

# Quantum Physics

- The photoelectric effect reveals the quantum nature of light:
  - ↳ the wave theory predicts that the energy of electrons depends on light intensity
  - ↳ but ↑ intensity actually resulted in more electrons with the same energy. Energy only depended on freq.
  - ↳ the EM field is quantised into **photons** with  $E = h\nu$
- A black body can be modelled as a cavity which supports a number of modes per unit volume. The energy density is given by the **Rayleigh-Jeans Law**:
 
$$\rho(\lambda, T) d\lambda = \frac{8\pi}{\lambda^4} k_B T d\lambda$$
  - ↳  $\rho(\lambda, T) \rightarrow \infty$  as  $\lambda \rightarrow 0$ . This erroneous prediction is the **ultraviolet catastrophe**
  - ↳ Planck solved this by quantising the energy modes
- Classically, accelerating charges radiate energy, so electrons should spiral into the nucleus.
  - ↳ Bohr proposed that the orbit's circumference must be an integer number of de Broglie wavelengths:  $2\pi r_n = n\lambda$
  - ↳ hence the angular momentum is quantised:  $L = n\hbar$
  - ↳ orbits have specific energies  $\propto \frac{1}{n^2}$ , explaining spectra.
- Electrons fired at a nickel crystal were shown to diffract
  - ↳ angles agree with the **de Broglie hypothesis**, i.e.  $p = \hbar k$

# Wavefunctions

- A **matter wave** is described by  $\Psi(\underline{r}, t) = A \exp\left[\frac{i}{\hbar}(p \cdot \underline{r} - Et)\right]$ 
  - ↳ the probability density of a particle existing somewhere when observed is  $P(x, t) = |\Psi(x, t)|^2$
  - ↳ the wavefunction evolves deterministically until observation
  - ↳ the wavevector and freq must be known, i.e. linear momentum and energy must be known (position unknown).
  - ↳  $\Psi$  is intrinsically complex.
- For a nonrelativistic particle,  $E = p^2/2m \Rightarrow \omega = \frac{\hbar}{2m} k^2$ 
  - ↳ i.e. quantum waves are dispersive
  - ↳  $\omega$  and  $k$  cannot be chosen independently.

## Localisation

- If we have any knowledge of position, then a plane wave is inadequate because it cannot be normalised. We need to **localise** the wavefunction by insisting  $|\Psi(\underline{r}, t)| \rightarrow 0$  as  $|\underline{r}| \rightarrow \pm\infty$ .
  - ↳ the region of localisation may change with time.
- We can construct a localised wavefunction with a weighted linear combination of plane waves with different wavevectors
 
$$\Psi(x, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i(kx - \omega t)} dk$$
  - ↳ if we consider  $t=0$  we can ignore  $\omega$  (a function of  $k$ )

↳ hence  $\psi(x)$  and  $g(k)$  form a Fourier pair:

complex  $\rightarrow g(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) e^{-ikx} dx$

↳  $g(k)$  is the momentum wavefunction and fully describes the state.  $|g(k)|^2$  is the pdf for momentum.

Hence knowledge of position is related to knowledge of momentum.

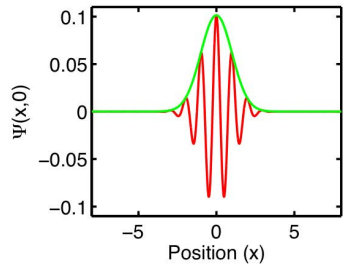
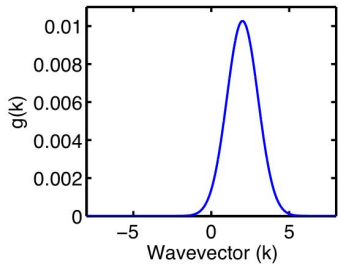
↳ this can be quantified by imposing a Gaussian momentum wavefunction, representing uncertain knowledge of  $p$ :

$$g(k) = \left(\frac{a^2}{\pi}\right)^{1/4} e^{-a^2(k-k_0)^2/2}$$

↳ hence  $\psi(x,0)$  can be found with the inverse FT.

$$\psi(x) = \left(\frac{1}{\pi a^2}\right)^{1/4} e^{ik_0 x} e^{-\frac{x^2}{2a^2}}$$

plane wave modulated by Gaussian



↳ as  $g(k)$  widens (smaller  $a$ ),  $\psi(x)$  narrows.

↳ since  $g(k)$  cannot go to infinity,  $x$  cannot be measured precisely.

This implies the uncertainty principle. For a Gaussian wavepacket it can be shown that  $\Delta x = \frac{a}{\sqrt{2}}$ ,  $\Delta p = \frac{\hbar}{a\sqrt{2}} \Rightarrow \Delta x \Delta p = \frac{\hbar}{2}$

↳ for general wavefunctions,  $\Delta x \Delta p \geq \frac{\hbar}{2}$

↳ the Gaussian wavepacket has minimum uncertainty

↳ in 3D, each dimension has its own uncertainty relation, i.e. orthogonal quantities can be measured precisely.

### Time evolution of wave packets

• for a wavefunction that is highly localised in  $k$  space, we can use a first-order approx to the dispersion relation to understand propagation

↳ let  $k = k_0 + \delta k$

$$\begin{aligned} \Rightarrow \psi(x,t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i(kx - \omega t)} dk \\ &= e^{i(k_0 x - \omega_0 t)} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i[\delta k x - \delta \omega t]} dk \end{aligned}$$

carrier envelope

$$\omega(k) \approx \omega(k_0) + \frac{d\omega}{dk} \Big|_{k_0} \delta k \Rightarrow \delta \omega = v_g \delta k$$

$$\therefore \psi(x,t) = e^{ik_0(x - v_g t)} f(x - v_g t)$$

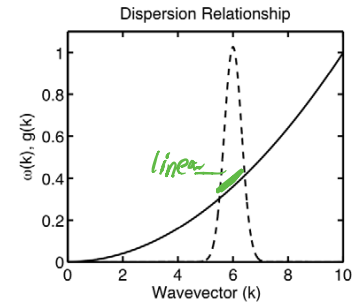
• In reality, the curvature of the dispersion relation over the wavepacket's spectral range may cause the wave to spread out.

• for a Gaussian wavepacket with constant spectral function:

$$g(k) = \left(\frac{a^2}{\pi}\right)^{1/4} e^{-a^2(k-k_0)^2/2}$$

↳ use a quadratic approx to the dispersion relation:

$$\omega(k) \approx \omega_0 + \frac{\hbar k_0}{m} \delta k + \frac{\hbar}{2m} (\delta k)^2$$



$$\Rightarrow |\Psi(x,t)|^2 = \left(\frac{a^2}{4\pi}\right)^{1/2} \underbrace{\frac{1}{(a^4/4 + \hbar^2 t^2/4m^2)^{1/2}}}_{\text{normalised for all time}} \exp\left\{\frac{-(x - \hbar k_0 t/m)^2}{(a^2 + \hbar^2 t^2/m^2 a^2)}\right\} e^{-\frac{(x - \hbar k_0 t/m)^2}{2a^2}}$$

↳ the centre of the packet (at  $x = \hbar k_0 t/m$ ) travels at  $v_g$

↳ the spread of the packet increases with time.

↳ we can alternatively derive the spreading using the uncertainty principle:

$$x(t) = x_0 + vt \quad \therefore (\Delta x)^2 = (\Delta x_0)^2 + (\Delta v t)^2$$

$$\Rightarrow (\Delta x)^2 = (\Delta x_0)^2 + (\hbar t/2m \Delta x_0)^2$$

### Momentum representation

• Rather than using  $g(k)$ , we can write everything more elegantly

in terms of momentum directly

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i(kx - \omega t)} dk$$

$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k,t) e^{ikx} dk$$

$$\therefore \Psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Phi(p,t) e^{ipx/\hbar} dk$$

$$\text{and } \Phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \Psi(x,t) e^{-ipx/\hbar} dx$$

- Thus the momentum repr. is the FT of the position repr.
- This hides the complications arising from the dispersion relation
- Each representation carries complete information about the state.

## Schrödinger's Equation

• For a general wavefunction  $\Psi = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} g(k) e^{i(kx - \omega t)} dk$ , taking partial derivatives results in a wave equation.

• Schrödinger's equation: 
$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x,t) \Psi$$

• This can be interpreted in the context of operators, which correspond to measurements being taken.

↳  $\hat{E} \equiv i\hbar \frac{\partial}{\partial t}$  is the total energy

↳  $\hat{p} \equiv -i\hbar \nabla$  is the momentum operator

↳  $\frac{\hat{p}^2}{2m} \equiv -\frac{\hbar^2}{2m} \nabla^2$  is the KE operator

• The Hamiltonian operator is equal to the total energy

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x,t) \quad \leftarrow \text{we often assume } \hat{H} \text{ is linear and has no time-dependence}$$

• In the time-independent case, we can view the Schrödinger equation as an eigenvalue equation: 
$$\hat{H} \Psi = E \Psi \quad \leftarrow \text{scalar}$$

↳ generally, the eigenvalues of an operator are the possible values that might be returned by an experiment.

### Probability current

- If the probability of a particle existing in one region decreases, it must increase elsewhere.
- This can be modeled as the flux of a probability current  $J$ .

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} \int_V \rho dV &= \int_V \psi^* \hat{H} \psi - (\hat{H} \psi^*) \psi dV \\
 &= -\frac{\hbar^2}{2m} \int_V \nabla \cdot [(\nabla \psi) \psi^* - (\nabla \psi^*) \psi] dV \\
 &= -\frac{\hbar^2}{2m} \oint_S (\nabla \psi) \psi^* - (\nabla \psi^*) \psi dV
 \end{aligned}$$

$$\Rightarrow \frac{\partial}{\partial t} \int_V \rho(x, t) dV = - \oint_S \underline{J}(x, t) \cdot d\underline{x}$$

- Conservation of probability implies  $\frac{\partial \rho}{\partial t} + \nabla \cdot \underline{J} = 0$
- $\underline{J}$  can be written succinctly in terms of  $\hat{p} = -i\hbar \nabla$ :

$$\underline{J}(x, t) = R \left[ \psi^* \frac{\hat{p}}{m} \psi \right]$$

### Unbound particles

- The time-independent Schrödinger equation implies wave behaviour:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = (E - V) \psi \Rightarrow \psi(x, t) = A \exp[i(kx - \omega t)]$$

with  $K = \pm \sqrt{\frac{2m(E - V)}{\hbar^2}}$

- ↳ if  $E > V$ , the solution is a travelling wave with real wavenumber and well-defined momentum
- ↳ if  $E < V$ ,  $K = i\kappa$  and the solution is evanescent, with  $\psi(x, t) = A e^{-\kappa x} e^{-i\omega t} \leftarrow e^{+\kappa x}$  not physical.

- A plane wave requires  $|A|^2 \rightarrow 0$  to normalise, but this is because it assumes an infinite number of particles. Hence we typically analyse either wavepackets or unbound particles in a potential landscape.
- To solve the TISE, we apply appropriate B.C.s:
  - ↳  $\psi$  finite and continuous
  - ↳  $\partial \psi / \partial x$  finite and continuous.
  - ↳ if  $V = \infty$ ,  $\psi = 0$  and  $\partial \psi / \partial x$  may be discontinuous.
- For a plane wave, the probability current is  $J = \frac{\hbar k}{m} |A|^2$

e.g Potential step

- Energy same on both sides so  $\omega$  constant

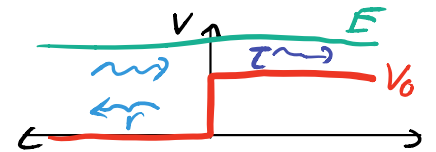
$$r = \frac{k_1 - k_2}{k_1 + k_2}$$

$$\tau = \frac{2k_1}{k_1 + k_2}$$

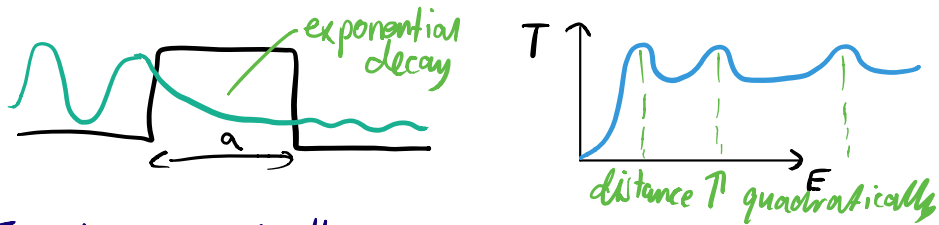
$$J_1^- = |A|^2 \frac{\hbar k_1}{m}$$

$$J_2^- = |At|^2 \frac{\hbar k_2}{m}$$

probability flux



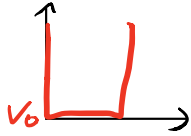
- If  $E < V$  for a potential step, the probability flux is completely reflected (although there is a nonzero chance of finding the particle in the barrier)
- For a barrier of finite width, it is possible for there to be flux on the far side - quantum tunnelling. There are resonances when  $ka = n\pi$ , resulting in perfect transmission.



