Classical and Quantum Mechanics
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Lecture 1. Introduction. Building blocks of matter, fundamental particles. Forces between particles. Electrostatics, Coulomb's Law.

Lecture 2. Classical mechanics. Particles and waves. Bond energy. Electrostatics and dielectric constant. Newton's Laws. Molecular modelling. Effects of electric fields, electrophoresis.

Lecture 3. Breakdown of classical mechanics. Wave-particle duality of matter and wavefunctions. De Broglie's relationship. Heisenberg's Uncertainty Principle. Zero-point energy.

Lecture 4. Boundary conditions and quantisation of energy. Particle in a box. Quantum numbers. Schrödinger's equation. Energy levels in molecules. Boltzmann and Maxwell-Boltzmann distribution.

Lecture 5. Atomic orbitals and quantum numbers. Orbital energies. Aufbau principle.

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N.C. Price, R.A. Dwek, R.G. Ratcliffe and M.R. Wormald (2001) "Principles and Problems in Physical Biochemistry for Biochemists", pub. Oxford – *the best basic text for biochemists – goes without saying really*.

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CONSTRAINTS IMPOSED ON BIOLOGICAL SYSTEMS BY THEIR ENVIRONMENT

Macroscopic level – Biological systems are living things that can move, grow and replicate. They can only do this by making use of the resources in their immediate vicinity. They also have to be able to survive the effects of the immediate vicinity as well.
- Abundance of the chemical elements
- External physical conditions - prevailing gravity, pressure, temperature, radiation levels
- External chemical environment - (either water or mixture of N_2 and O_2)
- Available energy sources - heat, light, unstable chemicals from the surroundings (usually other biological systems and thus indirectly from light).

CONSTRAINTS IMPOSED ON BIOLOGICAL SYSTEMS BY PHYSICS AND CHEMISTRY

Molecular level - Biological systems are just a large collection of spatially and temporally localised chemical reactions. These reactions follow the *same rules* whether they happen in a test tube or a cell.
- Chemical properties of the elements and their compounds - determined entirely by the covalent and non-covalent interactions between atoms.
    quantum mechanics
    macromolecular structure
- Energetic requirements of chemical reactions - the energy requirement must be met by the available energy sources, otherwise reactions cannot occur.
    thermodynamics
- Rates of chemical reactions - the rate of a reaction is determined by the nature of the process and its energy requirements.
    reaction kinetics

FUNDAMENTAL PARTICLES - A PHYSICISTS VIEW

Everything in the entire universe is made up of fundamental particles (defined as particles with no internal structure). There are three types of fundamental particles;
1. Leptons – e.g. electrons, neutrinos
2. Quarks – e.g. up, down, charm
3. Force carriers – e.g. photon

There are 6 leptons, 6 quarks and 4 force carriers.

Leptons can be directly detected. Quarks cannot be directly detected, we can only see particles made up of several quarks (the proton and neutron are both made of three quarks). We only know that quarks exist because the best theory available requires that they do. Force carriers mediate all the interactions between the other particles.

FUNDAMENTAL PARTICLES - A CHEMISTS VIEW

The only particles that are of interest to chemists (and thus biochemists) are;

proton	mass = 1	charge = +1
neutron	mass = 1	charge = 0
electron	mass = 0.0005	charge = -1
photon	mass = 0	charge = 0

Each of these particles can have two types of energy;
1. Kinetic energy associated with their velocity ($\frac{1}{2}mv^2$)
2. Potential energy associated with the interactions (forces) between the particles

TYPES OF FORCES - A PHYSICISTS VIEW

There are four (and only four) fundamental forces;
1. Strong force – holds nuclei together (only of interest to physicists)
2. Electromagnetic force – interactions between charges and between electromagnetic radiation and matter
3. Weak force – involved in radioactive decay (also only of interest to physicists)
4. Gravity - interaction between masses over very long range (only of interest on a macroscopic scale, e.g. astronomy).

The electromagnetic force determines ALL chemistry and hence all biochemistry.

ELECTROMAGNETIC FORCE

The electromagnetic force is responsible for;
• Holding electrons around nuclei in atoms (i.e. atomic structure)
• Covalent bonding between atoms (holding nuclei together, mediated by the electrons)
• Ionic bonding between ions (as in crystals)
• Non-covalent interactions between molecules (charged regions of the molecules interacting)
• Being able to write (electrons in your finger repel electrons in the pen, allowing you to push the pen)

The electromagnetic force has two parts;
• an electric interaction due to the presence of any charges (electrostatic interaction)
• a magnetic interaction as a result of moving charges.

We will only worry about the electric interaction because that it what is needed to understand atoms, molecules and intermolecular forces.

The magnetic interaction is only relevant in biochemistry in;
• Techniques such as Nuclear Magnetic Resonance spectroscopy

- Magnetoreceptors in some organisms (such as magnetite particles)

ELECTROSTATIC INTERACTION - COULOMB'S LAW

The force (F) of the interaction between two charges is;

$$F = \frac{1}{4\pi\varepsilon_o}\frac{q_1 q_2}{r^2}$$

where
q_1, q_2 – charges (C)
r – distance between charges (m)
ε_o – permittivity of free space (8.85×10^{-12} C^2 m^{-2} N^{-1})

In order to calculate the potential energy (E) of two charged species, we have to calculate the force required to push them together from infinity (where by definition E=0). This is equivalent to integrating Coulomb's Law between infinity and r.

$$E = \int_{\infty}^{r} -\frac{1}{4\pi\varepsilon_o}\frac{q_1 q_2}{r^2}\,dr = \frac{1}{4\pi\varepsilon_o}\frac{q_1 q_2}{r}$$

The charge on an electron is -1.6×10^{-19} C. The attraction between two species with opposite unit charges (e.g. Na^+ and Cl^-, or a glutamic acid residue and a lysine residue) at a separation of 10 Å (1×10^{-9} m) is
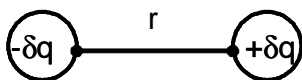
$$E = \frac{1}{4\times3.14\times8.85\times10^{-12}}\frac{(1.6\times10^{-19})\times(-1.6\times10^{-19})}{1\times10^{-9}} = -2.3\times10^{-19}\,J$$

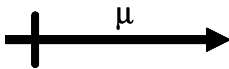Thermal energy at 300 K is 4×10^{-21} J.

