

# Introduction to Molecular Quantum Mechanics

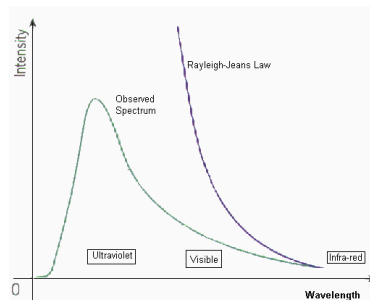
- Brief historical overview
- Wave-particle Duality
- What is Quantum mechanics doing for us now?
- The wavefunction,  $\Psi$
- Some background maths
- The Schrodinger Equations and some solutions
- Particle in a box, tunnelling, particle on a ring, the simple harmonic oscillator.

## The Failure of Classical Mechanics - Black Body Radiation

A hot body glows. The best classical explanation finds energy density/wavelength

$$\frac{dE}{d\lambda} = \frac{8\pi kT}{\lambda^4}$$

Which clearly fails and suggest even cold bodies should emit a pleasing blue glow, as the function increases to infinity as  $\lambda \rightarrow 0$



The mistake was to assume that an oscillator can have any frequency. Planck assumed the oscillator must be **quantised** and take the value  $E = nh\nu$  where n is an integer and obtained

$$\frac{dE}{d\lambda} = \frac{8\pi hc}{\lambda^5 [\exp(hc/kT) - 1]}$$

Which has the correct form, fits all data very well, reduces to the classical equation at high frequency and yields  $h = 6.63 \times 10^{-34}$  Js, which we now call **Planck's constant**.

## Some Other Triumphs of QM

- You are already familiar with the photoelectric effect, where classically the observed work function of a metal is inexplicable
- Similarly you have seen (1c24) how the spectrum of the H atom can be perfectly explained by quantization.
- In the textbooks you can see that heat capacity, which is classically constant with T reduces to 0 as  $T \rightarrow 0$ , explained again by quantization.



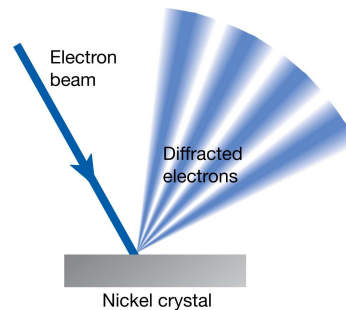
International Solvay Conference in 1927. Front row, left to right: I. Langmuir, M. Planck, M. Curie, H. A. Lorentz, A. Einstein, P. Langevin, C. E. Guye, C. T. R. Wilson, O. W. Richardson. Second row, left to right: P. Debye, M. Knudsen, W. L. Bragg, H. A. Kramers, P. A. M. Dirac, A. H. Compton, L. V. de Broglie, M. Born, N. Bohr. Standing, left to right: A. Piccard, E. Henriot, P. Ehrenfest, E. Herzen, T. De Donder, E. Schroedinger, E. Verschaffelt, W. Pauli, W. Heisenberg, R. H. Fowler, L. Brillouin

## The de Broglie Hypothesis - Wave Particle Duality

We have pretty much accepted that photons have particle properties – why should not particles have wave like properties?

They do: Davisson and Germer bombarded a Ni crystal with a collimated beam of electrons. The beam was *diffracted* from the rows of Ni atoms, exactly as in a Young's slit experiment.

More recently the same experiment has been performed with helium atoms.



In 1924 de Broglie suggested that the wavelength to be associated with a particle is given by

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

Where  $p$  is the particle momentum (mass x velocity).

## De Broglie Calculations

- What wavelengths are associated with particular particles? Let's start with something small – the electron. First we need its velocity.
- An electron is accelerated in a potential ( $V$ ) of 3kV.
- Energy is product of charge ( $e$ ) and potential
- $E = eV = 1.6 \times 10^{-19} \text{ C} \times 3000 \text{ V} = 4.8 \times 10^{-16} \text{ J}$  (note  $\text{J} \equiv \text{VC}$ )
- That energy is all kinetic
- $4.8 \times 10^{-16} \text{ J} = (1/2)mv^2$  electron mass =  $9.11 \times 10^{-31} \text{ kg}$
- $v = 3.25 \times 10^7 \text{ ms}^{-1}$
- The momentum is  $p = mv = 9.11 \times 10^{-31} \text{ kg} \times 3.25 \times 10^7 \text{ ms}^{-1} = 2.96 \times 10^{-23} \text{ kgms}^{-1}$ .
- The de Broglie wavelength is  $\lambda = h/p = 6.63 \times 10^{-34} \text{ Js} / 2.96 \times 10^{-23} \text{ kgms}^{-1}$
- $= 2.24 \times 10^{-11} \text{ m}$
- In the X-ray region

