\hat{A}|\Psi\rangle = \int \Psi(\mathbf{x})^* \hat{A}\Psi(\mathbf{x}) dV$$

- Heisenberg's uncertainty principle  $\Delta A \Delta B \geq \frac{1}{2} |\langle[\hat{A}, \hat{B}]\rangle|$

# Summary of operators

It is useful to summarise some of the fundamental operators in quantum mechanics

scalar

vector

position

$$\hat{x} = x$$

$$\hat{\mathbf{x}} = \mathbf{x}$$

linear momentum

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$\hat{\mathbf{p}} = -i\hbar \nabla$$

angular momentum

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{\mathbf{L}} = -i\hbar(\mathbf{x} \times \nabla)$$

energy

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

# Summary of operators

Composite operators are obtained by combining the fundamental operators as they appear in the classical formula: e.g.

kinetic energy  $\frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2$

harmonic potential  $\frac{1}{2}k\hat{x}^2 = \frac{1}{2}kx^2$

Coulomb potential  $\frac{Z_1Z_2e^2}{4\pi\epsilon_0|\hat{\mathbf{x}}_1 - \hat{\mathbf{x}}_2|} = \frac{Z_1Z_2e^2}{4\pi\epsilon_0|\mathbf{x}_1 - \mathbf{x}_2|}$

# The energy operator

The momentum operator generates translations in space. The energy operator generates translation in time, evolving the state forwards in time

$$\hat{E} = i\hbar \frac{\partial}{\partial t}$$

States of definite energy are eigenstates of the energy operator

$$\hat{E}|E_i\rangle = E_i|E_i\rangle$$

The quantum state is a linear superposition of energy states, with probability amplitudes  $c_i^E$ , and probabilities  $|c_i^E|^2$

$$|\Psi\rangle = \sum_i |E_i\rangle c_i^E \quad \langle E\rangle = \langle\Psi|\hat{E}|\Psi\rangle = \sum_i E_i |c_i^E|^2$$

# The Hamiltonian operator

The total energy is also equal to the kinetic energy plus the potential energy. This is called the *Hamiltonian*

Hamiltonian operator  $\hat{H} = \hat{T} + \hat{V}$

Kinetic energy  $\hat{T} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m} \nabla^2$

Potential energy depends on the interaction of the particle with its environment. e.g. an electron is attracted to a nucleus

$$\hat{V}(\mathbf{x}) = -\frac{Ze^2}{4\pi\epsilon_0|\mathbf{x} - \mathbf{R}|}$$

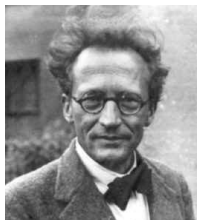
e.g. a particle in a harmonic energy well

$$\hat{V}(x) = \frac{1}{2}k(x - x_e)^2$$

# The Schrödinger equation

We now have two energy operators:  $\hat{E}$  and  $\hat{H}$ . Schrödinger's equation is nothing more than the statement that they are equivalent.

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$$



In terms of the wavefunction, Schrödinger's equation is

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t) = \hat{H} \Psi(\mathbf{x}, t)$$

It a formal solution that relates the wavefunction at time  $t = 0$  to the wavefunction at some time  $t$  later

$$\Psi(\mathbf{x}, t) = e^{-i\hat{H}t/\hbar} \Psi(\mathbf{x}, 0)$$

The Hamiltonian determines how the quantum state evolves in time

## Energy eigenfunctions are stationary states

If a quantum state has definite energy  $\hat{H}|E_i\rangle = E_i|E_i\rangle$ , then

$$i\hbar\frac{\partial}{\partial t}\Psi_i(\mathbf{x}, t) = E_i\Psi_i(\mathbf{x}, t)$$

In this case the time dependence of the wavefunction is

$$\Psi_i(\mathbf{x}, t) = e^{-iE_it/\hbar}\Psi_i(\mathbf{x}, 0)$$

- State at time  $t$  is just a phase  $e^{-iE_it/\hbar}$  times state at time  $t = 0$ .

Probability distribution is *independent of time*

$$P_x(\mathbf{x}, t) = |\Psi_i(\mathbf{x}, t)|^2 = |\Psi_i(\mathbf{x}, 0)|^2$$

Energy eigenstates  $|E_i\rangle$  are *stationary states*.

# The time-independent Schrödinger equation

States of definite energy are characteristic of the system and in QM we understand the behaviour of a system by examining energy eigenstates.

