

# Quantum Mechanics for Scientists and Engineers

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Cambridge

*To Pat, Andrew, and Susan*



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# Preface

This book introduces quantum mechanics to scientists and engineers. It can be used as a text for junior undergraduates onwards through to graduate students and professionals. The level and approach are aimed at anyone with a reasonable scientific or technical background looking for a solid but accessible introduction to the subject. The coverage and depth are substantial enough for a first quantum mechanics course for physicists. At the same time, the level of required background in physics and mathematics has been kept to a minimum to suit those also from other science and engineering backgrounds.

Quantum mechanics has long been essential for all physicists and in other physical science subjects such as chemistry. With the growing interest in nanotechnology, quantum mechanics has recently become increasingly important for an ever-widening range of engineering disciplines, such as electrical and mechanical engineering, and for subjects such as materials science that underlie many modern devices. Many physics students also find that they are increasingly motivated in the subject as the everyday applications become clear.

Non-physicists have a particular problem in finding a suitable introduction to the subject. The typical physics quantum mechanics course or text deals with many topics that, though fundamentally interesting, are useful primarily to physicists doing physics; that choice of topics also means omitting many others that are just as truly quantum mechanics, but have more practical applications. Too often, the result is that engineers or applied scientists cannot afford the time or cannot sustain the motivation to follow such a physics-oriented sequence. As a result, they never have a proper grounding in the subject. Instead, they pick up bits and pieces in other courses or texts. Learning quantum mechanics in such a piecemeal approach is especially difficult; the student then never properly confronts the many fundamentally counterintuitive concepts of the subject. Those concepts need to be understood quite deeply if the student is ever going to apply the subject with any reliability in any novel situation. Too often also, even after working hard in a quantum mechanics class, and even after passing the exams, the student is still left with the depressing feeling that they do not understand the subject at all.

To address the needs of its broad intended readership, this book differs from most others in three ways. First, it presumes as little as possible in prior knowledge of physics. Specifically, it does not presume the advanced classical mechanics (including concepts such as Hamiltonians and Lagrangians) that is often a prerequisite in physics quantum mechanics texts and courses. Second, in two background appendices, it summarizes all of the key physics and mathematics beyond the high-school level that the reader needs to start the subject. Third, it introduces the quantum mechanics that underlies many important areas of application, including semiconductor physics, optics, and optoelectronics. Such areas are usually omitted from quantum mechanics texts, but this book introduces many of the quantum mechanical principles and models that are exploited in those subjects.

It is also my belief and experience that using quantum mechanics in several different and practical areas of application removes many of the difficulties in understanding the subject. If quantum mechanics is only illustrated through examples that are found in the more esoteric

branches of physics, the subject itself can seem irrelevant and obscure. There is nothing like designing a real device with quantum mechanics to make the subject tangible and meaningful.

Even with its deliberately limited prerequisites and its increased discussion of applications, this book offers a solid foundation in the subject. That foundation should prepare the reader well for the quantum mechanics in either advanced physics or in deeper study of practical applications in other scientific and engineering fields. The emphasis in the book is on understanding the ideas and techniques of quantum mechanics rather than attempting to cover all possible examples of their use. A key goal of this book is that the reader should subsequently be able to pick up texts in a broad range of areas, including, for example, advanced quantum mechanics for physicists, solid state and semiconductor physics and devices, optoelectronics, quantum information, and quantum optics, and find they already have all the necessary basic tools and conceptual background in quantum mechanics to make rapid progress.

It is possible to teach quantum mechanics in many different ways, though most sequences will start with Schrödinger's wave equation and work forward from there. Even though the final emphasis in this book may be different from some other quantum mechanics courses, I have deliberately chosen not to take a radical approach here. This is for three reasons: first, most college and university teachers will be most comfortable with a relatively standard approach since that is the one they have most probably experienced themselves; second, taking a core approach that is relatively conventional will make it easier for readers (and teachers) to connect with the many other good physics quantum mechanics books; third, this book should also be accessible and useful to professionals who have previously studied quantum mechanics to some degree, but need to update their knowledge or connect to the modern applications in engineering or applied sciences.

The background requirements for the reader are relatively modest, and should represent little problem for students or professionals in engineering, applied sciences, physics, or other physical sciences. This material has been taught with apparent success to students in applied physics, electrical engineering, mechanical engineering, materials science, and other science and engineering disciplines, from 3<sup>rd</sup> year undergraduate level up to graduate students. In mathematics, the reader should have a basic knowledge in calculus, complex numbers, elementary matrix algebra, geometrical vectors, and simple and partial differential equations. In physics, the reader should be familiar with ordinary Newtonian classical mechanics and elementary electricity and magnetism. The key requirements are summarized in two background appendices in case the reader wants to refresh some background knowledge or fill in gaps. A few other pieces of physics and mathematics are introduced as needed in the main body of the text. It is helpful if the student has had some prior exposure to elementary modern physics, such as the ideas of electrons, photons, and the Bohr model of the atom, but no particular results are presumed here. The necessary parts of Hamiltonian classical mechanics will be introduced briefly when required in later Chapters.

This book goes deeper into certain subjects, such as the quantum mechanics of light, than most introductory physics texts. For the later Chapters on the quantum mechanics of light, additional knowledge of vector calculus and electromagnetism to the level of Maxwell's equations are presumed, though again these are summarized in appendices.

One intent of the book is for the student to acquire a strong understanding of the concepts of quantum mechanics at the level beyond mere mathematical description. As a result, I have chosen to try to explain concepts with limited use of mathematics wherever possible. With the ready availability of computers and appropriate software for numerical calculations and

simulations, it is progressively easier to teach principles of quantum mechanics without as heavy an emphasis on analytical techniques. Such numerical approaches are also closer to the methods that an engineer will likely use for calculations in real problems anyway, and access to some form of computer and high-level software package is assumed for some of the problems. This approach substantially increases the range of problems that can be examined both for tutorial examples and for applications.

Finally, I will make one personal statement on handling the conceptual difficulties of quantum mechanics in texts and courses. Some texts are guilty of stating quantum mechanical postulates, concepts and assumptions as if they should be obvious, or at least obviously acceptable, when in fact they are far from obvious even to experienced practitioners or teachers. In many cases, these are subjects of continuing debate at the highest level. I try throughout to be honest about those concepts and assumptions that are genuinely unclear as to their obviousness or even correctness. I believe it is a particularly heinous sin to pretend that some concept should be clear to the student when it is, in fact, not even clear to the professor (an overused technique that preserves professorial ego at the expense of the student's!).

It is a pleasure to acknowledge the many teaching assistants who have provided much useful feedback and correction of my errors in this material as I have taught it at Stanford, including Aparna Bhatnagar, Julien Boudet, Eleni Diamanti, Onur Fidaner, Martina Gerken, Noah Helman, Ekin Kocabas, Bianca Nelson, Tomas Sarmiento, and Scott Sharpe. I would like to thank Ingrid Tarien for much help in preparing many parts of the course material, and Marjorie Ford for many helpful comments on writing.

I am also pleased to acknowledge my many professorial colleagues at Stanford, including Steve Harris, Walt Harrison, Jelena Vuckovic, and Yoshi Yamamoto in particular, for many stimulating, informative, and provocative discussions about quantum mechanics. I would especially like to thank Jelena Vuckovic, who successfully taught the subject to many students despite having to use much of this material as a course reader, and who consequently corrected numerous errors and clarified many points. All remaining errors and shortcomings are, of course, my sole responsibility, and any further corrections and suggestions are most welcome.

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*Stanford, California, September 2007*

# How to use this book

## For teachers

The entire material in this book could be taught in a one-year course. More likely, depending on the interests and goals of the teacher and students, and the length of time available, only some of the more advanced topics will be covered in detail. In a two-quarter course sequence for senior undergraduates and for engineering graduate students at Stanford, the majority of the material here will be covered, with a few topics omitted and some covered in lesser depth.

The core material (Chapters 1 – 5) on Schrödinger's equation and on the mathematics behind quantum mechanics should be taught in any course. Chapter 4 gives a more explicit introduction to the ideas of linear operators than is found in most texts. Chapter 4 also explains and introduces Dirac notation, which is used from that point onwards in the book. This introduction of Dirac notation is earlier than in many older texts, but it saves considerable time thereafter in describing quantum mechanics. Experience teaching engineering students in particular, most of whom are quite familiar with linear algebra and matrices from other applications in engineering, shows that they have no difficulties with this concept.

Aside from that core there are many possible choices about the sequence of material and on what material needs to be included in a course. The prerequisites for each Chapter are clearly stated at the beginning of the Chapter. There are also some Sections in several of the Chapters that are optional, or that may only need to be read through when first encountered. These Sections are clearly marked. The discussion of methods for one-dimensional problems in Chapter 11 can come at any point after the material on Schrödinger's equations (Chapters 2 and 3). The core transfer matrix part could even be taught directly after the time-independent equation (Chapter 2). The material is optional in that it is not central to later topics, but in my experience students usually find it stimulating and empowering to be able to do calculations with simple computer programs based on these methods. This can make the student comfortable with the subject, and begin to give them some intuitive feel for many quantum mechanical phenomena. (These methods are also used in practice for the design of real optoelectronic devices.)

For a broad range of applications, the approximation methods of quantum mechanics (Chapter 6 and 7) are probably the next most important after Chapters 1 - 5. The specific topic of the quantum mechanics of crystalline materials (Chapter 8) is a particularly important topic for many applications, and can be introduced at any point after Chapter 7; it is not, however, required for subsequent Chapters (except for a few examples, and some optional parts at the end of Chapter 11), so the teacher can choose how far he or she wants to progress through this Chapter. For fundamentals, angular momentum (Chapter 9) and the hydrogen atom (Chapter 10) are the next most central topics, both of which can be taught directly after Chapter 5 if desired. After these, the next most important fundamental topics are spin (Chapter 12) and identical particles (Chapter 13), and these should probably be included in the second quarter or semester if not before.

Chapter 14 introduces the important technique of the density matrix for connecting to statistical mechanics, and it can be introduced at any point after Chapter 5; preferably the student would also have covered Chapters 6 and 7 so they are familiar with perturbation theory, though that is not required. The density matrix material is not required for subsequent Chapters, so this Chapter is optional.

The sequence of Chapters 15 – 17 introduces the quantum mechanics of electromagnetic fields and light, and also the important technique of second quantization in general, including fermion operators (a technique that is also used extensively in more advanced solid state physics). The inclusion of this material on the quantum mechanics of light is the largest departure from typical introductory quantum mechanics texts. It does however redress a balance in material that is important from a practical point of view; we cannot describe even the simplest light emitter (including an ordinary light bulb.) or light detector without it, for example. This material is also very substantial quantum mechanics at the next level of the subject. These Chapters do require almost all of the preceding material, with the possible exceptions of Chapters 8, 11, and 14.

The final two Chapters, Chapter 18 on a brief introduction to quantum information concepts and Chapter 19 on the interpretation of quantum mechanics, could conceivably be presented with only Chapters 1 – 5 as prerequisites. Preferably also Chapters 9, 10, 12, and 13 would have been covered, and it is probably a good idea that the student has been working with quantum mechanics successfully for some time before attempting to grapple with the tricky conceptual and philosophical aspects in these final Chapters. The material in these Chapters is well suited to the end of a course, when it is often unreasonable to include any further new material in a final exam, but yet one wants to keep the students' interest with stimulating ideas.

Problems are introduced directly after the earliest possible Sections rather than being deferred to the ends of the Chapters, thus giving the greatest flexibility in assigning homework. Some problems can be used as substantial assignments, and all such problems are clearly marked. These can be used as “take-home” problems or exams, or as extended exercises coupled with tutorial “question and answer” sessions. These assignments may necessarily involve some more work, such as significant amounts of (relatively straightforward) algebra or calculations with a computer. I have found, though, that students gain a much greater confidence in the subject once they have used it for something beyond elementary exercises, exercises that are necessarily often artificial. At least, these assignments tend to approach the subject from the point of view of a problem to be solved rather than an exercise that just uses the last technique that was studied. Some of these larger assignments deal with quite realistic uses of quantum mechanics.

At the very end of the book, I also include a suggested list of simple formulae to be memorized in each Chapter. These lists could also be used as the basis of simple quizzes, or as required learning for “closed-book” exams.

## **For students**

### **Necessary background**

Students will come to this book with very different backgrounds. You may recently have studied a lot of physics and mathematics at college level. If so, then you are ready to start. I suggest you have a quick look at Appendices A and B just to see the notations used in this book before starting Chapter 2.

For others, your mathematical or physics background may be less complete, or it may be some time since you have seen or used some of the relevant parts of these subjects. Rest assured, first of all, that in writing this book I have presumed the least possible knowledge of mathematics and physics consistent with teaching quantum mechanics, and much less than the typical quantum mechanics text requires. Ideally, I expect you have had the physics and mathematics typical of first or second year college level for general engineering or physical science students. You do absolutely have to know elementary algebra, calculus, and physics to a good pre-college level, however. I suggest you read the Background Mathematics Appendix A and the Background Physics Appendix B to see if you understand most of that. If not too much of that is new to you, then you should be able to proceed into the main body of this book. If you find some new topics in these Appendices, there is in principle enough material there to “patch over” those holes in knowledge temporarily so that you can use the mathematics and physics needed to start quantum mechanics; these Appendices are not, however, meant to be a substitute for learning these topics in greater depth.

## Study aids in this book

### Lists of concepts introduced

Because there are many concepts that the student needs to understand in quantum mechanics, I have summarized the most important ones at the end of the Chapters in which they are introduced. These summaries should help both in following the “plot” of the book, and in revising the material.

### Appendices

The book is as reasonably self-contained as I can make it. In addition to the background Appendices A and B covering the overall prerequisite mathematics and physics, additional background material needed later on is introduced in Appendices C and D (vector calculus and electromagnetism), and one specific detailed derivation is given in Appendix E. Appendix F summarizes the early history of quantum mechanics, Appendix G collects and summarizes most of the mathematical formulae that will be needed in the book, including the most useful ones from elementary algebra, trigonometric functions, and calculus. Appendix H gives the Greek alphabet (every single letter of it is used somewhere in quantum mechanics), and Appendix I lists all the relevant fundamental constants.

### Problems

There are about 160 problems and assignments, collected at the ends of the earliest possible Sections rather than at the ends of the Chapters.

### Memorization list

Quantum mechanics, like many aspects of physics, is not primarily about learning large numbers of formulae, but rather understanding the key concepts clearly and deeply. It will, however, save a lot of time (including in exams!) to learn a few basic formulae by heart, and certainly if you also understand these well, you should have a good command of the subject.

At the very end of the book, there is a list of formulae worth memorizing in each Chapter of the book. None of these formulae is particularly complicated – the most complicated ones are the Schrödinger wave equation in its two forms. Many of the formulae are simply short definitions of key mathematical concepts. If you learn these formulae chapter by chapter as you work through the book, there are not very many formulae to learn at any one time.

The list here is not of the formulae themselves, but rather is of descriptions of them so you can use this list as an exercise to test how successfully you have learned these key results.

## Self-teaching

If you are teaching yourself quantum mechanics using this book, first of all, congratulations to you for having the courage to tackle what most people typically regard as a daunting subject. For someone with elementary college level physics and mathematics, I believe it is quite an accessible subject in fact. *But*, the most important point is that you must not start learning quantum mechanics “on the fly” by picking and choosing just the bits you need from this book or any other. Trying to learn quantum mechanics like that would be like trying to learn a language by reading a dictionary. You cannot treat quantum mechanics as just a set of formulae to be substituted into problems, just as you cannot translate a sentence from one language to another just by looking up the individual words in a dictionary and writing down their translations. There are just so many counterintuitive aspects about quantum mechanics that you will never understand it in that piecemeal way, and most likely you would not use the formulae correctly anyway. Make yourself work on all of the first several Chapters, through at least Chapter 5; that will get you to a first plateau of understanding. You can be somewhat more selective after that. For the next level of understanding, you need to study angular momentum, spin and identical particles (Chapters 9, 12, and 13). Which other Chapters you use will depend on your interests or needs. Of course, it is worthwhile studying all of them if you have the time!

Especially if you have no tutor of whom you can ask questions, then I also expect that you should be looking at other quantum mechanics books as well. Use this one as your core, and when I have just not managed to explain something clearly enough or to get it to “click” for you, look at some of the others, such as the ones listed in the Bibliography. My personal experience is that a difficult topic finally becomes clear to me once I have five books on it open on my desk. One hope I have for this book is that it enables readers to access the more specialized physics texts if necessary. Their alternative presentations may well succeed where mine fail, and those other books can certainly cover a range of specific topics impossible to include here.





# Chapter 1

## Introduction

### 1.1 Quantum mechanics and real life

Quantum mechanics, we might think, is a strange subject, one that does not matter for daily life. Only a few people, therefore, should need to worry about its difficult details. These few, we might imagine, run about in the small dark corners of science, at the edge of human knowledge. In this unusual group, we would expect to find only physicists making ever larger machines to look at ever smaller objects, chemists examining the last details of tiny atoms and molecules, and perhaps a few philosophers absently looking out of windows as they wonder about free will. Surely quantum mechanics therefore should not matter for our everyday experience. It could not be important for designing and making real things that make real money and change real lives. Of course, we would be wrong.

Quantum mechanics is everywhere. We do not have to look far to find it. We only have to open our eyes. Look at some object, say a flower pot or a tennis ball. Why is the flower pot a soothing terra-cotta orange color and the tennis ball a glaring fluorescent yellow? We could say each object contains some appropriately colored pigment or dye, based on a material with an intrinsic color, but we are not much further forward in understanding. (Our color technology would also be stuck in medieval times, when artists had to find all their pigments in the colors in natural objects, sometimes at great cost<sup>1</sup>.) The particularly bright yellow of our modern tennis ball would also be quite impossible if we restricted our pigments to naturally occurring materials.

Why does each such pigment have its color? We have no answer from the “classical” physics and chemistry developed before 1900. But quantum mechanics answers such questions precisely and completely<sup>2</sup>. Indeed, the beginning of quantum mechanics comes from one

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<sup>1</sup> They had to pay particularly dearly for their ultramarine blue, a pigment made by grinding up the gemstone *lapis lazuli*. The Spanish word for blue, *azul*, and the English word *azure* both derive from this root. The word ultramarine refers to the fact that the material had to be brought from “beyond (ultra) the sea (marine)” – i.e., imported, presumably also at some additional cost. Modern blue coloring is more typically based on copper phthalocyanine, a relatively cheap, man-made chemical.

<sup>2</sup> In quantum mechanics, photons, the quantum mechanical particles of light, have different colors depending on their tiny energies; materials have energy levels determined by the quantum mechanics of electrons, energy levels separated by similarly tiny amounts. We can change the electrons from one energy level to another by absorbing or emitting photons. The specific color of an object comes from the specific separations of the energy levels in the material. A few aspects of color can be explained without quantum mechanics. Color can be sometimes result from scattering (such as the blue of the sky or the

particular aspect of color. Classical physics famously failed to explain the color of hot objects<sup>3</sup>, such as the warm yellow of the filament in a light bulb or the glowing red of hot metal in a blacksmith's shop. Max Planck realized in 1900 that if the energy in light existed only in discrete steps, or quanta, he could get the right answer for these colors. And so quantum mechanics was born.

The impact of quantum mechanics in explaining our world does not end with color. We have to use quantum mechanics in explaining most properties of materials. Why are some materials hard and others soft? For example, why can a diamond scratch almost anything, but a pencil lead will slide smoothly, leaving a black line behind it?<sup>4</sup> Why do metals conduct electricity and heat easily, but glass does not? Why is glass transparent? Why do metals reflect light? Why is one substance heavy and another light? Why is one material strong and another brittle? Why are some metals magnetic and others are not? We need, of course, a good deal of other science, such as chemistry, materials science, and other branches of physics, to answer such questions in any detail; but in doing so all of these sciences will rely on our quantum mechanical view of how materials are put together.

So, we might now believe, the consequences of quantum mechanics are essential for understanding the ordinary world around us. But is quantum mechanics useful? If we devote our precious time to learning it, will it let us make things we could not make before? One science in which the quantum mechanical view is obviously essential is chemistry, the science that enables most of our modern materials. No-one could deny that chemistry is useful.

