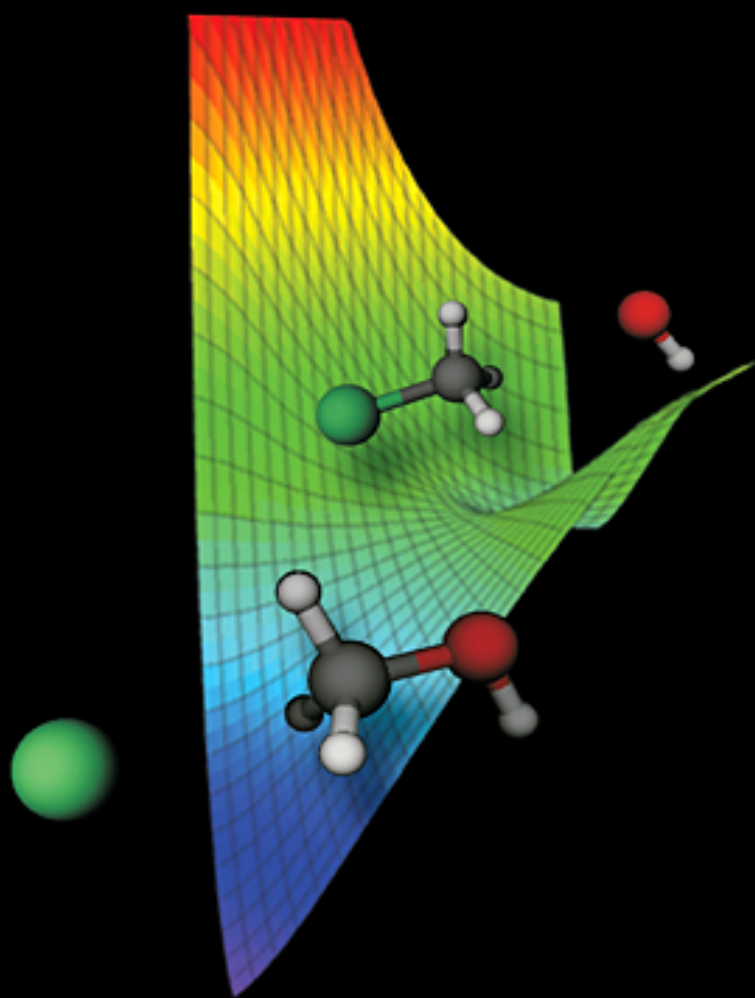




THIRD EDITION

QUANTUM CHEMISTRY



JOHN P. LOWE • KIRK A. PETERSON

Quantum Chemistry

Third Edition

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John P. Lowe

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania

Kirk A. Peterson

Department of Chemistry
Washington State University
Pullman, Washington



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To
Nancy
-J. L.

THE MOLECULAR CHALLENGE

Sir Ethylene, to scientists fair prey,
(Who dig and delve and peek and push and pry,
And prove their findings with equations sly)
Smoothed out his ruffled orbitals, to say:
“I stand in symmetry. Mine is a way
Of mystery and magic. Ancient, I
Am also deemed immortal. Should I die,
Pi would be in the sky, and Judgement Day
Would be upon us. For all things must fail,
That hold our universe together, when
Bonds such as bind me fail, and fall asunder.
Hence, stand I firm against the endless hail
Of scientific blows. I yield not.” Men
And their computers stand and stare and wonder.

W.G. LOWE

Contents

Preface to the Third Edition	xvii
Preface to the Second Edition	xix
Preface to the First Edition	xxi
1 Classical Waves and the Time-Independent Schrödinger Wave Equation	1
1-1 Introduction	1
1-2 Waves	1
1-3 The Classical Wave Equation	4
1-4 Standing Waves in a Clamped String	7
1-5 Light as an Electromagnetic Wave	9
1-6 The Photoelectric Effect	10
1-7 The Wave Nature of Matter	14
1-8 A Diffraction Experiment with Electrons	16
1-9 Schrödinger's Time-Independent Wave Equation	19
1-10 Conditions on ψ	21
1-11 Some Insight into the Schrödinger Equation	22
1-12 Summary	23
Problems	24
Multiple Choice Questions	25
Reference	26
2 Quantum Mechanics of Some Simple Systems	27
2-1 The Particle in a One-Dimensional "Box"	27
2-2 Detailed Examination of Particle-in-a-Box Solutions	30
2-3 The Particle in a One-Dimensional "Box" with One Finite Wall	38
2-4 The Particle in an Infinite "Box" with a Finite Central Barrier	44
2-5 The Free Particle in One Dimension	47
2-6 The Particle in a Ring of Constant Potential	50
2-7 The Particle in a Three-Dimensional Box: Separation of Variables	53
2-8 The Scattering of Particles in One Dimension	56
2-9 Summary	59
Problems	60
Multiple Choice Questions	65
References	68