## Try one yourself

- A lead bullet of volume  $2 \text{ cm}^3$  is fired at you at a velocity of  $400 \text{ ms}^{-1}$ . How worried should you be (about the extent of delocalisation of the bullet)? (you may note that the density of lead is  $11.3 \text{ g/cm}^3$ )

## Does QM Still Matter?

- Many chemical, analytical (spectroscopy), material (semi-conductors) and biomedical (X-ray, MRI scans) phenomena are understood today only because QM was understood first.
- To an extent those are developments from the 'glorious' past of QM (let us brush over it sometimes less than glorious contribution to weapons development); what of the future?
- The future is small – nanoscience will increasingly appear in everyday life, through improved material properties, faster computers and more compact devices...
- These developments are essential to a sustainable world (smaller devices use less energy and put out less pollution)
- Implementation of nanotechnology poses immense scientific and social challenges
- The scientific challenges will require use and further development of quantum mechanics – **QM matters!**

## Two Examples

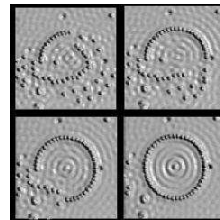
Moore's law tells us that 'transistor density will double every few years' (ditto Intel profits).

At the current level (wires ca 50 nm thick) quantum properties of the devices become important (at these sizes the **de Broglie** wavelength is significant). Even the spectrum is size dependent (see fig.).

How do you know that a wire is only 50 nm? You can measure it by electron **diffraction** (using the **de Broglie wavelength** of the electron) or by scanning tunnelling microscopy, a technique which relies on **quantum mechanical tunnelling** (see later). **For the manipulation, measurement and interpretation of nanoscience, we need QM**



*Cd:Se 'quantum dots which differ only in their particle size.*

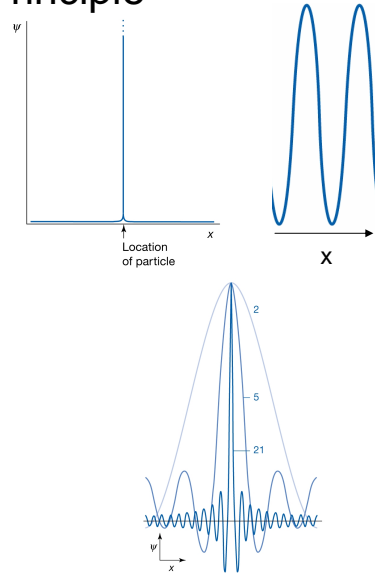


*The image shows individual copper atoms being located and imaged in a 'quantum corral'.*

## Wave Particle Duality And The Heisenberg Uncertainty Principle

- Classically we believe we can localise a particle in space, e.g a particle moving in the x-direction can be localised at position x.
- Quantum mechanically we describe the particle by a wave (what we shall soon call a **wavefunction**). We know that a single sine wave, for example repeats endlessly, and is not localised.
- However, if we add an infinite number of different wavelengths which all share a common origin at x then destructive interference will yield a completely localised result.
- The result of course is that complete certainty about x **requires complete uncertainty about p!**
- Heisenberg formulated his famous uncertainty relation as

$$\Delta p \cdot \Delta x \geq h/4\pi$$



## Heisenberg Uncertainty Relation – Some Consequences

- We can see that if either  $p$  or  $x$  are known exactly (e.g.  $\Delta p = 0$ ) the uncertainty relation requires the other partner to be infinitely uncertain (e.g.  $\Delta x = \infty$ ).
- Note how this violates the underlying principles of classical mechanics – that if the initial trajectories of the particles in a system are known the future of the system is completely predictable. A quantum universe is less predictable – we don't know exactly where we are going (or even exactly where we are).
- At a more concrete level, suppose the uncertainty in an electron's velocity is  $3 \times 10^5 \text{ ms}^{-1}$ . What is the minimum uncertainty in its position?