Suppose even that we set chemistry and materials themselves aside, and ask a harder question: do we need quantum mechanics when we design devices – objects intended to perform some worthwhile function? After all, the washing machines, eye-glasses, staplers, and automobiles of everyday life need only 19<sup>th</sup> century physics for their basic mechanical design, even if we employ the latest alloys, plastics or paints to make them. Perhaps we can concede such macroscopic mechanisms to the classical world. But when, for example, we look at the technology to communicate and process information, we have simply been forced to move to quantum mechanics. Without quantum theory as a practical technique, we would not be able to design the devices that run our computers and our internet connections.

The mathematical ideas of computing and information had begun to take their modern shape in the 1930's, 1940's and 1950's. By the 1950's, telephones and broadcast communication were well established, and the first primitive electronic computers had been demonstrated. The transistor and integrated circuit were the next key breakthroughs. These devices made complex computers and information switching and processing practical. These devices relied heavily on the quantum mechanical physics of crystalline materials.

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white of some paints), diffraction (for example by a finely ruled grating or a hologram), or interference (such as the varied colors of a thin layer of oil on the surface of water), all of which can be explained by classical wave effects. All such classical wave effects are also explained as limiting cases of quantum mechanics, of course.

<sup>3</sup> This problem was known as the “ultraviolet catastrophe”, because classical thermal and statistical physics predicted that any warm object would emit ever increasing amounts of light at ever shorter wavelengths. The colors associated with such wavelengths would necessarily extend past the blue, into the ultraviolet – hence the name.

<sup>4</sup> Even more surprising here is that diamond and pencil lead are both made from exactly the same element, carbon.

A well-informed devil's advocate could still argue, though, that the design of transistors and integrated circuits themselves was initially still an activity using classical physics. Designers would still use the idea of resistance from 19<sup>th</sup> century electricity, even if they added the ideas of charged electrons as particles carrying the current, and would add various electrical barriers (or "potentials") to persuade electrons to go one way or another. No modern transistor designer can ignore quantum mechanics, however. For example, when we make small transistors, we must also make very thin electrical insulators. Electrons can manage to penetrate through the insulators because of a purely quantum mechanical process known as tunneling. At the very least, we have to account for that tunneling current as an undesired, parasitic process in our design.

As we try to shrink transistors to ever smaller sizes, quantum mechanical effects become progressively more important. Naively extrapolating the historical trend in miniaturization would lead to devices the size of small molecules in the first few decades of the 21<sup>st</sup> century. Of course, the shrinkage of electronic devices as we know them cannot continue to that point. But as we make ever-tinier devices, quantum mechanical processes become ever more important. Eventually, we may need new device concepts beyond the semi-classical transistor; it is difficult to imagine how such devices would not involve yet more quantum mechanics.

We might argue, at least historically, about the importance of quantum mechanics in the design of transistors. We could have no comparable debate when we consider two other technologies crucial for handling information – optical communications and magnetic data storage.

Today nearly all the information we send over long distances is carried on optical fibers – strands of glass about the thickness of a human hair. We very carefully put a very small light just at one end of that fiber. We send the "ones" and "zeros" of digital signals by rapidly turning that light on and off and looking for the pattern of flashes at the fiber's other end. To send and receive these flashes, we need optoelectronic devices – devices that will change electrical signals into optical pulses and *vice versa*. All of these optoelectronic devices are quantum mechanical on many different levels. First, they mostly are made of crystalline semiconductor materials, just like transistors, and hence rely on the same underlying quantum mechanics of such materials. Second, they send and receive photons, the particles of light Einstein proposed to expand upon Planck's original idea of quanta. Here these devices are exploiting one of the first of many strange phenomena of quantum mechanics, the photoelectric effect. Third, most modern semiconductor optoelectronic devices used in telecommunications employ very thin layers of material, layers called quantum wells. The properties of these thin layers depend exquisitely on their thicknesses through a text-book piece of quantum mechanics known as the "particle-in-a-box" problem. That physics allows us to optimize some of the physical processes we already had in thicker layers of material and also to create some new mechanisms only seen in thin layers. For such devices, engineering using quantum mechanics is both essential and very useful.

When we try pack more information onto the magnetic hard disk drives in our computers, we first have to understand exactly how the magnetism of materials works. That magnetism is almost entirely based on a quantum mechanical attribute called "spin" – a phenomenon with no real classical analog. The sensors that read the information off the drives are also often now based on sophisticated structures with multiple thin layers that are designed completely with quantum mechanics.

Quantum mechanics is, then, a subject increasingly necessary for engineering devices, especially as we make small devices or exploit quantum mechanical properties that only occur in small structures. The examples given above are only a few from a broad and growing field

that can be called nanotechnology. Nanotechnology exploits our expanding abilities to make very small structures or patterns. The benefits of nanotechnology come from the new properties that appear at these very small scales. We get most of those new properties from quantum mechanical effects of one kind or another. Quantum mechanics is therefore essential for nanotechnology.

## 1.2 Quantum mechanics as an intellectual achievement

Any new scientific theory has to give the same answers as the old theories everywhere these previous models worked, and yet successfully describe phenomena that previously we could not understand. The prior theories of mechanics, Newton's Laws, worked very well in a broad range of situations. Our models for light similarly were quite deep and had achieved a remarkable unification of electricity and magnetism (in Maxwell's equations). But when we would try to make a model of the atom, for example, with electrons circling round some charged nucleus like satellites in orbit round the earth, we would meet major contradictions. Existing mechanics and electromagnetic theory would predict that any such orbiting electron would constantly be emitting light; but atoms simply do not do that.

The challenge for quantum mechanics was not an easy one. To resolve these problems of light and the structure of matter we actually had to tear down much of our view of the way the world works, to a degree never seen since the introduction of natural philosophy and the modern scientific method in the Renaissance. We were forced to construct a completely new set of principles for the physical world. These were, and still are in many cases, completely bizarre and certainly different from our intuition. Many of these principles simply have no analogs in our normal view of reality.

We mentioned above one of the bizarre aspects of quantum mechanics: the process of "tunneling" allows particles to penetrate barriers that are classically too high for them to overcome. This process is, however, actually nothing like the act of digging a tunnel; we are confronting here the common difficulty in quantum mechanics of finding words or analogies from everyday experience to describe quantum mechanical ideas. We will often fail.

There are many other surprising aspects of quantum mechanics. The typical student starting quantum mechanics is confused when told, as he or she often will be, that some question simply does not have an answer. The student will, for example, think it perfectly reasonable to ask what are the position and momentum (or, more loosely, speed) of some particle, such as an electron. Quantum mechanics (or in practice its human oracle, the professor) will enigmatically reply that there is no answer to that question. We can know one or the other precisely, but not both at once. This particular enigma is an example of Heisenberg's uncertainty principle.

Quantum mechanics does raise more than its share of deep questions, and it is arguable that we still do not understand quantum mechanics. In particular, there are still major questions about what a measurement really is in the quantum world. Erwin Schrödinger famously dramatized the difficulty with the paradox of his cat. According to quantum mechanics, an object may exist in a superposition state, in which it is, for example, neither definitely on the left, nor on the right. Such superposition states are not at all unusual – in fact they occur all the time for electrons in any atom or molecule. Though a particle might be in a superposition state, when we try to measure it, we always find that the object is at some specific position, e.g., definitely on the left or on the right. This mystical phenomenon is known as "collapse of the wavefunction". We might find that a bizarre idea, but one that, for something really tiny like an electron, we could perhaps accept.

But now Schrödinger proposes that we think not about an electron, but instead about his cat. We are likely to care much more about the welfare of this “object” than we did about some electron. An electron is, after all, easily replaced with another just the same<sup>5</sup>; there are plenty of them, in fact something like  $10^{24}$  electrons in every cubic centimeter of any solid material. And Schrödinger constructs a dramatic scenario. His cat is sealed in a box with a lethal mechanism that may go off as a result of, e.g., radioactive decay. Before we open the box to check on it, is the cat alive, dead, or, as quantum mechanics might seem to suggest, in some “superposition” of the two?

The superposition hypothesis now seems absurd. In truth, we cannot check it here; we do not know how to set up an experiment to test such quantum mechanical notions with macroscopic objects. In trying to repeat such an experiment we cannot set up the same starting state exactly enough for something as complex as a cat. Physicists disagree about the resolution of this paradox. It is an example of a core problem of quantum mechanics: the process of measurement, with its mysterious “collapse of the wavefunction”, cannot be explained by quantum mechanics.<sup>6</sup> The proposed solutions to this measurement problem can be extremely bizarre; in the “many worlds” hypothesis, for example, the world is supposed continually to split into multiple realities, one for each possible outcome of each possible measurement.

Another important discussion centers round whether quantum mechanics is complete. When we measure a quantum mechanical system, there is at least in practice some randomness in the result. If, for example, we tried to measure the position of an electron in an atom, we would keep getting different results. Or if we measured how long it took a radioactive nucleus to decay, we would get different numbers each time. Quantum mechanics would correctly predict the average position we would measure for the electron and the average decay time of the nucleus, but it would not tell us the specific position or time yielded by any particular measurement.

We are, of course, quite used to randomness in our ordinary classical world. The outcome of many lotteries is decided by which numbered ball appears out of a chute in a machine. The various different balls are all bouncing around inside the machine, driven probably by some air blower. The process is sufficiently complicated that we cannot practically predict which ball will emerge, and all have equal chance. But we do tend to believe classically that, if we knew the initial positions and velocities of all the air molecules and the balls in the machine, we could in principle predict which ball would emerge. Those variables are in practice hidden from us, but we do believe they exist. Behind the apparent randomness of quantum mechanics, then, are there just similarly some hidden variables? Could we actually predict outcomes precisely if we knew what those hidden variables were? Is the apparent randomness of quantum mechanics just because of our lack of understanding of some deeper theory and its starting conditions, some “complete” theory that would supersede quantum mechanics?

Einstein believed that indeed quantum mechanics was not complete, that there were some hidden variables that, once we understood them, would resolve and remove its apparent randomness. Relatively recent work, centered round a set of relations called Bell’s inequalities, shows rather surprisingly that there are no such hidden variables (or at least, not local ones that

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<sup>5</sup> Indeed, in quantum mechanics electrons can be absolutely identical, much more identical than the so-called “identical” toys from an assembly line or “identical” twins in a baby carriage.

<sup>6</sup> If at this point the reader raises an objection that there is an inconsistency in saying that quantum mechanics will only answer questions about things we can measure but quantum mechanics cannot explain the process of measurement, the reader would be quite justified in doing so!

propagate with the particles), and that, despite its apparent absurdities, quantum mechanics may well be a complete theory in this sense.

It also appears that quantum mechanics is “non-local”: two particles can be so “entangled” quantum mechanically that measuring one of them can apparently instantaneously change the state of the other one, no matter how far away it is (though it is not apparently possible to use such a phenomenon to communicate information faster than the velocity of light).<sup>7</sup>

Despite all its absurdities and contradictions of common sense, and despite the initial disbelief and astonishment of each new generation of students, quantum mechanics works. As far as we know, it is never wrong; we have made no experimental measurement that is known to contradict quantum mechanics, and there have been many exacting tests. Quantum mechanics is both stunningly radical and remarkably right. It is an astonishing intellectual achievement.

The story of quantum mechanics itself is far from over. We are still trying to understand exactly what are all the elementary particles and just what are the implications of such theories for the nature of the universe.<sup>8</sup> Many researchers are working on the possibility of using some of the strange possibilities of quantum mechanics for applications in handling information transmission. One example would send messages whose secrecy was protected the laws of quantum physics, not just the practical difficulty of cracking classical codes. Another example is the field of quantum computing, in which quantum mechanics might allow us to solve problems that would be too hard ever to be solved by any conventional machine.

### 1.3 Using quantum mechanics

At this point, the poor student may be about to give up in despair. How can one ever understand such a bizarre theory? And if one cannot understand it, how can one even think of using it? Here is the good news: whether we think we understand quantum mechanics or not, and whether there is yet more to discover about how it works, quantum mechanics is surprisingly easy to use.

The prescriptions for using quantum mechanics in a broad range of practical problems and engineering designs are relatively straightforward. They use the same mathematical techniques most engineering and science students will already have mastered to deal with the “classical” world<sup>9</sup>. Because of a particular elegance in its mathematics<sup>10</sup>, quantum mechanical calculations can actually be easier than those in many other fields.

The main difficulty the beginning student has with quantum mechanics lies in knowing which of our classical notions of the world have to be discarded, and what new notions we have to

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<sup>7</sup> This non-locality is often known through the original “EPR” thought experiment or paradox proposed by Einstein, Podolsky and Rosen.

<sup>8</sup> Such theories require relativistic approaches that are unfortunately beyond the scope of this book.

<sup>9</sup> In the end, most calculations require performing integrals or manipulating matrices. Many of the underlying mathematical concepts are ones that are quite familiar to engineers used to Fourier analysis, for example, or other linear transforms.

<sup>10</sup> Quantum mechanics is based entirely and exactly on linear algebra. Unlike most other uses of linear algebra, the fundamental linearity of quantum mechanics is apparently *not* an approximation.

use to replace them.<sup>11</sup> The student should expect to spend some time in disbelief and conflict with what is being asserted in quantum mechanics – that is entirely normal! In fact, a good fight with these propositions is perhaps psychologically necessary, like the clarifying catharsis of an old-fashioned bar-room brawl.

And there is a key point that simplifies all the absurdities and apparent contradictions: provided we only ask questions about quantities that can be measured, there are no philosophical problems that need worry us, or at least that would prevent us from calculating anything that we could measure.<sup>12</sup> As we use quantum mechanical principles in tangible applications, such as electronic or optical devices and systems, the apparently bizarre aspects become simply commonplace and routine. The student may soon stop worrying about quantum mechanical tunneling and Heisenberg's uncertainty principle. In the foreseeable future, such routine comprehension and acceptance may also extend to concepts such as non-locality and entanglement as we press them increasingly into practical use.

Understanding quantum mechanics does certainly mark a qualitative change in one's view of how the world actually works.<sup>13</sup> That understanding gives the student the opportunity to apply this knowledge in ways that others cannot begin to comprehend<sup>14</sup>. Whether the goal is basic understanding or practical exploitation, learning quantum mechanics is, in this author's opinion, certainly one of the most fascinating things one can do with one's brain.

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<sup>11</sup> The associated teaching technique of breaking down the student's beliefs and replacing them with the professor's "correct" answers has a lot in common with brainwashing!

<sup>12</sup> This philosophical approach of only dealing with questions that can be answered by measurement (or that are purely logical questions within some formal system of logic), and regarding all other questions as meaningless, is essentially what is known in the philosophical world as "logical positivism". It is the most common approach taken in dealing with quantum mechanics, at least at the elementary philosophical level, and, by allowing university professors to dismiss most student questions as meaningless, saves a lot of time in teaching the subject!

<sup>13</sup> It is undoubtedly true that, if one does not understand quantum mechanics, one does not understand how the world actually works. It may also, however, be true that, even if one does understand quantum mechanics, one still may not understand how the world works.

<sup>14</sup> Despite the inherent sense of superiority such an understanding may give the student, it is, however, as many physicists have already regrettably found, not particularly useful to point this out at parties.



# Chapter 2

## Waves and quantum mechanics – Schrödinger's equation

Prerequisites: Appendix A Background mathematics. Appendix B Background physics.

If the world of quantum mechanics is so different from everything we have been taught before, how can we even begin to understand it? Minuscule electrons seem so remote from what we see in the world around us that we do not know what concepts from our everyday experience we could use to get started. There is, however, one lever from our existing intellectual toolkit that we can use to pry open this apparently impenetrable subject, and that lever is the idea of waves. If we just allow ourselves to suppose that electrons might be describable as waves, and follow the consequences of that radical idea, the subject can open up before us. Astonishingly, we will find we can then understand a large fraction of those aspects of our everyday experience that can only be explained by quantum mechanics, such as color and the properties of materials. We will also be able to engineer novel phenomena and devices for quite practical applications.

On the face of it, proposing that we describe particles as waves is a strange intellectual leap in the dark. There is apparently nothing in our everyday view of the world to suggest we should do so. Nevertheless, it was exactly such a proposal historically (de Broglie's hypothesis) that opened up much of quantum mechanics. That proposal was made before there was direct experimental evidence of wave behavior of electrons. Once that hypothesis was embodied in the precise mathematical form of Schrödinger's wave equation, quantum mechanics took off.

Schrödinger's equation remains to the present day one of the most useful relations in quantum mechanics. Its most basic application is to model simple particles that have mass, such as a single electron, though the extensions of it go much further than that. It is also a good example of quantum mechanics, exposing many of the more general concepts. We will use these concepts as we go on to more complicated systems, such as atoms, or to other quite different kinds of particles and applications, such as photons and the quantum mechanics of light. Understanding Schrödinger's equation is therefore a very good way to start understanding quantum mechanics. In this Chapter, we introduce the simplest version of Schrödinger's equation – the time-independent form – and explore some of the remarkable consequences of this wave view of matter.

### 2.1 Rationalization of Schrödinger's equation

Why do we have to propose wave behavior and Schrödinger equation for particles such as electrons? After all, we are quite sure electrons are particles, because we know that they have definite mass and charge. And we do not see directly any wave-like behavior of matter in our

everyday experience. It is, however, now a simple and incontrovertible experimental fact that electrons can behave like waves, or at least in some way are “guided” by waves. We know this for the same reasons we know that light is a wave – we can see the interference and diffraction that are so characteristic of waves. At least in the laboratory, we see this behavior routinely.

We can, for example, make a beam of electrons by applying a large electric field in a vacuum to a metal, pulling electrons out of the metal to create a monoenergetic electron beam (i.e., all with the same energy). We can then see the wave-like character of electrons by looking for the effects of diffraction and interference, especially the patterns that can result from waves interacting with particular kinds or shapes of objects.

One common situation in the laboratory is, for example, to shine such a beam of electrons at a crystal in a vacuum. Davisson and Germer did exactly this in their famous experiment in 1927, diffracting electrons off a crystal of nickel. We can see the resulting diffraction if, for example, we let the scattered electrons land on a phosphor screen as in a television tube (cathode ray tube); we will see a pattern of dots on the screen. We would find that this diffraction pattern behaved rather similarly to the diffraction pattern we might get in some optical experiment; we could shine a monochromatic (i.e., single frequency) light beam at some periodic structure<sup>1</sup> whose periodicity was of a scale comparable to the wavelength of the waves (e.g., a diffraction grating). The fact that electrons behave both as particles (they have a specific mass and a specific charge, for example) and as waves is known as a “wave-particle duality.”<sup>2</sup>

The electrons in such wave diffraction experiments behave as if they have a wavelength

$$\lambda = \frac{h}{p} \quad (2.1)$$

where  $p$  is the electron momentum, and  $h$  is Planck's constant

$$h \cong 6.626 \times 10^{-34} \text{ Joule} \cdot \text{seconds} .$$

(This relation, Eq. (2.1), is known as de Broglie's hypothesis). For example, the electron can behave as if it were a plane wave, with a “wavefunction”  $\psi$ , propagating in the  $z$  direction, and of the form<sup>3</sup>

$$\psi \propto \exp(2\pi iz / \lambda) . \quad (2.2)$$

If it is a wave, or is behaving as such, we need a wave equation to describe the electron. We find empirically<sup>4</sup> that the electron behaves like a simple scalar wave (i.e., not like a vector wave, such as electric field,  $\mathbf{E}$ , but like a simple acoustic (sound) wave with a scalar amplitude; in acoustics the scalar amplitude could be the air pressure). We therefore propose that the electron wave obeys a scalar wave equation, and we choose the simplest one we know, the

<sup>1</sup> I.e., a structure whose shape repeats itself in space, with some spatial “period” or length.

<sup>2</sup> This wave-particle duality is the first, and one of the most profound, of the apparently bizarre aspects of quantum mechanics that we will encounter.

<sup>3</sup> We have chosen a complex wave here,  $\exp(2\pi iz / \lambda)$ , rather than a simpler real wave, such as  $\sin(2\pi z / \lambda)$  or  $\cos(2\pi z / \lambda)$ , because the mathematics of quantum mechanics is set up to require the use of complex numbers. The choice does also make the algebra easier.

<sup>4</sup> At least in the absence of magnetic fields or other magnetic effects.

