INTRODUCTION TO QUANTUM MECHANICS

THIRD EDITION

DAVID J. GRIFFITHS
DARRELL F. SCHROETER

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Third edition

Changes and additions to the new edition of this classic textbook include:

- A new chapter on Symmetries and Conservation Laws
- New problems and examples
- Improved explanations
- More numerical problems to be worked on a computer
- New applications to solid state physics
- Consolidated treatment of time-dependent potentials

David J. Griffiths received his BA (1964) and PhD (1970) from Harvard University. He taught at Hampshire College, Mount Holyoke College, and Trinity College before joining the faculty at Reed College in 1978. In 2001–2002 he was visiting Professor of Physics at the Five Colleges (UMass, Amherst, Mount Holyoke, Smith, and Hampshire), and in the spring of 2007 he taught Electrodynamics at Stanford. Although his PhD was in elementary particle theory, most of his research is in electrodynamics and quantum mechanics. He is the author of over fifty articles and four books: *Introduction to Electrodynamics* (4th edition, Cambridge University Press, 2013), *Introduction to Elementary Particles* (2nd edition, Wiley-VCH, 2008), *Introduction to Quantum Mechanics* (2nd edition, Cambridge, 2005), and *Revolutions in Twentieth-Century Physics* (Cambridge, 2013).

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Preface

Unlike Newton's mechanics, or Maxwell's electrodynamics, or Einstein's relativity, quantum theory was not created—or even definitively packaged—by one individual, and it retains to this day some of the scars of its exhilarating but traumatic youth. There is no general consensus as to what its fundamental principles are, how it should be taught, or what it really "means." Every competent physicist can "do" quantum mechanics, but the stories we tell ourselves about what we are doing are as various as the tales of Scheherazade, and almost as implausible. Niels Bohr said, "If you are not confused by quantum physics then you haven't really understood it"; Richard Feynman remarked, "I think I can safely say that nobody understands quantum mechanics."

The purpose of this book is to teach you how to *do* quantum mechanics. Apart from some essential background in Chapter 1, the deeper quasi-philosophical questions are saved for the end. We do not believe one can intelligently discuss what quantum mechanics *means* until one has a firm sense of what quantum mechanics *does*. But if you absolutely cannot wait, by all means read the Afterword immediately after finishing Chapter 1.

Not only is quantum theory conceptually rich, it is also technically difficult, and exact solutions to all but the most artificial textbook examples are few and far between. It is therefore essential to develop special techniques for attacking more realistic problems. Accordingly, this book is divided into two parts;[1] Part I covers the basic theory, and Part II assembles an arsenal of approximation schemes, with illustrative applications. Although it is important to keep the two parts *logically* separate, it is not necessary to study the material in the order presented here. Some instructors, for example, may wish to treat time-independent perturbation theory right after Chapter 2.

This book is intended for a one-semester or one-year course at the junior or senior level. A one-semester course will have to concentrate mainly on Part I; a full-year course should have room for supplementary material beyond Part II. The reader must be familiar with the rudiments of linear algebra (as summarized in the Appendix), complex numbers, and calculus up through partial derivatives; some acquaintance with Fourier analysis and the Dirac delta function would help. Elementary classical mechanics is essential, of course, and a little electrodynamics would be useful in places. As always, the more physics and math you know the easier it will be, and the more you will get out of your study. But quantum mechanics is not something that flows smoothly and naturally from earlier theories. On the contrary, it represents an abrupt and revolutionary departure from classical ideas, calling forth a wholly new and radically counterintuitive way of thinking about the world. That, indeed, is what makes it such a fascinating subject.