- Tunneling is what allows  $\alpha$  particles to escape the nucleus during radioactive decay. The rate of escape depends exponentially on the KE of the particle.

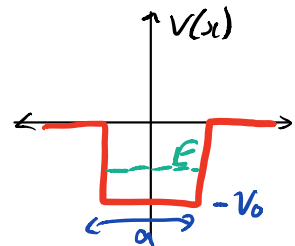
## Bound particles

- When a particle is **bound**, the solutions of Schrödinger's equation form a set discrete states.
- For an infinite square well of depth  $V_0$ , the particle can only exist in bound states.
  - ↳ B.C.s  $\Rightarrow k = \frac{n\pi}{a} \Rightarrow E_n - V_0 = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$
  - ↳  $n$  is the **quantum number**, specifying a state.
  - ↳ the particle cannot be stationary, so there is a **zero point energy** corresponding to  $n=1$
- The wavefunctions are the eigenfunctions of the Hamiltonian:  $\hat{H}\psi = E\psi$ , with eigenvalues  $E$ 
  - ↳ because of the confinement, we have discrete  $E_n, \psi_n$ .
  - ↳ the normalised wavefunctions are orthonormal.



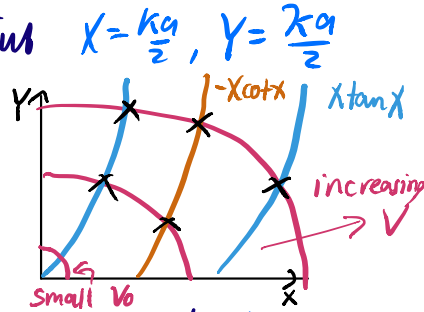
### Finite square well

- For  $E > 0$ , there is a continuous range of unbound solutions
- For  $-V_0 < E < 0$ , bound states exist.
- We fit a solution of the form:
- This gives rise to two classes of solution:



- $$\begin{array}{l}
 e^{\kappa x} \quad \left[ \begin{array}{l} A \sin kx \\ + B \cos kx \end{array} \right] \quad e^{-\kappa x} \\
 \left. \begin{array}{l} 1. \text{ Odd within well } k_1 \cot\left(\frac{k_1 a}{2}\right) = -\kappa \\ 2. \text{ Even within well } k_1 \tan\left(\frac{k_1 a}{2}\right) = \kappa \end{array} \right\} \begin{array}{l} \text{from } \psi, \psi' \\ \text{B.C.} \end{array}
 \end{array}$$

- These must be solved graphically. Sub  $X = \frac{kq}{2}, Y = \frac{\lambda q}{2}$
- ↳  $X^2 + Y^2 = \frac{ma^2}{2\hbar^2} V_0$ , corresponding to a circle on the XY plane
- ↳ plot e.g.  $X \tan X$  for the even solutions and find intersections



- ↳ energies/probabilities then depend on X and Y.
- Characteristics of the solutions can be derived from the graph:
  - ↳ the ground state is even
  - ↳ states alternate between even and odd
  - ↳ always at least one bound state no matter how small  $V_0$  - the minimum-energy bound state is even.

### Quantum Harmonic Oscillators

- Many real potentials can be modelled as locally quadratic.
- Classically, we can write such a potential as  $V(x) = \frac{1}{2} m \omega^2 x^2$
- Using the TISE:  $\frac{\partial^2 \psi}{\partial x^2} + \left[ \frac{2mE}{\hbar^2} - \frac{m^2 \omega^2 x^2}{\hbar^2} \right] \psi = 0$

↳ let  $q = x \sqrt{\frac{m\omega}{\hbar}}, \quad \epsilon = \frac{2E}{\hbar\omega}$   
 ↳ sub  $\chi(q) = \psi(x) = \psi(q \sqrt{\frac{\hbar}{m\omega}})$

∴  $\frac{\partial^2 \chi(q)}{\partial q^2} + (\epsilon - q^2) \chi(q) = 0$

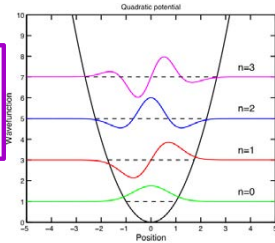
- Far away from the well, as  $|q| \rightarrow \infty$ , we have  $\chi \propto e^{-q^2/2}$
- We can assume a solution of the form  $\chi(q) = H(q) e^{-q^2/2}$

⇒  $\frac{\partial^2 H(q)}{\partial q^2} - 2q \frac{\partial H(q)}{\partial q} + (\epsilon - 1) H(q) = 0$  *Hermite's equation*

↳ the Hermite polynomials can be generated with the Rodrigues formula:  $H_n(q) = (-1)^n e^{q^2} \frac{d^n}{dq^n} (e^{-q^2})$

↳ the energy eigenvalues are then  $E_n = (n + \frac{1}{2}) \hbar \omega$ , with associated eigenfunction

$\psi_n(x) = \frac{1}{[\frac{2^n n! \sqrt{\pi}}{\hbar}]^{1/2}} H_n(x \sqrt{\frac{m\omega}{\hbar}}) e^{-\frac{m\omega}{2\hbar} x^2}$



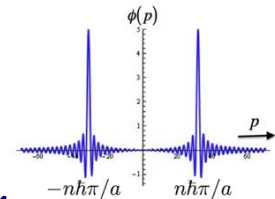
↳ the solutions are orthonormal

### The correspondence principle

- In the limit of large quantum numbers, QM tends to classical mechanics.
- e.g. the infinite square well can be modelled as  $\psi(x) = [e^{inx/a} + e^{-inx/a}] S(x)$  ← top-hat

↳ in momentum space, this is two deltas convolved with sinc (by FT)

↳ as n increases, the sines tend to deltas, i.e. the particle is either moving left or right with a perfectly-specified momentum (classical case)



- The potential energy of a diatomic molecule can be modelled as a harmonic oscillator with a reduced mass  $\mu = \frac{m_1 m_2}{m_1 + m_2}$
- The excitation of a state is governed by the Boltzmann dist:  $P_n \propto e^{-\beta E_n}$ ,  $\beta = \frac{1}{k_B T}$ ,  $E_n = (n + \frac{1}{2}) \hbar \omega$

↳ for the normalised distribution:

$$\langle E \rangle = \frac{\sum_{n=1}^{\infty} (n + \frac{1}{2}) \hbar \omega e^{-(n + \frac{1}{2}) \hbar \omega \beta}}{\sum_{n=1}^{\infty} e^{-(n + \frac{1}{2}) \hbar \omega \beta}}$$

evaluate geometric series

$$\Rightarrow \langle E \rangle = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\hbar \omega \beta} - 1} \leftarrow \text{Planck distribution}$$

- The vibrational heat capacity of  $N$  diatomic molecules is given by  $C_{vib} = N \frac{\partial \langle E \rangle}{\partial T}$ . This tends to the classical limit as  $T \rightarrow \infty$ .

## Operator Algebra

- An element in a vector space can be written as a ket vector  $|a\rangle$ . This can be used to represent e.g. column vector, matrix, function etc.
- For every ket vector there is a unique bra vector  $\langle b|$  which exists in the dual space (for matrices, the bra is the conjugate-transpose of the ket)
- The inner product returns a complex number  $\langle a|b\rangle = c = \langle b|a\rangle^*$ 
  - ↳ vectors are orthogonal if  $\langle a|b\rangle = 0$
  - ↳ the norm of a vector is  $[\langle a|a\rangle]^{1/2}$
  - ↳ in an orthonormal vector space,  $\langle a_n|a_m\rangle = \delta_{nm}$
- Vectors can be written as linear combinations of basis vectors  $|a\rangle = \sum_n a_n |a_n\rangle$ 
  - ↳ functions must be square-integrable to have a series representation of the form  $\psi(x) = \sum_{n=1}^{\infty} a_n \psi_n(x)$
  - ↳ basis functions depend on boundary conditions
  - ↳ for this to be true for any  $|a\rangle$ , the basis set must be complete, i.e.  $\sum_n |a_n\rangle \langle a_n| = \hat{I}$
  - ↳ to find the coefficients, we exploit orthonormality. e.g. the  $m^{\text{th}}$  coefficient is given by  $a_m = \langle \psi_m | \psi \rangle$
  - ↳ this is equivalent to projecting  $|\psi\rangle$  onto a basis vector.

• For a continuous vector space,  $\psi(x) = \int_{-\infty}^{\infty} \underbrace{\phi(k)}_{\text{weighting}} \underbrace{\chi(k,x)}_{\text{basis functions}} dk$   
 ↳ needed for unbound particles  
 ↳ the orthogonality condition is  $\int_{-\infty}^{\infty} \chi^*(k_1, x) \chi(k_2, x) dx = \delta(k_2 - k_1)$

↳ the completeness relation  $\int_{-\infty}^{\infty} \chi(k_1, x) \chi^*(k_2, x) dx = \delta(x_1 - x_2)$ .

↳ this is satisfied for  $\chi(k, x) = \frac{1}{\sqrt{2\pi}} e^{ikx}$ , giving the Fourier Transform

• Operators map between two vectors:  $|\phi\rangle = \hat{A}|\psi\rangle$   
 ↳ the outer product of two vectors  $|b\rangle\langle a|$  is an operator.

↳ operators are distributive:  $(\hat{A} + \hat{B})|a\rangle = \hat{A}|a\rangle + \hat{B}|a\rangle$

• The commutator of two operators describes the degree to which two operators commute:  $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$

• An operator may be represented in a given basis:

$$\hat{A}|a\rangle = \hat{I}\hat{A}\hat{I}|a\rangle = \sum_n \sum_m \underbrace{|u_n\rangle\langle u_n|}_{\hat{I}} \hat{A} \underbrace{|u_m\rangle\langle u_m|}_{\hat{I}} |a\rangle$$

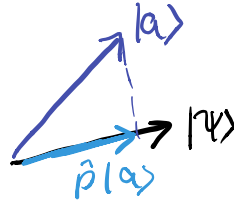
↳  $\langle u_n | \hat{A} | u_m \rangle$  is just a complex number, which we write as  $A_{nm}$ . These are the matrix elements of  $\hat{A}$ .

$$\Rightarrow \hat{A} \equiv \sum_n \sum_m A_{nm} |u_n\rangle\langle u_m|$$

↳ i.e. project  $|a\rangle$  onto basis  $\{|u_m\rangle\}$ , operate on the projection, then reconstruct.

↳ for square-integrable functions,  $A_{nm} = \int \psi_n^* \hat{A} \psi_m dx$

• Any operator of the form  $\hat{p} = |\psi\rangle\langle\psi|$  is a projection operator, projecting the operand onto the vector  $|\psi\rangle$ .



• An operator  $\hat{A}$  maps kets to kets. The corresponding operator in dual space (i.e. mapping the bras) is the adjoint of  $\hat{A}$ ,  $\hat{A}^\dagger$

↳ defined by  $\langle u_m | \hat{A} | u_n \rangle = \langle u_n | \hat{A}^\dagger | u_m \rangle^*$   $\forall n, m$   
 ↳ the matrix elements can be found with the conjugate transpose.