“Helmholtz” wave equation for a monochromatic wave. In one dimension, the Helmholtz equation is

$$\frac{d^2\psi}{dz^2} = -k^2\psi \quad (2.3)$$

This equation has solutions such as  $\sin(kz)$ ,  $\cos(kz)$ , and  $\exp(ikz)$  (and  $\sin(-kz)$ ,  $\cos(-kz)$ , and  $\exp(-ikz)$ ), that all describe the spatial variation in a simple wave. In three dimensions, we can write this as

$$\nabla^2\psi = -k^2\psi \quad (2.4)$$

where the symbol  $\nabla^2$  (known variously as the Laplacian operator, “del squared”, and “nabla”, and sometimes written  $\Delta$ ) means

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad (2.5)$$

where  $x$ ,  $y$ , and  $z$  are the usual Cartesian coordinates, all at right angles to one another. This has solutions such as  $\sin(\mathbf{k}\cdot\mathbf{r})$ ,  $\cos(\mathbf{k}\cdot\mathbf{r})$ , and  $\exp(i\mathbf{k}\cdot\mathbf{r})$  (and  $\sin(-\mathbf{k}\cdot\mathbf{r})$ ,  $\cos(-\mathbf{k}\cdot\mathbf{r})$ , and  $\exp(-i\mathbf{k}\cdot\mathbf{r})$ ), where  $\mathbf{k}$  and  $\mathbf{r}$  are vectors. The wavevector magnitude,  $k$ , is defined as

$$k = 2\pi / \lambda \quad (2.6)$$

or, equivalently, given the empirical wavelength exhibited by the electrons (de Broglie's hypothesis, Eq. (2.1))

$$k = p / \hbar \quad (2.7)$$

where

$$\hbar = h / 2\pi \cong 1.055 \times 10^{-34} \text{ Joule} \cdot \text{seconds}$$

(a quantity referred to as “h bar”). With our expression for  $k$  (Eq. (2.7)), we can rewrite our simple wave equation (Eq. (2.4)) as

$$-\hbar^2 \nabla^2 \psi = p^2 \psi \quad (2.8)$$

We can now choose to divide both sides by  $2m_o$ , where, for the case of the electron,  $m_o$  is the free electron rest mass

$$m_o \cong 9.11 \times 10^{-31} \text{ kg}$$

to obtain

$$-\frac{\hbar^2}{2m_o} \nabla^2 \psi = \frac{p^2}{2m_o} \psi \quad (2.9)$$

But we know for Newtonian classical mechanics, where  $p = m_o v$  (with  $v$  as the velocity), that

$$\frac{p^2}{2m_o} \equiv \text{kinetic energy of an electron} \quad (2.10)$$

and, in general,

$$\text{Total energy } (E) = \text{Kinetic energy} + \text{Potential energy } (V(\mathbf{r})) \quad (2.11)$$

Note that this potential energy  $V(\mathbf{r})$  is the energy that results from the physical position (the vector  $\mathbf{r}$  in the usual coordinate space) of the particle.<sup>5</sup>

Hence, we can postulate that we can rewrite our wave equation (Eq. (2.9)) as

$$-\frac{\hbar^2}{2m_o}\nabla^2\psi = (E - V(\mathbf{r}))\psi \quad (2.12)$$

or, in a slightly more standard way of writing this,

$$\left(-\frac{\hbar^2}{2m_o}\nabla^2 + V(\mathbf{r})\right)\psi = E\psi \quad (2.13)$$

which is the time-independent Schrödinger equation for a particle of mass  $m_o$ .

Note that we have not “derived” Schrödinger’s equation. We have merely suggested it as an equation that agrees with at least one experiment. There is in fact no way to derive Schrödinger’s equation from first principles; there are no “first principles” in the physics that precedes quantum mechanics that predict anything like such wave behavior for the electron. Schrödinger’s equation has to be postulated, just like Newton’s laws of motion were originally postulated. The only justification for making such a postulate is that it works.<sup>6</sup>

## 2.2 Probability densities

We find in practice that the probability  $P(\mathbf{r})$  of finding the electron near any specific point  $\mathbf{r}$  in space is proportional to the modulus squared,  $|\psi(\mathbf{r})|^2$ , of the wave  $\psi(\mathbf{r})$ . The fact that we work with the squared modulus for such a probability is not so surprising. First of all, it assures that we always have a positive quantity (we would not know how to interpret a negative probability). Second, we are already aware of the usefulness of squared amplitudes with waves. The squared amplitude typically tells us the intensity (power per unit area) or energy density in a wave motion such as a sound wave or an electromagnetic wave. Given that we know that the intensity of electromagnetic waves also corresponds to the number of photons arriving per unit area per second, we would also find in the electromagnetic case that the probability of finding a photon at a specific point was proportional to the squared wave amplitude; if we chose to use complex notation to describe an electromagnetic wave, we would find that we would use the modulus squared of the wave amplitude to describe the wave intensity, and hence also the probability of finding a photon at a given point in space.<sup>7</sup>

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<sup>5</sup> Though the symbol  $V$  is used, it does not refer to a voltage, despite the fact that the potential energy can be (and often is) an electrostatic potential. It (and other energies in quantum mechanical problems) is often expressed in electron-volts, this being a convenient unit of energy, but it is always an energy, not a voltage.

<sup>6</sup> The reader should get used to this statement. Again and again, we will simply postulate things in quantum mechanics, with the only justification being that it works.

<sup>7</sup> Though the analogy between electromagnetic waves and quantum mechanical wave amplitudes may be helpful here, the reader is cautioned not to take this too far. The wave amplitude in a classical wave, such as an acoustic wave or the classical description of electromagnetic waves, is a measurable and meaningful quantity, such as air pressure or electric field (which in turn describes the actual force that would be experienced by a charge). The wave amplitude of a quantum mechanical wave does not describe any real quantity, and it is actually highly doubtful that it has any meaning at all other than as a

The fact that the probability is given by the modulus squared of some quantity, in this case the wavefunction  $\psi$ , leads us also to call that quantity the “probability amplitude” or “quantum mechanical amplitude.” Note that this probability amplitude is quite distinct from the probability itself; to repeat, the probability is proportional to the modulus squared of the probability amplitude. The probability amplitude is one of those new concepts that is introduced in quantum mechanics that has little or no precedent in classical physics or, for that matter, classical statistics. For the moment, we think of that probability amplitude as being the amplitude of a wave of some kind; we will find later that the concept of probability amplitudes extends into quite different descriptions, well beyond the idea of quantum mechanical waves, while still retaining the concept of the modulus squared representing a probability.

This use of probability amplitudes in quantum mechanics is an absolutely central concept, and a crucial but subtle one for the student to absorb. In quantum mechanics, we always first calculate this amplitude (here a wave amplitude) by adding up all contributions to it (e.g., all the different scattered waves in a diffraction experiment), and then take the squared modulus of the result to come up with some measurable quantity. We do not add the measurable quantities directly. The effect of adding the amplitudes is what gives us interference, allowing cancellation between two or more amplitudes, for example. We will not see such a cancellation phenomenon if we add the measurable quantities or probabilities from two or more sources (e.g., electron densities) directly. A good example to understand this point is the diffraction of electrons by two slits.

## 2.3 Diffraction by two slits

With our postulation of Schrödinger's equation, Eq. (2.13), and our interpretation of  $|\psi(\mathbf{r})|^2$  as proportional to the probability of find the electron at position  $\mathbf{r}$ , we are now in a position to calculate a simple electron diffraction problem, that of an electron wave being diffracted by a pair of slits<sup>8</sup>. We need some algebra and wave mechanics to set up this problem, but it is well worth the effort. This behavior is not only one we can use relatively directly to see and verify the wave nature of electrons; it is also a conceptually important “thought experiment” in understanding some of the most bizarre aspects of quantum mechanics, and we will keep coming back to it.

We consider two open slits, separated by a distance  $s$ , in an otherwise opaque screen (see Fig. 2.1). We are shining a monochromatic electron beam of wavevector  $k$  at the screen, in the

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way of calculating other quantities. A second very important difference is that, whereas a classical wave with higher intensity would be described by a larger amplitude of wave, in general the states of quantum mechanical systems with many electrons (or with many photons) cannot be described by quantum mechanical waves simply with larger amplitudes. Instead, the description of multiparticle systems involves products of the wave amplitudes of the waves corresponding to the individual particles, and sums of those products, in a much richer set of possibilities than a simple increase of the amplitude of a single wave. A third problem is that, in a proper quantum mechanical description of optics, there are many situations possible in which we have photons, but in which there is not anything very like the classical electromagnetic wave. Electromagnetic waves are not then actually analogous in a rigorous sense to the quantum mechanical wave that describes electron behavior.

<sup>8</sup> In optics, this apparatus is known as Young's slits, demonstrated by Thomas Young in about 1803. It is a remarkable experiment that enables us both to see the wave nature directly, and also to measure the wavelength without having to have some object at the same size scale as the wavelength itself. An instrument on a size scale of the wavelength of light (less than one micron) would have been unimaginable in 1803.

direction normal to the screen. For simplicity, we presume the slits to be very narrow compared to both the wavelength  $\lambda = 2\pi/k$  and the separation  $s$ . We also presume the screen is far away from the slits for simplicity, i.e.,  $z_o \gg s$ , where  $z_o$  is the position of the screen relative to the slits.

For simplicity of analysis, we will regard the slits as essentially point sources<sup>9</sup> of expanding waves, in the spirit of Huygens' principle. We write could write these waves in the form  $\exp(ikr)$ , where  $r$  is the radius from the source point<sup>10</sup>. We have therefore one source (slit) at  $x = s/2$ , and another at  $x = -s/2$ . The net wave should be the sum of the waves from these two sources. Remembering that in the  $x$ - $z$  plane the equation of a circle of radius  $r$  centered about a point  $x = a$  and  $z = 0$  is  $r^2 = (x - a)^2 + z^2$ , the net wave at the screen is

$$\psi_s(x) \propto \exp\left[ik\sqrt{(x - s/2)^2 + z_o^2}\right] + \exp\left[ik\sqrt{(x + s/2)^2 + z_o^2}\right] \quad (2.14)$$

where the first term corresponds to a wave expanding from the upper slit, and the second corresponds similarly with the wave from the lower slit. Note that we are adding the wave amplitudes here. If we presume we are only interested in the pattern on the screen for relatively small angles, i.e.,  $x \ll z_o$ , then<sup>11</sup>

$$\begin{aligned} \sqrt{(x - s/2)^2 + z_o^2} &= z_o \sqrt{1 + (x - s/2)^2 / z_o^2} \cong z_o + (x - s/2)^2 / 2z_o \\ &= z_o + x^2 / 2z_o + s^2 / 8z_o - sx / 2z_o \end{aligned} \quad (2.15)$$

and similarly for the other exponent (though with opposite sign for the term in  $s$ ). Hence, using  $2\cos(\theta) = \exp(i\theta) + \exp(-i\theta)$ , we obtain

$$\psi_s(x) \propto \exp(i\phi) \cos(ksx / 2z_o) = \exp(i\phi) \cos(\pi sx / \lambda z_o) \quad (2.16)$$

where  $\phi$  is a real number ( $\phi = k(z_o + x^2 / 2z_o + s^2 / 8z_o)$ ), so  $\exp(i\phi)$  is simply a phase factor. Hence, on the screen,

$$|\psi_s(x)|^2 \propto \cos^2(\pi sx / \lambda z_o) = \frac{1}{2} [1 + \cos(2\pi sx / \lambda z_o)] \quad (2.17)$$

So, if we shine a beam of monoenergetic electrons at the slits, and put some phosphorescent screen (like our cathode ray tube screen) some distance behind the slits, we should expect to see a (co)sinusoidal interference pattern, or "fringes", on the screen, with the fringes separated by a distance  $d_s = \lambda z_o / s$ .<sup>12</sup> This simple fringe pattern is somewhat idealized; with a more

<sup>9</sup> To be strictly correct, we should actually consider them as line sources since they extend in the direction out of the paper in Fig. 2.1. To consider such line sources rigorously that would complicate our mathematics to no real benefit in this explanation, however.

<sup>10</sup> More rigorously, for spherically expanding waves, we ought to write them in the form  $\exp(ikr)/r$  because they must get weaker with distance, but since we are considering essentially one large distance for the position of the screen, and we can neglect the  $r$  in the denominator.

<sup>11</sup> Remember the power series expansion  $\sqrt{1+a} \cong 1 + a/2 + \dots$  for small  $a$ , which can be proved by Taylor (or Maclaurin) expansion.

<sup>12</sup> Note, incidentally, that because the distance  $z_o$  is much greater than the slit separation, we can effectively measure the wavelength in such an experiment without ever having a measuring device that is the size of the wavelength, which is one of the other beauties of this experiment.

sophisticated diffraction model, and with finite width for the slits, the intensity of the fringes falls off for larger  $x$ , but the basic interference fringes we predict here will be observed near the axis as long as the slit separation is much larger than the slit width.

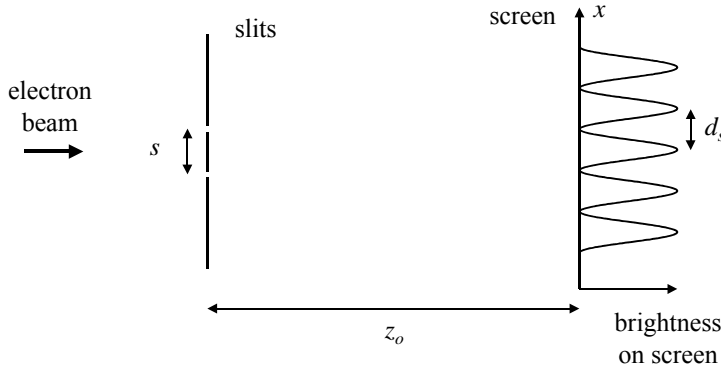


Fig. 2.1 A top view of diffraction from two slits, showing the form of the brightness of the interference pattern on a phosphorescent screen.

The existence of these interference effects for the quantum mechanical amplitudes has some bizarre consequences that we simply cannot understand classically. For example, suppose that we block one of the slits so the electrons can only go through one slit. Then we would not see the interference fringes. Near the axis we would see a broad featureless band<sup>13</sup> that is readily understood from wave diffraction from a single slit. Such a broad band is already difficult to explain based on a classical model of a particle; in a classical model, with the electron particles all traveling from left to right in straight lines, we would expect to see a relatively sharp spot on the screen. If we were determined to explain this broad band classically we might come up with some explanation, involving electrons bouncing off the edges of the slit, that would at least be qualitatively plausible (if ultimately incorrect). If we now uncover the second slit, however, we see something that cannot be explained by a classical particle picture – parts of the screen that were formerly bright now become dark (the minima of the (co)sinusoidal interference pattern described above). How can we explain that opening a second source of particles actually reduces the number of particles arriving at some point in the screen?

We might try to argue that the particles from the second slit were somehow bouncing off the ones from the first slit, and hence avoiding some particular part of the screen because of these collisions. If we repeat the experiment with extremely low electron currents so that there are never two electrons in the apparatus at a given time, and take a time-exposure picture of the phosphorescent screen, we will, however, see exactly the same interference pattern emerge, and we cannot now invoke some explanation that involves particles colliding with one

<sup>13</sup> The actual intensity diffraction pattern from a single slit of width  $w$  is, in this simple Huygens diffraction model, of the form  $\{[2z_o/kx][\sin(kxw/2z_o)]\}^2$ , which has a central “bright” band of width  $4\pi z_o/kw$ , and progressively weaker bands each half this width. This band will be much larger in size than the interference fringe separation in the two slit interference experiment as long as the slit width is much less than the slit separation. Note, incidentally, that the function  $(\sin x)/x$  is equal to 1 for  $x=0$ . If the reader is not familiar with this function, also often known as the “sinc” function, now would be a good time to graph it and understand how it behaves (it will come up again later).

another.<sup>14</sup> Hence we are forced even qualitatively to describe the behavior of the electrons in terms of some process involving interference of amplitudes, and we also find that the wave description postulated above does explain the behavior quantitatively.

Though a “two-slit” diffraction experiment of exactly the form described here might be quite difficult to perform in practice with electrons, diffraction phenomena such as this can be seen quite readily with electrons. Such diffraction is routinely used as a diagnostic and measurement tool. Electrons can be accelerated by electric fields and, if necessary, focused using magnetic and electric techniques. The wavelength associated with such accelerated electrons can be very small (e.g., an Ångstrom (1 Å), which is 0.1 nm). Diffractive effects are particularly strong when the wavelength is comparable to the size of an object (e.g., comparable to the slit spacing,  $s$ , above). Electrons can diffract quite strongly off crystal surfaces, for example, where the spacings between the atoms are on the order of Ångstroms or fractions of a nanometer.

One diagnostic technique, reflection high-energy electron diffraction (RHEED), for example, monitors the form of a crystal surface during the growth of crystalline layers; an electron beam incident at a shallow angle relative to the surface (i.e., nearly parallel with the crystal surface) is reflected and diffracted onto a phosphorescent screen to give a diffraction pattern characteristic of the precise form of the surface. Electron diffraction is also intrinsic to the operation of some kinds of electron microscope. In general, the fact that the electron wavelength can be so small means that electron microscopes can be used to view very small objects; it is practically difficult to image objects much smaller than a wavelength with any optical or wave-based technique because of diffractive effects, but the small wavelength possible in electron beams means that small objects or features can be seen.

## Problems

2.3.1 Suppose we have a screen that is opaque to electrons except for two thin slits separated by 5 nm. (We might imagine a plane of atoms with two missing rows of atoms, 5 nm apart, for example, as one way we might make such a structure.) We accelerate electrons, which are initially stationary, through 1 V of potential. These electrons arrive at the back of the screen perpendicular to the surface. A phosphorescent surface (e.g., like a cathode ray tube screen) is placed 10 cm away from the other side of the screen and parallel to it.

- (i) What is the spatial period of the bright and dark stripes seen on the phosphorescent surface (i.e., the distance between the centers of the bright stripes)?
- (ii) What is the period of the stripes if we use protons (hydrogen nuclei) instead of electrons? (The mass of a proton is  $\sim 1.67 \times 10^{-27}$  kg.)

2.3.2 In an electron diffraction experiment, consider a screen with a single vertical slit of finite width,  $d$ , in the  $x$  direction, “illuminated” from behind by a plane monochromatic electron wave of wavelength  $\lambda$ , with the wave fronts parallel to the plane of the slit (i.e., the wave is propagating perpendicularly to the screen). Presume that we take the simple “Huygens’ principle” model of diffraction, and, as above model the slit as a source of a spherically expanding (complex) wave (and hence each vertical line in the slit is a source of a circularly expanding wave).

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<sup>14</sup> Such experiments with single electrons and two slits raise other very interesting questions that probe the heart of the bizarre nature of quantum mechanics. Classically, we are tempted to ask, for any given electron passing through the slits to give one of the flashes on our screen that goes to make up the interference pattern over time on our photographic plate, which slit did the electron go through? In quantum mechanics that is apparently a meaningless question. Any attempt to measure which slit the electron goes through apparently destroys the interference pattern, so there is no measurable situation that corresponds to the question we wish to ask, and hence the question can be thrown out!



- (a) Find an approximate analytic expression for the form of the wave amplitude (by “form” we mean here that you may neglect any constant factor multiplying the wave amplitude) at a plane a distance  $z_o$  from the screen (assuming  $z_o \gg d$ ).
- (b) For a slit of width  $d = 1 \mu\text{m}$ , with an electron wavelength of  $\lambda = 50 \text{ nm}$ , plot the magnitude of the light intensity we would see on a phosphorescent screen placed 10 cm in front of the slit, as a function of the lateral distance in the  $x$  direction. Continue your plot sufficiently far in  $x$  to illustrate all of the characteristic behavior of this intensity.
- (c) Consider now two such slits in the screen, positioned symmetrically a distance  $5 \mu\text{m}$  apart in the  $x$  direction, but with all other parameters identical to part (b) above. Plot the intensity pattern on the phosphorescent screen for this case.

[Notes: You may presume that, in the denominator, the distance  $r$  from a slit to a point on the screen is approximately constant at  $r \approx z_o$  (though you must not make this assumption for the numerator in the calculation of the phase). You may also presume that for all  $x$  of interest on the screen,  $x \ll z_o$ , a so-called paraxial approximation. You will probably want to use a computer program or high-level mathematical computer package to plot the required functions. With this particular problem, you may find that you may want to avoid asking the program to calculate the amplitude or brightness at exactly  $x = 0$  since there may be a formal (though not actual) problem with evaluating the function there.]

