GROUP THEORY FOR ATOMS, MOLECULES AND SOLIDS

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Preface

This text has arisen out of a course of lectures on the physical applications of group theory, given for several years at Heriot-Watt University, and a longer course on group theory and semiconductor energy-band theory given at North Texas State University.

The aim is to establish, at a level suitable for those new to the ideas of group theory, the basic requirements for understanding the electronic band structure of solids and those transitions between the energy levels that can be excited by incident electromagnetic radiation. In so doing the groundwork is developed for an understanding of absorption selection rules in atoms and molecules as well as solids, of the vibrational properties of molecules and solids, and of non-radiative scattering processes in solids.

The text is divided into five parts. Part One contains chapters on the basic ideas of group theory, in Part Two group theory is used to solve the classical problem of the oscillations of a harmonically coupled system, and the electronic quantum states of atoms and molecules are discussed in Part Three. Part Four is concerned primarily with selection rules for transitions between electronic states and between states of the quantized coupled oscillators. Finally in Part Five the symmetries of crystalline materials are described and applied to the modelling of electron energy bands of solids.

In general each of the nineteen chapters of the text relies on material presented in earlier chapters. Rather than present all of the concepts of group theory in an initial section, they are introduced as they are needed, in the context of the problem being tackled. Thus, for example, direct product groups do not appear until Chapter 13. Equally Wigner's theorem is introduced in Chapter 7, to bridge the gap between symmetry ideas and the physical problems of interest. This theorem is introduced for use in the normal-mode problem, which is considered to be more intuitive than the quantum problems tackled in Chapters 9–19.

The course has been given as a final year course, corresponding in length to a US one-semester course, and as part of a course for experimental post-graduate students wishing to become familiar with the notation and the essential techniques of group theory. However, very little background knowledge is demanded. Success in use of the text demands a willingness to think in three dimensions and patience in bearing with the new vocabulary until it is used in physical situations. A small amount of previous experience of matrices, harmonic oscillation and semiconductor physics is useful but not essential. The reader will need to be familiar with the basic ideas of quantum mechanics.

My thanks are due to many people for helping me put this text together; to my family for putting up with my absences, to Art Smirl who conned me into writing up my notes in the first place, to the students who suffered the growing pains of the text, and to my typists – Becky, June and Janice.

Brian S. Wherrett

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PART ONE

SYMMETRY IDEAS

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1

An introduction to group theory

Group theory, in its application to physics, is concerned with the necessary consequences of symmetry.

By use of group theory one obtains physically significant results that are a consequence purely of the symmetry of the system under investigation. The techniques of group theory are deceptively simple, enabling conclusions to be drawn without recourse to detailed mathematics. The underlying theme of symmetry and the elegance of the methods of application combine to produce in applied group theory one of the most beautiful theoretical topics in physics.

Throughout most of this text group theory will be used to exploit the symmetrical configurations of atoms that occur in many molecules and solids. It is, however, worth mentioning briefly some well-known results of other forms of symmetry, which emphasize its significance throughout physics. From a classical viewpoint continuous translational symmetry, that is the absence of a force or the invariance of the energy of a system with respect to some direction in space, leads to the conservation of the linear momentum of the system. Continuous rotational symmetry, the invariance of energy with angle or the absence of a torque about some axis, leads to the conservation of angular momentum about the axis. Also continuous temporal symmetry is equivalent to conservation of energy. Conservation properties form the very root of physics as a discipline; without conservation we would find great difficulty in any attempt to model nature mathematically.

From a quantum-mechanical viewpoint it is necessary to include the ideas of boundary conditions in a discussion of symmetry. Thus, for example, bounded periodic, rather than continuous, translational symmetry leads to

the use of discrete **k**-wavevectors to label the states of crystal excitations, and leads to discrete energy eigenvalues. The rotational symmetry of atoms, coupled with the finite and single-valued properties of electronic eigenfunctions, leads to discrete angular momenta and energies and to the use of good quantum numbers to label eigenstates.