For multiple charges, the potential energy is just the sum of all the pairwise interactions.

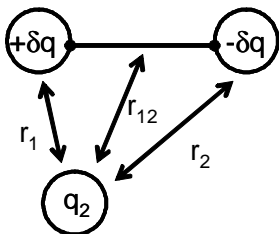$$E = \frac{1}{4\pi\varepsilon_o}\sum_{\substack{all\ i,j \\ pairs}}\frac{q_i q_j}{r_{ij}}$$

ELECTROSTATIC INTERACTION - DIPOLES

A dipole consists of two opposite charges separated by a fixed distance.

Dipole moment (μ) = $\delta q \times r$

The interaction between a charge and a dipole can be calculated in the usual way

$$E = \frac{1}{4\pi\varepsilon_o}\frac{\delta q \times q_2}{r_1} - \frac{1}{4\pi\varepsilon_o}\frac{\delta q \times q_2}{r_2}$$

or this can be rewritten as;

$$E = \frac{\mu \times q_2}{4\pi\varepsilon_o}\times\frac{t}{r_{12}^2}$$

where t is a triganometric term depending on the position of the charge relative to the dipole.

The interaction between two dipoles can be calculated in the same basic way, or can be written as

$$E = \frac{\mu_1 \times \mu_2}{4\pi\varepsilon_o} \times \frac{t}{r_{12}{}^3}$$

where t is a triganometric term depending on relative orientations of the dipoles.

$$E = \frac{\mu_1 \times \mu_2}{4\pi\varepsilon_o} \times \frac{t}{r_{12}{}^3}$$

Classical and Quantum Mechanics 2

Summary so far ...

- All matter is made of charged particles (nuclei and electrons).
- These particles interact via the electromagnetic force.
- The potential energy of the electrostatic interaction between two charged particles is

$$E = \frac{1}{4\pi\varepsilon_o} \frac{q_1 q_2}{r}$$

THE CLASSICAL WORLD

Matter consists of particles (e.g. atoms). Energy is either associated with particles (e.g. kinetic energy) or consists of waves (e.g. light). One form of matter can be converted into another form of matter. Similarly, one form of energy can be converted into another form of energy, but matter and energy are fundamentally different and cannot interconvert.

Waves;
- have no mass, and thus no momentum
- have no single position
- spread out from a point
- are characterised by a wavelength and an intensity
- energy is related to the intensity

The interaction between two waves is called interference. The two interacting waves add (constructive interference) and/or subtract (destructive interference) to give a resultant wave.

Particles;
- have mass (m) and thus momentum (mv)
- have a single position (x,y,z coordinates)
- have a well defined velocity (v)
- travel in straight lines
- energy = kinetic energy + potential energy

Kinetic energy is due to the velocity of the particle – $\frac{1}{2}mv^2$. Potential energy is due to the position of the particle – there are many forms of potential energy, e.g. due to the position of the particle in a gravitational field, an electric field, a chemical bond, etc.

CHEMICAL BOND - CLASSICAL APPROACH

Consider a molecule which consists of two atoms joined by a bond. The equilibrium bond length is b_e. This is just like two weights on a spring. When the actual bond length is b_e the potential energy of the bond is at a minimum. If the actual bond length is shorter or longer than this, the potential energy will be higher, i.e. there will be a force trying to return the atoms to their equilibrium positions.

$$E_{potential} = K_b(b - b_e)^2$$

where K_b is the bond force constant, which can be measured by vibrational spectroscopy.

For a vibrating bond:
- when the bond length is either at its maximum or minimum value, the potential energy is a maximum and the atoms are stationary so the kinetic energy is zero.
- when the bond length is the equilibrium value, the potential energy is a minimum and the atoms are moving quickly so the kinetic energy is a maximum.

$$E_{total} = K_b(b - b_e)^2 + \frac{1}{2}mv^2$$
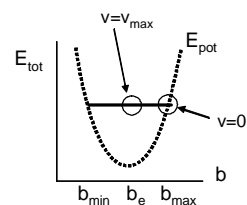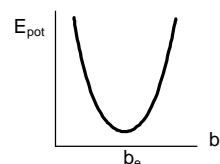
ELECTROSTATIC INTERACTION - ROLE OF THE MEDIUM

We can deal with solvent by explicitly calculating the electrostatic interactions between all the particles present. However, this is very complex so it is easier to make an approximation and treat the medium as a continuum (ignore the fact that it is made of molecules).

$$F = \frac{1}{4\pi\varepsilon_o\varepsilon}\frac{q_1 q_2}{r^2} \quad : \quad E = \frac{1}{4\pi\varepsilon_o\varepsilon}\frac{q_1 q_2}{r}$$

where ε is the dielectric constant of the medium. It is a measure of how much the surroundings shield one charge from the other. The larger the value of ε, the weaker is the interaction. This is equivalent to saying that the interaction is shorter range.

