

Quantum Mechanics

This book has developed from the author's four decades of zealous teaching of classical mechanics, quantum theory, and atomic physics at premium IITs in India, and from his lectures on these subjects delivered for the popular National Programme on Technology Enhanced Learning (NPTEL) and SWAYAM PRABHA online channels, which are effective initiatives of the Government of India.

Quantum Mechanics: Formalism, Methodologies, and Applications covers the current curriculum requirements of most courses offered in different programs of physics. It will be particularly useful for masters and PhD students taking core courses on quantum mechanics, atomic, molecular, and optical physics, condensed matter, and nuclear and particle physics. It will also be useful to students learning quantum information science and quantum computing. It discusses a wide range of topics beginning with a pedagogical formulation of quantum mechanics including vector space formalism, matrix mechanics, path integrals, and also relativistic quantum mechanics. Quantum mechanics of many-electron atoms is discussed, and applications in spectroscopy and quantum collisions are covered. Topics like the optical and the reciprocity theorems, Eisenbud–Wigner–Smith scattering time delay, and an introduction to quantum computing and teleportation are also included. These topics represent major milestones in the advances in our understanding of atomic physics and condensed matter. They have propelled revolutions in nanosciences and nanotechnologies, atomic clocks and ultrafast dynamics, and quantum information science and quantum computing. *Quantum Mechanics: Formalism, Methodologies, and Applications* would serve a modern graduate curriculum very well, since it provides a rapid but gentle ramp-up from the basics of quantum mechanics to the methodologies of its applications in the frontiers technology.

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Formalism, Methodologies, and Applications

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*To my teachers with much gratitude
and
to my students with best wishes*

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Foreword

Since its formulation during the first part of the twentieth century, quantum mechanics has fascinated everybody who has tried to grasp it. Classical physics regarded the world to be deterministic; it claimed that if we just knew everything with enough precision, we should be able to predict what will happen tomorrow. Laws of nature, however, can be best explained by quantum mechanics, which is very different from classical physics: only the probability of a certain outcome of an experiment can be predicted. There is also a fundamental limit to how precisely certain pairs of physical quantities can be measured: when we improve the precision of measurement of one quantity, we lose it on another! Even more mind-boggling is the concept of entanglement. Two entangled particles can travel far from each other and still have a connection so that measurements on one of them immediately forces the other into a specific quantum state, regardless of the distance between them. Through the history of quantum mechanics, accomplished scholars and students alike have found this hard to accept, and argued that the theory must not be complete, that we are still waiting for its final version. Nevertheless, quantum mechanics has been proven to be a very successful theory. As far as we know, its predictions are all correct and technologies based on quantum mechanics are nowadays used everywhere: the smart electronic devices in our pockets, the energy efficient LED lamps, and the solar panels that harvest sunlight – deep inside they function because of the laws of nature explained by quantum mechanics.

It is often said that it is not possible to really understand quantum mechanics. This might be true, but with enough effort it is certainly possible to learn to master its machinery and use it to explain physical phenomena and develop new technology. Professor Pranawa Deshmukh writes in this book: “Quantum theory may shock and confuse us, but it is a successful theory of the physical world. It is cast in a mathematical framework which must be learned with patience and rigour.”

As a university teacher I know that the first course in quantum mechanics brings something special to many students. While classical physics seems to be completely settled and just for new generations to learn, quantum mechanics comes with surprises, riddles, and philosophical discussions. This book acknowledges this fascination; it does not compromise with the mathematical tools needed to be able to use the theory. Starting with the question of measurement and the wave–particle duality, the book continues along a path that takes the reader from the solutions of a particle in a box, through the harmonic oscillator and to the hydrogen atom, but it does not stop there. A whole chapter is devoted to many-electron systems. Here the necessity to approximate the many-problem is elaborated and several common approximations are explained. Advanced topics such as the path integral formulation of quantum mechanics, the role of symmetry, and the

relativistic equation of Dirac are also covered and carefully integrated with the more traditional textbook content. The book comes with many solved problems, invaluable for the serious students and each chapter of the book starts with an historical photograph and an interesting quote from an important scientist, which nicely sets the theme for the following pages.

This is a broad and modern approach to the subject. It includes material for a longer graduate course that will prepare students in many subfields of physics. Its strength is the coverage of important applications of quantum mechanics, often subjects of contemporary research. Ample space has been provided, for example, to the use of transitions from one quantum state to another. Radiation waves emitted or absorbed during such transitions are fingerprints of the particular atom or molecule and can be used to analyse the element composition and temperature of distant stars and galaxies. Even the atmosphere of extra-terrestrial planets can today be studied with such spectroscopic methods. Collisions, involving both particles and photons, are treated with equal care and include a discussion on how time-reversal symmetry relates the seemingly different processes of particle scattering and photoionization.