The key equation is the time-independent energy eigenvalue equation:

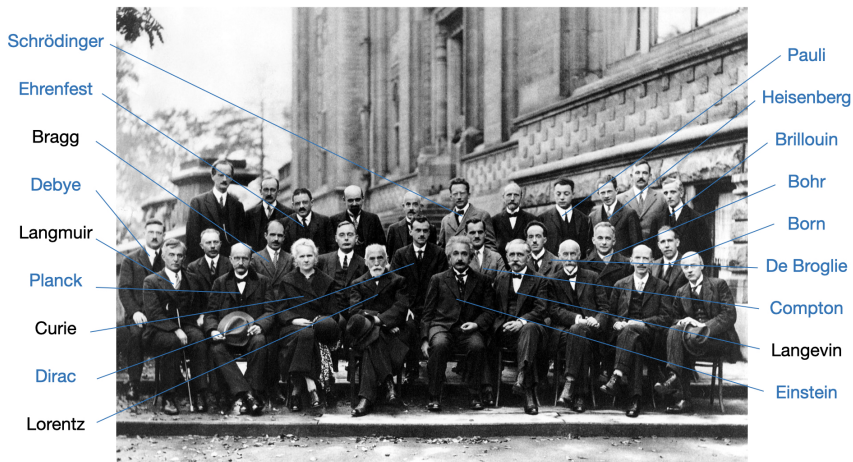
Schrödinger's time-independent wave equation

$$\hat{H}\Psi_i(\mathbf{x}) = E_i\Psi_i(\mathbf{x})$$

Our central goal is to solve this equation, exactly or approximately, of a system of interest.

In this way we can understand the properties of the system, where the particles are and how they are moving, the way the system can absorb or release energy and how it will behave if we perturb it through some interaction.

# The Postulates of Quantum Mechanics



Solvay conference 1927

# The Postulates of Quantum Mechanics

1. The state of a system of  $N$  particles is fully described by a function  $\Psi(\mathbf{r}, t)$  called the *wavefunction*.
2. For every physical observable  $A$  there is an associated operator  $\hat{A}$  that acts on the wavefunction and is both linear and hermitian.
3. The only possible result of the measurement of an observable  $A$  is one of the eigenvalues  $a_i$  of the corresponding operator  $\hat{A}$ .
4. For a state  $|\Psi\rangle = \sum_i c_i |a_i\rangle$ , the probability that a measurement of observable  $A$  returns eigenvalue  $a_i$  is  $|c_i|^2$ .
5. Immediately after the measurement of an observable  $A$  has yielded a value  $a_i$ , the state of the system is the normalized eigenstate  $|a_i\rangle$ .
6. The evolution of  $\Psi(\mathbf{r}, t)$  with time  $t$  is governed by Schrödinger's equation  $i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$ .

# The free particle

System: A particle of mass  $m$  moving in 1-d, free from external forces

Hamiltonian:  $\hat{H} = \hat{T} + \hat{V}$        $\hat{T} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$        $\hat{V} = 0$

Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x) = E \Psi(x)$$

General solution for energy eigenstates

$$\Psi(x) = Ae^{i\sqrt{2mE}x/\hbar} + Be^{-i\sqrt{2mE}x/\hbar}$$

There is an alternative route to the solution that is more instructive

# The free particle

Notice that momentum operator and the Hamiltonian operator commute

$$[\hat{H}, \hat{p}_x] = \frac{\hat{p}_x^2}{2m} \hat{p}_x - \hat{p}_x \frac{\hat{p}_x^2}{2m} = 0$$

- Eigenfunctions of the momentum operator are also eigenfunctions of the Hamiltonian operator with eigenvalues  $E = p_x^2/2m$

$$\hat{p}_x |p_x\rangle = p_x |p_x\rangle \quad \longrightarrow \quad \hat{H} |p_x\rangle = \frac{\hat{p}_x^2}{2m} |p_x\rangle = \frac{p_x^2}{2m} |p_x\rangle$$

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There are two momentum states with the same energy:  $|+p_x\rangle$  and  $|-p_x\rangle$

Any superposition is an eigenfunction of  $\hat{H}$  with eigenvalue  $E = p_x^2/2m$ .

$$\Psi(x) = \frac{c_1}{\sqrt{2\pi\hbar}} e^{ip_x x/\hbar} + \frac{c_2}{\sqrt{2\pi\hbar}} e^{-ip_x x/\hbar}$$

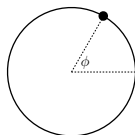
$|+p_x\rangle$  and  $|-p_x\rangle$  interfere to give a sinusoidal probability distribution.