Medium	ε	r_{max}
Vacuum	1	540 Å
Middle of a lipid bilayer	~2	260 Å
Middle of a protein	~4	130 Å
Water	80	6 Å

r_{max} – longest distance over which the interaction of two ions of unit charge is significant at 300 K.

THE ENERGY OF A MOLECULE

We can obtain a simple classical relationship for all the forms of potential energy that a molecule possesses. This is called a molecular force field and allows us to calculate the energy of a whole molecule (or assembly of molecules).

$$E_{potential} = \sum_{bonds} K_b\left(b\text{-}b_{eq}\right)^2 + \sum_{angles} K_\theta\left(\theta\text{-}\theta_{eq}\right)^2 + \sum_{dihedrals} \frac{V_n}{2}\left[1+\cos\left(n\phi - \gamma\right)\right] + \sum_{i<j}\left[\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} + \frac{1}{4\pi\varepsilon_o\varepsilon}\frac{q_i q_j}{r_{ij}}\right]$$

Energy minimisation - We can calculate the potential energy for lots of different arrangements of atoms for the molecule (different bond lengths, bond angles, conformations) and choose the one(s) with the lowest energy. This will give us the most stable arrangement(s) of atoms, i.e. the most probable structure(s) for the molecule.

NEWTON'S LAWS OF MOTION

The behaviour of particles is governed by Newton's Law of motion (17th century).

1st Law : Every object in a state of uniform motion tends to remain in that state of motion unless an external force is applied to it.

2nd Law: The relationship between an object's mass m, its acceleration a, and the applied force F is F = ma. The direction of acceleration is the same as the direction of the applied force.

3rd Law: For every action there is an equal and opposite reaction.

Molecular dynamics - We can calculate the force on each atom in the molecule and use Newton's 2nd law to predict where each will move to after a short time. We can then repeat the calculation to build up a model of how the atoms in the molecule moves. This gives us information about the range of structures that a molecule can adopt and the dynamic properties (flexibility) of these structures.

CHARGED SPECIES IN AN ELECTRIC FIELD

A charged species in an applied electric field, Φ, will have an additional potential energy term due to its position in the field. A positive charge will be lower in energy in a negative electric field and higher in energy in a positive electric field.

$$E = q \times \Phi$$

A charged species in a field gradient will experience a force tending to make it move up or down the gradient (depending on its charge).

$$F = q \times \frac{d\Phi}{dr}$$

ELECTROPHORESIS

In electrophoresis, a charged molecule is placed in a medium (usually a gel) and an electric field gradient applied to the gel. The molecule experiences two forces;
1. an electrostatic force in the direction of the field gradient.
2. a frictional force in the opposite direction to motion, $F=f \times v$, where f is the frictional coefficient which depends on the interaction between the molecule and the medium.


Direction of motion with velocity v
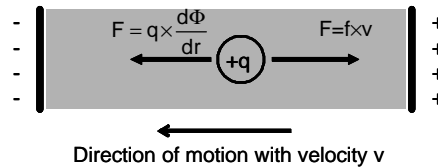
The molecule will initially accelerate in the direction of the electrostatic force until its velocity is sufficient for the frictional force to balance the electrostatic force. At that point the molecule will continue moving at constant velocity, v_{eq}.

$$q \times \frac{d\Phi}{dr} = f \times v_{eq}$$

$$\text{Electrophoretic mobility } (\mu) = \frac{v_{eq}}{d\Phi/dr} = \frac{q}{f}$$

μ depends on the charge, size and shape of the molecule.

A dipole will tend to align with an electric field.
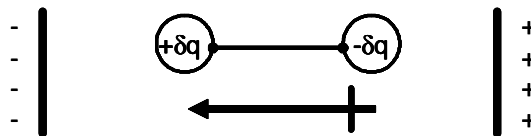
Summary so far ...

- Classical mechanics can be used to explain the macroscopic world.
- The classical world consists of particles and waves
- The behaviour of classical particles is governed by Newton's Laws.

CLASSICAL MECHANICS

Properties of a particle :
- It has mass
- Its position in space can be defined completely at any point in time (x, y, z co-ordinates or their equivalent).
- Its energy (given by the sum of kinetic and potential energies) can be defined completely at any point in time.
- It can have any amount of energy from zero to infinity.

Properties of a continuous wave :
- It extends from $+\infty$ to $-\infty$ and thus by definition has no position.
- It has no mass.
- It has a well defined frequency.
- Its energy is related to its intensity.
- As a wave can have any intensity, it can have any energy from zero to infinity.

BREAKDOWN OF CLASSICAL MECHANICS

Waves can behave as particles :-
- Shining light on a metal surface can provide a measurable force. Light has momentum and thus mass.

The energy of light does not depend on its intensity but its wavelength :-
- Shining light on a metal surface can cause electrons to be emitted. Using long wavelength light, even at very high intensity, does not produce electrons. Using short wavelength light, even at very low intensity, does produce electrons. At higher intensity more electrons are produced but each electron still has the same amount of residual kinetic energy. At shorter wavelength each electron produced has more residual kinetic energy.

Particles can behave as waves :-
- Electrons, neutrons and hydrogen nuclei can be diffracted by using an atomic diffraction grating (crystal) in exactly the same way that light can. They are not scattered randomly in all directions, but behave as though they are interacting waves.

Particles do not posses continuously varying energy :-
- Rotational, vibrational and electronic spectra of molecules consist of radiation emitted or absorbed at a series of discrete frequencies. Thus, molecules cannot rotate, vibrate, etc., at any speed but only at selected, predefined speeds.