↳ for an operation  $\hat{A}|\psi\rangle = |\phi\rangle$ , the dual is  $\langle\psi| \hat{A}^\dagger = \langle\phi|$   
 ↳ to compose adjoints,  $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$   
 ↳ every linear operator has a unique adjoint

### Hermitian operators

• A self-adjoint (Hermitian) operator satisfies  $\hat{A}^\dagger = \hat{A}$ .  
 • The act of measuring a physical quantity in QM is represented by a Hermitian operator.

↳ hence the expected values are real

$$\langle A \rangle \equiv \langle\psi| \hat{A} |\psi\rangle = \langle\psi| \hat{A}^\dagger |\psi\rangle^* = \langle A \rangle^*$$

↳ Observable  $\Leftrightarrow$  Hermitian

• It is easy to show  $\hat{p}$  is Hermitian with I.P. so  $\hat{p}^2$  is also Hermitian and real  $V(x) \Rightarrow \hat{A}$  is Hermitian.



- For a composite operator  $\hat{A}\hat{B}$  to be Hermitian,  $\hat{A}$  and  $\hat{B}$  must be Hermitian and commute.
  - ↳ if they do not commute, we can use the **anti-commutator** to construct an operator that commutes
 
$$\{\hat{A}\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$$
  - ↳  $\hat{C} = \{\hat{A}\hat{B}\}$  is then Hermitian if  $\hat{A}$  and  $\hat{B}$  are.
- The commutator is not an observable, but can be made so by multiplying with  $i$ .

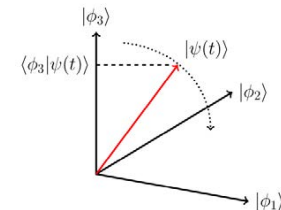
### Eigenstates

- The eigenvector relationship is  $\hat{A}|a_n\rangle = a_n|a_n\rangle$ 
  - $a_n$ : eigenvalue
  - $|a_n\rangle$ : eigenvector
  - a.k.a. eigenstate
- Eigenvectors form a complete orthogonal basis set. If we represent an operator in the eigenbasis, it is in its **diagonal form**:  $\hat{A} = \sum_m a_m |a_m\rangle \langle a_m|$
- Hermitian operators have real eigenvalues.
  - ↳ consider two eigenvectors  $|a_m\rangle, |a_n\rangle$ .
 
$$\langle a_m | \hat{A} | a_n \rangle = \langle a_n | \hat{A}^\dagger | a_m \rangle^*$$
  - ⇒  $a_n \langle a_m | a_n \rangle = a_m^* \langle a_m | a_n \rangle \therefore (a_m - a_n^*) \langle a_m | a_n \rangle = 0$ 
    - ↳ if  $n=m$ , we must have  $a_n = a_n^*$
    - ↳ otherwise,  $\langle a_m | a_n \rangle = 0$ , so eigenvectors corresponding to distinct eigenvalues are orthogonal.
- It can be shown that the eigenvectors form a complete set, i.e.  $|\psi\rangle = \sum_n c_n |a_n\rangle$

- Eigenvectors with the same eigenvalue correspond to **degenerate states**. Any linear combination of degenerate states is also an eigenstate.
- The expected value of an operator on an eigenstate is just the eigenvalue.
- Once an observable is measured, the wavefunction collapses (randomly) to one of the eigenfunctions of the observable. Hence a second measurement is certain.
- For a general state  $|\psi\rangle$ , the expected value of  $\hat{A}$  is
 
$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle = \sum c_n \langle \psi | \hat{A} | a_n \rangle \leftarrow \text{by completeness}$$

$$= \sum c_n a_n \langle \psi | a_n \rangle \leftarrow \text{eigenvector}$$

$$\Rightarrow \langle \hat{A} \rangle = \sum a_n |c_n|^2 \leftarrow \text{Fourier trick}$$
  - ↳ agrees with the special case where  $|\psi\rangle$  is an eigenstate
  - ↳ i.e. probability of collapsing to a certain eigenfunction depends on that eigenfunction's coefficient in the expansion.
  - ↳ this easily extends to continuous basis sets.
- The state vector  $|\psi(t)\rangle$  evolves in time according to Schrödinger's equation. A measurement collapses  $|\psi(t)\rangle$  to the eigenstate of the operator with probability  $|\langle \psi(t) | \phi_n \rangle|^2$ . If a different measurement is made,  $|\psi\rangle$  will collapse to one of that operator's eigenstates.



## Compatibility of observables

If two observables commute, they are **compatible**, i.e. they can both be measured to perfect precision.

↳ let  $\hat{A}, \hat{B}$  be two commuting operators

↳ assume  $\hat{A}$  has distinct eigenvalues

↳  $\hat{A}\hat{B}|a_n\rangle = \hat{B}\hat{A}|a_n\rangle = a_n\hat{B}|a_n\rangle$

$\hat{A}(\hat{B}|a_n\rangle) = a_n(\hat{B}|a_n\rangle) \Rightarrow \hat{B}|a_n\rangle$  is an eigenstate.

↳ but since  $\hat{B}|a_n\rangle$  has the same eigenvalue as  $|a_n\rangle$ ,

we must have  $\hat{B}|a_n\rangle \propto |a_n\rangle = b_n|a_n\rangle$

↳ hence  $|a_n\rangle$  is an eigenstate of both  $\hat{A}$  and  $\hat{B}$ , so each gives a precise measurement regardless of the order.

• Both the energy and momentum of a plane wave  $e^{-ikx}$  can be measured precisely since  $e^{-ikx}$  is an eigenfunction of both  $\hat{p}$  and  $\hat{H}$ , and  $[\hat{H}, \hat{p}] = 0$ .

## Generalised uncertainty

• Any incompatible pair of observables will have an uncertainty relation.

• Define  $\hat{A}_d \equiv \hat{A} - \langle A \rangle \Rightarrow (\Delta A)^2 = \langle A_d^2 \rangle$   
and likewise  $(\Delta B)^2 = \langle B_d^2 \rangle$ .

• For a general state  $|\psi\rangle$ , consider  $|\phi\rangle = (\hat{A}_d + i\lambda\hat{B}_d)|\psi\rangle$

↳ the norm of this vector must be positive

$$\begin{aligned} \langle \phi | \phi \rangle &= \langle \psi | (\hat{A}_d - i\lambda\hat{B}_d)(\hat{A}_d + i\lambda\hat{B}_d) | \psi \rangle \\ &= (\Delta A)^2 + \lambda^2(\Delta B)^2 + \lambda \langle i[\hat{A}_d, \hat{B}_d] \rangle \geq 0 \end{aligned}$$

↳  $i[\hat{A}_d, \hat{B}_d]$  is hermitian so  $\langle i[\hat{A}_d, \hat{B}_d] \rangle$  is real.

↳  $[\hat{A}_d, \hat{B}_d] = [\hat{A}, \hat{B}]$  by expanding

↳ we can find the tightest bound by minimising w.r.t  $\lambda$ ;

$\langle \phi | \phi \rangle_{\min}$  must still be  $> 0$

$$\Rightarrow \Delta A \Delta B \geq \frac{1}{2} |\langle i[\hat{A}, \hat{B}] \rangle| \quad \leftarrow \text{true for any observables.}$$

• The **minimum uncertainty state** for any two operators is when  $\langle \phi | \phi \rangle = 0$ , i.e.  $(\hat{A}_d + i\lambda\hat{B}_d)|\psi\rangle = 0$ .

↳ e.g. for  $\hat{x}$  and  $\hat{p}$ :

$$(\hat{x}_d + i\lambda\hat{p}_d)|\psi\rangle = 0$$

$$\Rightarrow [(x - \langle x \rangle) + i\lambda(-i\hbar \frac{\partial}{\partial x} - \langle p \rangle)] \psi(x) = 0$$

$$\Rightarrow \frac{\partial \psi}{\partial x} = \left[ -\frac{(x - \langle x \rangle)}{\lambda\hbar} + \frac{i\langle p \rangle}{\hbar} \right] \psi(x)$$

↳ solving this differential equation gives the min uncertainty state, in this case the Gaussian wavepacket

$$\psi(x) = e^{-(x - \langle x \rangle)^2 / 2\lambda^2} e^{ipx/\hbar}$$

↳  $\Delta x$  and  $\Delta p$  can be calculated from the standard expressions  $\int_{-\infty}^{\infty} \psi^* x \psi dx$  and  $\int_{-\infty}^{\infty} \psi^* \frac{\hbar}{i} \frac{\partial}{\partial x} \psi dx$ .

## Ladder operators

- The QHO is  $\hat{H} = \frac{1}{2m}\hat{p}^2 + \frac{m\omega^2}{2}\hat{x}^2$ . Introduce the operator  $\hat{a}$  and its Hermitian conjugate  $\hat{a}^\dagger$ :

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \frac{1}{\sqrt{2m\hbar\omega}} \hat{p} \quad \hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \hat{x} - i \frac{1}{\sqrt{2m\hbar\omega}} \hat{p}$$

↳ it can be shown that  $[\hat{a}, \hat{a}^\dagger] = 1$

↳ the Hamiltonian can be expressed in terms of  $\hat{a}$ :

$$\hat{H} = \hbar\omega(\hat{a}^\dagger\hat{a} + \frac{1}{2}) = \hbar\omega(\hat{a}\hat{a}^\dagger - \frac{1}{2})$$

- Consider an eigenstate  $|\phi\rangle$  of  $\hat{H}$  such that  $\hat{H}|\phi\rangle = E|\phi\rangle$   
↳ we can then show that:

$$\begin{aligned} \hat{H}\hat{a}|\phi\rangle &= (E - \hbar\omega)\hat{a}|\phi\rangle \\ \hat{H}\hat{a}^\dagger|\phi\rangle &= (E + \hbar\omega)\hat{a}^\dagger|\phi\rangle \end{aligned}$$

↳  $\hat{a}^\dagger$  is the **creation (raising)** operator because it increases the energy of the system by a quantum.

↳  $\hat{a}$  is the **annihilation (lowering)** operator.

- They both constitute **ladder operators**:

$$\hat{a}^\dagger|\phi_n\rangle = |\phi_{n+1}\rangle \quad \hat{a}|\phi_n\rangle = |\phi_{n-1}\rangle$$

- $\hat{a}^\dagger\hat{a}$  is an observable called the **number operator**  $\hat{N}$ .

$$\hat{H} = \hbar\omega(\hat{N} + \frac{1}{2})$$

↳ it measures the number of quantum excitations (e.g. photons)

↳ i.e. the number of unique times a photon can be removed then replaced.

- The **ground state** is such that  $\hat{a}|\phi_0\rangle = |0\rangle$ , i.e. the lowering sequence must terminate with  $E = \hbar\omega/2$

↳ all states can then be generated:  $|\phi_n\rangle = (\hat{a}^\dagger)^n |\phi_0\rangle$

↳ the associated energies are  $n\hbar\omega + \frac{\hbar\omega}{2}$

- $|\phi_n\rangle$  is an eigenstate of both  $\hat{H}$  and  $\hat{N}$ , with eigenvalues  $E$  and  $n = E/\hbar\omega - \frac{1}{2}$  respectively. Thus one quantity determines the other with zero uncertainty.

$$\therefore \hat{H}|\phi_n\rangle = E_n|\phi_n\rangle \text{ with } E_n = (n + \frac{1}{2})\hbar\omega$$

- We can normalise as follows:

$$\hat{a}|\phi_n\rangle = c_n|\phi_{n-1}\rangle \Rightarrow \langle\phi_n|\hat{a}^\dagger\hat{a}|\phi_n\rangle = |c_n|^2\langle\phi_{n-1}|\phi_{n-1}\rangle$$

↳ so if  $|\phi_{n-1}\rangle$  is normalised,  $c_n = \sqrt{n}$

$$\therefore \hat{a}|\phi_n\rangle = \sqrt{n}|\phi_{n-1}\rangle$$

and likewise  $\hat{a}^\dagger|\phi_n\rangle = \sqrt{n+1}|\phi_{n+1}\rangle$

↳ a general state is thus given as

$$|\phi_n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} |\phi_0\rangle$$

- The different **number states** form an orthogonal complete set, so arbitrary states can be repr. as a LC.

