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Classically Quantum

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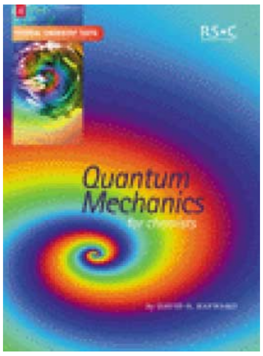

Quantum Mechanics for Chemists

David O. Hayward

Royal Society of Chemistry, Cambridge, U.K.
2002, 200 pp.
ISBN 0-85404-607-0
Softcover, 13 GBP.

The problem with a title like *Quantum Mechanics for Chemists* is that it immediately puts us on our guard. What does it mean? Is the author suggesting that quantum mechanics comes in different flavours and that the present book confines its attention to the version that governs chemistry? Surely not, since quantum mechanics is held to be a universal truth that permeates all of the physical sciences and binds them into a unified whole. Perhaps, then, the book's scope is restricted to those aspects of quantum mechanics that a chemist would find interesting? Or, maybe, those aspects that a chemist would be able to understand…? But neither of these can be right, for the family of chemists includes a wide variety of species and it seems inconceivable that any one glove could possibly fit them all.

Fortunately, the back cover sheds some light on the matter, informing us that the book is designed to provide chemistry undergraduates with a basic understanding of quantum mechanics and that it is intended to follow a basic course in organic and/or inorganic chemistry. The Preface adds that the book should therefore be used either towards the end of the first undergraduate year, or in the second year, after introductory courses on bonding have been given. Chemistry students at Nottingham are given an intense four-week course on atomic and molecular structure at the beginning of First Year and I have therefore examined Dr Hayward's book with such students in mind.

The back cover notes that the approach taken is rather different from that in most books on quantum chemistry, for wavefunctions are introduced first (chapter 1), followed by Schrödinger equations (chapter 4) and, finally, by Hamiltonians (chapter 7). Why does the author present his material in this way? Because he believes that it is pedagogically sound. He writes that 'although [the reverse] approach is logical, it seems to leave most students feeling bewildered' and those of us who have tried this experiment ourselves can certainly recall students who fit this description. Furthermore, it must be admitted that the author's ordering is faithful to the historical development of the subject: de Broglie, then Schrödinger, then the formalists. Nonetheless, I am not convinced that the book entirely achieves its aims.

Chapter 1 concerns itself with particle–wave duality and begins with a potted history that mentions Newton, Huygens, Young, Planck, Einstein, Millikan, Compton, de Broglie, and culminates in the Davisson–Germer experiment. The discussion leans heavily on electron diffraction experiments and makes extensive use of metallic surfaces, rather than atoms or molecules, for illustration. Will target students feel at home with this introduction? Perhaps, but it felt strangely eclectic to me.

Chapter 2 is short and is devoted to the description of a quantum mechanical particle in a one-dimensional box. The time-independent wavefunctions appear but their form is justified by the classical and time-dependent assertion that 'the particle will be continually colliding with the walls and having its momentum reversed.' Will such an explanation seem plausible to the thoughtful student? Or will it simply lead to the misapprehension that quantum mechanics is a time-averaged form of classical mechanics? The chapter then turns to applications of the model and its discussions of an electron trapped in a semiconductor quantum well and of a π electron in a conjugated molecule are chemically interesting. The chapter concludes with a selection of relevant problems.

Chapter 3 is also short and introduces the notion of the Heisenberg uncertainty principle. As in chapter 1, the diffraction of electrons from metal surfaces is used to illustrate the key points but, unfortunately, the presentation is again marred by the use of a dubious classical analogy. Contrary to the implications of the author's discussion, there is no uncertainty principle for the motion of a wave in classical mechanics.

In chapter 4, we meet the Schrödinger equation and things get better. Being able to abandon his strained analogies with classical mechanics, the author shows neatly how the de Broglie relation can be combined with a general wave equation and the result used to understand both the harmonic oscillator and tunnelling. From these, he sheds light on both the infrared spectra of diatomic molecules and the principles behind the scanning tunnelling microscope. Despite the presence of a brief and unhelpful detour back into classical mechanics (in a section entitled 'Can particles really have negative kinetic energy?'), I would recommend that a student using this book skip straight to this chapter.

Chapter 5 deals with rotational motion and discusses the particle on a ring and the particle on a sphere. There is not much chemistry here and most of the target students will find the maths overwhelming but, for those who survive, this leads to a helpful discussion of the spherical harmonics. The section on spin is problematic, for it begins with the statement that 'many elementary particles have an intrinsic angular momentum which can be considered to arise from the particle spinning on its axis' and, once again, a needless return to classical mechanics risks leaving our target student bewildered and confused. Electron spin does *not* result from the rotation of the electron on its axis. Electrons are *not* the tiny billiard balls shown in Figure 5.15 and we should not mislead our students by stating otherwise. If we remove this classical analogy, the remainder of the chapter is very good and it concludes with some helpful problems.

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Chapter 6 presents a detailed description of the orbitals in a hydrogen atom but I suspect that this is much too late. In a book specifically designed for chemists, one would surely expect to encounter atoms before the antepenultimate chapter! The treatment of the radial and angular parts of the hydrogenic orbitals is clear and well illustrated but, once again, problems arise when the author tries to illuminate his subject by reverting to a classical description. It is simply not true that 'an s electron must undergo an oscillatory motion in a straight line through the nucleus, similar to that of a harmonic oscillator' and the associated diagram (Figure 6.8) is meaningless and misleading. A page or two later, we learn that a p electron 'is circulating around the nucleus in the *xy* plane.' This may be the picture that emerges from the old Bohr theory, but it is certainly not the modern quantum mechanical one.

Chapter 7 introduces the Hamiltonian operator and develops the independent-electron model for many-electron atoms. The presentation here is clear and purposeful and the reader is shown the simplicity that underlies the Hartree–Fock approximation. Electron correlation should not merit much space in an elementary textbook but the author's assessment that 'it is very difficult to make proper allowance for [correlation] in calculations' is at least thirty years out of date. The Aufbau principle and Hund's rule are explained well and the periodicity of atomic ionization energies is also lucidly presented. The problems at the end of the chapter illustrate the chapter's key points reasonably well.

The final chapter is entitled 'The Structure of Molecules' and is deservedly the longest (42 pages) in the book. The reader is led through the variation principle and the Born–Oppenheimer approximation to the concept of the molecular orbital and the potential energy surface. Here is real chemistry, where bonds are formed and broken! The description of the orbital energies of homonuclear and heteronuclear diatomics is fulsome and is well illustrated with both diagrams and tables. Valence Bond Theory and Molecular Orbital Theory are then briefly compared and the chapter ends with a description of Hückel theory and ten problems that, as usual, illuminate the major issues covered in the chapter.

The book's strengths are its approachable size (184 pages), its attention to scientific history, its end-of-chapter problems (with answers), and its uncluttered layout. Its weaknesses are its devotion to dubious classical interpretations of quantum mechanical phenomena, its dated content, and, in my view, its backwards chapter ordering. Quantum mechanics is a difficult subject to teach because, as Feynmann remarked, no-one really understands it. However, it is important that the modern chemistry graduate is familiar with its chemical consequences and can use it to comprehend structure, bonding, and reactivity. This book touches upon some of these matters but its treatment lacks the clarity and, sometimes, the correctness of books such as *Physical Chemistry* by Peter Atkins.

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