## 2.4 Linearity of quantum mechanics: multiplying by a constant

Note that, in Schrödinger's equation (2.15), we could multiply both sides by a constant  $a$  and the equation would still hold. In other words, if  $\psi$  is a solution of Schrödinger's equation, so also is  $a\psi$ . This may seem a trivial property to point out, but the reason why this is possible is because Schrödinger's equation is *linear*. The wavefunction only appears in first order (i.e., to the power one) in the equation; there are no second-order terms, such as  $\psi^2$ , or any other terms that are higher order in  $\psi$ . The linearity (in this particular sense) of equations in quantum mechanics is of profound importance and generality. As far as we understand it, all quantum mechanical equations are linear in this sense (i.e., linear in the quantum mechanical amplitude for which the equation is being solved).

With classical fields, we often use linear equations, such as the differential equations that allow us to solve for small oscillatory motion of, say, a pendulum. In such a classical case, the linear equation is an approximation; a pendulum with twice the amplitude of oscillation will not oscillate at exactly the same frequency, for example. Hence we cannot take the solution derived at one amplitude of oscillation of the pendulum and merely scale it up for larger amplitudes of oscillation, except as a first approximation. We should emphasize right away, however, that, in quantum mechanics, this linearity of the equations with respect to the quantum mechanical amplitude is not an approximation of any kind; it is apparently an absolute property. Among other things, this linearity allows us to use the full power of linear algebra to handle the mathematics of quantum mechanics, a point to which we shall return later in some detail.

### Problems

- 2.4.1 Which of the following differential equations is linear, in the sense that, if some function  $\psi(z)$  is a solution (and this may well be a different function for each equation below), so also is the function  $\phi(z) = a\psi(z)$ , where  $a$  is an arbitrary constant? Justify your answers.

(i)  $z \frac{d\psi(z)}{dz} + g(z)\psi(z) = 0$  where  $g(z)$  is some specific function

- (ii)  $\psi(z) \frac{d\psi(z)}{dz} + \psi(z) = 0$
- (iii)  $\frac{d^2\psi(z)}{dz^2} + b \frac{d\psi(z)}{dz} = c\psi(z)$  where  $b$  and  $c$  are constants.
- (iv)  $\frac{d^3\psi(z)}{dz^3} = 1$
- (v)  $\frac{d^2\psi(z)}{dz^2} + \left(1 + |\psi(z)|^2\right) \frac{d\psi(z)}{dz} = g\psi(z)$  where  $g$  is a constant

[Note: you do not need to solve these equations for the function  $\psi(z)$ . Merely show that if  $\psi(z)$  is a solution, then  $a\psi(z)$  is or is not also a solution. Hint: is the equation for  $\phi(z)$  identical to the equation for  $\psi(z)$ , or does  $a$  unavoidably appear in the equation for  $\phi(z)$ , meaning  $\phi(z)$  is necessarily a solution of a different equation if we insist on arbitrary  $a$ ?]

## 2.5 Normalization of the wavefunction

We have postulated above that the probability  $P(\mathbf{r})$  of finding a particle near a point  $\mathbf{r}$  in space is  $\propto |\psi(\mathbf{r})|^2$ . So that we can use the concept of probability in its exact statistical sense, we should be more precise about this definition. Specifically, let us define  $P(\mathbf{r})$  as the probability per unit volume of finding the particle near the point  $\mathbf{r}$ ;  $P(\mathbf{r})$  can then rigorously be viewed as a “probability density”. Then, for some very small (infinitesimal) volume  $d^3\mathbf{r}$  around  $\mathbf{r}$ ,<sup>15</sup> the probability of finding the particle in that volume is  $P(\mathbf{r})d^3\mathbf{r} \propto |\psi(\mathbf{r})|^2 d^3\mathbf{r}$ . Presumably, we know that the particle is somewhere in the total volume of interest. Hence, the sum of such probabilities, considering all possible such infinitesimal volumes, should equal unity, i.e.,

$$\int P(\mathbf{r})d^3\mathbf{r} = 1 \quad (2.18)$$

where the integral is over the whole volume of interest. In general, unless we have been very cunning or very lucky, we will find that our first attempt at solving Schrödinger’s equation will lead to a solution  $\psi$  for which  $\int |\psi(\mathbf{r})|^2 d^3\mathbf{r} \neq 1$ . This integral will, however, be real (because it is an integral of a real quantity,  $|\psi(\mathbf{r})|^2$ ), so we will in general have

$$\int |\psi(\mathbf{r})|^2 d^3\mathbf{r} = \frac{1}{|a|^2} \quad (2.19)$$

where  $a$  is some number (possibly complex).<sup>16</sup> But we know from the discussion above on linearity that, if  $\psi$  is a solution, so also is  $\psi_N = a\psi$ , and we now have

$$\int |\psi_N(\mathbf{r})|^2 d^3\mathbf{r} = 1 \quad (2.20)$$

<sup>15</sup> Here  $d^3\mathbf{r}$  is just a shorthand for the volume element  $dx dy dz$  (in conventional Cartesian coordinates  $x$ ,  $y$ , and  $z$ )

<sup>16</sup> Functions that can be normalized in this way, i.e., that give a finite answer for an integral of their squared modulus, are sometimes referred to as “square integrable”, or, slightly more specifically in mathematical language, as being  $L^2$  functions. Here the “ $L$ ” refers to the name Lebesgue, and the superscript “2” refers to the fact that we are talking about an integral of the square of the function. The “Lebesgue” in turn refers to a formal method of integration that is more tolerant to some kinds of badly behaved functions than the “Riemann” integration that we normally perform, though gives the same answers for all normal situations. These details will not concern us here, and we mention these various terms just in case the reader comes across them in other contexts. See Appendix A.

This wavefunction solution  $\psi_N$  is referred to as a “normalized” wavefunction, and now there is a direct correspondence between probability density and the modulus squared of the wavefunction, i.e.,  $P(\mathbf{r}) = |\psi_N(\mathbf{r})|^2$ . The use of such normalized wavefunctions is quite convenient in the algebra of quantum mechanics.

Note, incidentally, that our plane wave, Eq. (2.2), cannot always be normalized in this way if we take the space of interest to be infinite. There is no way we can normalize a plane wave over an infinite space, for example, using this definition of normalization. Such problems can often be removed by considering that the particle is confined to some finite box, even if we take that box to be very large.<sup>17</sup>

## 2.6 Particle in an infinitely deep potential well (“particle in a box”)

Now that we have introduced the (time-independent) Schrödinger equation and some basic concepts like probability density and wavefunction normalization, we can proceed to solve some simple problems, starting with the so-called “particle in a box”. In following Sections, we will look at solutions for waves incident on steps, the particle in a box of finite depth, the harmonic oscillator, and various problems related to linearly varying potentials. These problems, and the hydrogen atom problem to which we will return in Chapter 10, are some of the main, exactly solvable problems in quantum mechanics. There are, unfortunately, relatively few other useful problems that can be solved exactly. Nearly all other practical problems have to be solved by approximation techniques, to which we will return in Chapter 6.<sup>18</sup>

The exactly solvable problems do give us much insight into quantum mechanics in general, and we will use these problems to illustrate a number of basic concepts in quantum mechanics. These problems are also at the root of the solution of many other actual practical problems. The particle-in-a-box problem is used routinely to design the so-called “quantum well” optoelectronic structures that are at the core of a large fraction of modern semiconductor optoelectronic devices, for example. The harmonic oscillator problem allows us to understand vibrating systems of many kinds, including, for example, acoustic vibrations in solids, and also electromagnetic waves, where it leads to the concept of photons (Chapter 15). The linearly varying potential is important for understanding the quantum mechanics of accelerating particles in fields, and has direct practical uses in semiconductor optical modulators and biased semiconductor devices generally.

We consider the simple problem of a particle, of mass  $m$ , with a spatially-varying potential  $V(z)$  in the  $z$  direction. We will not consider yet the fact that in a real structure the particle may also be able to move in the  $x$  and  $y$  directions. In fact, for a simple problem like a particle in a cubic box (or, more generally, a cuboidal box, i.e., one with rectangular faces), that motion can be considered separately and its consequences added in later.<sup>19</sup>

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<sup>17</sup> We will return to another way of normalizing functions like the plane wave in Section 5.4.

<sup>18</sup> The fact that there are only a few problems that are exactly solvable in quantum mechanics is more a statement about the limitations of mathematics than about the limitations of quantum mechanics. There are also relatively few problems that can be solved exactly in classical mechanics.

<sup>19</sup> Strictly, such a simple quantum-mechanical problem is “separable” mathematically in the three directions.

The (time-independent) Schrödinger equation for the particle's motion in the  $z$ -direction in our "one-dimensional" box is, then, the simple differential equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(z)}{dz^2} + V(z)\psi(z) = E\psi(z) \quad (2.21)$$

where  $E$  is the energy of the particle and  $\psi(z)$  is the wavefunction.

We are particularly interested in the case where the potential is a simple "rectangular" potential well (sometimes known also as a "square" potential well), i.e., one in which the potential energy is constant inside the well and rises abruptly at the walls. We choose the thickness of the well to be  $L_z$ . We can choose the value of  $V$  in the well to be zero for simplicity (this is only a choice of energy origin, and makes no difference to the physical meaning of the final results).

On either side of the well (i.e., for  $z < 0$  or  $z > L_z$ ), the potential,  $V$ , for this first problem, is presumed infinitely high. (Such a structure is sometimes called an infinite potential well.) Because these potentials are infinitely high, but the particle's energy  $E$  is presumably finite, we presume there can be no possibility of finding the particle in these regions outside the well. Hence the wavefunction  $\psi$  must be zero inside the walls of the well, and, to avoid a discontinuity in the wavefunction, we therefore reasonably ask that the wavefunction must also go to zero inside the well at the walls<sup>20</sup>. Formally putting this "infinite well" potential into Eq. (2.21), we have

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(z)}{dz^2} = E\psi(z) \quad (2.22)$$

within the well, subject to the boundary conditions

$$\psi = 0; \quad z = 0, L_z \quad (2.23)$$

The solution to Eq. (2.22) is very simple. The reader may well recognize the form of the equation (2.22). The general solution to this equation can be written

$$\psi(z) = A \sin(kz) + B \cos(kz) \quad (2.24)$$

where  $A$  and  $B$  are constants, and  $k = \sqrt{2mE/\hbar^2}$ . The requirement that the wavefunction goes to zero at  $z = 0$  means that  $B = 0$ . Because we are now left only with the sine part of (2.24), the requirement that the wavefunction goes to zero also at  $z = L_z$  then means that  $k = n\pi/L_z$ , where  $n$  is an integer. Hence, we find that the solutions to this equation are, for the wave,

$$\psi_n(z) = A_n \sin\left(\frac{n\pi z}{L_z}\right) \quad (2.25)$$

where  $A_n$  is a constant that can be any real or complex number, with associated energies

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<sup>20</sup> If the reader is bothered by the arguments here to justify these boundary conditions based on infinities (and is perhaps mathematically troubled by the discontinuities we are introducing in the wavefunction derivative), the reader can be assured that, if we take a well of finite depth, and solve that problem with boundary conditions that are more mathematically reasonable, the present "infinite well" results are recovered in the limit as the walls of the well are made arbitrarily high.

$$E_n = \frac{\hbar^2}{2m} \left( \frac{n\pi}{L_z} \right)^2 \quad (2.26)$$

We can restrict  $n$  to being a positive integer, i.e.,

$$n = 1, 2, \dots \quad (2.27)$$

for the following reasons. Since  $\sin(-a) = -\sin(a)$  for any real number  $a$ , the solutions with negative  $n$  are actually the same solutions as those with positive  $n$ ; all we would have to do to turn one into the other is change the sign of the constant  $A_n$ , and the sign of that is arbitrary anyway. The solution with  $n = 0$  is a trivial case; the wavefunction would be zero everywhere. If the wavefunction is zero everywhere, the particle is simply not anywhere, so the  $n = 0$  solution can be discarded. The resulting energy levels and wavefunctions are sketched in Fig. 2.2.

Solutions such as these, with a specific set of allowed values of a parameter (here energy) and with a particular function solution associated with each such value, are called eigen solutions; the parameter value is called the eigenvalue, the equation that gives rise to such solutions (here Eq. (2.21)) is called the eigenequation and the function is called the eigenfunction. It is possible to have more than one eigenfunction associated with a given eigenvalue, a phenomenon known as degeneracy. The number of such states with the same eigenvalue is sometimes called the degeneracy. Here, since the parameter is an energy, we can also call these eigenvalues the eigenenergies, and can refer to the eigenfunctions as the energy eigenfunctions.

Incidentally, we can see that the eigenfunctions in Fig. 2.2 have a very definite symmetry with respect to the middle of the well. The lowest ( $n = 1$ ) eigenfunction is the same on the right as on the left. Such a function is sometimes called an “even” function, or, equivalently, is said to have “even parity”. The second ( $n = 2$ ) eigenfunction is an exact inverted image, with the value at any point to the right of the center being exactly minus the value of the mirror image point on the left of the center. Such a function is correspondingly called an “odd” function or has “odd parity”. For this particular problem, the functions alternate between being even and odd, and all of the solutions are either even or odd, i.e., all the solutions have a definite parity. It is quite possible for solutions of quantum mechanical problems not to have either odd or even behavior; such a situation could arise if the form of the potential was not itself symmetric. In situations where the potential is symmetric, however, such odd and even behavior is very common, and can be quite useful since it can enable us to conclude that certain integrals and other quantum mechanical calculated properties will vanish exactly, for example.

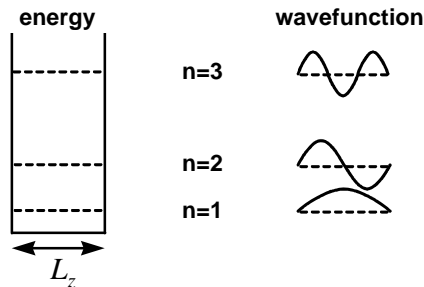


Fig. 2.2. Sketch of the energy levels in an infinitely deep potential well and the associated wavefunctions.

For completeness in this solution, we can normalize the eigenfunctions. We have

$$\int_0^{L_z} |A_n|^2 \sin^2\left(\frac{n\pi z}{L_z}\right) dz = |A_n|^2 \frac{L_z}{2} \quad (2.28)$$

To have this integral equal one for a normalized wavefunction, we therefore should choose  $|A_n| = (2/L_z)^{1/2}$ . Note that  $A_n$  can in general be complex, and it should be noted that the eigenfunctions are arbitrary within a constant complex factor; i.e., even the normalized eigenfunction can be arbitrarily multiplied by any factor  $\exp(i\theta)$  (where  $\theta$  is real). By convention, here we choose these eigenfunctions to be real quantities for simplicity, so the normalized wavefunctions become

$$\psi_n(z) = \sqrt{\frac{2}{L_z}} \sin\left(\frac{n\pi z}{L_z}\right) \quad (2.29)$$

Now we have mathematically solved this problem. The question is, what does this solution mean physically? We started out here by considering the known fact that electrons behave in some ways like propagating waves, as shown by electron diffraction effects. We constructed a simple wave equation that could describe such effects for monochromatic (and hence monoenergetic) electrons. What we have now found is that, if we continue with this equation that assumes the particle has a well-defined energy and put that particle in a box, there are only discrete values of that energy possible, with specific wavefunctions associated with each such value of energy. We are now going beyond the wave-particle duality we discussed before. This problem is showing us our first truly "quantum" behavior in the sense of the discreteness (or "quantization") of the solutions and the "quantum" steps in energy between the different allowed states.

There are several basic points about quantum confinement that emerge from this "particle-in-a-box" behavior that are qualitatively generally characteristic of such systems where we confine a particle in some region, and are very different from what we expect classically.

First, there is only a discrete set of possible values for the energy (Eq. (2.26)).

Second, there is a minimum possible energy for the particle, which is above the energy of the classical "bottom" of the box. In this problem, the lowest energy corresponds to  $n = 1$ , with the corresponding energy being  $E_1 = (\hbar^2 / 2m)(\pi / L_z)^2$ . This kind of minimum energy is sometimes called a "zero point" energy.

Third, the particle, as described by the modulus squared,  $|\psi_n|^2$ , of the appropriate eigenfunction, is not uniformly distributed over the box, and its distribution is different for different energies. It is never found very near to the walls of the box. In general, the probability of finding the electron at a particular point in the box obeys a kind of standing wave pattern. In the lowest state ( $n = 1$ ), it is most likely to be found near the center of the box. In higher states, there are points inside the box, away from the walls and corresponding to the other zeros of the sinusoidal eigenfunctions, where the particle will never be found.

All of these behaviors are very unlike the classical behavior of a classical particle (e.g., a billiard ball) inside a box.

We can also note that each successively higher energy state has one more "zero" in the eigenfunction (i.e., one more point where the function changes sign from positive to negative or *vice versa*). This is a very common behavior in quantum mechanics.

We can use this simple example to get some sense of orders of magnitude in quantum mechanics. Suppose we confine an electron in a box that is  $5 \text{ \AA}$  ( $0.5 \text{ nm}$ ) thick, a characteristic size for an atom or a unit cell in a crystal. Then the first allowed level for the electron is found at  $E_1 = (\hbar^2 / 2m_o)(\pi / 5 \times 10^{-10})^2 \cong 2.4 \times 10^{-19} \text{ J}$ .

In practice in quantum mechanics, it is usually inconvenient to work with energies in Joules. A more useful practical unit is the electron-Volt (eV). An electron-Volt is the amount of energy acquired by an electron in moving through an electric potential change of 1 V. Since the magnitude of the electronic charge is

$$e \cong 1.602 \times 10^{-19} \text{ C}$$

and the energy associated with moving such a charge through an electrostatic potential change of  $U$  is  $e \times U$ , then one electron-volt (1 eV) corresponds to an energy  $\cong 1.602 \times 10^{-19} \text{ J}$ . With this practical choice of energy units, the first allowed level in our  $5 \text{ \AA}$  wide well is  $2.4 \times 10^{-19} \text{ J} \cong 1.5 \text{ eV}$  above the energy of the bottom of the well. The separation between the first and second allowed energies ( $E_2 - E_1 = 3E_1$ ) is  $\sim 4.5 \text{ eV}$ , which is of the same magnitude as major energy separations between levels in an atom. (Of course, this one dimensional particle-in-a-box model is hardly a good one for an atom, but it does give a sense of energy and size scales.)

## Problems

- 2.6.1 An electron is in a potential well of thickness 1 nm, with infinitely high potential barriers on either side. It is in the lowest possible energy state in this well. What would be the probability of finding the electron between 0.1 and 0.2 nm from one side of the well?
- 2.6.2 Which of the following functions have a definite parity relative to the point  $x=0$  (i.e., we are interested in their symmetry relative to  $x=0$ )? For those that have a definite parity, state whether it is even or odd.
- $\sin(x)$
  - $\exp(ix)$
  - $(x-a)(x+a)$
  - $\exp(ix) + \exp(-ix)$
  - $x(x^2 - 1)$
- 2.6.3 Consider the problem of an electron in a one-dimensional “infinite” potential well of width  $L_z$  in the  $z$  direction (i.e., the potential energy is infinite for  $z < 0$  and for  $z > L_z$ , and, for simplicity, zero for other values of  $z$ ). For each of the following functions, in exactly the form stated, is this function a solution of the time-independent Schrödinger equation?
- $\sin(7\pi z / L_z)$
  - $\cos(2\pi z / L_z)$
  - $0.5 \sin(3\pi z / L_z) + 0.2 \sin(\pi z / L_z)$
  - $\exp(-0.4i) \sin(2\pi z / L_z)$
- 2.6.4 Consider an electron in a three-dimensional cubic box of side length  $L_z$ . The walls of the box are presumed to correspond to infinitely high potentials.
- Find an expression for the allowed energies of the electron in this box. Express your result in terms of the lowest allowed energy,  $E_1^\infty$ , of a particle in a one-dimensional box.
  - State the energies and describe the form of the wavefunctions for the 4 lowest energy states.
  - Are any of these states degenerate? If so, say which, and also give the degeneracy associated with any of the eigenenergies you have found that are degenerate.

[Note: This problem can be formally separated into three uncoupled one-dimensional equations, one for each direction, with the resulting wavefunction being the product of the three solutions, and the total energy being the sum of the three energies. This is easily verified by presuming this separation does work and finding that the product wavefunction is indeed a solution of the full three-dimensional equation.]

## 2.7 Properties of sets of eigenfunctions

### Completeness of sets – Fourier series

As we can see from Eq. (2.29), the set of eigenfunctions for this problem is the set of sine waves that includes all the harmonics of a sine wave that has exactly one half period within the well (i.e., sine waves with two half periods (one full period), three half periods, etc.). This set of functions has a very important property, very common in the sets of functions that arise in quantum mechanics, called “completeness”. We will discuss completeness in greater detail later, but we can illustrate it now through the relation of this particular set of functions to Fourier series.