- We can explicitly find the form of the ground state:

$$\hat{a}|\phi_0\rangle = 0 \Rightarrow \left[ \sqrt{\frac{m\omega}{2\hbar}} \hat{x} + i \frac{1}{\sqrt{2m\hbar\omega}} \hat{p} \right] \phi_0(x) = 0$$

$$\Rightarrow \phi_0(x) = \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} e^{-m\omega x^2/2\hbar} \quad \left. \vphantom{\phi_0(x)} \right\} \text{this is a minimum uncertainty state.}$$

↳ higher order states can be generated recursively, giving the Hermite polynomials as before.

- For the number states of the QHO:  $\Delta x \Delta p = (n + \frac{1}{2})\hbar$

## The density operator

• The density operator allows us to describe a classical ensemble of quantum states.

• The expectation of an operator can be written as a trace:

$$\langle A \rangle \equiv \langle \Psi | \hat{A} | \Psi \rangle = \text{Tr}[\langle \Psi | \hat{A} | \Psi \rangle] \leftarrow \text{it is just a number}$$

$$\therefore \langle A \rangle = \text{Tr}[\hat{A} |\Psi\rangle\langle\Psi|] \leftarrow \text{Tr}AB = \text{Tr}BA$$

↳ if  $\hat{A}$  is Hermitian,  $\langle \hat{A} \rangle$  is real so  $\langle \hat{A} \rangle = \text{Tr}[|\Psi\rangle\langle\Psi| \hat{A}]$

• In an ensemble, each member may exist in one of  $M$  states, each with probability  $P_i$ . The classical expectation is

$$\begin{aligned} \langle A \rangle &= \sum_{i=1}^M P_i \langle \Psi_i | \hat{A} | \Psi_i \rangle = \sum_{i=1}^M P_i \text{Tr}[|\Psi_i\rangle\langle\Psi_i| \hat{A}] \\ &= \text{Tr}\left[\sum_{i=1}^M P_i |\Psi_i\rangle\langle\Psi_i| \hat{A}\right] \end{aligned}$$

• This defines the **density operator**

$$\hat{O} \equiv \sum_{i=1}^M P_i |\Psi_i\rangle\langle\Psi_i| \Rightarrow \langle A \rangle = \text{Tr}[\hat{O} \hat{A}]$$

↳  $\hat{O}$  is Hermitian so is an observable

↳ **idempotent** when only one classical state is present, i.e.  $\hat{O}^n = \hat{O}$  for  $\hat{O} = |\Psi_i\rangle\langle\Psi_i|$  **pure state**

↳  $\text{Tr}[\hat{O}] = 1$  is a normalisation condition.

• Quantum states must be added **coherently**, i.e. including the phase.  $|\Psi\rangle = e^{i\phi_1} |\Psi_1\rangle + e^{i\phi_2} |\Psi_2\rangle$ .

• However, for a classical **mixed state**, there is no phase term:  $|\Psi\rangle\langle\Psi| = P_1 |\Psi_1\rangle\langle\Psi_1| + P_2 |\Psi_2\rangle\langle\Psi_2|$ .

## Functions of operators

• The function of an operator is defined to be the power-series of the function, with the variable replaced by the operator:

$$e^{-\hat{X}} = \hat{I} - \hat{X} + \frac{\hat{X}^2}{2} - \frac{\hat{X}^3}{3} + \dots$$

• If the operator  $\hat{X}$  is expressed in diagonal form, powers are just related to scalar powers of the eigenvalues

$$\hat{X} = \sum_i x_i |\Psi_i\rangle\langle\Psi_i| \Rightarrow \hat{X}^n = \sum_i x_i^n |\Psi_i\rangle\langle\Psi_i|$$

$$\Rightarrow \boxed{F(\hat{X}) = \sum_i F(x_i) |\Psi_i\rangle\langle\Psi_i|} \leftarrow \text{must be eigenbasis}$$

↳ i.e.  $F(\hat{X})$  has the same eigenvectors but eigenvalues  $F(x_i)$ , which is obvious since the eigenvalues are measured values.

↳ this analysis applies to an arbitrary state  $|\Phi\rangle$  as long as we are in the eigenbasis.

• In a classical thermodynamic system, energy states are distributed with pdf  $\frac{1}{Z} e^{-E_n/kT}$  where  $Z$  normalises.

↳ the density operator is then:

$$\hat{O} = \frac{1}{Z} \sum e^{-E_n/kT} |\Psi_n\rangle\langle\Psi_n| = \frac{1}{Z} e^{-\hat{H}/kT}, \quad Z = \text{Tr}[e^{-\hat{H}/kT}]$$

↳ where for a QHO,  $\hat{H}|\Phi_n\rangle = E_n|\Phi_n\rangle$ ,  $E_n = (n + \frac{1}{2})\hbar\omega|\Phi_n\rangle$ .

# Time-dependent QM

- The expected energy for a thermal state:  $\leftarrow$  i.e. classical ensemble

$$\begin{aligned} \text{Tr}[\rho \hat{H}] &= \frac{1}{Z} \text{Tr} \left[ \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} e^{-E_n/kT} |\phi_n\rangle \langle \phi_n| E_m |\phi_m\rangle \langle \phi_m| \right] \\ &= \frac{1}{Z} \text{Tr} \left[ \sum_{n=0}^{\infty} E_n e^{-E_n/kT} \right] \end{aligned}$$

$\hookrightarrow$  the normalisation can be explicitly calculated using

$$\frac{1}{Z} \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega/kT} = 1 \Rightarrow \frac{1}{Z} = 2 \sinh\left(\frac{\hbar\omega}{2kT}\right)$$

$$\Rightarrow \langle E \rangle = \hbar\omega \left[ \frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1} \right] \leftarrow \text{agrees with analysis of correspondence principle.}$$

## Commutation relations

- It is easy to show:  $[\hat{x}, \hat{p}^n] = i\hbar n \hat{p}^{n-1} = i\hbar \frac{\partial}{\partial \hat{p}} \hat{p}^n$   
 $[\hat{p}, \hat{x}^n] = -i\hbar n \hat{x}^{n-1} = -i\hbar \frac{\partial}{\partial \hat{x}} \hat{x}^n$
- We can generalise to functions of the operators

$$\begin{aligned} [\hat{x}, F(\hat{p}, \hat{x})] &= i\hbar \frac{\partial F(\hat{p}, \hat{x})}{\partial \hat{p}} \\ [\hat{p}, F(\hat{p}, \hat{x})] &= -i\hbar \frac{\partial F(\hat{p}, \hat{x})}{\partial \hat{x}} \end{aligned} \leftarrow \text{must preserve order.}$$

$\hookrightarrow$  i.e.  $[\hat{A}, F(\hat{A})] = \hat{O}$ ; intuitively obvious

$$\begin{aligned} \text{Useful formula: } [AB, C] &= A[B, C] + [A, C]B \\ [A, BC] &= B[A, C] + [A, B]C \end{aligned}$$

- Time is a parameter in QM - we never integrate to find the probability that an event occurred in some time period.
- A general state can be written as the LC of eigenstates of  $\hat{H}$ :  $|\Psi(t)\rangle = \sum_n c_n(t) |\phi_n\rangle$ . Since the eigenvectors are a complete basis for any  $t$ , the eigenvectors do not change with time.
- The time-dependent Schrödinger equation (TDSE) is  $i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$

$\hookrightarrow$  we then sub. the LC of eigenstates  $\leftarrow$  given by TDSE

$$\Rightarrow i\hbar \sum_n \frac{d c_n(t)}{dt} |\phi_n\rangle = \sum_n c_n(t) \hat{H} |\phi_n\rangle$$

$$\therefore \left[ i\hbar \frac{d c_n(t)}{dt} - c_n(t) E_n \right] = 0 \quad \forall n$$

$\hookrightarrow$  this ODE can be solved for  $c_n(t)$  to give

$$|\Psi(t)\rangle = \sum_n c_n(0) e^{-iE_n t/\hbar} |\phi_n\rangle$$

- $\hookrightarrow$  i.e. time dependence is associated with a superposition of frequency components, whose phase changes over time.
- $\hookrightarrow$  if there is only one freq component,  $|\Psi(t)\rangle$  is a stationary state.
- In the above formula, we have a LC of eigenvectors with weights that are functions of the eigenvalues of  $\hat{H}$ .

This can be rewritten using the definition of a function of an operator

$$|\psi(t)\rangle = e^{i\hat{H}t/\hbar} \sum_n c_n(0) |\phi_n\rangle$$

$$\therefore |\psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\psi(0)\rangle$$

↳ we can thus relate the current state to an earlier state using the **time shift** operator:

$$\hat{U}(t, t_0) = e^{-i\hat{H}(t-t_0)/\hbar} \Rightarrow |\psi(t)\rangle = \hat{U}(t, t_0) |\psi(t_0)\rangle$$

↳  $\hat{U}$  is unitary, so its adjoint equals its inverse.

↳  $\hat{U}$  preserves inner products and therefore normalisations.

↳  $[\hat{U}, \hat{H}] = 0$  so eigenstates of  $\hat{U}$  are energy eigenstates

### Ehrenfest's theorem

It does not make sense to consider the time derivative of an observable, only that of its expectation.

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

↳ in the Schrödinger approach to QM, observables are time-indep.

↳ if  $\hat{A}$  commutes with  $\hat{H}$ ,  $\langle \hat{A} \rangle$  is invariant.

↳ in a stationary state,  $\langle \hat{A} \rangle$  is invariant for any  $\hat{A}$ .

• However, Ehrenfest's theorem is not useful for actually calculating the coefficients.

$$|\psi(t)\rangle = \sum_n c_n(0) e^{-iE_n t/\hbar} |\phi_n\rangle$$

$$\Rightarrow \langle \psi(t) | = \sum_m c_m^*(0) e^{iE_m t/\hbar} \langle \phi_m |$$

$$\therefore \langle \hat{A} \rangle = \sum_m \sum_n c_m^* c_n e^{i(E_m - E_n)t/\hbar} A_{mn} \leftarrow \langle \phi_m | \hat{A} | \phi_n \rangle$$

• Consider a particle moving in a potential:

$$\frac{d\langle \hat{x} \rangle}{dt} = \frac{1}{\hbar} \langle i[\hat{A}, \hat{x}] \rangle, \quad \hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(\hat{x})$$

$$\hookrightarrow [\hat{p}^2, \hat{x}] = -2i\hbar \hat{p}, \quad [\hat{V}(\hat{x}), \hat{x}] = 0$$

$$\Rightarrow \frac{d\langle \hat{x} \rangle}{dt} = \frac{\langle \hat{p} \rangle}{m} \leftarrow \dot{x} = \frac{p}{m} \text{ classically}$$

$$\hookrightarrow \frac{d\langle \hat{p} \rangle}{dt} = \frac{1}{\hbar} \langle i[\hat{H}, \hat{p}] \rangle = \frac{i}{\hbar} \langle [\hat{V}(\hat{x}), \hat{p}] \rangle = - \left\langle \frac{d\hat{V}(\hat{x})}{d\hat{x}} \right\rangle$$

$$\therefore \frac{d\langle \hat{p} \rangle}{dt} = \left\langle F(\hat{x}) \right\rangle \leftarrow \text{ie NI is a consequence of QM}$$

↳  $\langle F(\hat{x}) \rangle \approx F(\langle \hat{x} \rangle)$  only when the QM uncertainties are small compared to the scale of the system

## Time-energy uncertainty

- The time-energy uncertainty principle is fundamentally of different character to  $x$ - $p$  uncertainty.
- From the generalised uncertainty principle,

$$\Delta E \Delta t \geq \frac{1}{2} |\langle i[A, \hat{A}] \rangle| = \frac{\hbar}{2} \left| \frac{d\langle \hat{A} \rangle}{dt} \right| \leftarrow \text{from Ehrenfest}$$

$$\therefore \Delta E \left( \frac{\Delta A}{\left| \frac{d\langle \hat{A} \rangle}{dt} \right|} \right) \geq \frac{\hbar}{2}$$

↳ this quantity can be interpreted as the  $\Delta t$  required for the expectation value to change by an amount equal to the uncertainty  $\Rightarrow \Delta E \Delta t \geq \frac{\hbar}{2}$

↳  $\Delta t$  is not an uncertainty

- For small  $\Delta E$ , it takes the particle a long time to significantly change the value of an observable.
- For a stationary state,  $\Delta t \rightarrow \infty$  so  $\langle \hat{A} \rangle$  is constant.