Given the extremely powerful results to which continuous symmetries lead it might well be expected that the discrete symmetries with which we are primarily concerned in this text are also to be associated with conservation properties of some sort, and with state labelling. As we shall discover the latter is one of the major results of group theory.

Now the basic problem of quantum mechanics, considered in detail in Chapter 8, is the solution of the Hamiltonian equation in terms of eigenfunctions and energy eigenvalues. The problem can take the following mathematical forms:

$$\mathcal{H}\psi = E\psi; \tag{1.1}$$

$$[a]^{-1}[\mathcal{H}^f - ES^f][a] = [\mathcal{E} - E]; \tag{1.2}$$

$$[\mathcal{H}^f - E_n S^f]\begin{bmatrix} a_{1n} \\ a_{2n} \\ \vdots \end{bmatrix} = 0. \tag{1.3}$$

The details of these equations are not of immediate concern; we need only recognize that the first is a differential equation and that the latter two are *matrix equations*. Solution of the Hamilton equation leads to a set of eigenfunctions ψ_n that describe distributions of the particles in the allowed states of the quantum system, and the energies of these states. In turn a knowledge of the ψ_n allows one to determine how the system would respond to any given external influence (for example an incident beam of electromagnetic radiation, or an applied static field).

Group theory has the following uses in the quantum problem. Firstly it allows one to determine the symmetry properties of the possible states even though the precise form of the distribution functions, ψ_n, might not be known. Secondly, it is often the case that for a given E_n there is more than one distinct eigenfunction; such functions are said to be degenerate. The second use of group theory is in determining such degeneracies of the states of a system. With a knowledge of the state symmetries, further application of group theory allows the form of a response of the system to be predicted. For example one can determine whether or not radiation can excite a molecule from any one particular state to another.

Additionally, if one does wish to solve the matrix equations, which generally requires computational methods, group theory may be used to reduce the dimensions of the matrices one has to deal with, with considerable savings in time.

Because it is difficult to think intuitively about quantum-mechanical eigenfunctions, the techniques of applied group theory will be introduced here by considering instead the coupled-oscillator problem. This problem is solved in classical physics by exactly the same matrix methods as those required for the above quantum problem. Thus if we imagine a set of masses mutually attached by springs, there will be some equilibrium condition—a configuration of the system as a whole—for which all the masses are stationary. The coupled oscillator problem sets out to answer the question: 'If the system is displaced slightly from equilibrium, then what is the subsequent motion of each mass?' Mathematically this problem is manifested by matrix equations which have identical form to equations (1.2) and (1.3) above:

$$[\alpha]^{-1}[K^d - M^d\omega^2][\alpha] = [\Omega - \omega^2 I] \tag{1.4}$$

or

$$[K^d - M^d\omega_i^2]\begin{bmatrix} \alpha_{1i} \\ \alpha_{2i} \\ \vdots \end{bmatrix} = 0. \tag{1.5}$$

In these equations K^d and M^d are known as force and mass matrices and are obtained from a knowledge of the potential and kinetic energies of the system of masses under a set of displacements from their equilibrium positions (Chapter 6). For a system containing N masses, each able to move in any of three perpendicular directions, there are $3N$ solutions for ω_i, and $3N$ associated sets of α_{ji} values. Each solution represents a normal mode of oscillation of the system.

To appreciate the simplicity of the consequences of symmetry consider the model, pictured in Figure 1.1, which is trivial to construct.

I want to concentrate on the motion, along their line of connection, of the two symmetrically placed 100 gramme masses. This system has just two degrees of freedom; the smaller mass is uniquely positioned once the positions of the others are set. Hence any displacement can be defined in terms of two vectors. If mass 1 is displaced by a small amount and mass 2 held at the equilibrium, on releasing the masses, 1 begins to oscillate but its amplitude is damped rapidly and 2 oscillates. The converse occurs and then the motion repeats periodically. However, as far as each mass is concerned, it does not undergo a simple harmonic motion. By direct contrast if both masses are moved to the same side, by the same small amplitude, and released, then they oscillate back and forth, in phase, at some frequency ω_1. Alternatively if they are given equal but opposite initial displacements they subsequently oscillate π out of phase, at a frequency ω_2. These two modes of motion of the system are termed the normal modes; ω_1, ω_2 are the natural frequencies. The more complex motion obtained from any other initial conditions may be modelled by some linear combination of the normal mode displacements.