The reader may well be aware that we could describe, for example, the movement of the loudspeaker in an audio system either in terms of the actual displacements of the loudspeaker cone at each successive instant in time, or, equivalently, in terms of the amplitudes (and phases) of the various frequency components that make up the music being played. These two descriptions are entirely equivalent, and both are “complete”; any conceivable motion can be described by the list of actual positions in time (so that approach is “complete”), or equivalently by the list of the amplitudes and phases of the frequency components.

The calculation of the frequency components required to describe the motion from the actual displacements in time is called Fourier analysis, and the resulting way of representing the motion in terms of these frequency components is called a Fourier series.

There are a few specific forms of Fourier series<sup>21</sup>. For a situation where we are interested in the behavior from time zero to time  $t_o$ , an appropriate Fourier series to represent the loudspeaker displacement,  $f(t)$  would be

$$f(t) = \sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi t}{t_o}\right) \quad (2.30)$$

where the  $a_n$  are the relevant amplitudes.<sup>22</sup>

We can see now that we could similarly represent any function  $f(z)$  between the positions  $z = 0$  and  $z = L_z$  as what we will now call, using a more general notation, an “expansion in the set of (eigen)functions”,  $\psi_n(z)$  from Eq. (2.29),

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<sup>21</sup> Fourier series can be constructed with combinations of sine functions, combinations of cosine functions, combinations of sine and cosine functions, and combinations of complex exponential functions.

<sup>22</sup> Strictly, with this choice of sine Fourier series, we have to exclude the end points  $t = 0$  and  $t = t_o$ , because there the function would have to be zero if we use this expansion. We can use this expansion to deal with functions that have finite values at any finite distance from these end points, however, so if we exclude the end points, this expansion is complete.



$$f(z) = \sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi z}{L_z}\right) = \sum_{n=1}^{\infty} b_n \psi_n(z) \quad (2.31)$$

where  $b_n = \sqrt{L_z/2} a_n$  to account for our formal normalization of the  $\psi_n$ . The coefficients  $a_n$  are the so-called “expansion coefficients” in the expansion of the function  $f(z)$  in the functions  $\sin(n\pi z/L_z)$ . Similarly the coefficients  $b_n$  are the expansion coefficients of  $f(z)$  in the functions  $\psi_n(z)$ .

Thus we have found that we can express any function between positions  $z = 0$  and  $z = L_z$  as an expansion in terms of the eigenfunctions of this quantum mechanical problem. We justified this expansion through our understanding of Fourier analysis. There are many other sets of functions that are also complete, and we will return to generalize these concepts later.

A set of functions such as the  $\psi_n$  that can be used to represent an arbitrary function  $f(z)$  is referred to as a “basis set of functions” or, more simply, a “basis”. The set of coefficients (amplitudes),  $b_n$ , would then be referred to as the “representation” of  $f(z)$  in the basis  $\psi_n$ . Because of the completeness of the set of basis functions  $\psi_n$ , this representation is just as good a one as the set of the amplitudes at every point  $z$  between zero and  $L_z$  required to specify or “represent” the function  $f(z)$  in ordinary space.

The eigenfunctions of differential equations are very often complete sets of functions. We will find quite generally that the sets of eigenfunctions we encounter in solving quantum mechanical problems are complete sets, a fact that turns out to be mathematically very useful, as we will see in later Chapters.

## Orthogonality of eigenfunctions

The set of functions  $\psi_n(z)$  have another important property, which is that they are “orthogonal”. In this context, two functions  $g(z)$  and  $h(z)$  are orthogonal<sup>23</sup> (formally, on the interval 0 to  $L_z$ ) if<sup>24</sup>

$$\int_0^{L_z} g^*(z)h(z)dz = 0 \quad (2.32)$$

It is easy to show for the specific  $\psi_n$  sine functions (Eq. (2.29)) that

$$\int_0^{L_z} \psi_n^*(z)\psi_m(z)dz = 0 \text{ for } n \neq m \quad (2.33)$$

and hence that the different eigenfunctions are orthogonal to one another. Indeed, it is obvious from parity considerations, without performing the integral algebraically, that this integral will vanish if  $\psi_n$  and  $\psi_m$  have opposite parity; in such a case, the product function will have odd parity with respect to the center of the well, and the net integral of any odd function is zero. Hence all the cases where  $n$  is an even number and  $m$  is an odd number, or where  $n$  is an odd number and  $m$  is an even number, lead to a net zero integral. The other cases are not quite so

<sup>23</sup> We formally presume that neither of these functions is zero everywhere (which would have made this orthogonality integral trivial).

<sup>24</sup>  $g^*(z)$  is the complex conjugate of  $g(z)$ . This explicit use of the complex conjugate may seem redundant given that the specific eigenfunctions we have considered so far have all been real, but this gives a more general statement of the orthogonality condition.

obvious, but performing the actual integration shows zero net integral for all cases where  $n \neq m$ .<sup>25</sup> For  $n = m$ , the integral reduces to the normalization integral already performed (Eq. (2.28)). Introducing the notation known as the Kronecker delta

$$\begin{aligned}\delta_{nm} &= 0, \quad n \neq m \\ \delta_{nn} &= 1\end{aligned}\tag{2.34}$$

we can therefore write

$$\int_0^{L_z} \psi_n^*(z) \psi_m(z) dz = \delta_{nm}\tag{2.35}$$

The relation Eq. (2.35) expresses both the fact that all different eigenfunctions are orthogonal to one another, and that the eigenfunctions are also normalized. A set of functions obeying a relation like Eq. (2.35) is said to be “orthonormal”, i.e., both orthogonal and normalized, and Eq. (2.35) is sometimes described as the orthonormality condition. Orthonormal sets turn out to be particularly convenient mathematically, so most basis sets are chosen to be orthonormal.

The property of the orthogonality of different eigenfunctions is again a very common one in quantum mechanics, and is not at all restricted to this specific simple problem where the eigenfunctions are sine waves.

## Expansion coefficients

The orthogonality (and orthonormality) of a set of functions makes it very easy to evaluate the expansion coefficients. Suppose we want to write the function  $f(x)$  in terms of a complete set of orthonormal functions  $\psi_n(x)$ , i.e.,

$$f(x) = \sum_n c_n \psi_n(x)\tag{2.36}$$

In general, incidentally, it is simple to evaluate the expansion coefficients  $c_n$  in Eq. (2.36). Explicitly, multiplying Eq. (2.36) on the left by  $\psi_m^*(x)$  and integrating, we have

$$\begin{aligned}\int \psi_m^*(x) f(x) dx &= \int \psi_m^*(x) \left[ \sum_n c_n \psi_n(x) \right] dx \\ &= \sum_n c_n \int \psi_m^*(x) \psi_n(x) dx = \sum_n c_n \delta_{nm} \\ &= c_m\end{aligned}\tag{2.37}$$

## Problems

2.7.1 Which of the following pairs of functions are orthogonal on the interval  $-1$  to  $+1$ ?

- (i)  $x, x^2$
- (ii)  $x, x^3$
- (iii)  $x, \sin x$

---

<sup>25</sup> Note that  $\sin(n\theta)\sin(m\theta) = (1/2)[\cos(n-m)\theta - \cos(n+m)\theta]$ . With  $\theta = \pi z/L_z$ , the integration limits for  $\theta$  become  $0$  to  $\pi$ . For a function  $\cos p\theta$ , except for  $p = 0$ , the function is either “odd” round about the middle of the integration interval (i.e., round about  $\pi/2$ ), so its integral is zero, or the integration is over a complete number of periods of the cosine functions, so its integral is again zero.  $p = 0$  occurs only for  $n = m$  in the first cosine term, and then the integration reduces to the normalization integral already performed.

- (iv)  $x, \exp(i\pi x/2)$   
 (v)  $\exp(-2\pi ix), \exp(2\pi ix)$

2.7.2 Suppose we wish to construct a set of orthonormal functions so that we can use them as a basis set.

We wish to use them to represent any function of  $x$  on the interval between  $-1$  and  $+1$ . We know that the functions  $f_0(x) = 1, f_1(x) = x, f_2(x) = x^2, \dots, f_n(x) = x^n, \dots$  are all independent, that is, we cannot represent one as a combination of the others, and in this problem we will form combinations of them that can be used as this desired orthonormal basis.

- (i) Show that not all of these functions are orthogonal on this interval. (You may prove this by finding a counter example.)
- (ii) Construct a set of orthogonal functions by the following procedure:
  - a) Choose  $f_0(x)$  as the (unnormalized) first member of this set, and normalize it to obtain the resulting normalized first member,  $g_0(x)$ .
  - b) Find an (unnormalized) linear combination of  $g_0(x)$  and  $f_1(x)$  of the form  $f_1(x) + a_{10}g_0(x)$  that is orthogonal to  $g_0(x)$  on this interval (this is actually trivial for this particular case), and normalize it to give the second member,  $g_1(x)$ , of this set.
  - c) Find a linear combination of the form  $f_2(x) + a_{20}g_0(x) + a_{21}g_1(x)$  that is orthogonal to  $g_0(x)$ , and  $g_1(x)$  on this interval, and normalize it to obtain the third member,  $g_2(x)$  of this set.
  - d) Write a general formula for the coefficient  $a_{ij}$  in the  $i+1$ th unnormalized member of this set.
  - e) Find the normalized fourth member,  $g_3(x)$ , of this set, orthogonal to all the previous members.
  - f) Is this the only set of orthogonal functions for this interval that can be constructed from the powers of  $x$ ? Justify your answer.

[Note: The above kind of procedure is known as Gram-Schmidt orthogonalization, and you should succeed in constructing a version of the Legendre polynomials by this procedure.]

## 2.8 Particles and barriers of finite heights

### Boundary conditions

Thus far, we have only considered a potential  $V$  that is either zero or infinite, which led to very simple boundary conditions for the problem (the wavefunction was forced to be zero at the boundary with the infinite potential). We would like to consider problems with more realistic, finite potentials, though for simplicity of mathematical modeling we would still like to be able to deal with abrupt changes in potential, such as a finite potential step.<sup>26</sup>

In particular, we would like to know what the boundary conditions should be on the wavefunction,  $\psi$ , and its derivative,  $d\psi/dz$ , at such a step. We know from the basic theory of second-order differential equations that, if we know both of these quantities on the boundaries,

<sup>26</sup> Any abrupt change in potential should really be regarded as unphysical. It is, however, practically useful to set up problems with such abrupt steps, essentially as simple models of more realistic systems with relatively steep changes in potential. We then, however, have to find mathematical constructions that get us out of the mathematical problems we have created by this abruptness, and these boundary conditions are such a construction. The choice of boundary conditions is really one that appears not to create any physical problems (such as losing particles or particle current), and would be a limiting case as a potential was made progressively more abrupt. The boundary conditions given here are not quite as absolute as one might presume, however. For example, if the mass of the particle varies in space (as does happen in some semiconductor problems), the boundary condition given here on the derivative of the wavefunction is not correct. The boundary condition of continuity of  $(1/m)(d\psi/dz)$  is then often substituted instead of continuity of  $d\psi/dz$ .

we can solve the equation. We are interested in solutions of Schrödinger's equation, Eq. (2.21), for situations where  $V$  is presumably finite everywhere, and where the eigenenergy  $E$  is also a finite number. If  $E$  and  $V$  are to be finite, then, for  $\psi(z)$  to be a solution to the equation,  $d^2\psi/dz^2$  must also be finite everywhere. For  $d^2\psi/dz^2$  to be finite,

$$d\psi/dz \text{ must be continuous} \quad (2.38)$$

(if there were a jump in  $d\psi/dz$ ,  $d^2\psi/dz^2$  would be infinite at the position of the jump), and  $d\psi/dz$  must be finite (otherwise  $d^2\psi/dz^2$  could also be infinite, being a limit of a difference involving an infinite quantity). For  $d\psi/dz$  to be finite,

$$\psi \text{ must be continuous} \quad (2.39)$$

These two conditions, Eqs. (2.38) and (2.39), will be the boundary conditions we will use to solve problems with finite steps in the potential.

## Reflection from barriers of finite height

Let us first remind ourselves of what a classical particle, such as a ball, does when it encounters a finite potential barrier. If the barrier is abrupt, like a wall, the ball is quite likely to reflect off the wall, even if the kinetic energy of the ball is more than the potential energy it would have at the top of the wall. (We loosely refer to the potential energy the ball or particle would have at the top of the barrier as the "height" of the barrier, hence expressing this "height" in energy units (usually electron-volts) rather than distance units.) If the barrier is a smoothly rising one, such as a gentle slope, the ball will probably continue over the barrier if its kinetic energy exceeds the (potential energy) height of the barrier. We certainly would not expect that the ball could get to the other side of the barrier if its kinetic energy was less than the barrier height. We also would never expect that the ball could be found inside the barrier region in that case. The behavior of a quantum mechanical particle at a potential barrier is quite different. As we shall see, it both can be found within the barrier and can get to the other side of the barrier, even if its energy is less than the height of the potential barrier.

We start by considering a barrier of finite height,  $V_o$ , but of infinite thickness, as shown in Fig. 2.3. For convenience, we choose the potential to be zero in the region to the left of the barrier (it would not matter if we chose it to be something different, since only energy differences actually matter in these kinds of quantum mechanical calculations).

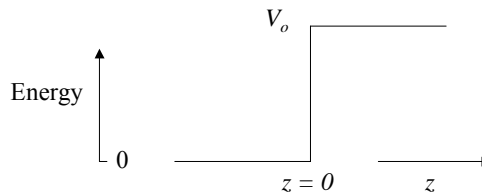


Fig. 2.3 Potential barrier of finite height, but infinite thickness.

We presume that a quantum mechanical wave is incident from the left on the barrier, and we presume that the energy,  $E$ , associated with this wave, is positive (i.e.,  $E > 0$ ). We are not going to be looking for eigenfunction solutions in this problem; we are merely considering what will happen to a monoenergetic particle wave as it interacts with the barrier, presuming that the energy  $E$  that we will consider is a valid one for the system overall.

We will also allow for possible reflection of the wave from the barrier into the region on the left. We can allow for both of these possibilities by allowing the wave on the left hand side to be the general solution of the wave equation in this region. That equation is the same as the Eq.

(2.22) we used above for the region inside the potential well, because in both cases the potential is presumed to be zero in this region. The general solution could be written as in Eq. (2.24), but here we choose instead to write the solution,  $\psi_{left}$ , for  $z < 0$  in terms of complex exponential waves

$$\psi_{left}(z) = C \exp(ikz) + D \exp(-ikz) \quad (2.40)$$

where we have, as before,  $k = \sqrt{2mE/\hbar^2}$ . Such a way of writing the solution can, of course, be exactly equivalent mathematically to that of Eq. (2.24).<sup>27</sup> The complex exponential form is conventionally used to represent running waves. In the convention we will use,  $\exp(ikz)$  represents a wave traveling to the right (i.e., in the positive  $z$  direction), and  $\exp(-ikz)$  represents a wave traveling to the left (i.e., in the negative  $z$  direction). The right traveling wave,  $C \exp(ikz)$ , is the incident wave, and the left-traveling wave,  $D \exp(-ikz)$ , represents the wave reflected from the barrier.

Now let us presume that  $E < V_o$ , i.e., we are presuming that the particle represented by the wave does not have enough energy classically to get over this barrier. Inside the barrier, the wave equation therefore becomes

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dz^2} = -(V_o - E)\psi \quad (2.41)$$

The mathematical solution of this equation is straightforward, being, for the wave,  $\psi_{right}$ , on the right (i.e., for  $z > 0$ ) in the general form,

$$\psi_{right}(z) = F \exp(\kappa z) + G \exp(-\kappa z) \quad (2.42)$$

where  $\kappa = (2m(V_o - E)/\hbar^2)^{1/2}$ .

We presume that  $F = 0$ . Otherwise the wave amplitude would increase exponentially to the right for ever, which does not appear to correspond to any classical or quantum mechanical behavior we see for particles incident from the left. (Also, the particle would never be found on the left because all of the probability amplitude would be arbitrarily far to the right because of the growing exponential.) Hence we are left with

$$\psi_{right}(z) = G \exp(-\kappa z) \quad (2.43)$$

Even this solution is strange. It proposes that the wave inside the barrier is not identically zero, but rather falls off exponentially as we move inside the barrier. Let us formally complete the mathematical solution here by using the boundary conditions (2.38) and (2.39). Continuity of the wavefunction, (2.39), gives us

$$C + D = G \quad (2.44)$$

and continuity of the derivative, (2.38), gives us

$$C - D = \frac{i\kappa}{k} G \quad (2.45)$$

Addition of Eqs. (2.44) and (2.45) gives us

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<sup>27</sup> Formally  $B = C + D$ ,  $A = -i(C - D)$ .

$$G = \frac{2k}{k+i\kappa}C = \frac{2k(k-i\kappa)}{k^2+\kappa^2}C = 2\frac{E-i\sqrt{(V_o-E)E}}{V_o}C \quad (2.46)$$

Subtraction of Eqs. (2.44) and (2.45) gives us

$$D = \frac{k-i\kappa}{k+i\kappa}C = \frac{2E-V_o-2i\sqrt{(V_o-E)E}}{V_o}C \quad (2.47)$$

Just as a check here, we find from Eq. (2.47) that  $|D/C|^2 = 1$ , so any incident particle is completely reflected.  $D/C$  is, however, complex, which means that there is a phase shift on reflection from the barrier, an effect with no classical precedent or meaning.

The most unusual aspect of this solution is the exponential decay of the wavefunction into the barrier. The fact that this exponential decay exists means that there must be some probability of finding the particle inside the barrier. This kind of behavior is sometimes called “tunneling” or “tunneling penetration”, by loose analogy with the classical idea that we could get inside or through a barrier that was too high simply by digging a tunnel. There is, however, little or no mathematical connection between the classical idea of a tunnel and this quantum mechanical process<sup>28</sup>.

The wavefunction has fallen off to  $1/e$  of its initial amplitude<sup>29</sup> in a distance  $1/\kappa$ . That distance is short when  $E \ll V_o$ , becoming longer as  $E$  approaches  $V_o$ ; the less is the energy deficit,  $V_o - E$ , the longer is the tunneling penetration into the barrier.

Let us look at some example numbers. Suppose that the barrier is  $V_o = 2$  eV high and that we are considering incident electrons with 1 eV energy. Then

$$\kappa = \sqrt{2 \times 9.1095 \times 10^{-31} \times (2-1) \times 1.602 \times 10^{-19} / (1.055 \times 10^{-34})^2} \cong 5 \times 10^9 \text{ m}^{-1}$$

In other words, the attenuation length of the wave amplitude into the barrier (i.e., the length to fall to  $1/e$  of its initial value) is  $1/\kappa \cong 0.2 \text{ nm} \cong 2 \text{ \AA}$ . Note that the probability density falls off twice as fast, i.e.,  $|\psi(z)|^2 \propto \exp(-2\kappa z)$ , so the penetration depth of the electron into the

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<sup>28</sup> Note, incidentally, that, though tunneling penetration is not a concept that has any meaning or precedent in the classical mechanics of classical particles, the phenomenon of tunneling is quite common when dealing with waves in general, including classical waves. Perhaps the best-known example is found in total internal reflection in optics. A wave inside a high refractive index medium, such as water or glass, at a sufficiently steep angle of incidence at the interface to the outside air (past the so-called critical angle), is totally reflected, just as the wave here is totally reflected by the barrier for energies below the barrier height. This phenomenon is well known to any swimmer who opens his or her eyes under water, with the water surface looking quite “silvery” and reflective for directions off at some angle. Though the reflection is total, there is an exponentially decaying field amplitude inside the air. Just as there is a phase shift here in reflecting the quantum mechanical wave from the barrier, so also is there a phase shift in this optical reflection. In optics, that phase shift leads to an effective sideways shift in the beam on reflection from this surface, known as the Goos-Hänchen shift. This optical tunneling is a routine part of the design and operation of optical waveguides, such as optical fibers. Once the mathematical equations are separated formally, leaving the forward waveguide propagation in another equation, the remaining equation for the wave in transverse direction is of the same form as we are discussing in this Section, with exactly analogous types of behavior. The propagating bound modes of an optical fiber are essentially the same concept as the bound states in a quantum potential well of finite depth, for example.