3	The One-Dimensional Harmonic Oscillator	69
3-1	Introduction	69
3-2	Some Characteristics of the Classical One-Dimensional Harmonic Oscillator	69
3-3	The Quantum-Mechanical Harmonic Oscillator	72
3-4	Solution of the Harmonic Oscillator Schrödinger Equation	74
3-5	Quantum-Mechanical Average Value of the Potential Energy	83
3-6	Vibrations of Diatomic Molecules	84
3-7	Summary	85
	Problems	85
	Multiple Choice Questions	88
4	The Hydrogenlike Ion, Angular Momentum, and the Rigid Rotor	89
4-1	The Schrödinger Equation and the Nature of Its Solutions	89
4-2	Separation of Variables	105
4-3	Solution of the R , Θ , and Φ Equations	106
4-4	Atomic Units	109
4-5	Angular Momentum and Spherical Harmonics	110
4-6	Angular Momentum and Magnetic Moment	115
4-7	Angular Momentum in Molecular Rotation—The Rigid Rotor	117
4-8	Summary	119
	Problems	120
	Multiple Choice Questions	125
	References	126
5	Many-Electron Atoms	127
5-1	The Independent Electron Approximation	127
5-2	Simple Products and Electron Exchange Symmetry	129
5-3	Electron Spin and the Exclusion Principle	132
5-4	Slater Determinants and the Pauli Principle	137
5-5	Singlet and Triplet States for the $1s2s$ Configuration of Helium	138
5-6	The Self-Consistent Field, Slater-Type Orbitals, and the Aufbau Principle	144
5-7	Electron Angular Momentum in Atoms	149
5-8	Overview	159
	Problems	160
	Multiple Choice Questions	164
	References	165
6	Postulates and Theorems of Quantum Mechanics	166
6-1	Introduction	166
6-2	The Wavefunction Postulate	166
6-3	The Postulate for Constructing Operators	167
6-4	The Time-Dependent Schrödinger Equation Postulate	168
6-5	The Postulate Relating Measured Values to Eigenvalues	169
6-6	The Postulate for Average Values	171
6-7	Hermitian Operators	171

6-8	Proof That Eigenvalues of Hermitian Operators Are Real	172
6-9	Proof That Nondegenerate Eigenfunctions of a Hermitian Operator Form an Orthogonal Set	173
6-10	Demonstration That All Eigenfunctions of a Hermitian Operator May Be Expressed as an Orthonormal Set	174
6-11	Proof That Commuting Operators Have Simultaneous Eigenfunctions	175
6-12	Completeness of Eigenfunctions of a Hermitian Operator	176
6-13	The Variation Principle	178
6-14	The Pauli Exclusion Principle	178
6-15	Measurement, Commutators, and Uncertainty	178
6-16	Time-Dependent States	180
6-17	Summary	185
	Problems	186
	Multiple Choice Questions	189
	References	189
7	The Variation Method	190
7-1	The Spirit of the Method	190
7-2	Nonlinear Variation: The Hydrogen Atom	191
7-3	Nonlinear Variation: The Helium Atom	194
7-4	Linear Variation: The Polarizability of the Hydrogen Atom	197
7-5	Linear Combination of Atomic Orbitals: The H_2^+ Molecule-Ion	206
7-6	Molecular Orbitals of Homonuclear Diatomic Molecules	220
7-7	Basis Set Choice and the Variational Wavefunction	231
7-8	Beyond the Orbital Approximation	233
	Problems	235
	Multiple Choice Questions	241
	References	242
8	The Simple Hückel Method and Applications	244
8-1	The Importance of Symmetry	244
8-2	The Assumption of σ - π Separability	244
8-3	The Independent π -Electron Assumption	246
8-4	Setting up the Hückel Determinant	247
8-5	Solving the HMO Determinantal Equation for Orbital Energies	250
8-6	Solving for the Molecular Orbitals	251
8-7	The Cyclopropenyl System: Handling Degeneracies	253
8-8	Charge Distributions from HMOs	256
8-9	Some Simplifying Generalizations	259
8-10	HMO Calculations on Some Simple Molecules	263
8-11	Summary: The Simple HMO Method for Hydrocarbons	268
8-12	Relation Between Bond Order and Bond Length	269
8-13	π -Electron Densities and Electron Spin Resonance Hyperfine Splitting Constants	271
8-14	Orbital Energies and Oxidation-Reduction Potentials	275
8-15	Orbital Energies and Ionization Energies	278
8-16	π -Electron Energy and Aromaticity	279

