

Course Aims

After completing each chapter of this course, you should be able to do the following.

Chapter 1 - Origins of QM

- Describe and explain some of the scientific discoveries that led to the breakdown of classical mechanics in the late 19th century.
- Describe what a **wavefunction** is, and explain how they can be calculated by solving the **Schrödinger Equation**. Describe what makes a wavefunction acceptable or not.
- Qualitatively explain the **Born Interpretation** of the wavefunction, and explain how it allows wavefunctions to be **normalised**. Be able to normalise simple wavefunctions via integration.
- Explain **operators and observables**, and how **observables** correspond to **operators**. Calculate observables from operators and simple wavefunctions.
- Explain why the **Hamiltonian Operator** is special, and explain what observable it calculates.
- Show that the Schrödinger Equation is a kind of **eigenvalue equation**. Be able to show that a wavefunction is an eigenfunction of a specific operator algebraically.
- Give the expression for the **expectation value** of an operator, and apply it to simple examples to calculate expectation values.
- Qualitatively explain **The Uncertainty Principle** in terms of position and momentum.
- Explain the significance of the **commutator** in quantum mechanics.
- Summarise the five **Postulates of Quantum Mechanics** given at the end of this chapter.

Chapter 2 - Translational Motion

- Describe the meaning of **translational motion** and give the **Hamiltonian** for a particle free to move in one dimension.
- Using a given wavefunction and Hamiltonian, be able to calculate the energy eigenvalue for a particle free to move in one dimension. Explain the significance of the quantity $k\hbar$.
- Qualitatively explain the concept of **quantisation of energy**, and explain how and when it arises.
- Being given all relevant wavefunctions and Hamiltonians, be able to derive an expression for the energy of a particle confined to a one dimensional box. Show algebraically why this energy is **quantised**.
- Explain the significance of the **quantum number** n .
- Sketch the first three wavefunctions for a particle in a box and explain the trend in energies using wavelength as an illustration. Explain how the spacing between adjacent levels changes as the quantum number increases.
- Explain the concept of the **zero-point energy** in quantum mechanics.

- Give a qualitative description of the **Quantum-Classical Correspondence Principle**, and illustrate the description with the probability distributions for a particle in a box at various values of n .

Chapter 3 - Vibrational Motion

- Explain what a **harmonic oscillator** is using classical mechanics. Understand **Hooke's Law**, including the significance of the force constant, k .
- Give an expression for the potential energy V , for a particle trapped in a **harmonic well**. Sketch how changing the value of k will affect the resulting potential.
- Give the Schrödinger Equation for a **quantum harmonic oscillator**. Quote the expression for the **vibrational energy levels**. Explain the significance of ω , with reference to both k and m .
- Sketch the first few vibrational energy levels in a sketch of a harmonic potential. Explain how the **level spacing** differs from a particle in a one dimensional box.
- Identify the **normalisation constant**, **Hermite Polynomial**, and **Gaussian Function** in a given general vibrational wavefunction.
- Sketch the first few vibrational wavefunctions and their probability distributions, using the sketches to illustrate both the **Quantum-Classical Correspondence Principle** and the **zero-point energy**.
- Explain the vibrational zero point energy in terms of a **classical pendulum**.

Chapter 4 - Rotational Motion

- Define **angular momentum**, **angular velocity**, and **moment of inertia** in classical terms. Contrast them to their linear analogues. Explain how angular momentum depends on moment of inertia.
- Give expressions for **rotational and translational kinetic energy**, in terms of both **velocity** and **momentum**.
- Sketch the **particle on a ring** system, and explain how the Hamiltonian is constructed in comparison to the translational Hamiltonian.
- Verify that given wavefunctions are eigenfunctions of the given Hamiltonian, and produce the energy eigenvalues. Explain the significance of the quantity $m_l \hbar$ in comparison to $k \hbar$ from translations.
- Explain qualitatively the meaning of the **cyclic boundary condition**. Show mathematically that this leads to **quantised angular momentum**.
- Explain the additional complexities that arise when moving from a **particle on a ring** to a **particle on a sphere**.
- State that the wavefunctions for the particle on a sphere are given by the **Spherical Harmonics**. Explain the significance of the spherical harmonics in the context of **atomic orbitals**.
- Explain the physical meanings of l and m_l . Be able to give a reasonable sketch of the **vector model**, and explain how it demonstrates **quantised angular momentum**.
- State the allowed values for l and m_l , and reflect on this in terms of **atomic orbitals**.
- Give the expression for the energies of a particle on a sphere, and comment on this in relation to known expressions from rotational spectroscopy.

Chapter 5 - The Born-Oppenheimer Approximation

- Outline why **The Born-Oppenheimer Approximation** is necessary in chemistry, and explain what it is in terms of the separability of nuclear and electronic wavefunctions.
- Explain in what circumstances we are able to invoke the Born-Oppenheimer Approximation, with a discussion of different **timescales** and **energies**.
- Describe how the Born-Oppenheimer Approximation allows molecular potential energy curves to be calculated.
- Explain why, as spectroscopists, we are able to **extend** the Born-Oppenheimer Approximation to encompass all different modes of molecular motion (translation, rotation, vibration, and electronic).
- State how this allows us to separate the **total molecular energy** into **constituent parts** from each type of molecular motion. Explain why this is useful for physical chemists.

Chapter 6 - Rotational and Vibrational Quantisation of Molecules

- Explain how spectroscopy can provide information about molecules by the **interaction of molecules and EM radiation**.
- State the **Bohr Frequency Condition**, and explain all the terms in the equation.
- State the expression for **rotational energy** in **wavenumbers**, and calculate **rotational constants** with given data.
- Derive the expression for the **rotational line spacing**, and explain how it changes as J increases.
- State the **gross** and **specific** rotational **selection rules**. Qualitatively explain their origins.
- Explain how the concept of the **reduced mass** allows diatomic molecules to be modelled as a simple **mass on a spring**. Calculate reduced masses using given data.
- State the expression for **vibrational energy** in **wavenumbers**, and calculate the value of $\tilde{\nu}$ using given data.
- Qualitatively explain the **limitations of the harmonic oscillator model**, and explain how using **anharmonicity** can get round them.
- Sketch a **harmonic potential** and a **Morse potential**, showing the key differences, and explaining why a **Morse potential** is more accurate for molecules.
- State the **gross** and **specific** vibrational **selection rules**. Explain qualitatively where they come from.