At first glance, this book may strike you as forbiddingly mathematical. We encounter Legendre, Hermite, and Laguerre polynomials, spherical harmonics, Bessel, Neumann, and Hankel functions, Airy functions, and even the Riemann zeta function—not to mention Fourier transforms, Hilbert spaces, hermitian operators, and Clebsch–Gordan coefficients. Is all this baggage really necessary? Perhaps not, but physics is like carpentry: Using the right tool makes the job *easier*, not more difficult, and teaching quantum mechanics without the appropriate mathematical equipment is like having a tooth extracted with a pair of pliers—it's possible, but painful. (On the other hand, it can be tedious and diverting if the instructor feels obliged to give elaborate lessons on the proper use of each tool. Our instinct is to hand the students shovels and tell them to start digging. They may develop blisters at first, but we still think this is the most efficient and exciting way to learn.) At any rate, we can assure you that there is no *deep* mathematics in this book, and if you run into something unfamiliar, and you don't find our explanation adequate, by all means *ask* someone about it, or look it up. There are many good books on mathematical methods—we particularly recommend Mary Boas, *Mathematical Methods in the Physical Sciences*, 3rd edn, Wiley, New York (2006), or George Arfken and Hans-Jurgen Weber, *Mathematical Methods for Physicists*, 7th edn, Academic Press, Orlando (2013). But whatever you do, don't let the mathematics—which, for us, is only a *tool*—obscure the physics.

Several readers have noted that there are fewer worked examples in this book than is customary, and that some important material is relegated to the problems. This is no accident. We don't believe you can learn quantum mechanics without doing many exercises for yourself. Instructors should of course go over as many problems in class as time allows, but students should be warned that this is not a subject about which *any*one has natural intuitions—you're developing a whole new set of muscles here, and there is simply no substitute for calisthenics. Mark Semon suggested that we offer a "Michelin Guide" to the problems, with varying numbers of stars to indicate the level of difficulty and importance. This seemed like a good idea (though, like the quality of a restaurant, the significance of a problem is partly a matter of taste); we have adopted the following rating scheme:

- ⋆ an *essential* problem that every reader should study;
- ⋆⋆ a somewhat more difficult or peripheral problem;
- ⋆⋆⋆ an unusually challenging problem, that may take over an hour.

(No stars at all means fast food: OK if you're hungry, but not very nourishing.) Most of the one-star problems appear at the end of the relevant section; most of the three-star problems are at the end of the chapter. If a computer is required, we put a mouse in the margin. A solution manual is available (to instructors only) from the publisher.

In preparing this third edition we have tried to retain as much as possible the spirit of the first and second. Although there are now two authors, we still use the singular ("I") in addressing the reader—it feels more intimate, and after all only one of us can speak at a time ("we" in the text means you, the reader, and I, the author, working together). Schroeter brings the fresh perspective of a solid state theorist, and he is largely responsible for the new chapter on symmetries. We have added a number of problems, clarified many explanations, and revised the Afterword. But we were determined not to allow the book to grow fat, and for that reason we have eliminated the chapter on the adiabatic approximation (significant insights from that chapter have been incorporated into Chapter 11), and removed material from Chapter 5 on statistical mechanics (which properly belongs in a book on thermal physics). It goes without saying that instructors are welcome to cover such other topics as they see fit, but we want the textbook itself to represent the essential core of the subject.

We have benefitted from the comments and advice of many colleagues, who read the original manuscript, pointed out weaknesses (or errors) in the first two editions, suggested improvements in the presentation, and supplied interesting problems. We especially thank P. K. Aravind (Worcester Polytech), Greg Benesh (Baylor), James Bernhard (Puget Sound), Burt Brody (Bard), Ash Carter (Drew), Edward Chang (Massachusetts), Peter Collings (Swarthmore), Richard Crandall (Reed), Jeff Dunham (Middlebury), Greg Elliott (Puget Sound), John Essick (Reed), Gregg Franklin (Carnegie Mellon), Joel Franklin (Reed),

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[1] This structure was inspired by David Park's classic text *Introduction to the Quantum Theory*, 3rd edn, McGraw-Hill, New York (1992).

Part I
Theory

1
The Wave Function

1.1 The Schrödinger Equation

Imagine a particle of mass *m*, constrained to move along the *x* axis, subject to some specified force $F(x,t)$ (Figure 1.1). The program of *classical* mechanics is to determine the position of the particle at any given time: $x(t)$. Once we know that, we can figure out the velocity $(v = dx/dt)$, the momentum $(p = mv)$, the kinetic energy $\left(T = (1/2)mv^2\right)$, or any other dynamical variable of interest. And how do we go about determining $x(t)$? We apply Newton's second law: $F = ma$. (For *conservative* systems—the only kind we shall consider, and, fortunately, the only kind that *occur* at the microscopic level—the force can be expressed as the derivative of a potential energy function,[1] $F = -\partial V/\partial x$, and Newton's law reads $m\, d^2x/dt^2 = -\partial V/\partial x$.) This, together with appropriate initial conditions (typically the position and velocity at $t = 0$), determines $x(t)$.