# Particle on a ring

Example of a system with angular momentum

A particle of mass  $m$  that moves around a ring

Angular momentum  $l_z$ , moment of inertia  $I = mr^2$



Hamiltonian

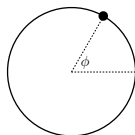
$$\hat{H} = \frac{\hat{l}_z^2}{2I} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$$

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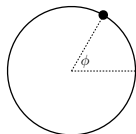
Notice that  $[\hat{H}, \hat{l}_z] = 0 \rightarrow$  look for eigenstates of  $\hat{l}_z$

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Hamiltonian

$$\hat{H} = \frac{\hat{l}_z^2}{2I} = -\frac{\hbar^2}{2I} \frac{\partial^2}{\partial \phi^2}$$

Notice that  $[\hat{H}, \hat{l}_z] = 0 \rightarrow$  look for eigenstates of  $\hat{l}_z$

$$-i\hbar \frac{\partial}{\partial \phi} \Psi_m(\phi) = l_m \Psi_m(\phi)$$

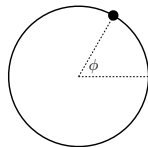
Analogous to eigenstates of linear momentum

$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{il_m \phi / \hbar}$$

# Particle on a ring

$$\hat{l}_z |m\rangle = l_m |m\rangle$$

$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{il_m\phi/\hbar}$$



Wavefunction must be *single valued*

- $l_m = \hbar m \quad m = 0, \pm 1, \pm 2 \dots$

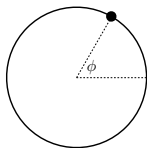
$$\Psi_m(\phi + 2\pi) = \Psi_m(\phi)$$

$$\frac{2\pi l_m}{\hbar} = 2\pi m$$

# Particle on a ring

$$\hat{I}_z|m\rangle = I_m|m\rangle$$

$$\Psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi/\hbar}$$



Wavefunction must be *single valued*

$$\Psi_m(\phi + 2\pi) = \Psi_m(\phi)$$

- $I_m = \hbar m \quad m = 0, \pm 1, \pm 2 \dots$

$$\frac{2\pi I_m}{\hbar} = 2\pi m$$

$|m\rangle$  has definite angular momentum  $\hbar m$  and definite energy  $\frac{m^2 \hbar^2}{2I}$

$m = \pm 2$  Particle has  $\pm 2\hbar$  angular momentum  $E_{\pm 2} = 4\hbar^2/2I$

$m = \pm 1$  Particle has  $\pm \hbar$  angular momentum  $E_{\pm 1} = \hbar^2/2I$

$m = 0$  Particle has no angular momentum  $E_0 = 0$

$$\hat{H}(c_1|+m\rangle + c_2|-m\rangle) = \frac{m^2 \hbar^2}{2I}(c_1|+m\rangle + c_2|-m\rangle)$$

# The Postulates of Quantum Mechanics

1. The state of a system of  $N$  particles is fully described by a function  $\Psi(\mathbf{r}, t)$  called the *wavefunction*.
2. For every physical observable  $A$  there is an associated operator  $\hat{A}$  that acts on the wavefunction and is both linear and hermitian.
3. The only possible result of the measurement of an observable  $A$  is one of the eigenvalues  $a_i$  of the corresponding operator  $\hat{A}$ .
4. For a state  $|\Psi\rangle = \sum_i c_i |a_i\rangle$ , the probability that a measurement of observable  $A$  returns eigenvalue  $a_i$  is  $|c_i|^2$ .
5. Immediately after the measurement of an observable  $A$  has yielded a value  $a_i$ , the state of the system is the normalized eigenstate  $|a_i\rangle$ .
6. The evolution of  $\Psi(\mathbf{r}, t)$  with time  $t$  is governed by Schrödinger's equation  $i\hbar \frac{\partial}{\partial t} |\Psi\rangle = \hat{H} |\Psi\rangle$ .

## Key equations

The quantum state is a linear superposition  $|\Psi\rangle = \int |\mathbf{x}\rangle \Psi(\mathbf{x}) = \sum_i |a_i\rangle c_i^a$

States of definite observable  $A = a_i$  are eigenfunctions  $\hat{A}|a_i\rangle = a_i|a_i\rangle$

The expectation value of  $A$  is  $\langle \Psi | \hat{A} | \Psi \rangle = \int \Psi(\mathbf{x})^* \hat{A} \Psi(\mathbf{x}) dV = \sum_i a_i |c_i^a|^2$

Uncertainty  $\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$ .