The discussion on the measurement problem does not stop with the debate between Bohr and Einstein in the 1930s. This discussion was in fact just the starting point for the field of quantum information science. The inequality that was formulated by John Bell took the question of realism from being a philosophical issue to speculate on, to a question that could be settled with experiments. Bell's inequality is here discussed in detail, as is quantum teleportation and the theoretical foundations of quantum computing. Today, 'entanglement' is not just something to be puzzled about, but a reality that can be utilized in quantum computers. The in-depth discussion on these issues underlines a contemporary approach to the subject taken in this textbook.

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Preface

A graduate course on quantum mechanics is a daunting task – for both students and teachers. Students come for such a course with a fair amount of background in classical physics, *classical* in the sense that it is time-tested. They are familiar with the works of Newton, Lagrange, Hamilton, Euler, etc. In this scheme, an object's physical state is described by its position q and momentum p , and temporal evolution by Hamilton's equations of motion for the time rates \dot{q} and \dot{p} . Their experience with classical physics entrenches their faith in it and builds their intuition, but they must now be taught that a physical theory that requires simultaneous knowledge of position and momentum is *fundamentally untenable*. Students must now settle with the fact that classical mechanics 'works' only when it is a very good approximation to a *more appropriate* theory of Nature, which is quantum mechanics. The foundational principles of quantum mechanics *conflict* with those of classical physics, causing confusion and doubt. Overcoming the resulting befuddlement involves learning what seems like an *abstract* formalism, which nonetheless turned out to be an unassailable theory of practical value. It changed our lives in the last century with quantum devices, and is now all set to take another leap into the second quantum revolution. It ushers in mind-blowing technology driven by entanglement and quantum computing.

The route to diligent applications of quantum mechanics begins with a *shock*. Students must grapple with formidable challenges on the path to comprehending consequential principles in a mystified territory. They have to develop proficiency in new methodologies involving abstract mathematics before they can see for themselves that quantum theory simply *works*; *nothing succeeds like success*. They can then use the theory to propel the frontiers of sciences, engineering, and technology. Amid this bewilderment, a graduate course in quantum mechanics is as romantic as it is challenging. One must learn to see beyond the corners of your vision, acquire rigorous capabilities in mathematics, enjoy luminous discourses between brilliant minds, cultivate an inventiveness to develop new technology that impacts human life, and understand the cosmos. *Quantum mechanics: formalism, methodologies, and applications* is a vast subject, very young compared to classical physics, but a very rich field to which some of the most outstanding intellectuals have made dazzling contributions during the past hundred odd years.

Some of my colleagues were surprised when a little over three years ago Cambridge University Press published my *Foundations of Classical Mechanics* (FoCM). They had expected that I would write a book on *quantum mechanics*, not *classical*. FoCM sets the stage for the present book: concepts, vocabulary, and notations employed in it are frequently referred to in *Quantum Mechanics: Formalism, Methodologies, and Applications*. This book has grown out of joyful improvisations I have labored over four decades to provide graduate students with a

rapid, but gentle, ramp-up from foundational principles of quantum theory to advances in its practices of contemporary interests. We emphasise that there aren't two sets of laws of Nature, one for the microscopic and the other for the macroscopic world. In Chapter 1, we jump without much ado into the vector space formulation of quantum mechanics with a brief comment on the incompatibility of measurement of position and momentum using the Heisenberg microscope. We discuss the *complete set of compatible observables* and proceed to deliberate on Heisenberg's principle of uncertainty, and also on the Schrödinger equation. Chapter 1 also compares, and contrasts, the energy–time uncertainty with that in position–momentum. We underscore the fact that a system has *discrete* or *continuum* energy eigenstates depending on the boundary conditions on the Schrödinger equation.

The sequencing of topics in this book is perhaps a bit untraditional, but purposefully so. Immediately after introducing foundational principles in Chapter 1, we introduce in Chapter 2 Feynman's path integral formulation, along with a discussion on the geometrical phase, because of the importance of the *phase* of the wavefunction. The mindboggling Aharonov–Bohm effect is also discussed in this chapter. Chapter 2 also includes a commentary on why classical mechanics works at all, when and where it does. Chapter 3 is primarily dedicated to simple one-dimensional problems, whose applications go as far as laying the foundations of nanoscience, but it also includes a relatively new method to solve quantum mechanical problems using the Lambert W function, developed by S. R. Valluri and Kenneth Roberts.