<sup>29</sup>  $e$  here is the base of the natural logarithms, not, obviously, the electronic charge.

barrier is  $\sim 1/2\kappa \cong 1 \text{ \AA}$ . This calculation also gives a sense of why the units of electron-volts and Ångstroms are commonly used in quantum mechanics for electrons.

Fig. 2.4 shows wavefunctions,  $\psi(z)$ , for an electron incident on such a barrier, and Fig. 2.5 shows the corresponding probability amplitudes,  $|\psi(z)|^2$ . (The real part of the wavefunction is shown in Fig. 2.4.<sup>30</sup>) Note in Fig. 2.4 and Fig. 2.5 that the reflection from the barrier (which is a total reflection in this case) leads to a standing wave pattern in the electron wavefunction and probability density. The position of the standing wave pattern depends on the phase change on reflection from the barrier, and this changes as the electron energy changes. For example, for a barrier that is very high compared to the electron energy, the phase change on reflection is  $\pi$  (i.e.,  $180^\circ$ , or, equivalently, phase reversal), and when the electron energy approaches the barrier energy, the phase change becomes  $\sim 0$ .

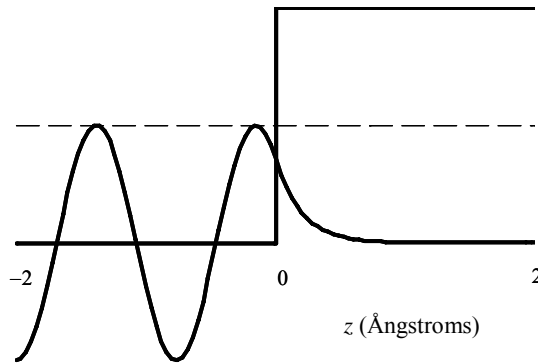


Fig. 2.4. Real part of the wavefunction  $\psi(z)$  for electrons with 1 eV of energy when incident on a barrier that is 2 eV high.

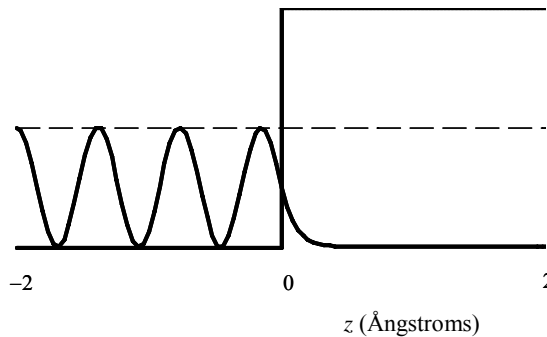


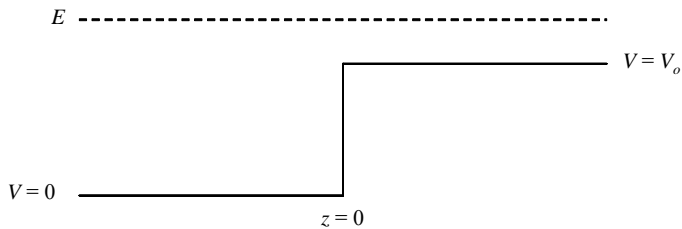
Fig. 2.5. Probability density  $\propto |\psi(z)|^2$  for electrons with the 1 eV of energy when incident on a barrier that is 2 eV high.

<sup>30</sup> For a solution of the time-independent Schrödinger equation, the complex conjugate of any solution  $\psi(z)$  is also a solution, as can be seen by taking the complex conjugate of both sides. Hence the sum of a solution and its complex conjugate is also a solution, so the real part of any solution is also a solution. This works because the terms that multiply or operate on the wavefunction  $\psi(z)$  are themselves real in the time-independent Schrödinger equation.

Problems

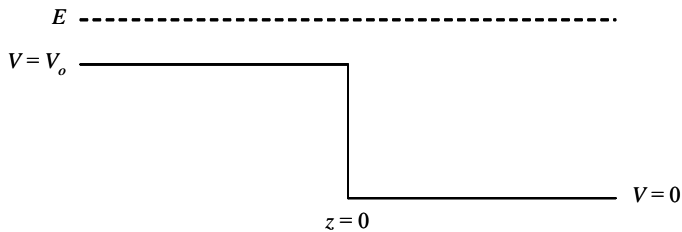
- 2.8.1 An electron of energy 1 eV is incident perpendicularly from the left on an infinitely high potential barrier. Sketch the form of the probability density for the electron, calculating a value for any characteristic distance you find in your result.
- 2.8.2 An electron wave of energy 0.5 eV is incident on an infinitely thick potential barrier of height 1 eV. Is the electron more likely to be found (a) within the first 1 Ångstrom of the barrier, or (b) somewhere further into the barrier?
- 2.8.3 Consider the one-dimensional problem, in the  $z$  direction, of an infinitely thick barrier of height  $V_o$ , at  $z = 0$ , beside an infinitely thick region with potential  $V = 0$ . We are interested in the behavior of an electron wave with electron energy  $E$ , where  $E > V_o$ .

(i) For the case where the barrier is to the right, i.e., the barrier is for  $z > 0$ , as shown below



and the electron wave is incident from the left,

- (a) solve for the wavefunction everywhere, within one arbitrary constant for the overall wavefunction amplitude
- (b) sketch the resulting probability density, giving explicit expressions for any key distances in your sketch, and being explicit about the phase of any standing wave patterns you find.



(ii) Repeat (i) but for the case where the barrier is on the left, i.e., for  $z < 0$ , the potential is  $V_o$ , and for  $z > 0$  the potential is  $V = 0$ , as shown in the second figure. The electron is still “incident” from the left (i.e., from within the barrier region in this case).

- 2.8.4 Graph the (relative) probability density as a function of distance for an electron wave of energy 1.5 eV incident from the left on a barrier of height 1 eV. Continue your graph far enough in distance on both sides of the barrier to show the characteristic behavior of this probability density.
- 2.8.5 Electrons with energy  $E$  are incident, in the direction perpendicular to the barrier, on an infinitely thick potential barrier of height  $V_o$  where  $E > V_o$ . Show that the fraction of electrons reflected from this barrier is

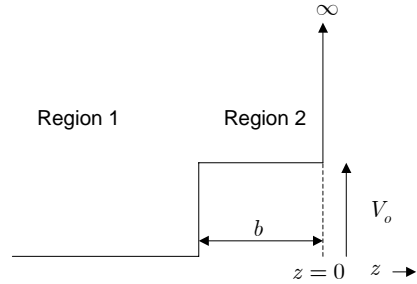
$$R = \left[ \frac{1 - a}{1 + a} \right]^2$$

where  $a = \sqrt{(E - V_o) / E}$ .

- 2.8.6 An electron wave of unit amplitude is incident from the left on the potential structure shown in the figure below. In this structure, the potential barrier at  $z = 0$  is infinitely high, and there is a potential step of height  $V_o$  and width  $b$  just to the left of the infinite potential barrier. The potential may be taken to be zero elsewhere on the left. For the purposes of this problem, we will only consider electron energies  $E > V_o$ .

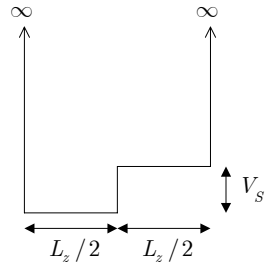


- (i) Show that the wavefunction in Region 2 may be written in the form  $\psi(z) = C \sin(fz)$  where  $C$  is a complex constant and  $f$  is a real constant.
- (ii) What is the magnitude of the wave amplitude of the reflected wave (i.e., the wave propagating to the left)?
- (iii) Find an expression for  $C$  in terms of  $E$ ,  $V_o$ , and  $b$ .
- (iv) Taking  $V_o = 1$  eV, and  $b = 10$  Å, sketch  $|C|^2$  as a function of energy from 1.1 eV to 3 eV.
- (v) Sketch the (relative) probability density in the structure at  $E = 1.356$  eV.
- (vi) Provide an explanation for the form of the curve in part (iv).



2.8.7 Consider an electron in the infinitely deep one-dimensional “stepped” potential well shown in the figure. The potential step is of height  $V_S$  and is located in the middle of the well, which has total width  $L_z$ .  $V_S$  is substantially less than  $(\hbar^2/2m_o)(\pi/L_z)^2$ .

- (i) Presuming that this problem can be solved, and that it results in a solution for some specific eigenenergy  $E_S$ , state the functional form of the eigenfunction solutions in each half of the well, being explicit about the values of any propagation constants or decay constants in terms of the eigenenergy  $E_S$ , the step height  $V_S$ , and the well width  $L_z$ . [Note: do not attempt a full solution of this problem – it does not have simple closed-form solutions for the eigenenergies. Merely state what the form of the solutions in each half would be if we had found an eigenenergy  $E_S$ .]
- (ii) Sketch the form of the eigenfunctions (presuming we have chosen to make them real functions) for each of the first two states of this well. In your sketch, be explicit about whether any zeros in these functions are in the left half, the right half, or exactly in the middle. [You may exaggerate differences between these wavefunctions and those of a simply infinitely deep well for clarity.]
- (iii) State whether each of these first two eigenfunctions have definite parity with respect to the middle of the structure, and, if so, whether that parity is even or odd.
- (iv) Sketch the form of the probability density for each of the two states.
- (v) State, for each of these eigenfunctions, whether the electron is more likely to be found in the left or the right half of the well.



## 2.9 Particle in a finite potential well

Now that we have understood the interaction of a quantum mechanical wave with a finite barrier, we can consider a particle in a “square” potential well of finite depth. This is a more realistic problem than the “infinite” (i.e., infinitely deep or with infinitely high barriers) square potential well. We presume a potential structure as shown in Fig. 2.6.

Here we have chosen the origin for the  $z$  position to be in the middle of the potential well (in contrast to the infinite well above where we chose one edge of the well). Such a choice makes no difference to the final results, but is mathematically more convenient now.

Such a problem is relatively straightforward to solve. Indeed, it is one of the few non-trivial quantum mechanical problems that can be solved analytically with relatively simple algebra and elementary functions, so it is a useful example to go through completely. It also has a close correspondence with actual problems in the design of semiconductor quantum well structures.

We consider for the moment to the case where  $E < V_o$ . Such solutions are known as bound states. For such energies, the particle is in some sense “bound” to the well. It certainly does not have enough energy classically to be found outside the well.

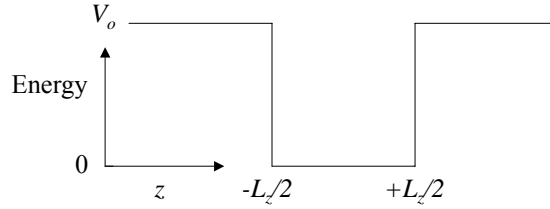


Fig. 2.6. A finite square potential well.

We know the nature of the solutions in the barriers (exponential decays away from the potential well) and in the well (sinusoidal), and we know the boundary conditions that link these solutions. We first need to find the values of the energy for which there are solutions to the Schrödinger equation, then deduce the corresponding wavefunctions.

The form of Schrödinger's equation in the potential well is the same as we had for the infinite well (i.e., Eq. (2.22)), and the solutions are of the same form (i.e., Eq. (2.24)), though the valid energies  $E$  and the corresponding values of  $k$  ( $=\sqrt{2mE/\hbar^2}$ ) will be different from the infinite well case. The form of the solution in the barrier is an exponential one as discussed above, except that the solution in the left barrier will be exponentially decaying to the left so that it does not grow as we move further away from the well. Hence, formally, the solutions are of the form

$$\begin{aligned}\psi(z) &= G \exp(\kappa z), \quad z < -L_z/2 \\ \psi(z) &= A \sin kz + B \cos kz, \quad -L_z/2 < z < L_z/2 \\ \psi(z) &= F \exp(-\kappa z), \quad z > L_z/2\end{aligned}\tag{2.48}$$

where the amplitudes  $A$ ,  $B$ ,  $F$ ,  $G$ , and the energy  $E$  (and consequently  $k$ , and  $\kappa = (2m(V_o - E)/\hbar^2)^{1/2}$ ) are constants to be determined. For simplicity of notation, we choose to write

$$X_L = \exp(-\kappa L_z/2), \quad S_L = \sin(kL_z/2), \quad C_L = \cos(kL_z/2)$$

so the boundary conditions give, from continuity of the wavefunction

$$GX_L = -AS_L + BC_L\tag{2.49}$$

$$FX_L = AS_L + BC_L\tag{2.50}$$

and from continuity of the derivative of the wavefunction

$$\frac{\kappa}{k}GX_L = AC_L + BS_L\tag{2.51}$$

$$-\frac{\kappa}{k}FX_L = AC_L - BS_L\tag{2.52}$$

Adding Eqs. (2.49) and (2.50) gives

$$2BC_L = (F + G)X_L\tag{2.53}$$

Subtracting Eq. (2.52) from Eq. (2.51) gives

$$2BS_L = \frac{\kappa}{k}(F+G)X_L \quad (2.54)$$

As long as  $F \neq -G$ , we can divide Eq. (2.54) by Eq. (2.53) to obtain

$$\tan(kL_z/2) = \kappa/k \quad (2.55)$$

Alternatively, subtracting Eq. (2.49) from Eq. (2.50) gives

$$2AS_L = (F-G)X_L \quad (2.56)$$

and adding Eqs. (2.51) and (2.52) gives

$$2AC_L = -\frac{\kappa}{k}(F-G)X_L \quad (2.57)$$

Hence, as long as  $F \neq G$ , we can divide Eq. (2.57) by Eq. (2.56) to obtain

$$-\cot(kL_z/2) = \kappa/k \quad (2.58)$$

For any situation other than  $F = G$  (which leaves Eq. (2.55) applicable but Eq. (2.58) not) or  $F = -G$  (which leaves Eq. (2.58) applicable but Eq. (2.55) not), the two relations (2.55) and (2.58) would contradict each other, so the only possibilities are (i)  $F = G$  with relation (2.55), and (ii)  $F = -G$  with relation (2.58).

For  $F = G$ , we see from Eqs. (2.56) and (2.57) that  $A = 0$ ,<sup>31</sup> so we are left with only the cosine wavefunction in the well, and the overall wavefunction is symmetrical from left to right (i.e., has even parity). Similarly, for  $F = -G$ ,  $B = 0$ , we are left only with the sine wavefunction in the well, and the overall wavefunction is antisymmetric from left to right (i.e., has odd parity). Hence, we are left with two sets of solutions.

To write these solutions more conveniently, we change notation. We define a useful energy unit, the energy of the first level in the infinite potential well of the same width  $L_z$ ,

$$E_1^\infty = \frac{\hbar^2}{2m} \left( \frac{\pi}{L_z} \right)^2 \quad (2.59)$$

and define a dimensionless energy

$$\varepsilon \equiv E / E_1^\infty \quad (2.60)$$

and a dimensionless barrier height

$$v_o \equiv V_o / E_1^\infty \quad (2.61)$$

Consequently,

$$\frac{\kappa}{k} = \sqrt{\frac{V_o - E}{E}} = \sqrt{\frac{v_o - \varepsilon}{\varepsilon}} \quad (2.62)$$

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<sup>31</sup> Note formally that  $C_L$  and  $S_L$  cannot both be zero at the same time, so the only way of satisfying both of these equations is for  $A$  to be zero.

$$\frac{kL_z}{2} = \frac{\pi}{2} \sqrt{\frac{E}{E_1^\infty}} = \frac{\pi}{2} \sqrt{\varepsilon} \quad (2.63)$$

$$\frac{\kappa L_z}{2} = \frac{\pi}{2} \sqrt{\frac{V_o - E}{E_1^\infty}} = \frac{\pi}{2} \sqrt{v_o - \varepsilon} \quad (2.64)$$

We can also conveniently define two quantities that will appear in the wavefunctions

$$c_L = \frac{C_L}{X_L} = \frac{\cos(kL_z/2)}{\exp(-\kappa L_z/2)} = \frac{\cos(\pi\sqrt{\varepsilon}/2)}{\exp(-\pi\sqrt{v_o - \varepsilon}/2)} \quad (2.65)$$

$$s_L = \frac{S_L}{X_L} = \frac{\sin(kL_z/2)}{\exp(-\kappa L_z/2)} = \frac{\sin(\pi\sqrt{\varepsilon}/2)}{\exp(-\pi\sqrt{v_o - \varepsilon}/2)} \quad (2.66)$$

and it will be convenient to define a dimensionless distance

$$\zeta = z/L_z \quad (2.67)$$

We can therefore write the two sets of solutions as follows.

#### *Symmetric solution*

The allowed energies satisfy

$$\sqrt{\varepsilon} \tan\left(\frac{\pi}{2}\sqrt{\varepsilon}\right) = \sqrt{v_o - \varepsilon} \quad (2.68)$$

The wavefunctions are

$$\begin{aligned} \psi(\zeta) &= Bc_L \exp(\pi\sqrt{v_o - \varepsilon}\zeta), \quad \zeta < -1/2 \\ \psi(\zeta) &= B \cos(\pi\sqrt{\varepsilon}\zeta), \quad -1/2 < \zeta < 1/2 \\ \psi(\zeta) &= Bc_L \exp(-\pi\sqrt{v_o - \varepsilon}\zeta), \quad \zeta > 1/2 \end{aligned} \quad (2.69)$$

#### *Antisymmetric solution*

The allowed energies satisfy

$$-\sqrt{\varepsilon} \cot\left(\frac{\pi}{2}\sqrt{\varepsilon}\right) = \sqrt{v_o - \varepsilon} \quad (2.70)$$

The wavefunctions are

$$\begin{aligned} \psi(\zeta) &= -As_L \exp(\pi\sqrt{v_o - \varepsilon}\zeta), \quad \zeta < -1/2 \\ \psi(\zeta) &= A \sin(\pi\sqrt{\varepsilon}\zeta), \quad -1/2 < \zeta < 1/2 \\ \psi(\zeta) &= As_L \exp(-\pi\sqrt{v_o - \varepsilon}\zeta), \quad \zeta > 1/2 \end{aligned} \quad (2.71)$$

Here  $A$  and  $B$  are normalization coefficients that will in general be different for each different solution.

The relations (2.68) and (2.70) do not give simple formulae for the allowed energies; these relations have to be solved to deduce the allowed energies, though this is straightforward in practice. A graphical illustration of the solutions of Eqs. (2.68) and (2.70) is shown in Fig. 2.7. Allowed energies  $\varepsilon$  correspond to the points where the appropriate solid curve (corresponding to the right hand side of these relations) intersects with one of the broken curves (corresponding to the left hand sides of these relations). Intersections with the dashed curves are solutions of Eq. (2.68) (corresponding to a symmetric solution), and intersections with the dot-dashed curves are solutions of Eq. (2.70) (corresponding to an antisymmetric solution).

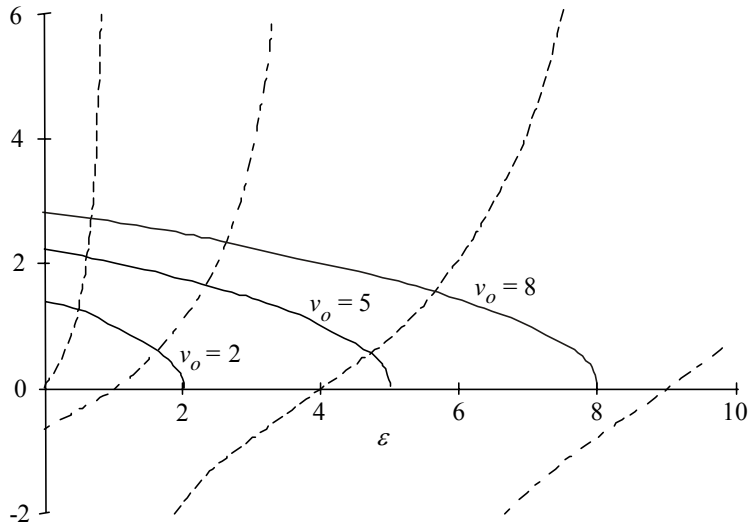


Fig. 2.7. Graphical solutions for equations (2.68) and (2.70) for the allowed energies in a finite potential well. The solid curves correspond to different values of the height of the potential barrier. The simple dashed lines correspond to Eq. (2.68), the symmetrical solutions, and the lines with alternating short and long dashes correspond to Eq. (2.70), the antisymmetric solutions. Allowed energy solutions correspond to the intersections of the solid and the various dashed curves.