WAVE-PARTICLE DUALITY OF EVERYTHING

As we have seen, particles can behave as waves and waves can behave as particles. Thus, the starting point is to come up with a description of matter and energy that explains this. It is probably easier to try and make a wave behave like a particle than visa-versa. Thus, we use a simple wave as a starting point.
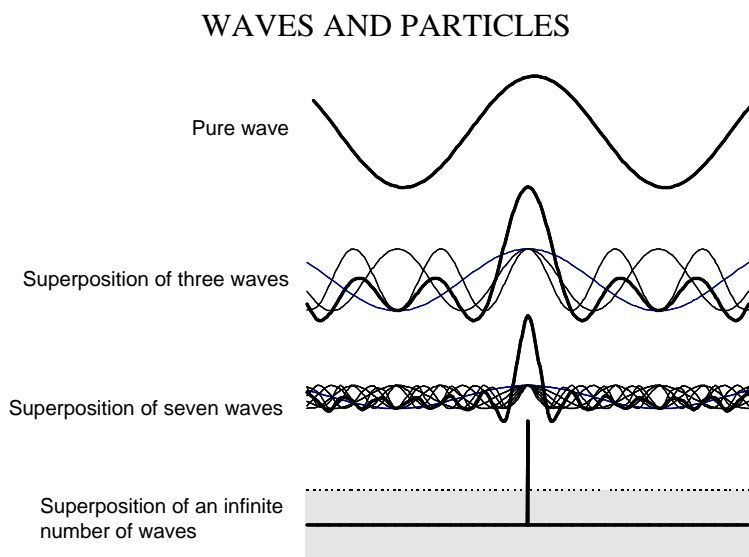
- Everything will be described as a wave or collections of wave.
        This description is called a wavefunction.
- Waves have **mass**.

This means that waves (and anything made by adding waves together) can have momentum.

- Particles will be described as **wave-packets**.

    This leads directly to the Uncertainty Principle and Zero-point energy.

- The **energy** of a wave-packet depends on its **wavelength**, not its intensity.

    The intensity is a measure of the number of wave-packets.

- **Localisation** of waves (or applying boundary conditions) gives rise to **quantisation** of energy (or energy levels).

The mathematical formalism of this is the Schrödinger equation (which we shall ignore).

WAVES AND PARTICLES

Pure wave

Superposition of three waves

Superposition of seven waves

Superposition of an infinite number of waves

Anything (light, electrons, nuclei, chairs, tables, etc.) behaves as a wave or a collection of waves. This is called the **wavefunction** of the object, usually given the symbol Ψ. Obviously, the more complex the object is, the more complex will be its wavefunction. For a wave, the square of Ψ at any point in space is simply its intensity - this is the same as classical mechanics. We use the square of the wavefunction because Ψ can be negative but we can't have a negative intensity.

Wave/Particle duality :-

For a "classical particle" (such as an electron) the square of Ψ at any point in space can be *interpreted* as the probability of finding the particle at that point [called the Born interpretation]. Usually we have to **normalise** the wavefunctions, so that the total probability of finding a particle somewhere in space is one. This does <u>not</u> mean that classical particles exist, they don't, it is simply a method of translating the wave properties of a particle into the classical properties that we find it easier to visualise.

THE DE BROGLIE RELATION

De Broglie provided a relationship between the momentum (p) of a particle and the wavelength (λ) of its associated wave (called the de Broglie wavelength).

$$\lambda = h / p$$

where h is Planck's constant. The kinetic energy (E) of a particle of mass m is given by;

$$E = \tfrac{1}{2} mv^2 = (mv)^2 / 2m = p^2 / 2m$$

These two equations can be combined to give;

$$E = \frac{h^2}{2m\lambda^2}$$

Consider an electron, mass of 9.109×10^{-31} kg, which has been accelerated to a velocity of 0.6×10^6 ms^{-1} (equivalent to an accelerating potential of approximately 1 V). The de Broglie wavelength is given by;

$$\lambda = \frac{h}{p} = \frac{h}{m\,v} = \frac{6.626 \times 10^{\cdot}}{(9.109 \times 10^{\cdot})\ x\ (0.6 \times 10^{\cdot})}$$

Thus;

$$\lambda = 1.2 \times 10^{-9} \text{ m} \quad \text{or} \quad 1.2 \text{ nm}$$

This is long compared to a typical chemical bond (0.1 nm) but short compared to the size of cell structures (such as membranes). So an electron microscope using electrons at this speed should be able to (and can) resolve major cellular components and membrane structure.

For an electron which has been accelerated to a velocity of 20×10^6 ms^{-1} (equivalent to an accelerating potential of approximately 1 kV), then;

$$\lambda \quad = 0.036 \text{ nm}$$

This is about one third the size of a typical chemical bond. So an electron microscope using electrons at this speed should be able to (and can in favourable cases) resolve the atomic structure of molecules.

HEISENBERG'S UNCERTAINTY PRINCIPLE

A pure wave has an absolute energy (the frequency is known) but the position is totally undefined.

A wave packet has an approximate position (not fully defined because it is spread out somewhat) and an approximate energy (not fully defined because a summation over many frequencies is required). The more frequencies we use, the better the position is defined and the worse the energy.

A classical particle has an absolute position (it exists at a single point) but the energy is totally undefined (to determine the energy requires the summation of an infinite number of frequencies).