States can only have definite values of  $A$  and  $B$  simultaneously if the operators commute  $[\hat{A}, \hat{B}] = 0$ . In general  $\Delta A \Delta B \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle|$ .

The operators for position, momentum and energy are

$$\hat{\mathbf{x}} = \mathbf{x} \quad \hat{\mathbf{p}} = -i\hbar \hat{\nabla} \quad \hat{E} = i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad \hat{E} = \hat{H} = \hat{T} + \hat{V}$$

Schrödinger's wave equation for time evolution of the quantum state

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}, t) = \hat{H} \Psi(\mathbf{x}, t)$$

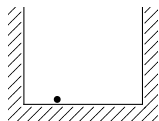
Eigenstates of the Hamiltonian have definite energy and are stationary states.

$$\hat{H} \Psi_i(\mathbf{x}) = E_i \Psi_i(\mathbf{x})$$

## Particle in a 1-d box

A particle of mass  $m$  free to move in a 1-d box

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{else} \end{cases}$$



Outside the box

$$\Psi(x) = 0 \text{ for } x \leq 0, x \geq L$$

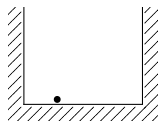
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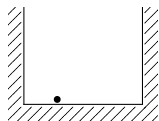
Has solutions

$$\begin{aligned} \Psi(x) &= Ae^{i\sqrt{2mEx}/\hbar} + Be^{-i\sqrt{2mEx}/\hbar} \\ &= (A + B) \cos(\sqrt{2mEx}/\hbar) + i(A - B) \sin(\sqrt{2mEx}/\hbar) \end{aligned}$$

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Continuous  $\Psi(x) \rightarrow A = -B$  and  $\sqrt{2mEL}/\hbar = n\pi \quad n = 1, 2, \dots$

# Particle in a 1-d box

This is an example where energy is *quantised*

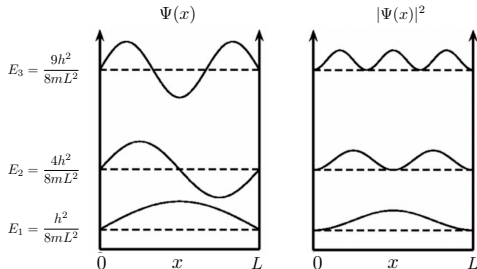
*Def.* Quantisation refers to the instance when the allowed values that a physical observable can take become discrete (quantised), rather than continuous.

Solutions:

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

$$E_n = \frac{n^2 h^2}{8mL^2}$$

$$n = 1, 2, \dots$$



Ground state  $\Psi_1(x)$  has non-zero energy  $E_1 = \frac{h^2}{8mL^2}$ : *zero point energy*

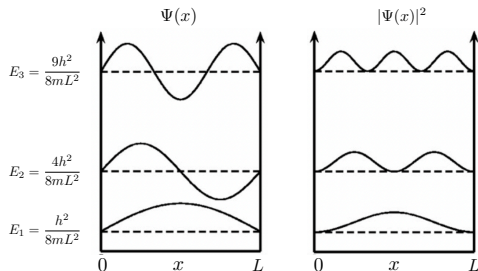
# Particle in a 1-d box

Energy eigenstates:

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$$E_n = \frac{n^2 h^2}{8mL^2}$$

$$n = 1, 2, \dots$$



Questions:

- What is  $\langle n | \hat{x} | n \rangle$ ?
- What is  $\langle n | \hat{p} | n \rangle$ ?
- What is  $\Delta x \Delta p$  for  $n = 1$ ?

## Free particle in 3-d

Let's consider a particle of mass  $m$  free to move in 3-d

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z) = E \Psi(x, y, z)$$

Since there is no coupling between  $x, y, z$ , the equation *factorises*

$$\left( \hat{T}_x + \hat{T}_y + \hat{T}_z \right) \Psi_x(x) \Psi_y(y) \Psi_z(z) = \left( E_x + E_y + E_z \right) \Psi_x(x) \Psi_y(y) \Psi_z(z)$$

Each of  $\Psi_x(x), \Psi_y(y), \Psi_z(z)$  obey a 1-d equation  $\hat{T}_x \Psi_x(x) = E_x \Psi_x(x)$

$$\Psi_x(x) = \frac{c_1}{\sqrt{2\pi\hbar}} e^{ip_x x/\hbar} + \frac{c_1}{\sqrt{2\pi\hbar}} e^{-ip_x x/\hbar}, \quad E_x = \frac{p_x^2}{2m}$$