8-17	Extension to Heteroatomic Molecules	284
8-18	Self-Consistent Variations of α and β	287
8-19	HMO Reaction Indices	289
8-20	Conclusions	295
	Problems	296
	Multiple Choice Questions	305
	References	306
9	Matrix Formulation of the Linear Variation Method	308
9-1	Introduction	308
9-2	Matrices and Vectors	308
9-3	Matrix Formulation of the Linear Variation Method	315
9-4	Solving the Matrix Equation	317
9-5	Summary	320
	Problems	320
	References	323
10	The Extended Hückel Method	324
10-1	The Extended Hückel Method	324
10-2	Mulliken Populations	335
10-3	Extended Hückel Energies and Mulliken Populations	338
10-4	Extended Hückel Energies and Experimental Energies	340
	Problems	342
	References	347
11	The SCF-LCAO-MO Method and Extensions	348
11-1	<i>Ab Initio</i> Calculations	348
11-2	The Molecular Hamiltonian	349
11-3	The Form of the Wavefunction	349
11-4	The Nature of the Basis Set	350
11-5	The LCAO-MO-SCF Equation	350
11-6	Interpretation of the LCAO-MO-SCF Eigenvalues	351
11-7	The SCF Total Electronic Energy	352
11-8	Basis Sets	353
11-9	The Hartree–Fock Limit	357
11-10	Correlation Energy	357
11-11	Koopmans’ Theorem	358
11-12	Configuration Interaction	360
11-13	Size Consistency and the Møller–Plesset and Coupled Cluster Treatments of Correlation	365
11-14	Multideterminant Methods	367
11-15	Density Functional Theory Methods	368
11-16	Examples of <i>Ab Initio</i> Calculations	370
11-17	Approximate SCF-MO Methods	384
	Problems	386
	References	388

12 Time-Independent Rayleigh–Schrödinger Perturbation Theory	391
12-1 An Introductory Example	391
12-2 Formal Development of the Theory for Nondegenerate States	391
12-3 A Uniform Electrostatic Perturbation of an Electron in a “Wire”	396
12-4 The Ground-State Energy to First-Order of Heliumlike Systems	403
12-5 Perturbation at an Atom in the Simple Hückel MO Method	406
12-6 Perturbation Theory for a Degenerate State	409
12-7 Polarizability of the Hydrogen Atom in the $n = 2$ States	410
12-8 Degenerate-Level Perturbation Theory by Inspection	412
12-9 Interaction Between Two Orbitals: An Important Chemical Model	414
12-10 Connection Between Time-Independent Perturbation Theory and Spectroscopic Selection Rules	417
Problems	420
Multiple Choice Questions	427
References	428
13 Group Theory	429
13-1 Introduction	429
13-2 An Elementary Example	429
13-3 Symmetry Point Groups	431
13-4 The Concept of Class	434
13-5 Symmetry Elements and Their Notation	436
13-6 Identifying the Point Group of a Molecule	441
13-7 Representations for Groups	443
13-8 Generating Representations from Basis Functions	446
13-9 Labels for Representations	451
13-10 Some Connections Between the Representation Table and Molecular Orbitals	452
13-11 Representations for Cyclic and Related Groups	453
13-12 Orthogonality in Irreducible Inequivalent Representations	456
13-13 Characters and Character Tables	458
13-14 Using Characters to Resolve Reducible Representations	462
13-15 Identifying Molecular Orbital Symmetries	463
13-16 Determining in Which Molecular Orbital an Atomic Orbital Will Appear	465
13-17 Generating Symmetry Orbitals	467
13-18 Hybrid Orbitals and Localized Orbitals	470
13-19 Symmetry and Integration	472
Problems	476
Multiple Choice Questions	481
References	483
14 Qualitative Molecular Orbital Theory	484
14-1 The Need for a Qualitative Theory	484
14-2 Hierarchy in Molecular Structure and in Molecular Orbitals	484
14-3 H_2^+ Revisited	485
14-4 H_2 : Comparisons with H_2^+	488