This leads to one statement of Heisenberg's Uncertainty principle, which is;
"It is impossible to specify simultaneously, with arbitrary precision, both the energy and the position of a particle."
This can be expressed quantitatively as follows;

$$\Delta p \times \Delta q \ \geq \ \tfrac{1}{2}\,\hbar$$

where;

      Δp -- uncertainty in momentum
      Δq -- uncertainty in position
      $\hbar$ -- Plank's constant (h) divided by 2π

This principle applies to many different pairs of quantities as well, such as energy and time.

Consider a 65 kg person (not very large) running at 10 ms^{-1} (i.e. very fast). If his/her velocity is known to an accuracy of 0.001 ms^{-1} (about what can be measured on a running track), then the uncertainty in his/her position is;

$$\Delta q \ = h\,/\,2\Delta p \ = h\,/\,2m\Delta v \ = \ 8.1 \times 10^{-34} \text{ m}$$

This is not a significant number.

If we consider a molecule of molecular weight 100 (g mol^{-1}) travelling at the same speed, then the uncertainty in its position is;

$$\Delta q = h / 2.(M.Wt . x 10^{-3} / A).\Delta v = 3.2 \times 10^{-7} \text{ m}$$

where A is Avogadro's number. This is a significant number, over 100 times bigger than the molecule.

ZERO POINT ENERGY

One important implication of the Heisenberg Uncertainty Principle is the idea of zero-point energy. A particle must always retain a small amount of energy in some form even at absolute zero (0 K), called the zero-point energy. If a particle was completely still then both its energy (zero) and its position would be completely known and this contradicts the Uncertainty Principle. Alternatively, if a particle's energy is zero, then the uncertainty in its momentum (Δp) must be zero and thus the uncertainty in position (Δq) is given by;

$$\Delta q \geq h / 2\Delta p \geq h / 0 \geq \infty$$

Thus, the particle must exists everywhere in the Universe at once (assuming the Universe is infinite).

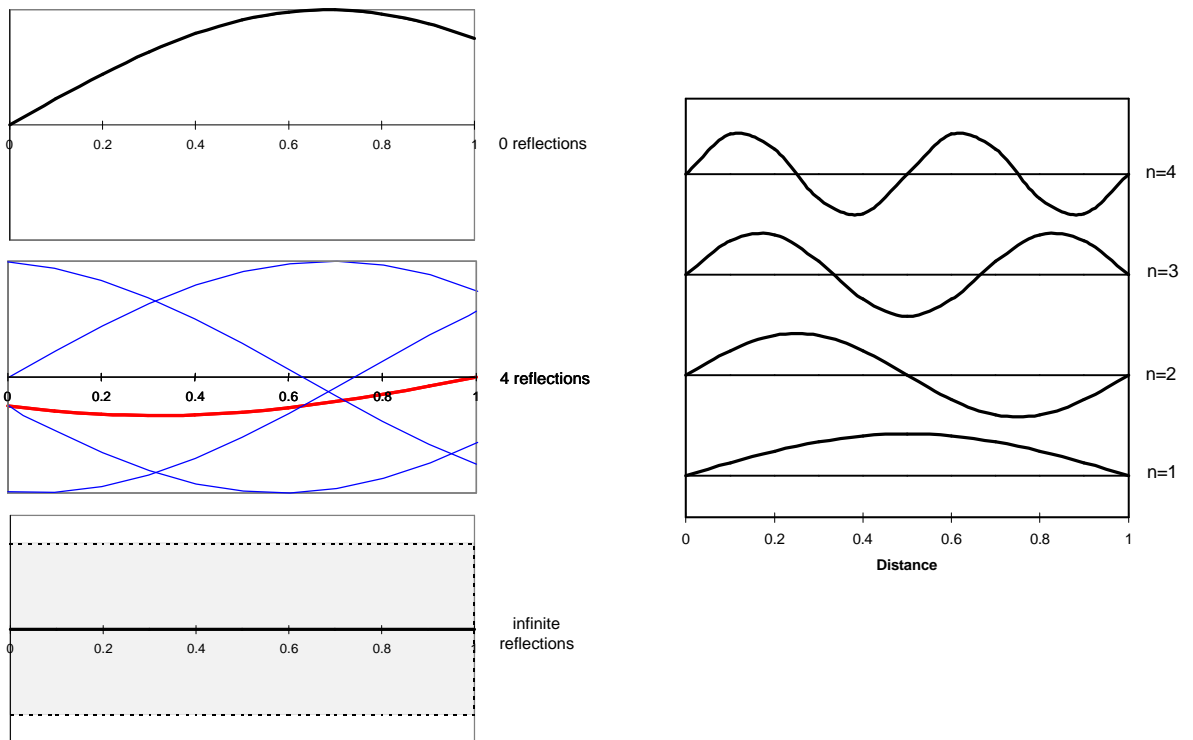# Classical and Quantum Mechanics 4

Summary so far …

- Classical mechanics doesn't work. Particles can behave as waves and visa versa.
- Everything can be described as a wave or a wave packet. A wave packet has the properties of both a wave and a particle.
- This description of an object is called its wavefunction.
- The wavelength of a "classical particle" can be determined from its momentum using the de Broglie relationship.
- Heisenberg's uncertainty principle and the idea of zero point energy are direct consequences of the wave nature of matter.

BOUNDARY CONDITIONS AND THE QUANTISATION OF ENERGY

A continuous wave (going from -∞ to +∞) can have any wavelength and so can have any energy. Similarly, a particle that is completely free can have any energy. Once a wave or particle becomes localised to a specific region of space (i.e. boundary conditions are applied that restrict its motion) then only certain wavelengths are allowed. Waves with other wavelengths cannot exist under these boundary conditions. As energy depends on wavelength, only certain energies (energy levels) are possible. This is the quantisation of energy.