## Heisenberg's approach

- Thus far we have used the Schrödinger approach, in which state vectors evolve but observables (and eigenstates) don't.
- The Heisenberg approach treats operators as time-dependent

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\psi(0)\rangle$$

$$\Rightarrow \langle A(t) \rangle = \langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi(0) | e^{i\hat{A}t/\hbar} \hat{A} e^{-i\hat{A}t/\hbar} | \psi(0) \rangle$$

- Hence the expectation can be written in terms of the time-dependent operator  $\hat{A}^H(t)$ :

$$\langle A(t) \rangle = \langle \psi(0) | \hat{A}^H(t) | \psi(0) \rangle \quad \hat{A}^H(t) = e^{i\hat{H}t/\hbar} \hat{A} e^{-i\hat{H}t/\hbar}$$

- The Heisenberg equation is the equivalent of the TDSE:

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

# QM in 3D

- For a wavefunction in 3D, we have  $P(\underline{r}) = |\Psi(\underline{r}, t)|^2 d^3\underline{r}$
- Operators become vector operators, e.g.  $\hat{p} = -i\hbar \nabla$ , as do eigenvalues.
- Position and momentum in orthogonal directions commute and can thus be measured precisely.  $[\hat{r}_j, \hat{p}_k] = i\hbar \delta_{jk}$
- Numerical methods are often used to solve the Schrödinger equation in spherical coordinates.

## Orbital angular momentum

$$L = \underline{r} \times \underline{p} = \begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} \Rightarrow \begin{aligned} \hat{L}_x &= \hat{y}\hat{p}_z - \hat{z}\hat{p}_y \\ \hat{L}_y &= \hat{z}\hat{p}_x - \hat{x}\hat{p}_z \\ \hat{L}_z &= \hat{x}\hat{p}_y - \hat{y}\hat{p}_x \end{aligned}$$

no ambiguity since orthogonal components commute.

- The 3D angular momentum operator is observable, i.e.  $\hat{L} = \hat{L}^\dagger$ .
- $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$  (and cyclic perms), so only one component of  $\hat{L}$  can be measured precisely (typically  $z$ ).
- The total angular momentum is  $\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$   
 $\hookrightarrow [\hat{L}^2, \hat{L}_i] = \hat{0}$ , so measuring any component is equivalent to measuring  $\hat{L}^2$   
 $\hookrightarrow$  i.e. only  $L$  and one of  $L_x, L_y, L_z$  can be precisely known.
- The ladder operators for  $\hat{L}_z$  are:

$$\begin{aligned} \hat{L}_+ &= \hat{L}_x + i\hat{L}_y \\ \hat{L}_- &= \hat{L}_x - i\hat{L}_y \end{aligned}$$

$\hookrightarrow$  they are clearly not observable

$\hookrightarrow$  useful commutation relation:

$$[\hat{L}_z, \hat{L}_\pm] = \hbar \hat{L}_\pm \Rightarrow \hat{L}_z \hat{L}_\pm = \hat{L}_\pm \hat{L}_z + \hbar \hat{L}_\pm$$

$\hookrightarrow$  consider an eigenstate  $|\phi_\alpha\rangle$  of  $\hat{L}_z$  with eigenvalue  $\alpha\hbar$ , where  $\alpha$  is a real number. If we apply the ladder then measure  $\hat{L}_z$ :

$$\hat{L}_z \hat{L}_+ |\phi_\alpha\rangle = (\alpha+1)\hbar \hat{L}_+ |\phi_\alpha\rangle$$

$$\hat{L}_z \hat{L}_- |\phi_\alpha\rangle = (\alpha-1)\hbar \hat{L}_- |\phi_\alpha\rangle$$

$\hookrightarrow$  hence  $L_z$  is being changed in units of  $\hbar$ , and measurements of  $L_z$  are quantised.

• However,  $\hat{L}_\pm$  does not change the magnitude of the total angular momentum:

$\hookrightarrow |\phi_\alpha\rangle$  is also an eigenstate of  $\hat{L}^2$  since  $\hat{L}^2$  and  $\hat{L}_z$  commute.  $\Rightarrow \hat{L}^2 |\phi_\alpha\rangle = \Lambda \hbar^2 |\phi_\alpha\rangle$

$\hookrightarrow [\hat{L}^2, \hat{L}_\pm] = 0 \Rightarrow \hat{L}^2 \hat{L}_\pm |\phi_\alpha\rangle = \Lambda \hbar^2 \hat{L}_\pm |\phi_\alpha\rangle$ , i.e. the eigenvalue is unchanged even after operating  $\hat{L}_\pm$

$\hookrightarrow$  but we must have  $\langle \hat{L}_z^2 \rangle \leq \langle \hat{L}^2 \rangle$ , so  $\alpha^2 \leq \Lambda$ .

$\hookrightarrow$  hence, unlike  $\hat{a}^\dagger$  and  $\hat{a}$ , angular momentum ladders have a max and min.

$\hookrightarrow$  hence  $\alpha$  can take integer values (because of symmetry) indexed by  $m_L = L, L-1, L-2, \dots, 0, \dots, -(L-1), -L$

$\hookrightarrow$  there are  $2L+1$  eigenvalues, including  $L=0$ .



The value of  $L$  depends on  $\alpha$ , which depends on the eigenvalue  $\Lambda \hbar^2$  of the total momentum operator.

↳ the explicit relation is derived by considering the highest eigenstate, such that  $\hat{L}_z |\phi_L\rangle = L\hbar |\phi_L\rangle$

↳ but  $\hat{L}_+ |\phi_L\rangle = 0$  to terminate the sequence

↳ consider  $\hat{L}_- \hat{L}_+ = \hat{L}^2 - \hat{L}_z^2 - \hbar \hat{L}_z$  and operate on the highest eigenstate.  $\Rightarrow 0 = \Lambda \hbar^2 - L^2 \hbar^2 - L\hbar^2$   
 $\Rightarrow \Lambda = L(L+1)$

↳  $L$  is called the **orbital angular momentum quantum number** and relates to the total  $L^2$

↳  $m_l \in L, L-1, \dots, 0, \dots, -L$  is the **azimuthal/magnetic angular momentum quantum number** and relates to a measurement of  $\hat{L}_z$ .

↳ summary:  $\hat{L}^2 |L, m_l\rangle = L(L+1)\hbar^2 |L, m_l\rangle$   
 $\hat{L}_z |L, m_l\rangle = m_l \hbar |L, m_l\rangle$

Normalisation constants can be found:

↳  $\hat{L}_- |L, m_l\rangle = C |L, m_l-1\rangle \rightarrow$  using  $\hat{L}_+^\dagger = \hat{L}_-$

$$\Rightarrow |C|^2 \langle L, m_l-1 | L, m_l-1 \rangle = \langle L, m_l | \hat{L}_+ \hat{L}_- |L, m_l\rangle = \langle L, m_l | \hat{L}^2 + \hbar \hat{L}_z - \hat{L}_z^2 |L, m_l\rangle$$

$$\therefore \hat{L}_\pm |L, m_l\rangle = \hbar \sqrt{L(L+1) - m_l(m_l \pm 1)} |L, m_l \pm 1\rangle$$

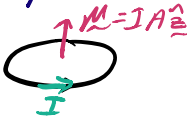
↳ the normalisation goes to zero for  $\hat{L}_\pm$  when  $m_l = \pm L$ , necessary to terminate the sequence.

Because angular momentum is quantised, so is the magnetic dipole moment. For a classical electron orbit:

$$\hookrightarrow \mu_z = IA = \frac{e}{2\pi r/v} \cdot \pi r^2 = \frac{e}{2m_e} L_z$$

$$\hookrightarrow \text{but } \langle \hat{L}_z \rangle = m_l \hbar \Rightarrow \mu_z = -\frac{e\hbar}{2m_e} m_l$$

↳  $\mu_B \equiv \frac{e\hbar}{2m_e}$  is the **Bohr magneton**, revealing that  $\mu_z = -\mu_B m_l$  so  $\mu_z$  is quantised.



### Orbital angular momentum eigenfunctions

The angular momentum operator in spherical coordinates is found by substituting  $\hat{p} = -i\hbar \nabla$  into  $L_x = y p_z - z p_y$  etc.

The ladder operators are then:  $\hat{L}_\pm = \hbar e^{\pm i\phi} \left( \pm \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right)$

Because all the angular momentum operators depend solely on  $\theta$  and  $\phi$ , the eigenfunctions must be angular  $Y_{l,m_l}(\theta, \phi)$   
 $\hat{L}_z Y = m_l \hbar Y \Rightarrow -i\hbar \frac{\partial}{\partial \phi} Y = m_l \hbar Y$   
 $\Rightarrow Y_{l,m_l}(\theta, \phi) = F_{l,m_l}(\theta) e^{im_l \phi}$

↳ since the wavefunction is single-valued,

$$Y_{l,m_l}(\theta, \phi + 2\pi) = Y_{l,m_l}(\theta, \phi) \Rightarrow e^{i2\pi m_l} = 1$$

↳ this explains why  $m_l$  must be integers.

$\hat{L}_+$  acting on the highest eigenstate ( $m_l = l$ ) must give zero  
 $\therefore \hat{L}_+ |l, l\rangle = 0 \Rightarrow \hbar e^{i\phi} \left( \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right) Y_{l,l}(\theta, \phi) = 0$

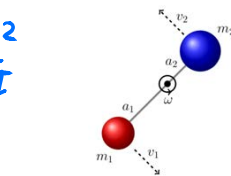
↳ using  $Y_{l,l}(\theta, \phi) = F_{l,l}(\theta) e^{il\phi}$ :  $Y_{l,l}(\theta, \phi) = C (\sin \theta)^l e^{il\phi}$

- $\hat{L}_-$  lowers the eigenstate so we can find  $Y_{l, m_l-1}(\theta, \phi)$   
 $\hat{L}_- Y_{l, m_l}(\theta, \phi) = \hbar e^{-i\phi} \left(-\frac{\partial}{\partial \theta} + \cot \theta \frac{\partial}{\partial \phi}\right) Y_{l, m_l}(\theta, \phi)$   
 $\hookrightarrow$  sub  $Y_{l, m_l-1}(\theta, \phi) = F_{l, m_l-1}(\theta) e^{i(m_l-1)\phi}$   
 $\hookrightarrow$  these eigenfunctions can then be normalised over all angles:  $\int_0^{2\pi} \int_0^\pi |Y_{l, m_l}(\theta, \phi)|^2 \sin \theta d\theta d\phi = 1$
- The orthonormal eigenfunctions that satisfy the relationships are **spherical harmonics**  
 e.g.  $Y_{2, \pm 2} \propto \sin^2 \theta e^{\pm 2i\phi}$  ← find by  $\hat{L}_+ |l, l\rangle = 0$   
 $Y_{2, \pm 1} \propto \sin \theta \cos \theta e^{\pm i\phi}$  ↘ apply lowering operator  
 $Y_{2, 0} \propto 3 \cos^2 \theta - 1$  ↘ operator  
 $\hookrightarrow$  they have useful symmetries, e.g.:  
 $Y_{l, -m_l}(\theta, \phi) = (-1)^{m_l} Y_{l, m_l}(\theta, \phi) = Y_{l, m_l}(\theta, \pi - \phi)$