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We can write a solution in terms of  $\mathbf{x} = (x, y, z)$  and  $\mathbf{p} = (p_x, p_y, p_z)$

$$\Psi(\mathbf{x}) = \left( \frac{1}{2\pi\hbar} \right)^{3/2} e^{i\mathbf{p}\cdot\mathbf{x}/\hbar} \quad E = \frac{\mathbf{p}^2}{2m}$$

## Particle in a 2-d box

The Hamiltonian for a particle in a 2-d box *factorises*. This is because the potential for the box is separable  $V(x, y) = V(x) + V(y)$

$$V(x) = \begin{cases} 0 & 0 < x < L \\ \infty & \text{else} \end{cases} \quad V(y) = \begin{cases} 0 & 0 < y < L \\ \infty & \text{else} \end{cases}$$

So we have

$$\left(\hat{H}_x + \hat{H}_y\right)\psi_n(x)\psi_m(y) = \left(E_n + E_m\right)\psi_n(x)\psi_m(y)$$

The solutions are quantised with quantum number  $n$  in  $x$  and  $m$  in  $y$

$$\hat{H}|nm\rangle = E_{nm}|nm\rangle ; \quad |nm\rangle = \frac{2}{L} \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi y}{L}\right)$$
$$n, m = 1, 2, \dots \quad E_{nm} = \frac{(n^2 + m^2)h^2}{8mL^2}$$

The zero point energy is the sum of the  $x$  and  $y$  contributions  $E_{11} = \frac{2h^2}{8mL^2}$

## Two particles in a 1-d box

The state of the system  $|\Psi\rangle$  is described by *joint* probability distributions  $P_x(x_1, x_2)$ ,  $P_p(p_1, p_2)$ .

The wavefunction is the probability amplitude

$$|\Psi\rangle = \iint |x_1\rangle |x_2\rangle \Psi(x_1, x_2) dx_1 dx_2$$

Where  $|\Psi(x_1, x_2)|^2 dx_1 dx_2$  is the probability of finding particle 1 within  $x_1$  and  $x_1 + dx_1$  at the *same time* as particle 2 within  $x_2$  and  $x_2 + dx_2$

The total energy operator is  $\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{V}_1 + \hat{V}_2 + \hat{V}_{12}$

- Kinetic energy of each particle  $T_1 + T_2$
- Potential energy of each particle due to any external forces  $V_1 + V_2$
- Potential energy of interaction  $V_{12}$

## Two non-interacting particles in a 1-d box

If there is no interaction, then the Hamiltonian for 2 particles in box *factorises* in a similar way to the 1 particle in a 2-d box example

$$\left(\hat{H}_1 + \hat{H}_2\right)\psi_{n_1}(x_1)\psi_{n_2}(x_2) = \left(E_{n_1} + E_{n_2}\right)\psi_{n_1}(x_1)\psi_{n_2}(x_2)$$

The solutions are quantised with quantum number  $n_1$  in  $x_1$  and  $n_2$  in  $x_2$

$$\hat{H}|n_1 n_2\rangle = E_{n_1 n_2}|n_1 n_2\rangle ; \quad |n_1 n_2\rangle = \frac{2}{L} \sin\left(\frac{n_1 \pi x_1}{L}\right) \sin\left(\frac{n_2 \pi x_2}{L}\right)$$
$$n_1, n_2 = 1, 2, \dots \quad E_{n_1 n_2} = \frac{(n_1^2 + n_2^2)h^2}{8mL^2}$$

The zero point energy is the sum of the  $x_1$  and  $x_2$  contributions

$$E_{11} = \frac{2h^2}{8mL^2}$$

## Constants of motion

A quantum state evolves forwards in time according to

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$$

A general state  $|\Psi(t)\rangle$  is not an energy eigenstate, so the probability distributions are time dependent. What is the time dependence of  $\langle A \rangle$ ?

$$\frac{d}{dt} \langle A \rangle = \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle$$

If  $[\hat{H}, \hat{A}] = 0$  then  $A$  is a **constant of the motion**

$$\begin{aligned} \frac{d}{dt} \langle \Psi | \hat{A} | \Psi \rangle &= \left\langle \frac{\partial \Psi}{\partial t} | \hat{A} | \Psi \right\rangle + \langle \Psi | \hat{A} | \frac{\partial \Psi}{\partial t} \rangle \\ &= \frac{i}{\hbar} \langle \Psi | \hat{H} \hat{A} | \Psi \rangle - \frac{i}{\hbar} \langle \Psi | \hat{A} \hat{H} | \Psi \rangle \\ &= \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle \end{aligned}$$