Application of boundary   ⇒   Quantisation of
conditions   energy

A WAVE (OR PARTICLE) IN A BOX

The allowed wavefunctions for a particle in a box must be zero at each edge of the box. Then the reflected wave always adds to the initial wave. Thus, the allowed wavelengths must satisfy the equation

$$L = \tfrac{1}{2}\, n\, \lambda$$

where L is the length of the box, and n is an integer.

QUANTUM NUMBERS

In the case of a particle in a box, there are an infinite number of allowed wavelengths, for all the possible values of the integer n.

n is called a quantum number.

A particle in a box is simply a one-dimensional problem, thus we only need one quantum number to describe the system.

A quantum number tells us something about the **shape** of the allowed wavefunction.

For the particle in a box, there are (n-1) nodes for any given wave. As the energy of a wave depends on its shape, quantum numbers can be used to help calculate the energy.

ENERGY LEVELS FOR A PARTICLE IN A BOX

As only certain wavelengths for the particle in a box are allowed, the particle can only have certain specific energies. Its energy is quantised.

From the de Broglie relation;

$$E = \frac{h^2}{2m\lambda^2}$$

For a 1D box, L = ½ n λ, thus;

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

In order to move from one level (n) to a higher level (n'), the correct amount of energy (ΔE) must be put in.

$$\Delta E = \frac{n'^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2} = \frac{\left(n'^2 - n^2\right)h^2}{8mL^2}$$

If the available energy does not match this criterion, then it cannot be absorbed.

Note -- the spacing of the energy levels depends on the size of the box. If L is very large, then the energy separation is very small and visa versa. This is a general property of waves, the smaller the region over which the boundary conditions apply, the greater the energy separation.

ENERGY LEVELS IN MOLECULES

Molecules can have many different types of energy and nearly all of them are quantised. The more localised a wave the greater is the separation between energy levels and the smaller the mass the greater the separation.

Nuclear energy levels	Involve protons and neutrons in the nucleus	Very, very large energy separations $10,000,000 \text{ cm}^{-1}$
Electronic energy levels	Involve electrons close to nuclei	Very large energy separations $10,000 \text{ cm}^{-1}$
Vibrational energy levels	Involve a few atoms in the molecule	Medium energy separations 500 cm^{-1}
Rotational energy levels	Involves the whole molecule	Small energy separations 5 cm^{-1}

Translational energy levels	Involves the whole molecule moving over large distances	Effectively a continuum (not quantised)

BOLTZMANN DISTRIBUTION

When we consider chemical systems, they are made up of a very large number of molecules. The thermal collisions between molecules (Brownian motion) mean that energy can pass from one molecule to another. Thus, they will not all have the same energy but there will be a random distribution over the available energy levels, given that the total energy must be constant. The Boltzmann distribution states that at a given temperature, T, the ratio of the number of molecules with energies E_i and E_j is given by;

$$\frac{n_i}{n_j} = \exp\left(\frac{-(E_i - E_j)}{kT}\right)$$

where k is the Boltzmann constant. Note: n_i must always be less than n_j if E_i is greater than E_j (i.e. the lower state is always more populated.

An alternative way of expressing the Boltzmann distribution is as the probability, $P(E_i)$, of a molecule having a specific energy, E_i. This is given by;

$$P(E_i) = \frac{n_i}{N} = \frac{\exp\left(\frac{-E_i}{kT}\right)}{\sum_j \exp\left(\frac{-E_j}{kT}\right)}$$

where N is the total number of molecules and the summation is taken over all occupied energy levels. Note: as before if E_i gets bigger, $P(E_i)$ gets smaller.
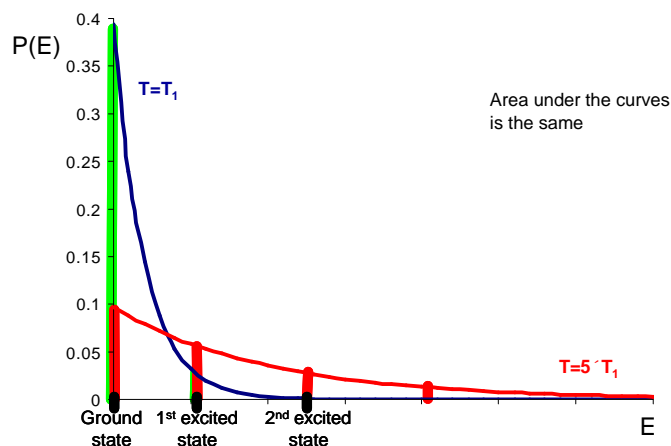
Consider the following typical separations between energy levels relevant to three different types of spectroscopy;

NMR	$\Delta E = 1.19 \times 10^{-2}$ J mol^{-1}
Rotational	$\Delta E = 11.9$ J mol^{-1}
Electronic	$\Delta E = 119 \times 10^3$ J mol^{-1}

As ΔE is in J mol^{-1}, we have to divide by Avogadro's number (L) to give ΔE in J per molecule. Thus;

$$\frac{n_{upper}}{n_{lower}} = \exp\left(\frac{-\Delta E}{LkT}\right)$$

At room temperature, this gives the ratio for n_{upper} to n_{lower} as follows;

NMR	0.9999952
Rotational	0.9952

Electronic	1.86×10^{-21}

The excited energy levels for both NMR and rotational spectroscopy are populated at room temperature whilst very nearly all molecules are in the electronic ground state.