### Diatomic molecules

- The energy levels depend on angular momentum eigenvalues (but specific dependence differs by system).
- For a rigid diatomic molecule,  $E = \frac{1}{2} I \omega^2 = \frac{L^2}{2I}$
- Hence the energy eigenvalues are:

$$E_l = \frac{l(l+1)\hbar^2}{2I} \quad \text{with degeneracy } 2l+1$$



- The heat capacity of a quantum system is  $\frac{\partial \langle E \rangle}{\partial T}$ . There is thus a rotational contribution to the heat capacity
- $C_{rot} \rightarrow 0$  as  $T \rightarrow 0$  and  $C_{rot} \rightarrow R$  as  $T \rightarrow \infty$

### Orbits with potentials

- The Hamiltonian in spherical coordinates can be written in terms of  $\hat{L}^2$ :

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2mr^2} + \hat{V}(r)$$

- $\hookrightarrow$  the eigenfunctions have the same angular dependence as before, but there is now radial behaviour:  
 $\Psi_{n, l, m_l}(r, \theta, \phi) = R_{n, l}(r) Y_{l, m_l}(\theta, \phi)$   
 $\hookrightarrow$  the radial eigenfunctions  $R_{n, l}(r)$  depend on  $n$ , the **principal quantum number**.  
 $\hookrightarrow$  states with the same  $n, l$  but different  $m_l$  are energy-degenerate.
- $\hat{H} \Psi_{n, l, m_l} = E_{n, l} \Psi_{n, l, m_l}$ . After operating, we can divide out  $Y_{l, m_l}(\theta, \phi)$  and substitute  $U_{n, l}(r) = r R_{n, l}(r)$ .  

$$-\frac{\hbar^2}{2m} \frac{\partial^2 U_{n, l}}{\partial r^2} + \left[ \frac{l(l+1)\hbar^2}{2mr^2} + V(r) \right] U_{n, l} = E_{n, l} U_{n, l}$$
  
 $\hookrightarrow$  this is the 1D TISE, except the effective potential is now  $V(r) + \frac{\langle \hat{L}^2 \rangle}{2mr^2}$

- For a hydrogen-like atom, there is a **central potential**  
 $V(r) = -\frac{ze^2}{4\pi\epsilon_0 r}$ . Substituting into the eigenfunction equation:  

$$\frac{\partial^2 U_{n, l}}{\partial r^2} - \left[ \frac{l(l+1)}{r^2} - \frac{A}{r} + \chi^2 \right] U_{n, l} = 0$$

← with suitable subs  $A, \chi^2$ .

$\hookrightarrow$  in the limit of large  $r$ ,  $U_{n,l} \propto e^{-\kappa r}$   
 $\hookrightarrow$  for small  $r$ ,  $U_{n,l} \propto r^{l+1}$   
 $\hookrightarrow$  hence we guess a solution  $U_{n,l} \propto G(r)r^{l+1}e^{-\kappa r}$ ,  
 which gives the associated Laguerre equation  

$$r^2 \frac{\partial^2 G}{\partial r^2} + 2(l+1-\kappa r) \frac{\partial G}{\partial r} + [A - 2\kappa(l+1)]G = 0$$

This can be solved with a power series  $G(r) = \sum_{q=0}^{\infty} C_q r^q$   
 $\Rightarrow C_{q+1} = C_q \frac{2\kappa(q+l+1) - A}{(q+1)[q+2(l+1)]}$

$\hookrightarrow$  in order to prevent exponential behaviour, we must terminate the series at some  $q=p$ .

$\hookrightarrow 2\kappa(p+l+1) - A = 0 \Rightarrow A/2\kappa$  is an integer.

$\hookrightarrow$  it turns out that  $A/2\kappa \equiv n$  is the principal quantum number.

$\hookrightarrow p = n - (l+1)$  and  $p \geq 0, l \geq 0 \Rightarrow l \leq n-1$  and  $n \geq 1$

$$\Rightarrow R_{n,l} \propto \sum_{q=0}^{n-(l+1)} C_q r^{q+l} e^{-\kappa r}$$

The energy levels are given by:

$$A = \frac{2m}{\hbar^2} \frac{ze^2}{4\pi\epsilon_0}, \quad \kappa^2 = \frac{-2mE_{n,l}}{\hbar^2}, \quad \frac{A^2}{4\kappa^2} = n^2.$$

$$\Rightarrow E_n = \frac{-\hbar^2 z^2}{2m a_0^2} \frac{1}{n^2}, \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \text{ is the Bohr radius.}$$

$\hookrightarrow$  energy only depends on  $n$ , not  $l$ .

$\hookrightarrow$  the degeneracy of state  $n$  is  $2 \sum_{l=0}^{n-1} (2l+1) = 2n^2$

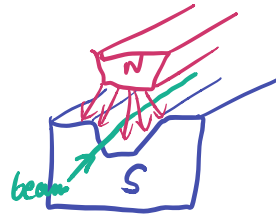
# Spin

The Stern-Gerlach Experiment showed that the magnetic dipole moment (related to  $L_z$ ) is quantised:

$\hookrightarrow$  non-uniform field so particle feels force depending on dipole moment  $F_z(z) = \mu_z \frac{\partial B_z(z)}{\partial z}$

$\hookrightarrow$  hence position on screen is related to  $L_z$

$\hookrightarrow$  the screen showed a discrete distribution.



However, rather than seeing an odd number of beams corresponding to the  $2l+1$  possible values of  $m_l$ , some experiments showed an even range

$\hookrightarrow$  this implies  $l$  is half-integer, which cannot be due to orbital angular momentum

$\hookrightarrow$  so we attribute it to spin, an intrinsic angular momentum unrelated to spatial motion.

It is assumed that the spin operator works the same way as the orbital angular momentum operator:

$$\hookrightarrow \hat{S} = i\hat{S}_x + j\hat{S}_y + k\hat{S}_z$$

$$\hookrightarrow [\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z \text{ and cyclic perms}$$

$\hookrightarrow \hat{S}^2$  is compatible with  $\hat{S}_z$ ; eigenvalues are  $s(s+1)\hbar^2$  and  $m_s\hbar$  respectively, with  $2s+1$  possible values of  $m_s$ :

$$m_s = -s, -s+1, \dots, s-1, s$$

The electron is a **spin-half particle** so can have spin angular momentum  $\pm \frac{\hbar}{2}$  for the **spin up/down** states.

↳ the total spin angular momentum is  $\sqrt{s(s+1)} \hbar = \frac{\sqrt{3}}{2} \hbar$

↳ it is convention to write the eigenstates as:

$$\hat{S}_z |\uparrow\rangle = +\frac{\hbar}{2} |\uparrow\rangle, \quad \hat{S}_z |\downarrow\rangle = -\frac{\hbar}{2} |\downarrow\rangle$$

↳ any spin state is a superposition:  $|\chi\rangle = c_1 |\uparrow\rangle + c_2 |\downarrow\rangle$

The **anticommutator** of two operators is  $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$

↳ for electrons,  $\{\hat{S}_i, \hat{S}_j\} = \frac{\hbar^2}{2} \delta_{ij}$

↳ this allows us to derive the commutation relations and eigenvalues.

We define spin ladder operators  $\hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$ :

$$\hat{S}_{\pm} |s, m_s\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)} |s, m_s \pm 1\rangle$$

$$|0\rangle \xleftarrow{\hat{S}_-} |\downarrow\rangle \xrightarrow{\pm\hbar} |\uparrow\rangle \xrightarrow{\hat{S}_+} |0\rangle$$

↳ using  $\hat{S}_x = \frac{\hat{S}_+ + \hat{S}_-}{2}$ :  $\hat{S}_x |\uparrow\rangle = \frac{\hbar}{2} |\downarrow\rangle$ ,  $\hat{S}_x |\downarrow\rangle = \frac{\hbar}{2} |\uparrow\rangle$

↳ similarly,  $\hat{S}_y |\uparrow\rangle = i\frac{\hbar}{2} |\downarrow\rangle$ ,  $\hat{S}_y |\downarrow\rangle = -i\frac{\hbar}{2} |\uparrow\rangle$

↳ this can be used to find eigenstates of  $\hat{S}_x$  and  $\hat{S}_y$

• Because  $|\uparrow\rangle$  is an eigenstate of  $\hat{S}_z$  (and  $\hat{S}^2$ ), there is no uncertainty in a measurement.

• But  $\hat{S}_x$  and  $\hat{S}_y$  are incompatible with  $\hat{S}_z$ .  $\Delta S_x = \Delta S_y = \frac{\hbar}{2}$ , so knowing that we are spin up/down does not give info about x-y components

## Total angular momentum

The total angular momentum  $\hat{J}$  is given by  $\hat{J} = \hat{L} + \hat{S}$

• Spin is not described by the time-space wavefunction of a particle - it is a result of additional degrees of freedom in the Dirac equation (relativistic).

$$\hookrightarrow |\Psi\rangle = |L, t\rangle |S\rangle$$

↳  $\hat{S}$  only acts on the  $|S\rangle$  portion while  $\hat{L}$  only acts on  $|L, t\rangle$

• Since components of  $\hat{L}$  commute with components of  $\hat{S}$ , we have  $[\hat{J}_x, \hat{J}_y] = i\hbar \hat{J}_z$  and cyclic permutations.

↳  $\hat{J}_z$  and  $\hat{J}^2$  are compatible, with eigenvalues  $m_j \hbar$  and  $j(j+1)\hbar^2$  respectively

↳  $m_j$  takes one of  $2j+1$  values.

• By vector addition,  $j_{\max} = L+S$ ,  $j_{\min} = |L-S|$

↳ the possible  $j$ s are integer steps between  $j_{\min}$  and  $j_{\max}$

↳ for each value of  $j$  we have  $2j+1$  values of  $m_j$ .

↳ for a spin-half system there are only two possible values of  $j$ , so  $2(2L+1)$  total states.

• In general, a particular orbital state can be written as:

$$|\Psi_{j, m_j}\rangle = \sum_{L, m_L, S, m_S} C_{L, m_L, S, m_S} |Y_{L, m_L}(\theta, \phi)\rangle |S, m_S\rangle$$

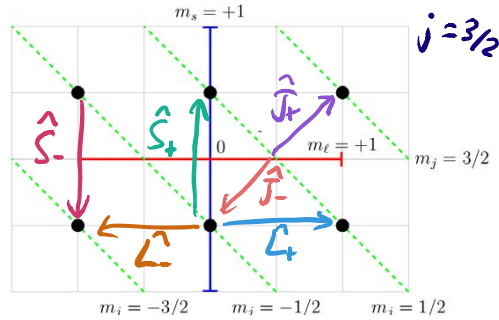
↳ all the states are orthogonal (useful!)

↳  $C_{L, m_L, S, m_S}$  are the **Clebsch-Gordan coefficients**

• Different states can be generated by using the total angular momentum ladder  $\hat{J}_{\pm} = \hat{L}_{\pm} + \hat{S}_{\pm}$

↳ can be visualised on a lattice

↳ for a given  $j$ , starting from the highest eigenstate we can generate all other states with  $\hat{J}_{-}$ .



$$\hat{J}_{\pm} |j, m_j\rangle = \hbar \sqrt{j(j+1) - m_j(m_j \pm 1)} |j, m_j \pm 1\rangle$$

↳ to find the coefficients in the highest eigenstate for a lower  $j$ , we cannot use  $\hat{J}_{-}$ . However, orthogonality may be used to write it down.

### Two-particle systems

• In a He atom, there are two electrons, which can each be spin up or spin down.

