## Lecture Synopses for Course A

### *Introduction to Quantum Mechanics: 12 lectures*

**Dr S. C. Althorpe**

The principles of Quantum Mechanics underlie all of chemistry at the molecular level, and provide a foundation on which the subsequent courses in Chemistry A are built. This course will introduce the fundamental ideas of quantum mechanics, and show how they may be applied to some simple but important examples: the harmonic oscillator, the rigid rotor and the hydrogen atom.

From there we shall move on to many-electron atoms and the consequences of electron spin, and finally show how the variation principle leads to an understanding of chemical bonding.

Mathematically, all that is required is some fluency with Part IA Mathematics (course A).

The practical course in the Michaelmas Term contains a set of computer-based exercises designed to illustrate the contents of this course.

### *Molecular Spectroscopy: 6 lectures*

**Dr P. D. Wothers**

Spectroscopy provides us with some of the best evidence for the quantization of energy. This course is integrated with the Quantum Mechanics course and illustrates how the key ideas may be used to understand the appearance of spectra and allow us to determine fundamental molecular parameters. The course also provides the background for the laboratory sessions where you will be able to put the theory into practice.

We shall start with the rotational spectra of diatomic molecules and its applications from microwave spectroscopy in the labs, which allows us to determine bond lengths in simple molecules, to radio astronomy which allows us to determine the composition of heavenly bodies. We shall then examine vibrational spectroscopy using both the harmonic oscillator and Morse oscillator as models. Finally, we shall touch on the electronic spectroscopy of atoms and simple molecules.

### *Symmetry and Bonding: 12 lectures*

**Dr J. H. Keeler**

Humans seem to have an innate ability to recognise and appreciate the symmetry of objects, and chemists seem to be especially fascinated by molecules or other structures which display high or unusual symmetry. In this course we will show how *Group Theory* provides a formal framework for describing the symmetry of molecules and how this theory can be used as a powerful tool for predicting the properties and behaviour of molecules. In particular we will look at how symmetry helps us to construct molecular orbital (MO) diagrams and then how these can be used to understand key properties such as shape or stability.

We will also see how symmetry helps us to understand the vibrations of molecules via a normal mode analysis. Finally, we will look at how we can actually calculate the energies

and form of the MOs in simple molecules using the Hückel approach. The application of symmetry to such calculations results in considerable simplification.

This course will take a relatively informal approach to Group Theory with the emphasis being on developing a practical set of tools which can be applied with ease.

> **Introducing Group Theory** Symmetry elements and symmetry operations. Point groups. Character tables. Representations. Direct products.
>
> **Applications** Vanishing integrals. Symmetry orbitals and molecular orbitals. Transition metal complexes. Walsh diagrams. Hückel MO calculations. Normal mode analysis and vibrational spectroscopy. Electronic states.

## *Molecular Energy Levels and Thermodynamics: 13 lectures*

### Dr M. A. Miller

Quantum mechanics provides us with a detailed description of the energy levels of single atoms and molecules, but when we are doing chemistry we deal not with one molecule at a time but vast numbers. The question is, then, how are the properties of bulk matter related to the energy levels of the molecules of which it is composed? The methods of *statistical thermodynamics*, which are introduced in this course, make this connection. In particular, we will see how the thermodynamic properties of matter (internal energy, entropy, Gibbs energy etc.) can be calculated from a knowledge of the molecular energy levels. As you will have seen in the earlier courses, these energy levels can be predicted by quantum mechanics and determined experimentally from spectroscopy. We will also investigate the Boltzmann distribution which is used to understand many molecular phenomena.

The course closes with a number of applications of the ideas developed in the earlier part. We will look at how it is possible to understand the temperature variation of heat capacities, and how it is possible to predict the values of equilibrium constants simply from spectroscopic data. Statistical thermodynamics can also be used to predict the values of reaction rate constants using transition state theory. We will look at how this is developed and the interpretation of the parameters involved.

> **Topics**  Review of thermodynamic ideas: the Second Law, internal energy, the Gibbs and Helmholtz functions. Microstates and macrostates: the canonical distribution function, the partition function and thermodynamics quantities.
>
> Evaluation of the partition function: translation, rotation and vibration.
>
> Internal energy and heat capacities; temperature variation. Calculation of absolute entropies.
>
> Chemical equilibrium and the prediction of equilibrium constants.
>
> Transition state theory: concept of a potential energy surface and the transition state; formulation in terms of partition functions; comparison with collision theory. Thermodynamic formulation.
>
> The Boltzmann distribution; applications in spectroscopy. Density of states.