The *shock* from the simultaneous immeasurability of position and momentum is accentuated by that of the impossibility of determining orthogonal components of angular momentum. We appreciate the role of symmetry and conservation laws in formulating laws of nature, and enter an analysis of the angular momentum in considerable detail in Chapter 4. In Chapter 5, we use it to understand quantum mechanics of the hydrogen atom from the standpoint of the geometrical, and also the dynamical, symmetry of the Coulomb interaction. Discrete bound states spectrum and the continuum eigenstates of the hydrogen atom are both discussed.

Approximation methods are dealt with in Chapter 6, but degenerate perturbation theory is deferred to Chapter 8 on Stark–Lu Surdo, Zeeman, and hyperfine spectroscopies. Perturbative interpretation of relativistic effects is discussed in the context of the Foldy–Wouthuysen transformations of the fully relativistic Dirac Hamiltonian in Chapter 7, which also presents a decoupling of the radial and the angular parts of the relativistic 4-component wavefunction – notwithstanding the presence of *odd* operators in the Dirac Hamiltonian. We stress that there aren't two laws, a *relativistic* law for particles moving at high speeds, and another *nonrelativistic* for those at low speeds. A fundamental particle *even at rest* has an intrinsic 'spin' angular momentum (discussed in Chapters 4 and 7, in particular), which requires *relativistic quantum mechanics* for its interpretation. It is this property that makes a particle a Fermion or a Boson.

The many-electron self-consistent field (Hartree–Fock) theory of the atomic structure is detailed in Chapter 9. In Chapter 10, on scattering theory, pedagogical treatment of the partial-waves analysis is boosted to explicate the role of time-reversal symmetry which connects solutions of quantum collisions with those from photoionization/photodetachment spectroscopy. This chapter discusses the optical theorem, reciprocity theorem, Eisenbud–Wigner–Smith time delay, Born approximations, Green function methods, etc.

We accentuate the fact that it is misleading to say that quantum theory is mind-boggling and counter-intuitive; rather, it is Nature which is – quantum theory describes it correctly. *Apparently* strange phenomena occur in Nature, not in theories. To an uneducated intuition, they appear strange. One requires a reinterpretation of *reality*, which paves the way to quantum computing and

to the *second* quantum revolution. Chapter 11 provides an introduction to quantum computing, teleportation, and dense coding.

Quantum mechanics is a vast subject. We attempt to lay down a strong foundational formalism, move up to exemplify intricate methodologies, and exhibit significant applications which impact advances in engineering and technology. We hope this approach will help students and researchers to gain confidence in deploying crucial quantum tools resourcefully. We celebrate the interlacing of mathematics with the physical laws of Nature and hope that the coverage of each topic is satisfactory. An attempt has been made to maintain the presentation simple by focusing on the main ideas, and relegating some details to either a few problems at the end of each chapter, or to an appendix. Chapter 5 (on the non-relativistic hydrogen atom) has five appendices, 5A–5E, to provide necessary details with regard to the continuum eigenfunctions of the hydrogen atom, and about the symmetry group of the Coulomb potential, which accounts for the degeneracy of its discrete eigenstates. There also are five appendices (A–E) at the *end* of the book. These include a brief commentary on the role of *discrete symmetries*, a summary of Schrödinger, Heisenberg, and Dirac pictures of quantum mechanics, a brief account of the spherical harmonics, a short introduction to *second* quantization, and a shorter introduction to the Variational Quantum Eigensolver to simulate a many-electron system using *qubits*. Readers would benefit by regarding the appendices and the end-of-chapter problems as *vital* and *integral* content of the subject matter.

The contents of this book provide a compilation of my lecture notes prepared for a number of courses I had the opportunity to teach over four decades at the Indian Institute of Technology Madras, at the Indian Institute of Technology Mandi, at the Indian Institute of Technology Tirupati, and at the Indian Institute of Science Engineering and Research Tirupati. The course contents also benefited from video-lecture courses I had the opportunity to deliver for the NPTEL (Physics - Select/Special Topics in Atomic Physics - YouTube, <https://www.youtube.com/playlist?list=PLbMVogVj5nJQAcTv17ETSh5-GNDbAo6BM>, and Physics - Special/Select Topics in the Theory of Atomic Coll - YouTube, <https://www.youtube.com/playlist?list=PLbMVogVj5nJSdsqPcC1J9SmCuKg5DIUwn>) and for SWAYAM PRABHA (Special/Select Topics in Classical and Quantum Physics - YouTube, https://www.youtube.com/playlist?list=PLJoALJA_KMOAbZCaNzL28v8zqa0mpewf7). Parts of the contents of Chapter 11 have also been taught at the Dayananda Sagar University, Bengaluru. I am indebted to each of these institutions for giving me an opportunity to teach their students which has been an amazing learning experience for me.

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