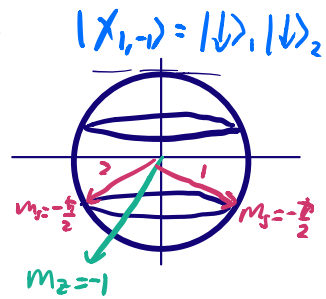
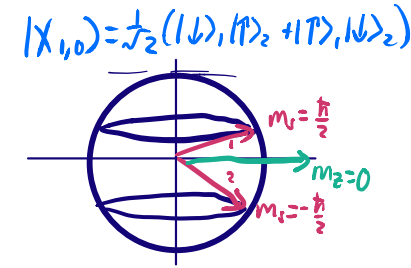
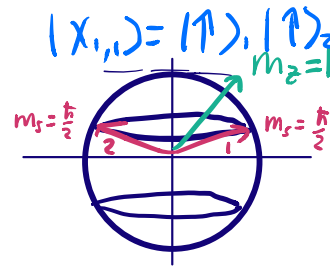
• We characterise the states in terms of the total spin  $S_z$  and the total  $z$  component  $m_z$ , i.e.  $|X_{S_z, m_z}\rangle$

• For a pair of electrons, the highest state is  $|X_{1,1}\rangle = |\uparrow\rangle_1 |\uparrow\rangle_2$

↳ other states can be found with ladders  $\hat{S}_{-} = \hat{S}_{1-} + \hat{S}_{2-}$ :

$$\begin{aligned} \hat{S}_{-} |X_{S_z, m_z}\rangle &= \hbar \sqrt{S_z(S_z+1) - m_z(m_z-1)} |X_{S_z, m_z-1}\rangle \\ &= (\hat{S}_{1-} + \hat{S}_{2-}) |X_{S_z, m_z}\rangle \end{aligned}$$

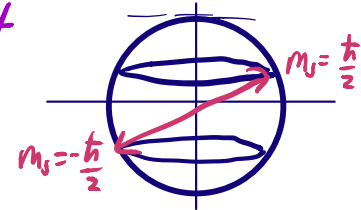
↳  $|X_{1,1}\rangle, |X_{1,0}\rangle, |X_{1,-1}\rangle$  are the triplet states



↳ the triplet states are symmetric if the particles are interchanged.

↳  $|X_{0,0}\rangle$  is an antisymmetric singlet state:

$$|X_{0,0}\rangle = \frac{1}{\sqrt{2}} (|\downarrow\rangle_1 |\uparrow\rangle_2 - |\uparrow\rangle_1 |\downarrow\rangle_2)$$



• A photon is a spin-one particle. It is thus able to impart its angular momentum to an electron to change it from spin-up to spin-down.

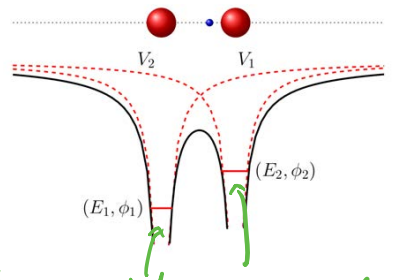
# Matrix Mechanics

- Heisenberg's matrix mechanics represents states by column vectors and operators by square matrices. It is especially effective when studying discrete systems with few states.
- For a given basis set, the matrix elements of an operator  $\hat{A}$  are given by  $A_{mn} = \langle \phi_m | \hat{A} | \phi_n \rangle$ 
  - ↳ the operator can be reconstructed from elements using  $\hat{A} = \sum_{mn} A_{mn} | \phi_m \rangle \langle \phi_n |$
  - ↳ if  $| \phi_n \rangle$  are eigenstates,  $A_{mn} = \lambda_n \delta_{mn}$  (diagonal)

## Two-level systems

- Matrix mechanics is suitable for two-level systems (e.g qubits).
- Consider a double potential well.
  - ↳ e.g in a diatomic molecule
  - ↳ the individual wells would each obey an eigenvalue equation:
 
$$\hat{H}_1 | \phi_{1i} \rangle = E_{1i} | \phi_{1i} \rangle$$

$$\hat{H}_2 | \phi_{2j} \rangle = E_{2j} | \phi_{2j} \rangle$$
 lowest energy states when isolated.



- To find the new eigenvalue equation, we form a basis consisting of  $\{ | \phi_{1i} \rangle, | \phi_{2j} \rangle \}$  - hybridisation.
  - ↳ we approximate as only needing  $\{ | \phi_1 \rangle, | \phi_2 \rangle \}$
  - ↳ for relatively isolated systems,  $\hat{H}_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$

- However, a particle may tunnel between basis states so the total Hamiltonian  $\hat{H}$  must include coupling terms:

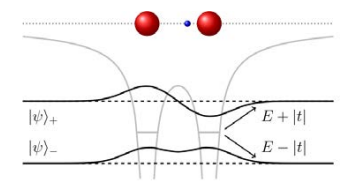
$$\hat{H} = \begin{pmatrix} E_1 & \tau \\ \tau^* & E_2 \end{pmatrix} \leftarrow \tau = \langle \phi_1 | \hat{H} | \phi_2 \rangle$$

- ↳ diagonalise to find eigenstates:
 
$$\begin{vmatrix} E_1 - \lambda & \tau \\ \tau^* & E_2 - \lambda \end{vmatrix} = 0 \Rightarrow \lambda = \frac{1}{2} (E_1 + E_2 \pm \sqrt{(E_2 - E_1)^2 + 4\tau^2})$$

- For two identical wells:  $\lambda_{\pm} = E \pm |\tau|$ 

$$\Rightarrow | \Psi \rangle_{\pm} = \frac{1}{\sqrt{2}} ( | \phi_1 \rangle \pm | \phi_2 \rangle )$$

- ↳ the lower eigenstate is symmetric; corresponds to bonding
- ↳ higher eigenstate is repulsion



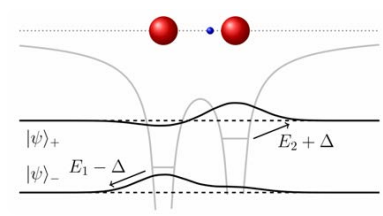
- ↳ if the two wells each had an electron, both occupy the lower state, reducing energy by  $2|\tau|$ . This is a covalent bond.
- Consider the case with  $E_1 < E_2$  and assume the coupling factor is small, i.e.  $\frac{|\tau|}{E_2 - E_1} \equiv \delta \ll 1$

- ↳ the energy levels become
 
$$\lambda = E_1 - (E_2 - E_1) \delta^2 = E_1 - \Delta \leftarrow \Delta \text{ is positive}$$

$$\lambda_+ = E_2 + (E_2 - E_1) \delta^2 = E_2 + \Delta$$

- ↳ using  $\delta \ll 1$ :  $| \Psi_- \rangle = \frac{1}{\sqrt{1+\delta^2}} ( | \phi_1 \rangle + \delta | \phi_2 \rangle )$ 

$$| \Psi_+ \rangle = \frac{1}{\sqrt{1+\delta^2}} ( -\delta | \phi_1 \rangle + | \phi_2 \rangle )$$



- ↳ if both wells had electrons, energy could be lowered by moving to  $E_1 - \Delta$ : ionic bonding.

# Multiparticle systems

• The hydrogen atom is effectively a one-particle system because we treat the proton as stationary.

• For a true two-particle system, the state depends on both positions:

$$|\Psi_{a,b}\rangle = \Psi(\underline{r}_a, \underline{r}_b, t)$$

↳ the distribution of positions is now a joint pdf:  $P(\underline{r}_a, \underline{r}_b) = |\Psi|^2 d^3r_a d^3r_b$

• For separable states,  $\Psi(\underline{r}_a, \underline{r}_b, t) = \Psi_a(\underline{r}_a) \Psi_b(\underline{r}_b)$

↳  $P_{a,b} = P_a P_b$  so the two particles behave independently.

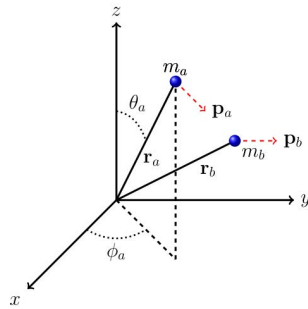
↳ in terms of abstract vectors,  $|\Psi_{a,b}\rangle = |\Psi_a\rangle |\Psi_b\rangle$ , i.e. the Cartesian product of  $|\Psi_a\rangle$  and  $|\Psi_b\rangle$ , which is a ket in higher-dimensional space.

↳  $|\Psi_{a,b}\rangle$  is normalised if both  $|\Psi_a\rangle$  and  $|\Psi_b\rangle$  are.

• Any two-particle state can be expanded in terms of separable basis vectors:  $|\Psi_{a,b}\rangle = \sum_m \sum_n C_{mn} \underbrace{|a_m\rangle |a_n\rangle}_{M \times N \text{ of these}}$

↳  $\{|a_m\rangle\}$  is a complete basis for measurements on  $a$ , and  $\{|b_n\rangle\}$  is a complete basis for measurements on  $b$ .

↳ QM postulates that  $\{|a_m\rangle |b_n\rangle\}$  is a complete basis for measurements on the system.



• These principles apply to  $N$  particles, but the number of basis states grows exponentially.

• For a separable state, measurements do not interfere. Consider two observables relating to  $a$  and  $b$  respectively:

$$\begin{aligned} \langle O_a O_b \rangle &= \langle \Psi_b | \langle \Psi_a | \hat{O}_a \hat{O}_b | \Psi_a \rangle | \Psi_b \rangle \\ &= \langle \Psi_b | \hat{O}_b | \Psi_b \rangle \langle \Psi_a | \hat{O}_a | \Psi_a \rangle = \langle a \rangle \langle b \rangle \end{aligned}$$

• For an entangled state, measurement on one subsystem may change the outcome of a measurement on the other.

↳ an example is  $|\Psi_{a,b}\rangle = \frac{1}{\sqrt{2}} (|a_1\rangle |b_2\rangle + |a_2\rangle |b_1\rangle)$ , for which there is maximal uncertainty about which particle is where

↳  $P(a \text{ in state } |a_1\rangle \text{ and } b \text{ in } |b_2\rangle) = |\langle b_2 | \langle a_1 | \Psi \rangle|^2 = 1/2$

↳  $P(a \text{ in state } |a_2\rangle \text{ and } b \text{ in } |b_1\rangle) = |\langle b_1 | \langle a_2 | \Psi \rangle|^2 = 1/2$ .

• However, operators still only act on their relevant wavefunction dependence, e.g.  $\hat{p}_a = -i\hbar \nabla_a = -i\hbar (\frac{\partial}{\partial x_a}, \frac{\partial}{\partial y_a}, \frac{\partial}{\partial z_a})$

↳ the commutation relations for a single particle are the same, i.e.  $[\hat{x}_a, \hat{p}_{x_a}] = [\hat{y}_a, \hat{p}_{y_a}] = [\hat{z}_a, \hat{p}_{z_a}] = i\hbar$

↳ however, the 'cross terms' commute:  $[\hat{r}_a, \hat{p}_b] = 0$   
 $[\hat{r}_a, \hat{r}_b] = 0$

↳ but measurements on  $a$  still affect the outcome of  $b$ .

• The Hamiltonian for the system is:  $\hat{H} = \frac{\hat{p}_a^2}{2m_a} + \frac{\hat{p}_b^2}{2m_b} + \hat{V}(\underline{r}_a, \underline{r}_b)$

↳  $\hat{V}$  includes both the external fields and the interactions

↳ if  $\hat{V}$  is only a function of separation, the problem simplifies.

## Interactions

- The total momentum operator is  $\hat{p} = \hat{p}_a + \hat{p}_b$ 
  - ↳ each component of  $\hat{p}$  commutes with any component of the relative position  $\hat{r} = \hat{r}_a - \hat{r}_b$ .
  - ↳ hence  $\hat{p}$  commutes with  $V(\hat{r})$
  - ↳  $\hat{p}$  also commutes with  $\hat{p}_a^2, \hat{p}_b^2$
  - ↳ hence  $\hat{p}$  commutes with  $\hat{H}$  and is thus conserved
- The position of the CoM is  $\underline{R} = \frac{m_a \underline{r}_a + m_b \underline{r}_b}{m_a + m_b}$

← Ehrenfest's theorem.