## *Electronic Structure and Properties of Solids: 16 lectures*

### Dr S. J. Jenkins and Prof S. R. Elliott

The objective of this course which spans the Lent and Easter terms is to introduce the concepts of structure and bonding that are required to explain the behaviour of electrons in solids. The course is designed in such as way that it builds upon the material presented

in all of the preceding courses in Chemistry A. At the heart of the course lie two contrasting models for the behaviour of electrons in solids – the free electron and the LCAO models.

Free electron theory is used as a starting point, because it is simple and it permits the introduction of essential concepts such as wavevectors, travelling waves and the fermi surface. However, this theory does not take account of the presence of atoms and orbitals and offers no structural predictions. LCAO theory is used to show how atomic orbitals may be used as a basis for constructing wavefunctions appropriate for solids. This theory is used to explain the bonding and energy bands in a wide variety of solids.

Many of the most important properties of solids are controlled by the presence of defects – semi-conductors provide the best example of this. The last part of the course shows that defects are inevitable and describes the effect they have upon the electronic structure of solids.

No prior knowledge of the structure of solids will be presumed. The course will provide a self contained and concise summary of the concepts that are required to understand the fundamentals of solid state electronic structure and how this structure determines the properties of crystalline solids.

**Lent Term**

> Introduction. Free electron theory of solids. Travelling waves, wavevectors and the Fermi surface. Fermi energies and Fermi levels. Electrical conductivity. Experimental techniques for investigating the electronic structure of solids. Failures of the free electron theory. Crystalline lattices described by repetition of a unit cell.

**Easter Term**

> The LCAO theory of solid, atomic orbitals and bands. Crystal wavefunctions and Bloch's theorem. One-dimensional chain of H atoms. Orbital topology. Electrical conductivity, effective mass and the concept of "holes". One-dimensional solids: polyacetylene and chain compounds.

> Atomic and electronic structure of solids. Crystal structures. One-dimensional solids. Two-dimensional solids. Band structures of three-dimensional solids.

> Semiconductors: Science and applications. Intrinsic semiconductors. Extrinsic semiconductors. Optical spectroscopy of solids. Applications of doped semiconductors.

## Recommended Books for Chemistry A

These recommended books should be in your College Library. They can also be consulted in the Departmental Library, and some are available on short loans.

### Quantum Mechanics

Green N.J.B. *Quantum Mechanics 1: Foundations*, Oxford Chemistry Primers, 1997.
For reference: McQuarrie, D.A, and Simon, J.D, *Physical Chemistry: A Molecular Approach*, University Science Books, 1997.
For reference: Atkins P.W. & Friedman R.S. *Molecular Quantum Mechanics*, 3rd edition, O.U.P., 1997.
Steiner E. *The Chemistry Maths Book*, O.U.P., 1996.

### Molecular Spectroscopy

Banwell, C. and McCash, E., *Fundamentals of Molecular Spectroscopy*, 4th edition, McGraw Hill
For reference: McQuarrie, D.A, and Simon, J.D, *Physical Chemistry: A Molecular Approach*, University Science Books, 1997.

### Symmetry and Bonding

Vincent A. *Molecular Symmetry and Group Theory*, 2nd edition, Wiley, 2001.
For reference: Cotton F.A. *Chemical Applications of Group Theory*, Wiley, 3rd Edn, 1990.
For reference: McQuarrie, D.A, and Simon, J.D, *Physical Chemistry: A Molecular Approach*, University Science Books, 1997.

### Molecular Energy Levels and Thermodynamics

Maczek A.O.S *Statistical Thermodynamics* (Oxford Chemistry Primers 58), OUP 1998.
Gasser R.P.H. and Richards W. G. *An Introduction to Statistical Thermodynamics*, World Scientific, 1995.

### Electronic Structure and Properties of Solids

Smart, L. and Moore, E., *Solid State Chemistry*, 2nd Edn, Chapman and Hall, 1996
West, A.R., *Basic Solid State Chemistry*, Wiley 1988
Cox P.A. *The Electronic Structure and Chemistry of Solids*, Oxford Science Publication, 1992.
For reference: Singleton J., *Band Theory and Electronic Properties of Solids*, OUP 2001.
For reference: Elliott S. R. *Physics and Chemistry of Solids*, Wiley 1998.