We can see, for example, that for  $v_o = 8$ , there are three possible solutions: (i) a symmetric solution at  $\varepsilon = 0.663$ ; (ii) an antisymmetric solution at  $\varepsilon = 2.603$ ; and (iii) a symmetric solution at  $\varepsilon = 5.609$ . These three solutions are shown in Fig. 2.8.

Note that these solutions for  $E < V_o$  have two important characteristics. First, there are solutions of the time-independent Schrödinger equation only for specific discrete energies. We already saw such behavior for the infinite potential well, and here we have found this kind of behavior for a finite number of states in this finite well.<sup>32</sup> A second characteristic of these bound states is that the particle is indeed still largely found in the vicinity of the potential well, in correspondence with the classical expectation, though there is some probability of finding the particle in the barriers near the well. (Note the penetration of the wavefunction into the

<sup>32</sup> It is not generally true that there are only finite numbers of bound states in problems with bound states. The hydrogen atom, for example, has an infinite number of bound states, though each of those has a specific eigenenergy, and there are separations between the different eigenenergies for these bound states.

barrier rises for the higher energy states, as we would have expected from the behavior with the single barrier discussed in the previous Section.)

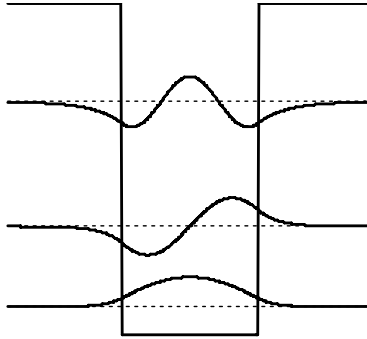


Fig. 2.8. First three solutions for a finite potential well of depth 8 units (the energy unit is the first confinement energy of an infinitely deep potential well of the same width). The dotted lines indicate the energies corresponding the three states. For convenience, these are used as the zeros for plotting the three eigenfunctions. Note the first and third levels have symmetric wavefunctions, and the second has an antisymmetric wavefunction.

We have considered only solutions to this problem for energies below the top of the potential well, i.e., for  $E < V_o$ . This problem can also be solved for energies above the top of the barrier, though we will omit this here. In that case, there are solutions possible for all energies, a so-called continuum of energy eigenstates, just as there are solutions possible for all energies in the simple problem where  $V$  is a constant everywhere (the well-known plane waves we have been using to discuss diffraction and waves reflecting from single barriers).

## Problems

2.9.1 Consider a one-dimensional problem with a potential barrier as shown below. A particle wave is incident from the left, but no wave is incident from the right. The energy,  $E$ , of the particle is less than the height,  $V_o$ , of the barrier.



- (i) Describe and sketch the form of the probability density in all three regions (i.e., on the left, in the barrier, and on the right). (Presume that the situation is one in which the transmission probability of the particle through the barrier is sufficiently large that the consequences of this finite transmission are obvious in the sketched probability density.)
- (ii) Show qualitatively how the probability density on the right of the barrier can be increased without changing the energy of the particle or the amplitude of the incident wave, solely by *increasing* the potential in some region to the left of the barrier. (This may require some creative thought!)

2.9.2 A one-dimensional potential well has a barrier of height 1.5 eV (relative to the energy of the bottom of the well) on the right hand side, and a barrier higher than this on the left hand side. We happen to know that this potential well has an energy eigenstate for an electron at 1.3 eV (also relative to the energy at the bottom of the well).

State the general form of the wavefunction solution (i.e., within a normalizing constant that you need not attempt to determine) in each of the following two cases, giving actual values for any wavevector magnitude  $k$  and/or decay constant  $\kappa$  in these wavefunctions

- (a) within the well
- (b) in the barrier on the right hand side

2.9.3 Consider a barrier, 10 Å thick and 1 eV high. An electron wave is incident on this barrier from the left (perpendicular to the barrier).

- (i) Plot the probability of the transmission of an electron from one side of this barrier to the other as a function of energy from 0 eV to 3 eV.
- (ii) Plot the probability density for the electron from 1 Å to the left of the barrier to 1 Å to the right of the barrier at an energy corresponding to the first maximum in the transmission for energies above the barrier.
- (iii) Attempt to provide a physical explanation for the form of the transmission as a function of energy for energies above the top of the barrier.

Hints:

- (1) The probability of transmission of the electron can be taken to be  $|\psi_{RF}|^2 / |\psi_{LF}|^2$ , where  $\psi_{LF}(z) \propto \exp(ikz)$  is the forward-going wave (i.e., the wave propagating to the right) on the left of the barrier, and  $\psi_{RF}(z) \propto \exp(ikz)$  is the forward-going wave on the right of the barrier.
- (2) Presume that there is a specific amplitude for the forward-going wave on the right, and no backward-going wave on the right (there is no wave incident from the right). This enables you to work the problem mathematically “backwards” from the right.
- (3) You may wish to use a computer program or high-level mathematical programming package to deal with this problem, or at least a programmable calculator. This problem can be done by hand, though it is somewhat tedious to do that.

2.9.4 In semiconductors, it is possible to make actual potential wells, quite similar to the finite potential well discussed above, by sandwiching a “well” layer of one semiconductor material (such as InGaAs) between two “barrier” layers of another semiconductor material (such as InP). In this structure, the electron has lower energy in the “well” material, and sees some potential barrier height  $V_o$  at the interface to the “barrier” materials. This kind of structure is used extensively in, for example, the lasers for telecommunications with optical fibers. In semiconductors, such potential wells are called “quantum wells”. In these semiconductors, the electrons in the conduction band behave as if they had an effective mass,  $m^*$ , that is different from the free electron mass,  $m_o$ , and this mass is different in the two materials, e.g.,  $m_w^*$  in the well and  $m_b^*$  in the barrier. Because the electron effective mass differs in the two materials, the boundary condition that is used at the interface between the two materials for the derivative of the wavefunction is not continuity of the derivative  $d\psi/dz$ ; instead, a common choice is continuity of  $(1/m)(d\psi/dz)$  where  $m$  is different for the materials in the well and in the barrier. (Without such a change in boundary conditions, there would not be conservation of electrons in the system as they moved in and out of the regions of different mass.) The wavefunction itself is still taken to be continuous across the boundary.

- (i) Rederive the relations for the allowed energies of states in this potential well (treating it like the one-dimensional well analyzed above), i.e., relations like (2.68) and (2.70) above, using this different boundary condition.
- (ii) InGaAs has a so-called “bandgap” energy of  $\sim 750$  meV. The bandgap energy is approximately the photon energy of light that is emitted in a semiconductor laser. This energy corresponds to a wavelength that is too long for optimum use with optical fibers. (The relation between photon energy,  $E_{photon}$ , in electron-volts and wavelength,  $\lambda$ , in meters is  $E_{photon} = hc/e\lambda$ , which becomes, for wavelengths in microns,  $E_{photon} \cong 1.24/\lambda_{(microns)}$ , a very useful relation to memorize.) For use with optical fibers we would prefer light with wavelength  $\sim 1.55$  microns. We wish to change the photon energy of emission from the InGaAs by making a quantum well structure with InGaAs between InP barriers. The confinement of electrons in this structure will raise the lowest possible energy for an electron in the conduction band by the “zero-point” energy of the electron (i.e. the energy of the first allowed state in the quantum well). Assuming for simplicity in this problem that the entire change in the bandgap is to come from this zero-

point energy of the electron, what thickness should the InGaAs layer be made? (For InGaAs, the electron effective mass is  $m_{InGaAs}^* \cong 0.041m_o$ , and for InP it is  $m_{InP}^* \cong 0.08m_o$ . The potential barrier seen by the electrons in the InGaAs at the interface with InP is  $V_o \cong 260$  meV.)

## 2.10 Harmonic oscillator

The second, relatively simple quantum mechanical problem that we will solve exactly is the harmonic oscillator. This system is one of the most useful in quantum mechanics, being the first approximation to nearly all oscillating systems. One of its most useful applications is in describing photons, and we will return to this point in Chapter 15. For the moment we will consider a simple mechanical oscillator.

Classical harmonic oscillators are ones that give a simple, sinusoidal oscillation in time. Such behavior results, for example, from linear springs whose (restoring) force,  $F$ , is proportional to distance,  $z$ , with some spring constant,  $s$ , i.e.,  $F = -sz$ . With a mass  $m$ , we obtain from Newton's second law ( $F = ma$  where  $a$  is acceleration,  $d^2z/dt^2$ )

$$m \frac{d^2z}{dt^2} = -sz \quad (2.72)$$

The solutions to such a classical motion are sinusoidal with angular frequency

$$\omega = \sqrt{s/m} \quad (2.73)$$

(e.g., of the form  $\sin \omega t$ ). To analyze such an oscillator quantum mechanically using Schrödinger's equation, we need to cast the problem in terms of potential energy. The potential energy,  $V(z)$ , is the integral of force exerted on the spring (i.e.,  $-F$ ) times distance, i.e.,

$$V(z) = \int_0^z -F dz = \frac{1}{2} sz^2 = \frac{1}{2} m\omega^2 z^2 \quad (2.74)$$

Hence, for a quantum mechanical oscillator, we have a Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dz^2} + \frac{1}{2} m\omega^2 z^2 \psi = E\psi \quad (2.75)$$

To make this more manageable mathematically, we define a dimensionless unit of distance

$$\xi = \sqrt{\frac{m\omega}{\hbar}} z \quad (2.76)$$

Changing to this variable, and dividing by  $-\hbar\omega$ , we obtain

$$\frac{d^2\psi}{d\xi^2} - \xi^2 \psi = -\frac{2E}{\hbar\omega} \psi \quad (2.77)$$

The reader might be astute enough to spot<sup>33</sup> that one specific solution to this equation is of the form  $\psi \propto \exp(-\xi^2/2)$  (with a corresponding energy  $E = \hbar\omega/2$ ). This suggests that we make a choice of form of function

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<sup>33</sup> It is, in fact, quite unlikely that any normal reader could possibly be astute enough to spot this. The reason why the author is astute enough to spot this is, of course, because he knows the answer already.



$$\psi_n(\xi) = A_n \exp(-\xi^2/2) H_n(\xi) \quad (2.78)$$

where  $H_n(\xi)$  is some set of functions still to be determined. Substituting this form in the Schrödinger equation (2.77), we obtain, after some algebra, the equation

$$\frac{d^2 H_n(\xi)}{d\xi^2} - 2\xi \frac{dH_n(\xi)}{d\xi} + \left( \frac{2E}{\hbar\omega} - 1 \right) H_n(\xi) = 0 \quad (2.79)$$

The solutions to this equation are known. This equation turns out to be the defining differential equation for the Hermite polynomials. Solutions exist provided

$$\frac{2E}{\hbar\omega} - 1 = 2n, \quad n = 0, 1, 2, \dots \quad (2.80)$$

i.e.,

$$E = \left( n + \frac{1}{2} \right) \hbar\omega \quad (2.81)$$

(Note that here  $n$  starts from zero, not 1.) Here we see the first remarkable property of the harmonic oscillator – the allowed energy levels are equally spaced, separated by an amount  $\hbar\omega$ , where  $\omega$  is the classical oscillation frequency. Like the potential well, there is also a “zero point energy” – the first allowed state is not at zero energy, but instead here at  $\hbar\omega/2$  compared to the classical minimum energy.

The first few Hermite polynomials are as follows.

$$H_0 = 1 \quad (2.82)$$

$$H_1(\xi) = 2\xi \quad (2.83)$$

$$H_2(\xi) = 4\xi^2 - 2 \quad (2.84)$$

$$H_3(\xi) = 8\xi^3 - 12\xi \quad (2.85)$$

$$H_4(\xi) = 16\xi^4 - 48\xi^2 + 12 \quad (2.86)$$

Note that the functions are either entirely odd or entirely even, i.e., they have a definite parity.

The polynomials have some other useful properties. In particular, they satisfy a recurrence relation

$$H_n(\xi) = 2\xi H_{n-1}(\xi) - 2(n-1)H_{n-2}(\xi) \quad (2.87)$$

which means that the successive Hermite polynomials can be calculated from the previous two.

The normalization coefficient,  $A_n$ , in the wavefunction (2.78) is

$$A_n = \sqrt{\frac{1}{\sqrt{\pi} 2^n n!}} \quad (2.88)$$

and the wavefunction can be written explicitly in the original coordinate system as

$$\psi_n(z) = \sqrt{\frac{1}{2^n n!} \sqrt{\frac{m\omega}{\pi\hbar}}} \exp\left(-\frac{m\omega}{2\hbar} z^2\right) H_n\left(\sqrt{\frac{m\omega}{\hbar}} z\right) \quad (2.89)$$

The first several harmonic oscillator eigenfunctions are shown in Fig. 2.9, together with the parabolic potential  $V (= \xi^2 / 2$  in the dimensionless units).

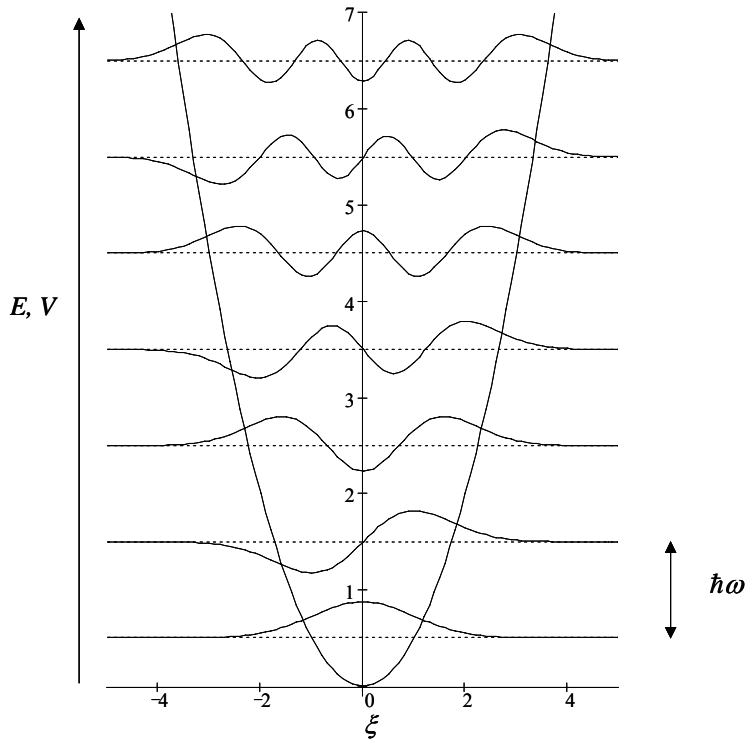


Fig. 2.9. Illustration of the eigenfunctions of a harmonic oscillator. Each eigenfunction is plotted relative to an origin that corresponds to the eigenenergy (i.e.,  $\hbar\omega/2$ ,  $3\hbar\omega/2$ , etc.). The parabolic harmonic oscillator potential is also shown.

The reader may be content that we have found the solution to Schrödinger's time-independent wave equation for the case of the harmonic oscillator, just as we did for the infinite and finite potential wells. But on reflection the reader may well now be perplexed. Surely this is meant to be an oscillator; then why is it not oscillating? We have calculated stationary states for this oscillator, including stationary states in which the oscillator has energy much greater than zero. This would appear to be meaningless classically; an oscillator that has energy ought to oscillate. To understand how we recover oscillating behavior, and indeed to understand the true meaning of the stationary eigenstates we have calculated, we need first to understand the time-dependent Schrödinger equation, which is the subject of the next Chapter.

## Problem

- 2.10.1 Suppose we have a "half harmonic oscillator" potential, e.g., exactly half of a parabolic potential on the right of the "center" and an infinitely high potential barrier to the left of the center. Compared to the normal harmonic oscillator, what are the (normalized) energy eigenfunctions and eigenvalues? [Hint: there is very little you have to solve here – this problem mostly requires thought, not mathematics.]

## 2.11 Particle in a linearly varying potential

(This topic can be omitted on a first reading, though it does give some very useful insights into wave mechanics, and is useful for several practical problems.)

Another situation that occurs frequently in quantum mechanics is that we have applied a uniform electric field,  $E$ , in some direction, say the  $z$  direction. For a charged particle, this leads to a potential that varies linearly in distance. For example, an electron, which is negatively charged with a charge of magnitude  $e$ , will see a potential energy, relative to that at  $z = 0$ , of

$$V = eEz \quad (2.90)$$

In practice, we find this kind of potential in many semiconductor devices. We use it when we are calculating the quantum mechanical penetration (tunneling) through the gate oxide in Metal-Oxide-Semiconductor (MOS) transistors, for example. We see it in semiconductor optical modulators,<sup>34</sup> which use optical absorption changes that result from electric fields. It is of basic interest also if we want to understand how an electron is accelerated by a field, a point to which we will return in the next Chapter.

The technique for solving for the electron states is just the same as before; we merely have to put this potential into the Schrödinger equation and solve the equation. The Schrödinger equation then becomes

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(z)}{dz^2} + eEz\psi(z) = E\psi(z) \quad (2.91)$$

The solutions to this equation are not obvious combinations of well-known functions. When one finds an equation such as this, the most productive practical technique for solving it is to look up a mathematical reference book<sup>35</sup> to see if someone has solved this kind of equation before. This particular kind of equation, with a linearly varying potential, has solutions that are so-called "Airy" functions. The standard form of differential equation that defines Airy functions is

$$\frac{d^2 f(\zeta)}{d\zeta^2} - \zeta f(\zeta) = 0 \quad (2.92)$$

The solutions of this equation are formally the Airy functions  $Ai(\zeta)$  and  $Bi(\zeta)$ , i.e., the general solution to this equation is

$$f(\zeta) = a Ai(\zeta) + b Bi(\zeta) \quad (2.93)$$

To get Eq. (2.91) into the form of Eq. (2.92), we make a change of variable to

$$\zeta = \left( \frac{2meE}{\hbar^2} \right)^{1/3} \left( z - \frac{E}{eE} \right) \quad (2.94)$$

<sup>34</sup> There are two closely related electroabsorption mechanisms used in semiconductors. The Franz-Keldysh effect in bulk semiconductors, and the quantum-confined Stark effect in quantum wells, both of which rely on this underlying physics.

<sup>35</sup> A very comprehensive reference is M. Abramowitz and I. A. Stegun, "Handbook of Mathematical Functions" (National Bureau of Standards, Washington, 1972)

The reader can verify this change of variable does work by substituting the right hand side of Eq. (2.94) each time for  $\zeta$  in Eq. (2.92), which will give Eq. (2.91) after minor manipulations.

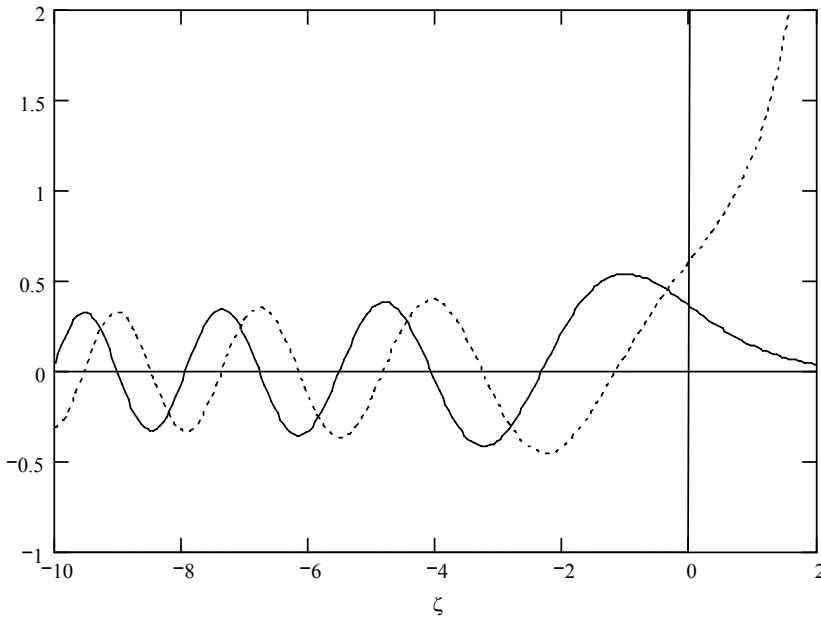


Fig. 2.10. Airy functions  $Ai(\zeta)$  (solid line) and  $Bi(\zeta)$  (dashed line).