The sensitivity of a spectroscopic technique depends on the population difference between the ground and excited states. If this difference is small then only a few molecules can be excited before the system becomes saturated (the same number of molecules in both states). At room temperature, the ratio for n_{upper} to n_{lower} are as follows;

NMR	0.9999952
Rotational	0.9952
Electronic	1.86×10^{-21}

For NMR only one molecule in every one hundred thousand will give a signal, whereas in electronic spectroscopy every molecule will give a signal. Thus, electronic spectroscopy is potentially one hundred thousand times more sensitive than NMR.
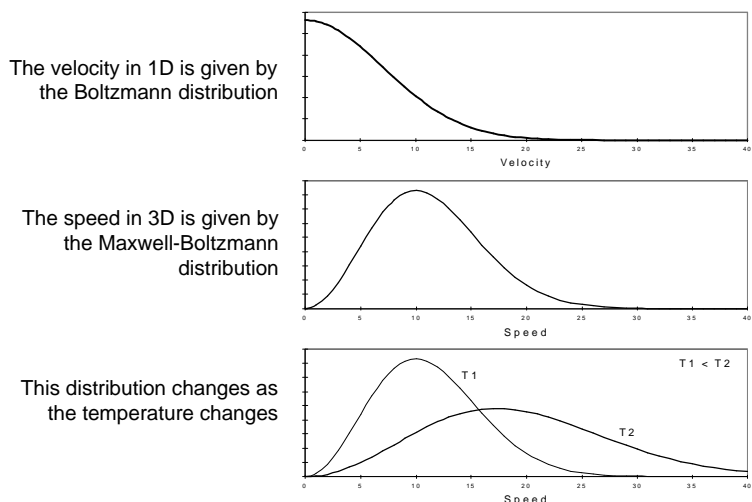
MAXWELL-BOLTZMANN DISTRIBUTION

When considering the translational motion of molecules, the situation is slightly more complex because molecules can move in three dimensions. However, we are usually interested in how fast a molecule is moving, not in which direction it is going.

Velocities in any one $\Rightarrow$ Boltzmann
dimension   distribution

To get the distribution of speeds, we need to consider the sum of the probabilities in all three directions. This tends to emphasise medium speeds.

Low speed	Must be going slowly in all three dimensions	Low probability
Medium speed	Could be; 1.going slowly in two dimensions and fast in onegoing a medium speed in all three dimensions	High probability
High speed	Must be going fast in all three dimensions	Low probability

The velocity in 1D is given by the Boltzmann distribution

The speed in 3D is given by the Maxwell-Boltzmann distribution

This distribution changes as the temperature changes

Summary so far …

- Classical mechanics doesn't work. Particles can behave as waves and visa versa.
- Wave theory leads directly to the Uncertainty Principle and the idea of Zero-point Energy.
- Localisation of a wave (applying boundary conditions) results in only certain wavefunctions being allowed. These are characterised by quantum numbers. This leads to the quantisation of energy.
- The probability of finding a molecule in a specific energy state is given by the Boltzmann distribution.
- When considering translational motion in three-dimensions rather than one, the range of speeds is given by the Maxwell-Boltzmann distribution.

WAVE PICTURE OF AN ATOM

Electrons behave as waves and are localised around the nucleus. As they are localised waves, only certain wavefunctions will be allowed and so their energies will be quantised. These allowed wavefunctions are called atomic orbitals. As atoms are small and electrons have a very small mass, the energy separation between allowed states will be large. The energy of an electron in an orbital is determined by the electrostatic interactions with the nucleus and with other electrons.

Electrons orbit the nucleus of an atom and so can be considered as particles on the surface of a sphere. We can treat this problem in an identical way to that of a particle in a box, but as a sphere is a bit difficult to visualise we will start with a wave on a circle.
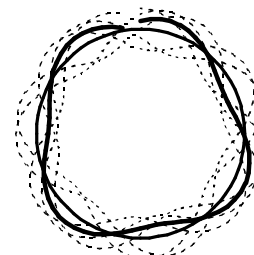
QUANTISATION OF WAVES ON A CIRCLE
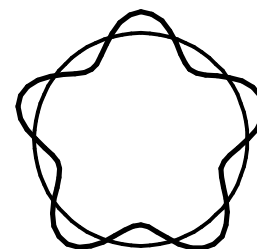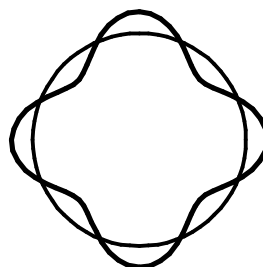
For a wave of arbitrary wavelength;

Superposition of 2 waves   Superposition of 5 waves
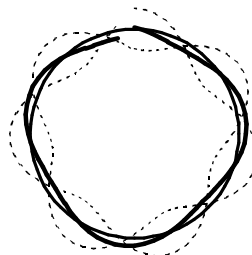
As before the superposition of many waves will lead to perfect cancellation, unless the waves always add. This will happen if the circumference of the circle is an exact multiple of the wavelength.
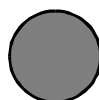

ALLOWED WAVES ON A CIRCLE

These are based on the allowed wavefunctions of a particle on a sphere (the three dimensional equivalent of a particle on a circle). The angular quantum number for a particle on a circle is l, which gives the number of angular nodes.
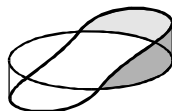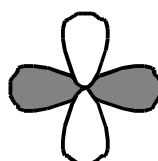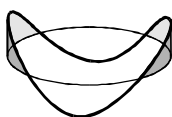
l = 0

s-orbital

l = 1

p-orbital

l = 2

d-orbital

ORBITAL QUANTUM NUMBERS

Quantum number	Value		Description
n	0,1,2, ...	radial	Distance from the nucleus
l	0,1,...,(n-1)	angular	Number of angular nodes
m	0,±1,...,±l	angular	Angular direction

These three are exactly analogous to simple polar co-ordinates (r,ϕ,ψ). However, they do not give the exact spatial co-ordinates of the electron (as polar co-ordinates do in classical mechanics) but instead give the probability that an electron will be found at that point in space.