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{h}{4\pi m\Delta v}$$

$$\Delta x = \frac{6.63 \cdot 10^{-34}}{4 \cdot \pi \cdot 9.11 \cdot 10^{-31} \cdot 3 \cdot 10^5} = 1.93 \cdot 10^{-10} \text{ m}$$

(Which is not small for an electron!)

## Try the following calculation

- That bullet was fired at you along the  $x$ -axis at  $400 \pm 1 \text{ ms}^{-1}$ . How far off the  $x$ -axis do you need to move to be sure of getting out of its way?
- Recalling that the mass was  $22.6 \times 10^{-3} \text{ kg}$  the maximum uncertainty in the momentum is
- 

## Where are we now?

- We can be pretty sure where we are, but less certain about electrons.
- At the microscopic or molecular level the direction or location of a particle is not explicable by a classical trajectory – the particle has wave like properties
- We will have to describe the trajectory with a wave equation, and we will describe the particle in terms of a **wavefunction**.
- We give the **wavefunction** the symbol  $\Psi$ .
- $\Psi$  is pronounced *psi* (though sigh is sometimes heard).
- In the next few slides we will be concerned with some of the properties of the wavefunction.
- Next we will consider why the wavefunction has these properties, which requires us to engage a little with the math of quantum mechanics, and in particular the **Schroedinger equation**.
- Thus equipped we will be able to predict the properties of some simple systems.

# Ψ

- The wavefunction contains all there is to know about the dynamics of the system it describes – i.e. the momenta as a function of time of all the particles in the system. Properly written  $\Psi(\rho, t)$ .
- The **Born Interpretation** of the wavefunction is helpful. Born interprets the wavefunction as the probability that a particle is at a given point in space. Specifically if  $\Psi$  has some value in a volume of space  $d\tau$  (where  $d\tau$  is an infinitesimal volume,  $d\tau = dx.dy.dz$ ) then the probability that the particle is located there is

$$|\Psi|^2 d\tau$$

- Where  $|\Psi|$
- Means the modulus of the wavefunction (as it may be negative) and

$$|\Psi|^2 = \Psi^* \Psi$$

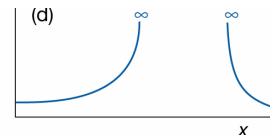
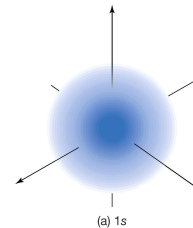
- Where  $\Psi^*$  means the complex conjugate of the wavefunction (as it may be a complex function)

## What does Ψ Look Like?

- If we know  $\Psi$  we can evaluate  $\Psi^2$  for all  $d\tau$ , and build up a 3D picture of the spatial distribution of our particle. You are already familiar with these – the 1s orbital of the H atom is a good example.
- If a particle exists, then it must exist somewhere, so if we look (integrate) over all space the probability of finding the particle is 1. Mathematically

$$N^2 \int \Psi^2 d\tau = 1$$

- Where N is called the normalization factor (a constant).
- This gives us some more information about  $\Psi$ . If the integration is to take the value 1 and  $N \neq 0$  (a trivial result) the value of  $\Psi$  can never go to infinity. **The wavefunction is finite everywhere** (the figure shows a forbidden form for  $\Psi$ )



## Further Properties of the Wavefunction

- The Born interpretation calculates a probability for a given value of  $\Psi$  at a particular position. Logically a particle cannot be in two places at the same time. **The wavefunction must be single valued.**
- When we come to evaluate wave functions using the Schrodinger equation we will take their first and second derivatives of the function. These must be well behaved (not go to zero or infinity). If you recall some basic calculus this implies that  $\Psi$  must have no steps or sharp kinks. **The wavefunction must be continuous.** Thus the wavefunctions shown are also not permitted.
- These restrictions severely limit the form of the allowed wave functions. The particles are not free to be anywhere, so cannot adopt any energy – the energy is **quantised**, as in the H atom problem (1C24).



Multiply valued



Discontinuous

## Consider the Following

- Which of these are legitimate wavefunctions?
- (a)  $\exp(-x)$  for  $0 < x < \infty$  (b)  $\exp(-x)$  for  $-\infty < x < \infty$  (c)  $x^{-1}$  for  $0 < x < \infty$
- Assume we determine  $\Psi = N \exp(-ax)$ . What is the correct value for the normalisation constant  $N$ .