The functions  $Ai$  and  $Bi$  are plotted in Fig. 2.10. Though they are not very common functions, they are usually available in advanced mathematics programs as built-in functions.<sup>36</sup> Note that

- (i) both functions are oscillatory for negative arguments, with a shorter and shorter period as the argument becomes more negative.
- (ii) The  $Ai$  function decays in an exponential-like fashion for positive arguments.
- (iii) The  $Bi$  function diverges for positive arguments.

Now let us examine solutions to some specific problems.

### Linear potential without boundaries

The simplest situation mathematically is just a potential that varies linearly without any additional boundaries or walls. This is somewhat unphysical since it presumes some source of potential, such as an electric field, that continues forever in some direction, but it is a simple idealization when we are far from any boundary. The mathematics allows for two possible solutions, one based on the  $Ai$  function, and the other based on the  $Bi$  function. Physically, we discard the  $Bi$  solution here because it diverges for positive arguments, becoming larger and larger. Any attempt at normalizing this function would fail, and the particle would have increasing probability of being found at arbitrarily large positive  $z$ . This is the same argument we used to ignore the exponentially growing solution when considering penetration into an infinitely thick barrier. We are left only with the  $Ai$  function in this case. Substituting back from the change of variable, Eq. (2.94), the  $Ai(\zeta)$  solution becomes explicitly

<sup>36</sup> The Airy functions are also related to Bessel functions of  $1/3$  fractional order.

$$\psi_E(z) = Ai\left(\left(\frac{2meE}{\hbar^2}\right)^{1/3}\left(z - \frac{E}{eE}\right)\right) \quad (2.95)$$

This solution is sketched, for a specific eigenenergy  $E_o$ , together with the potential energy, in Fig. 2.11.

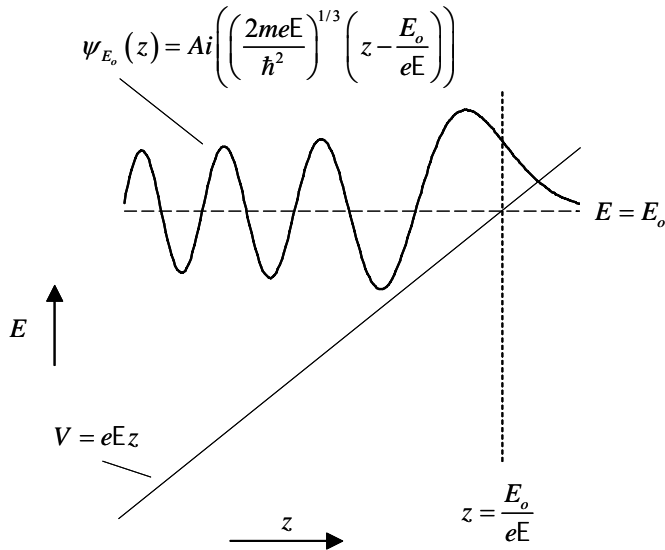


Fig. 2.11. Sketch of a linearly varying potential, and the Airy function solution of the resulting Schrödinger equation.

There are several interesting aspects about this solution.

- (i) Since we have introduced no additional boundary conditions, there are mathematical solutions for any possible value of the eigenenergy  $E$ . This behavior reminds us of the simple case of a uniform zero potential (i.e.,  $V = 0$  everywhere), which leads to plane wave solutions for any positive energy. In the present case also, the allowed values of the eigenenergies are continuous, not discrete. Like the case of a uniform potential, the eigenstates are not bound within some finite region (at least for negative  $z$ ).
- (ii) The solution is oscillatory when the eigenenergy is greater than the potential energy, which occurs on the left of the point  $z = E_o/eE$ , and it decays to the right of this point. This point is known as the classical turning point, because it is the furthest to the right that a classical particle of energy  $E_o$  could go.
- (iii) The eigenfunction solutions for different energies are the same except they are shifted sideways (i.e., shifted in  $z$ ).
- (iv) Unlike the uniform potential case, the solutions here are not running waves; rather, they are standing waves, which is more like the case of the particle in a box.

We again find, just like the harmonic oscillator case, that we have been able to derive eigenstates, i.e., states that are stable in time. Just as in the harmonic oscillator case, where classically we would have expected to get an oscillation if we have finite energy, here we would have expected classically to get states that correspond to the electron being accelerated. Simply put, we have put an electron in an electric field, and the electron is not moving. Again,

to resolve this paradox, we need to consider the time-dependent Schrödinger equation, which we will cover in the next Chapter.

How is it that we could even have a standing wave in this case? In the case of a particle in a box, we can easily rationalize that the particle is reflecting off the walls. In the present case, we could presumably readily accept that the particle should bounce off the increasing potential seen at or near the classical turning point, so it is relatively easy to see why there is a reflection at the right. There is also here reflection from the left; the reason for this reflection is that, from the point of view in general of wave mechanics, any change in potential (or change of impedance in the case of acoustic or electromagnetic waves), even if it is smooth rather than abrupt, leads to reflections. Effectively, there is a distributed reflection on the left from the continuously changing potential there. The fact that there is such a distributed reflection explains why the wave amplitude decreases progressively as we go to the left. The fact that we have a standing wave is apparently because, integrated up, that reflection does eventually add up to 100%.

Why does the period of the oscillations in the wave decrease (i.e., the oscillations become faster) as we move to the left? Suppose in Schrödinger's equation we divide both sides by  $\psi$ , then we have

$$\frac{-\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dz^2} + V(z) = E \quad (2.96)$$

For any eigenstate of the Schrödinger equation,  $E$  is a constant (the eigenenergy). In such a state, if  $V$  decreases, then  $-(1/\psi)(d^2\psi/dz^2)$  (which we can visualize as the degree of curvature of the wavefunction) must increase. If we imagine that we have an oscillating wave, which we presume is locally approximately sinusoidal, of the form  $\sim \sin(kz + \theta)$  for some phase angle  $\theta$ ,

$$\frac{-1}{\psi} \frac{d^2\psi}{dz^2} = k^2 \quad (2.97)$$

Hence, if  $V$  decreases, the wavevector  $k$  must increase, i.e., the period must decrease. Viewed from the perspective of the particle, we could imagine that the particle is going increasingly fast as it goes towards the left, being accelerated by the field, or equivalently, is going increasingly slowly as it goes towards the right, being decelerated by the field, either of which is consistent with smaller periods as we go to the left. This view of particle motion is not very rigorous, though there is a kernel of truth to it, but for a full understanding in terms of particle motion, we need the time-dependent Schrödinger equation of the next Chapter.

### Triangular potential well

If we put a hard barrier on the left, we again get a discrete set of eigenenergies. Formally, we can consider an electron, still in a uniform electric field  $E$ , with an infinitely high potential barrier at  $z = 0$  (i.e., the potential is infinite for all negative  $z$ ) as shown in Fig. 2.12, with the potential taken to be zero at  $z = 0$  (or at least just to the right of  $z = 0$ ).

For all  $z > 0$ , we have the same potential as we considered above. Again we can discard the  $Bi$  solution because it diverges, so we are left with the  $Ai$  solution. Now we have the additional boundary condition imposed by the infinitely high potential at  $z = 0$ , which means the wavefunction must go to zero there. This is easily achieved with the  $Ai$  function if we position it laterally so that one of its zeros is found at  $z = 0$ . The  $Ai(\zeta)$  function will have zeros for a

set of values  $\zeta_i$ . These can be found in mathematical tables, or are relatively easily calculated numerically in advanced mathematics programs.

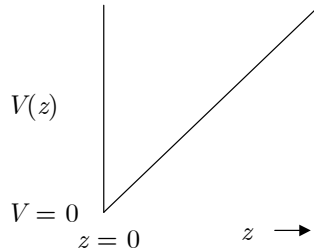


Fig. 2.12 Triangular potential well.

The first few of these zeros are

$$\begin{aligned}\zeta_1 &\approx -2.338 \\ \zeta_2 &\approx -4.088 \\ \zeta_3 &\approx -5.521 \\ \zeta_4 &\approx -6.787 \\ \zeta_5 &\approx -7.944\end{aligned}\tag{2.98}$$

To get the solution Eq. (2.95) to be zero at  $z = 0$  means therefore that

$$Ai\left(\left(\frac{2mE}{\hbar^2}\right)^{1/3}\left(0 - \frac{E}{eE}\right)\right) = 0\tag{2.99}$$

i.e., the argument of this function must be one of the zeros of the  $Ai$  function,

$$\left(\frac{2mE}{\hbar^2}\right)^{1/3}\left(-\frac{E}{eE}\right) = \zeta_i\tag{2.100}$$

or, equivalently, the possible energy eigenvalues are

$$E_i = -\left(\frac{\hbar^2}{2m}\right)^{1/3} (eE)^{2/3} \zeta_i\tag{2.101}$$

Fig. 2.13 shows the results of a specific calculation, for the case of an electric field of  $1 \text{ V/\AA}$  ( $10^{10} \text{ V/m}$ ). As can be seen, the wavefunctions for the different levels are simple shifted versions of one another, with the wavefunction being truncated at the infinitely high potential barrier at position 0, at which point each wavefunction is zero in amplitude. As in the simple rectangular potential wells, the lowest energy function has no zeros (other than at the left and right ends), and each successive, higher-energy solution has one more zero.

### Infinite potential well with field

We can take the triangular well one step further, by including also an infinitely high barrier on the right. This makes the potential structure into an infinite potential well with field (or a skewed infinite potential well).

The equations remain the same, except we have the additional boundary condition that the potential is infinite, and hence the wavefunction is zero, at  $z = L_z$ . Now we cannot discard the

*Bi* solution; the potential forces the wavefunction to zero at the right wall, so there will be no wavefunction amplitude to the right of this wall, and so the divergence of the *Bi* function no longer matters for normalization (we would only be normalizing inside the box). Hence we have to work with the general solution, Eq. (2.93), with both *Ai* and *Bi* functions.

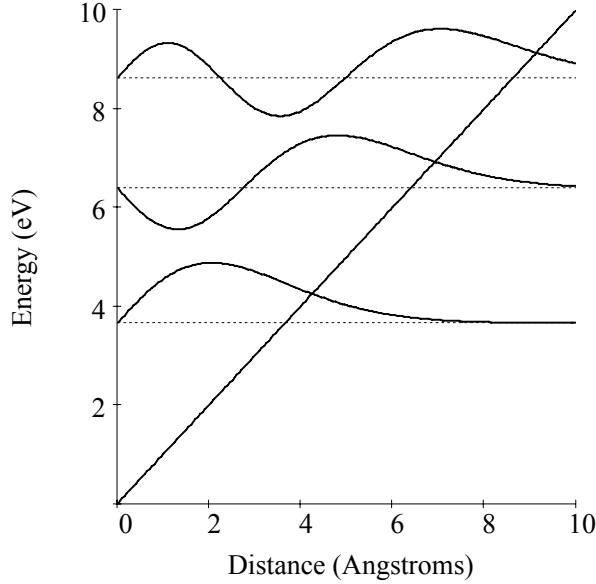


Fig. 2.13. Graphs of wavefunctions and energy levels for the first three levels in a triangular potential well, for a field of  $1\text{V}/\text{\AA}$ .

This solution requires some more mathematical work, but is ultimately straightforward. The two boundary conditions are that the wavefunction must be zero at  $z = 0$  and at  $z = L_z$ , or equivalently at  $\zeta = \zeta_0$  and  $\zeta = \zeta_L$ , where

$$\zeta_0 \equiv -\left(\frac{2m}{\hbar^2 e^2 E^2}\right)^{1/3} E \quad (2.102)$$

$$\zeta_L \equiv \left(\frac{2meE}{\hbar^2}\right)^{1/3} \left(L_z - \frac{E}{eE}\right) \quad (2.103)$$

These boundary conditions will establish what the possible values of  $E$  are, i.e., the energy eigenvalues. The conditions result in two equations

$$a Ai(\zeta_0) + b Bi(\zeta_0) = 0 \quad (2.104)$$

$$a Ai(\zeta_L) + b Bi(\zeta_L) = 0 \quad (2.105)$$

or, in matrix form

$$\begin{bmatrix} Ai(\zeta_0) & Bi(\zeta_0) \\ Ai(\zeta_L) & Bi(\zeta_L) \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix} = 0 \quad (2.106)$$

The usual condition for a solution of such equations is



$$\begin{vmatrix} Ai(\zeta_0) & Bi(\zeta_0) \\ Ai(\zeta_L) & Bi(\zeta_L) \end{vmatrix} = 0 \quad (2.107)$$

or, equivalently,

$$Ai(\zeta_0)Bi(\zeta_L) - Ai(\zeta_L)Bi(\zeta_0) = 0 \quad (2.108)$$

The next mathematical step is to find for what values of  $\zeta_L$  Eq. (2.108) can be satisfied. This can be done numerically.

First, we will change to appropriate dimensionless units. In this problem, there are two relevant energies. One is the natural unit for discussing potential well energies, which is the energy of the lowest state in an infinitely deep potential well,  $(\hbar^2 / 2m)(\pi / L_z)^2$  (as in Eq. (2.26)), which here we will call  $E_1^\infty$  to avoid confusion with the final energy eigenstates for this problem; we will use this as the energy unit. Hence we will use the dimensionless “energy”

$$\varepsilon \equiv E / E_1^\infty$$

The second energy in the problem is the potential drop from one side of the well to the other resulting from the electric field, which is

$$V_L = eEL_z \quad (2.109)$$

or, in dimensionless form

$$\nu_L = V_L / E_1^\infty \quad (2.110)$$

With these definitions, we can rewrite Eqs. (2.102) and (2.103) as, respectively,

$$\zeta_0 \equiv - \left( \frac{\pi}{\nu_L} \right)^{2/3} \varepsilon \quad (2.111)$$

$$\zeta_L = \left( \frac{\pi}{\nu_L} \right)^{2/3} (\nu_L - \varepsilon) \quad (2.112)$$

Now we choose a specific  $\nu_L$ , which corresponds to choosing the electric field for a given well width. Suppose, for example, that we consider a 6 Å wide well with a field of 1 V/Å. Then  $E_1^\infty \approx 1.0455$  eV, and  $\nu_L \approx 5.739$  (i.e., the potential change from one side of the well to the other is  $\approx 5.739 E_1^\infty$ ). Next we numerically find the values of  $\varepsilon$  that make the determinant function from Eq. (2.108),

$$D(\varepsilon) = Ai(\zeta_0(\varepsilon))Bi(\zeta_L(\varepsilon)) - Ai(\zeta_L(\varepsilon))Bi(\zeta_0(\varepsilon)) \quad (2.113)$$

equal to zero. One way to do this is to graph this function from  $\varepsilon = 0$  upwards to find the approximate position of the zero crossings, and use a numerical root finder to find more accurate estimates. With these eigenvalues of  $\varepsilon$  it is now straightforward also to evaluate the wavefunctions. From Eq. (2.104), we have for the coefficients  $a$  and  $b$  of the general solution, Eq. (2.93), for each eigenenergy  $\varepsilon_i$ ,

$$\frac{b_i}{a_i} = - \frac{Ai(\zeta_0(\varepsilon_i))}{Bi(\zeta_0(\varepsilon_i))} \quad (2.114)$$

Given that we know the ratio  $b_i/a_i$ , we can normalize the wavefunction by integrating from 0 to  $L_z$  to find the specific values of both  $a_i$  and  $b_i$  for each  $i$  if we wish. The resulting wavefunction is therefore, for a given energy eigenstate, using the same notation as for Eqs. (2.111) and (2.112) with the dimensionless energies

$$\psi_i(z) = a_i Ai \left( \left( \frac{\pi}{v_L} \right)^{2/3} \left( v_L \frac{z}{L_z} - \varepsilon \right) \right) + b_i Bi \left( \left( \frac{\pi}{v_L} \right)^{2/3} \left( v_L \frac{z}{L_z} - \varepsilon \right) \right) \quad (2.115)$$

For the example numbers here, we have

	$\varepsilon_i$	$E_i$ (eV)	$b/a$
First level ( $i = 1$ )	3.53	3.69	-0.04
Second level ( $i = 2$ )	6.95	7.27	-2.48
Third level ( $i = 3$ )	11.93	12.47	-0.12

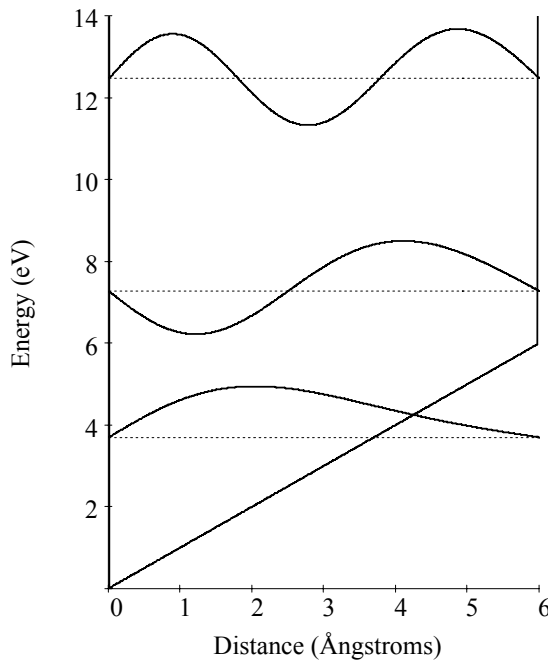


Fig. 2.14. First three eigenstates in a 6 Å potential well with infinitely high barriers at each side, for an electron in a field of 1 V/Å. The potential is also sketched.

The resulting solutions are plotted in Fig. 2.14. Note that

- (i) All the wavefunctions go to zero at both sides of the well, as required by the infinitely high potential energies there.
- (ii) The lowest solution is almost identical in energy and wavefunction to that of the lowest state in the triangular well. (The fraction of the  $Bi$  Airy function is very small, -0.04). The energy is actually slightly higher because the wavefunction is slightly more confined.
- (iii) The second solution is now quite strongly influenced by the potential barrier at the right, with a significantly higher energy than in the triangular well.

(iv) The third solution is very close in form to that of the third level of a simple rectangular well. To the eye, it looks to be approximately sinusoidal, though the period is slightly shorter on the left hand side, consistent with our previous discussion of the effect on the wavefunction oscillation period from changes in potential.

We can see in the lowest state that the electron has been pulled closer to the left hand side, which is what we would expect classically from such an electric field. Note, though, that our classical intuition does not work for the higher levels. In fact, in the second level, a detailed calculation shows that the electron is actually substantially more likely to be in the right half (~64%) of the well than in the left half (~36%).<sup>37</sup>

## Problems

- 2.11.1 Give actual energy levels in electron volts to three significant figures for the first three levels in the triangular well as in Fig. 2.13 (i.e., with a field of 1 V/Å).
- 2.11.2 Repeat the calculation of problem 2.11.1 for electrons in the semiconductor GaAs, for specific electric fields of 1 V/μm and 10 V/μm. Instead of using the free electron mass, use the effective mass of an electron in GaAs,  $m_{eff} \approx 0.07m_o$ . Also, calculate the distance from the interface to the classical turning point in each case.
- 2.11.3 For the following two fields, calculate the first three energy levels (in electron-volts) for an electron in a 100 Å GaAs potential well with infinitely high barriers, and plot the probability densities in units of Å<sup>-1</sup> for each of the three states. State the energies relative to the energy of the center of the well (*not* relative to the lower corner). Presume that the electron can be treated as having an effective mass of  $m_{eff} \approx 0.07m_o$ . (For this problem, mathematical software will be required. You need to be able to find roots numerically, evaluate the Airy functions, and perform numerical integration for normalization.)
- (i) zero field
  - (ii) 20 V/μm

## 2.12 Summary of concepts

This Chapter has seen the introduction, mostly by example, of various of the unusual concepts in quantum mechanics, and of some key results and equations. We list these briefly here. (See also the memorization list at the end of the book for those formulae particularly worth learning by heart.)

### Wave-particle duality

The idea that particles, such as electrons, also behave in some ways as if they were waves (e.g., showing diffraction).

### Time-independent Schrödinger wave equation

Single particles with mass, such as a non-relativistic electron in the absence of a magnetic field, often obey the (time-independent) Schrödinger wave equation

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<sup>37</sup> The reader is likely surprised at the large difference in probabilities between the right and left halves of the well; by eye, the wavefunction perhaps does not look so unbalanced between the two halves. Remember, though, that it is the modulus squared of the wavefunction that gives the probability. The left half contains the zero crossing, and there is little contribution to the square from the region near the zero crossing. The small difference in the magnitude of the peak of the wavefunction in the two halves is also magnified by taking the square.