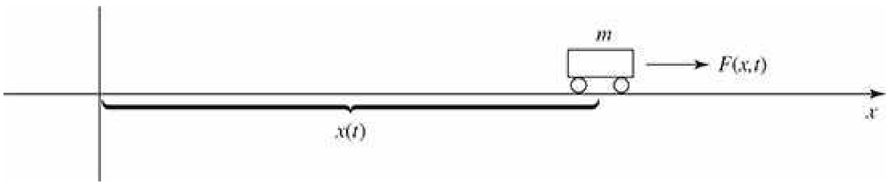

Figure 1.1: A "particle" constrained to move in one dimension under the influence of a specified force.

Quantum mechanics approaches this same problem quite differently. In this case what we're looking for is the particle's **wave function**, $\Psi(x,t)$, and we get it by solving the **Schrödinger equation**:

$$\boxed{i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V\Psi.} \tag{1.1}$$

Here *i* is the square root of -1, and $\hbar$ is Planck's constant—or rather, his *original* constant (*h*) divided by 2π:

$$\hbar = \frac{h}{2\pi} = 1.054573 \times 10^{-34}\ \text{J s}. \tag{1.2}$$

The Schrödinger equation plays a role logically analogous to Newton's second law: Given suitable initial conditions (typically, $\Psi(x,0)$), the Schrödinger equation determines $\Psi(x,t)$ for all future time, just as, in classical mechanics, Newton's law determines $x(t)$ for all future time.[2]

1.2 The Statistical Interpretation

But what exactly *is* this "wave function," and what does it do for you once you've *got* it? After all, a particle, by its nature, is localized at a point, whereas the wave function (as its name suggests) is spread out in space (it's a function of x, for any given t). How can such an object represent the state of a *particle*? The answer is provided by Born's **statistical interpretation**, which says that $|\Psi(x,t)|^2$ gives the *probability* of finding the particle at point x, at time t—or, more precisely,[3]

$$\boxed{\int_a^b |\Psi(x,t)|^2\,dx = \left\{\begin{array}{c}\text{probability of finding the particle}\\ \text{between } a \text{ and } b,\text{ at time } t.\end{array}\right\}} \tag{1.3}$$

Probability is the *area* under the graph of $|\Psi|^2$. For the wave function in Figure 1.2, you would be quite likely to find the particle in the vicinity of point A, where $|\Psi|^2$ is large, and relatively *un*likely to find it near point B.

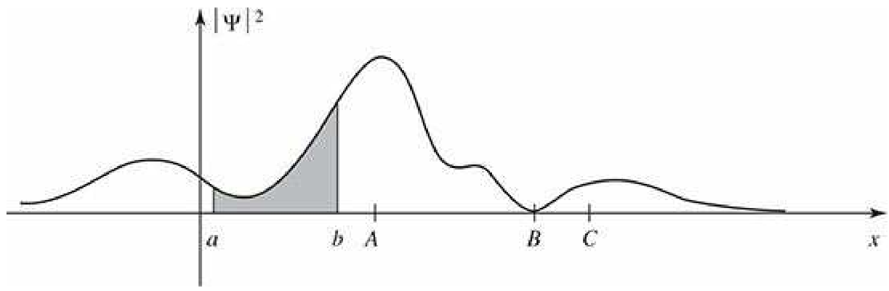

Figure 1.2: A typical wave function. The shaded area represents the probability of finding the particle between a and b. The particle would be relatively likely to be found near A, and unlikely to be found near B.

The statistical interpretation introduces a kind of **indeterminacy** into quantum mechanics, for even if you know everything the theory has to tell you about the particle (to wit: its wave function), still you cannot predict with certainty the outcome of a simple experiment to measure its position—all quantum mechanics has to offer is *statistical* information about the *possible* results. This indeterminacy has been profoundly disturbing to physicists and philosophers alike, and it is natural to wonder whether it is a fact of nature, or a defect in the theory.