ORBITAL SHAPES

1s
n=1 l=0 m=0

2s
n=2 l=0 m=0

2p$_x$
n=2 l=1 m=-1

2p$_y$
n=2 l=1 m=+1

2p$_z$
n=2 l=1 m=0

3s
n=3 l=0 m=0

3p$_x$
n=3 l=1 m=-1

3d$_{xy}$
n=3 l=2 m=+2

3d$_{x2-y2}$
n=3 l=2 m=-2
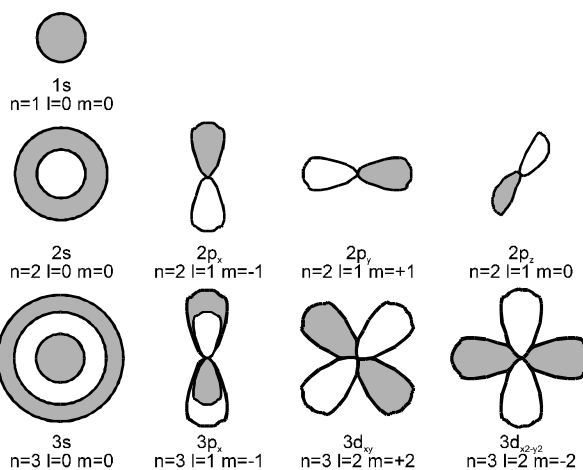
ORBITAL ENERGIES

The energy of a given orbital depends on the *electrostatic interactions* that occur between;
1. The electron and the nucleus (attraction)
2. The electron and other electrons (repulsion)

in the atom. These electrostatic interactions depend on the distances between the electrons and nucleus and thus on the shapes and sizes of the orbitals.

For the orbitals within a specific atom;
- The closer the electron is to the nucleus (smaller value of n) the lower the energy.
- The more diffuse the orbital (smaller value of l) the less electron-electron repulsion there is.

This leads to the general order;

$$1s < 2s < 2p < 3s < 3p < 3d$$

for any atom with more than one electron.

Examples –

The 2s orbital in H is at the same energy as the 2p orbital because there is only one electron and so electron-electron repulsion is not relevant and energies are only determined by distance from the nucleus.

The 2s orbital in Li is at a lower energy than the 2p orbital because there is now more than one electron and there is greater electron-electron repulsion for an electron in a 2p orbital (l=1) than in a 2s orbital (l=0)

RELATIVE ORBITAL ENERGIES IN DIFFERENT ATOMS

For a given atomic orbital (n, l, m), the only difference between atoms is the nuclear charge and the number of electrons. The increased attraction from the larger nuclear charge always outweighs the increased repulsion from more electrons.

Examples –

The 1s orbital in Li is lower in energy than the 1s orbital in H because the atomic charge of the former is greater (3 compared to 1).

The 2s orbital in Li is at about the same energy as the 3s orbital in Na because the increase in distance for the latter (n=3 for Na compared to n=2 for Li) and increase in electron-electron repulsion (there are 10 other electrons present in Na compared to 2 in Li) is counterbalanced by an increase in nuclear charge (11 for Na compared to 3 for Li).

ELECTRON SPIN

Electrons have an extra property i.e. they have a magnetic moment. This arises from the internal motion of the electron (not the motion around the nucleus), called the electron spin.

Quantum number Value		Description
s	$\pm \frac{1}{2}$	Direction of the internal motion of the electron

PAULI EXCLUSION PRINCIPLE

"No two electrons can have the same set of quantum numbers"

i.e. no two electrons can continuously occupy the same space. If they do occupy the same space (n, l and m the same), then their time evolution (s) must be different. This means that only two electrons can occupy any one orbital. Another implication of the Pauli Exclusion Principle is that electrons in the same shell (n, l) with the same spin will repel each other less than those with opposite spins, i.e. two electrons in the same shell with the same spin are more stable than with opposite spins.

AUFBAU (BUILDING UP) PRINCIPLE

The electron configuration can be determined by always putting the next electron into the lowest energy orbital available. This will give the ground state (lowest energy state) for the atom.

Given the large energy separation between orbital energy levels, only the ground state will be populated at normal temperatures.
e.g.

H	1 electron	$1s^1$
He	2 electrons	$1s^2$
Li	3 electrons	$1s^2 \, 2s^1$
F	9 electrons	$1s^2 \, 2s^2 \, 2p^5$
Si	14 electrons	$1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^2$

For part filled orbitals, the electrons will prefer to be unpaired.

VALENCE ELECTRONS AND CHEMISTRY

Valence electrons are the electrons that can be involved in bonding. These are the highest energy electrons, i.e. the electrons in the highest energy atomic orbitals.

The chemical properties of an element are determined by the:
- number of valence electrons;
- energies of the valence electrons;
- size and shape of the atomic orbitals containing the valence electrons.

The energies of the valence electrons:
- decrease rapidly across the periodic table;
- increase slowly down the periodic table.