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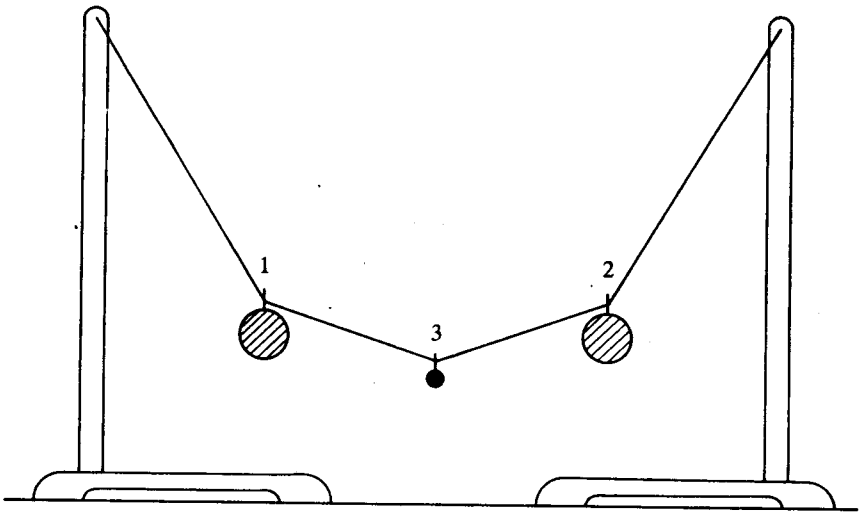

Figure 1.1 Model of a system that demonstrates the symmetry of normal modes. Masses 1 and 2 are 100 grammes each. Mass 3 is far lighter. Effectively the system acts, in the plane of the masses, like a pair of harmonic oscillators coupled together by the connecting line and the small mass. A weak spring can in principle be used instead to couple masses 1 and 2, but the demonstration is easier to set up as indicated.

The most important point to be brought out here though is that both normal modes are highly symmetric—in some way they display the symmetry of the system.

The classical coupled oscillator is a useful macroscopic model for the vibrational motion of the nuclei in a molecule; the nuclei are coupled through the electrostatic forces between all the particles in the molecule. Therefore the first type of problem to which we shall apply group theory will correspond to the analysis of the vibrations of a polyatomic molecule, such as NH_3 (ammonia) or C_6H_6 (benzene) which have high symmetry. In the benzene case it would require the construction and diagonalization of a 36×36 matrix in order to determine the number of distinct natural frequencies, their values and the displacements. Group theory tells us almost immediately that there are only 24 such frequencies and that the solution of eight 2×2 matrices and two 4×4 matrices will give us the remaining information.

Having obtained a set of eigenvectors and frequencies or, in quantum mechanics, a set of eigenfunctions and energy eigenvalues, the next question one asks is how can one excite the vibrations, or how can transitions be

excited from one energy level to another. Again group theory can provide the answer. Whether the excitation is to be by the absorption of radiation, or by some scattering process, group theory will tell us if it can be accomplished.

What group theory itself will not tell us, without recourse to further analysis, is the magnitude of any of the parameters discussed above—the value of natural frequencies or energies, or the strengths of excitation—the so-called transition matrix elements. Group theory gives us yes–no selection rules.

The remaining chapters in Part 1 are included in order to introduce the basic concepts and to build up the vocabulary of group theory. Where possible group theoretical ideas are introduced by inspection of particular groups of symmetry operations; certain important results are given without any attempt at rigorous proof. The reader is referred to the more abstract mathematical texts on group theory for these proofs, as indicated in the bibliography at the end of the book.

The problems provided with each chapter serve two purposes. Problems marked with an asterisk should be considered as essential exercises; they are included in order to allow the reader to test his/her understanding of the text material. Other problems are included in order to indicate some of the features of group theory that are not considered to be crucial to progress through the present text.

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