Suppose I *do* measure the position of the particle, and I find it to be at point C.[4] *Question:* Where was the particle just *before* I made the measurement? There are three plausible answers to this question, and they serve to characterize the main schools of thought regarding quantum indeterminacy:

1. The **realist** position: *The particle was at C.* This certainly seems reasonable, and it is the response Einstein advocated. Note, however, that if this is true then quantum mechanics is an *incomplete* theory, since the particle *really was* at C, and yet quantum mechanics was unable to tell us so. To the realist, indeterminacy is not a fact of nature, but a reflection of our ignorance. As d'Espagnat put it, "the position of the particle was never indeterminate, but was merely unknown to the experimenter."[5] Evidently Ψ is not the whole story—some additional information (known as a **hidden variable**) is needed to provide a complete description of the particle.

2. The **orthodox** position: *The particle wasn't really anywhere.* It was the act of measurement that forced it to "take a stand" (though how and why it decided on the point C we dare not ask). Jordan said it most starkly: "Observations not only *disturb* what is to be measured, they *produce* it …We *compel* [the particle] to assume a definite position."[6] This view (the so-called **Copenhagen interpretation**), is associated with Bohr and his followers. Among physicists it has always been the most widely accepted position. Note, however, that if it is correct there is something very peculiar about the act of measurement—something that almost a century of debate has done precious little to illuminate.

3. The **agnostic** position: *Refuse to answer.* This is not quite as silly as it sounds—after all, what sense can there be in making assertions about the status of a particle *before* a measurement, when the only way of knowing whether you were right is precisely to *make* a measurement, in which case what you get is no longer "before the measurement"? It is metaphysics (in the pejorative sense of the word) to worry about something that cannot, by its nature, be tested. Pauli said: "One should no more rack one's brain about the problem of whether something one cannot know anything about exists all the same, than about the ancient question of how many angels are able to sit on the point of a needle."[7] For decades this was the "fall-back" position of most physicists: they'd try to sell you the orthodox answer, but if you were persistent they'd retreat to the agnostic response, and terminate the conversation.

Until fairly recently, all three positions (realist, orthodox, and agnostic) had their partisans. But in 1964 John Bell astonished the physics community by showing that it makes an *observable* difference whether the particle had a precise (though unknown) position prior to the measurement, or not. Bell's discovery effectively eliminated agnosticism as a viable option, and made it an *experimental* question whether 1 or 2 is the correct choice. I'll return to this story at the end of the book, when you will be in a better position to appreciate Bell's argument; for now, suffice it to say that the experiments have decisively confirmed the orthodox interpretation:[8] a particle simply does not have a precise position prior to measurement, any more than the ripples on a pond do; it is the measurement process that insists on one particular number, and thereby in a sense *creates* the specific result, limited only by the statistical weighting imposed by the wave function.

What if I made a *second* measurement, immediately after the first? Would I get C again, or does the act of measurement cough up some completely new number each time? On this question everyone is in agreement: A repeated measurement (on the same particle) must return the same value. Indeed, it would be tough to prove that the particle was really found at C in the first instance, if this could not be confirmed by immediate repetition of the measurement. How does the orthodox interpretation account for the fact that the second measurement is bound to yield the value C? It must be that the first measurement radically alters the wave function, so that it is now sharply peaked about C (Figure 1.3). We say that the wave function **collapses**, upon measurement, to a spike at the point C (it soon spreads out again, in accordance with the Schrödinger equation, so the second measurement must be made quickly). There are, then, two entirely distinct kinds of physical processes: "ordinary" ones, in which the wave function evolves in a leisurely fashion under the Schrödinger equation, and "measurements," in which Ψ suddenly and discontinuously collapses.[9]

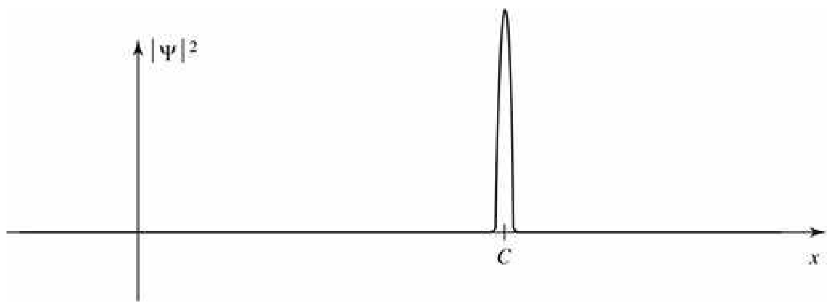

Figure 1.3: Collapse of the wave function: graph of $|\Psi|^2$ immediately *after* a measurement has found the particle at point C.