↳ it can be shown that  $[\hat{R}, \hat{A}] = i\hbar \frac{\hat{p}}{m_a + m_b}$   
 ↳ hence  $\frac{d\langle \hat{R} \rangle}{dt} = \frac{\langle \hat{p} \rangle}{M}$  as expected.  
 $M \leftarrow M = m_a + m_b$

We may wish to express the Hamiltonian as the sum of a CoM part and internal part, i.e. in terms of  $\underline{R} = (X, Y, Z)$

$$\underline{r} = \underline{r}_b - \underline{r}_a = (x, y, z)$$

$$\hat{p}_a = -i\hbar \frac{\partial}{\partial \underline{r}_a} = -i\hbar \left\{ \frac{\partial x}{\partial x_a} \frac{\partial}{\partial x} + \frac{\partial y}{\partial x_a} \frac{\partial}{\partial y} + \frac{\partial z}{\partial x_a} \frac{\partial}{\partial z} \right\}$$

$$= \frac{m_a}{M} \frac{\partial}{\partial x} - \frac{\partial}{\partial x}$$

↳ this gives  $\hat{p}$  corresponding to the CoM and  $\hat{p}_r$  associated with the relative motion of a and b

$$\hat{p}_a = \frac{m_a}{M} \hat{p} - \hat{p}_r ; \quad \hat{p}_b = \frac{m_b}{M} \hat{p} - \hat{p}_r$$

↳ we can compute  $\hat{p}_a^2, \hat{p}_b^2$  to give the overall Hamiltonian

$$\hat{H} = \underbrace{\frac{\hat{p}^2}{2M}}_{\text{CoM}} + \underbrace{\frac{\hat{p}_r^2}{2\mu}}_{\text{reduced mass}} + V(r)$$

← assuming V only func. of separation  
 ↳ between

- The wavefunction can be transformed to the new coordinate system:  $(\hat{A}_{\text{com}} + \hat{A}_r) \Psi(\underline{R}, \underline{r}) = E \Psi(\underline{R}, \underline{r})$ 
  - ↳ if  $V$  is only a function of separation, the equation separates
    - $-\frac{\hbar^2}{2M} \nabla_R^2 U(\underline{R}) = E_{\text{com}} U(\underline{R}) \rightarrow$  free particle
    - $(-\frac{\hbar^2}{2\mu} \nabla_r^2 + V(r)) u(r) = E_r u(r) \rightarrow$  spherical harmonic etc.
  - ↳ the overall wavefunction is  $\exp[i(\hat{p} \cdot \hat{R} / \hbar)] \Psi_{n, l, m_l}(r)$
- Translationally it acts as a single composite free particle.
- Vibration as if one particle of mass  $\mu$  is moving in a central  $V(r)$
- Rotation same as a rigid rotor at fixed distance from origin.

## N identical particles

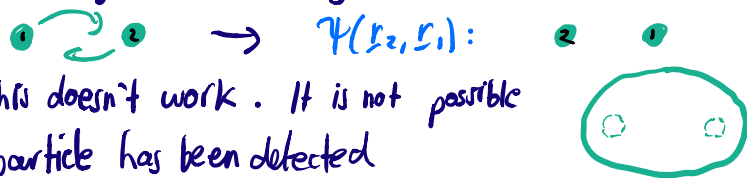
- The many-particle Schrödinger equation is  $\hat{H}_N \Psi_N = E_N \Psi_N$
- The  $N$ -particle Hamiltonian must be invariant to swapping identical particles. This leads to exchange degeneracies.
  - ↳  $\hat{H}_N \equiv \hat{A}(\underline{r}_1, \dots, \underline{r}_i, \underline{r}_j, \dots, \underline{r}_N; \underline{p}_1, \dots, \underline{p}_i, \underline{p}_j, \dots, \underline{p}_N)$
  - $= \hat{A}(\underline{r}_1, \dots, \underline{r}_j, \underline{r}_i, \dots, \underline{r}_N; \underline{p}_1, \dots, \underline{p}_j, \underline{p}_i, \dots, \underline{p}_N)$
  - ↳ in fact, identical particles may be defined as those which are exchange-symmetric under all possible observables
  - ↳ it is convention to write  $\Psi_N \equiv \Psi(\xi_i, \xi_j)$  where  $\xi_i$  encodes the dynamical variables of particle  $i$ .
  - ↳ identical particles thus obey  $\hat{A}(\xi_i, \xi_j) = \hat{A}(\xi_j, \xi_i)$  for all  $\hat{A}$
- Classically, identical particles may still be distinguished from one another.  $\Psi(\underline{r}_1, \underline{r}_2): e^- \quad 1 \quad 2 \quad e^-$



↳ we could track trajectories as they move, and thus find  $\psi(r_2, r_1)$ .

↳ but in QM this doesn't work. It is not possible to say which particle has been detected

↳ the states are the same:  $|\psi(r_1, r_2)|^2 = |\psi(r_2, r_1)|^2$ ,  
different to saying that  $\hat{A}(r_i, r_j) = \hat{A}(r_j, r_i)$



## Exchange symmetries

• Given the indistinguishability of states, there are two possible **exchange symmetries**. This has a physical meaning.

$$|\psi(r_1, r_2)|^2 = |\psi(r_2, r_1)|^2 \Rightarrow \psi(r_1, r_2) = \pm \psi(r_2, r_1)$$

• From the perspective of state vectors, an  $N$ -particle basis set

is represented by the **Hartree product**  $|r_1\rangle |r_2\rangle \dots |r_N\rangle$

↳ each  $|r_i\rangle$  is a set of quantum numbers for particle

↳ basis set because all possible outcomes are contained.

• Eg for a two particle spin system, a possible basis set is:

$$\{ |\uparrow_1\rangle |\uparrow_2\rangle, |\uparrow_1\rangle |\downarrow_2\rangle, |\downarrow_1\rangle |\uparrow_2\rangle, |\downarrow_1\rangle |\downarrow_2\rangle \}$$

↳ but due to indistinguishability, the middle two should be physically identical. We thus construct two new states that show exchange symmetry → result is same as the eigenstates.

$$|s\rangle = \frac{1}{\sqrt{2}} (|\uparrow_1\rangle |\downarrow_2\rangle + |\downarrow_1\rangle |\uparrow_2\rangle) \quad |a\rangle = \frac{1}{\sqrt{2}} (|\uparrow_1\rangle |\downarrow_2\rangle - |\downarrow_1\rangle |\uparrow_2\rangle)$$

$$\Rightarrow |\uparrow_1\rangle |\downarrow_2\rangle = \frac{1}{\sqrt{2}} (|s\rangle + |a\rangle), \quad |\downarrow_1\rangle |\uparrow_2\rangle = \frac{1}{\sqrt{2}} (|s\rangle - |a\rangle)$$

↳ so we have a new basis  $\{ |\uparrow\rangle |\uparrow\rangle, |s\rangle, |a\rangle, |\downarrow\rangle |\downarrow\rangle \}$ .

↳ this basis has the same number of degrees of freedom, even though we eliminated one using identical particles

⇒  $|s\rangle$  and  $|a\rangle$  correspond to two fundamentally different kinds of particle

↳ the new basis has maximum uncertainty about which particle we find in which state.

• **Bosons** are exchange-symmetric, i.e.  $\psi(r_1, r_2) = \psi(r_2, r_1)$ .

• **Fermions** are exchange-antisymmetric, i.e.  $\psi(r_1, r_2) = -\psi(r_2, r_1)$ .

• The **symmetrisation postulate** states that  $N$  identical particles are either exchange-symmetric or exchange-antisymmetric; there are no mixed states and bosons/fermions are fundamentally different objects

• In the two-particle spin system (i.e. He),  $|\uparrow\rangle |\uparrow\rangle$  and  $|\downarrow\rangle |\downarrow\rangle$  correspond to two bosons in the same state. But no antisymmetric wavefunction permits two particles to be in the same state.

• The **Pauli Exclusion Principle** states that no two identical fermions can be in the same state (i.e. share quantum numbers).

• The **spin-statistics theorem** relates particle spin to exchange symmetry. Half-integer spin  $\Leftrightarrow$  fermions; integer spin  $\Leftrightarrow$  bosons.

• Bosons obey **Bose-Einstein statistics**:  $\langle n_j \rangle = \frac{1}{e^{(\epsilon_j - \mu)/kT} - 1}$   
↳ unbounded  $j$  is a particular quantum state.

• Fermions obey **Fermi-Dirac statistics**:  $\langle n_j \rangle = \frac{1}{e^{(\epsilon_j - \mu)/kT} + 1}$   
↳ less than unity.

## Multi-particle exchange

• In a general system of  $N$  particles, let a given state  $r$  of particle  $i$  be denoted by  $|\xi_i^r\rangle$ .

• If all particles are identical, a suitable basis is:  
 $|\xi^a\rangle \dots |\xi^r\rangle \dots |\xi^z\rangle$

↳ terms with  $r=s$  have an exchange symmetry, but terms for which  $r \neq s$  do not:

$$|\xi^a\rangle \dots |\xi^r\rangle |\xi^s\rangle \dots |\xi^z\rangle \neq |\xi^a\rangle \dots |\xi^s\rangle |\xi^r\rangle \dots |\xi^z\rangle$$

↳ but these should be indistinguishable, so as with the two-particle spin system, we must symmetrise it.

• To do this, we combine all possible permutations then **renormalise** the resulting vector:

$$\underbrace{|\underbrace{a, \dots, r, \dots, z}\rangle^s}_{\text{Exchange symmetric vector}} = \frac{1}{\underbrace{\sqrt{N! / (\prod_n m_n!)}}_{\text{counts } \# \text{ permutations with repeated elements}}} \sum_{\text{perms}} |\xi^a\rangle \dots |\xi^r\rangle \dots |\xi^z\rangle$$

↳ this must be done for each  $a, \dots, r, \dots, z$  combination

• We can also form antisymmetric states when  $a, \dots, r, \dots, z$  are all different. These correspond to arrangements of fermions.

$$|\underbrace{a, \dots, r, \dots, z}\rangle^s = \frac{1}{\sqrt{N!}} \sum_{\text{perms}} \text{sgn}(p) |\xi^a\rangle \dots |\xi^r\rangle \dots |\xi^z\rangle$$

• Both the symmetric and antisymmetric states are needed to form the new basis.

e.g 3 particles, each with 3 states.

• i.e.  $|\xi^a\rangle |\xi^b\rangle |\xi^c\rangle$  with  $a, b, c \in \{1, 2, 3\}$

•  $|1, 1, 1\rangle$  is symmetric, but  $|1, 1, 2\rangle$  isn't

• Symmetrise:  $|1, 1, 2\rangle^s = \frac{1}{\sqrt{3}} [ |1, 1, 2\rangle + |1, 2, 1\rangle + |2, 1, 1\rangle ]$

• Now  $|1, 1, 2\rangle^s = |1, 2, 1\rangle^s = |2, 1, 1\rangle^s$

• There is only one antisymmetric state:

$$|1, 2, 3\rangle^a = \frac{1}{\sqrt{3!}} [ |1, 2, 3\rangle - |1, 3, 2\rangle + |2, 3, 1\rangle + \dots - |3, 2, 1\rangle ]$$

• The antisymmetric states can also be represented as the

Slater determinant:  $|N\rangle^a = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\xi^1\rangle & |\xi^1\rangle & \dots & |\xi^1\rangle \\ |\xi^2\rangle & |\xi^2\rangle & \dots & |\xi^2\rangle \\ \vdots & \vdots & \dots & \vdots \\ |\xi^N\rangle & |\xi^N\rangle & \dots & |\xi^N\rangle \end{vmatrix}$

↳ because  $\det A = \epsilon_{i_1 \dots i_n} a_{1i_1} \dots a_{ni_n}$

↳ swapping columns corresponds to swapping particles, so the sign changes as required.

• All  $N$  fermions exist in different states, but at sufficiently low temperatures the bosons can all be in the same state

↳ this is called a **Bose-Einstein condensate**.

↳ the state vector is  $|\xi^1\rangle \dots |\xi^1\rangle \dots |\xi^1\rangle$