Example 1.1

Electron Interference. I have asserted that particles (electrons, for example) have a wave nature, encoded in Ψ. How might we check this, in the laboratory?

The classic signature of a wave phenomenon is *interference*: two waves *in phase* interfere constructively, and out of phase they interfere destructively. The wave nature of light was confirmed in

1801 by Young's famous double-slit experiment, showing interference "fringes" on a distant screen when a monochromatic beam passes through two slits. If essentially the same experiment is done with *electrons*, the same pattern develops,[10] confirming the wave nature of electrons.

Now suppose we decrease the intensity of the electron beam, until only one electron is present in the apparatus at any particular time. According to the statistical interpretation each electron will produce a spot on the screen. Quantum mechanics cannot predict the precise *location* of that spot—all it can tell us is the *probability* of a given electron landing at a particular place. But if we are patient, and wait for a hundred thousand electrons—one at a time—to make the trip, the accumulating spots reveal the classic two-slit interference pattern (Figure 1.4). [11]

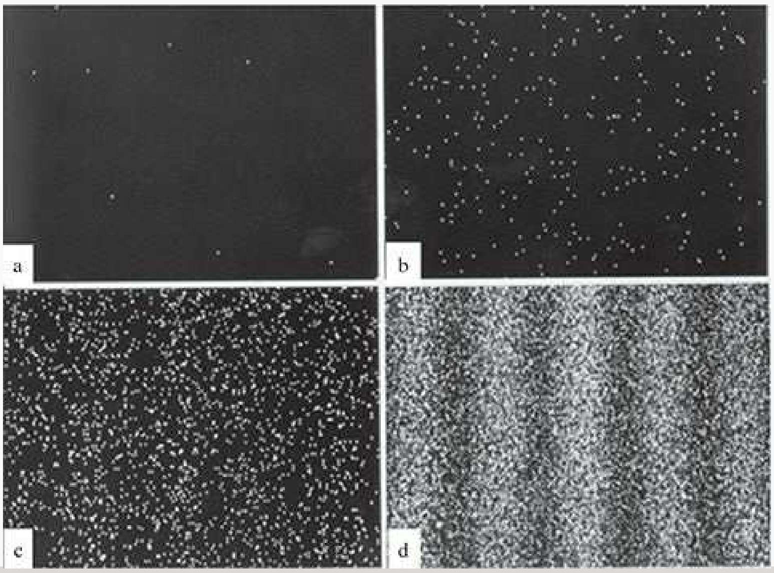

Figure 1.4: Build-up of the electron interference pattern. (a) Eight electrons, (b) 270 electrons, (c) 2000 electrons, (d) 160,000 electrons. Reprinted courtesy of the Central Research Laboratory, Hitachi, Ltd., Japan.

Of course, if you close off one slit, or somehow contrive to detect which slit each electron passes through, the interference pattern disappears; the wave function of the emerging particle is now entirely different (in the first case because the boundary conditions for the Schrödinger equation have been changed, and in the second because of the collapse of the wave function upon measurement). But with both slits open, and no interruption of the electron in flight, each electron interferes with itself; it didn't pass through one slit or the other, but through both at once, just as a water wave, impinging on a jetty with two openings, interferes with itself. There is nothing mysterious about this, once you have accepted the notion that particles obey a wave equation. The truly *astonishing* thing is the blip-by-blip assembly of the pattern. In any classical wave theory the pattern would develop smoothly and continuously, simply getting more intense as time goes on. The quantum process is more like the pointillist painting of Seurat: The picture emerges from the cumulative contributions of all the individual dots.[12]