14-5	Rules for Qualitative Molecular Orbital Theory	490
14-6	Application of QMOT Rules to Homonuclear Diatomic Molecules	490
14-7	Shapes of Polyatomic Molecules: Walsh Diagrams	495
14-8	Frontier Orbitals	505
14-9	Qualitative Molecular Orbital Theory of Reactions	508
	Problems	521
	References	524
15	Molecular Orbital Theory of Periodic Systems	526
15-1	Introduction	526
15-2	The Free Particle in One Dimension	526
15-3	The Particle in a Ring	529
15-4	Benzene	530
15-5	General Form of One-Electron Orbitals in Periodic Potentials— Bloch's Theorem	533
15-6	A Retrospective Pause	537
15-7	An Example: Polyacetylene with Uniform Bond Lengths	537
15-8	Electrical Conductivity	546
15-9	Polyacetylene with Alternating Bond Lengths—Peierls' Distortion	547
15-10	Electronic Structure of All- <i>Trans</i> Polyacetylene	551
15-11	Comparison of EHMO and SCF Results on Polyacetylene	552
15-12	Effects of Chemical Substitution on the π Bands	554
15-13	Poly-Paraphenylene—A Ring Polymer	555
15-14	Energy Calculations	562
15-15	Two-Dimensional Periodicity and Vectors in Reciprocal Space	562
15-16	Periodicity in Three Dimensions—Graphite	565
15-17	Summary	576
	Problems	578
	References	580
Appendix 1	Useful Integrals	582
Appendix 2	Determinants	584
Appendix 3	Evaluation of the Coulomb Repulsion Integral Over 1s AOs	587
Appendix 4	Angular Momentum Rules	591
Appendix 5	The Pairing Theorem	601
Appendix 6	Hückel Molecular Orbital Energies, Coefficients, Electron Densities, and Bond Orders for Some Simple Molecules	605
Appendix 7	Derivation of the Hartree–Fock Equation	614
Appendix 8	The Virial Theorem for Atoms and Diatomic Molecules	624

Contents	xv
Appendix 9 Bra-ket Notation	629
Appendix 10 Values of Some Useful Constants and Conversion Factors	631
Appendix 11 Group Theoretical Charts and Tables	636
Appendix 12 Hints for Solving Selected Problems	651
Appendix 13 Answers to Problems	654
Index	691



Preface to the Third Edition

We have attempted to improve and update this text while retaining the features that make it unique, namely, an emphasis on physical understanding, and the ability to estimate, evaluate, and predict results without blind reliance on computers, while still maintaining rigorous connection to the mathematical basis for quantum chemistry. We have inserted into most chapters examples that allow important points to be emphasized, clarified, or extended. This has enabled us to keep intact most of the conceptual development familiar to past users. In addition, many of the chapters now include multiple choice questions that students are invited to solve in their heads. This is not because we think that instructors will be using such questions. Rather it is because we find that such questions permit us to highlight some of the definitions or conclusions that students often find most confusing far more quickly and effectively than we can by using traditional problems. Of course, we have also sought to update material on computational methods, since these are changing rapidly as the field of quantum chemistry matures.

This book is written for courses taught at the first-year graduate/senior undergraduate levels, which accounts for its implicit assumption that many readers will be relatively unfamiliar with much of the mathematics and physics underlying the subject. Our experience over the years has supported this assumption; many chemistry majors are exposed to the requisite mathematics and physics, yet arrive at our courses with poor understanding or recall of those subjects. That makes this course an opportunity for such students to experience the satisfaction of finally seeing how mathematics, physics, and chemistry are intertwined in quantum chemistry. It is for this reason that treatments of the simple and extended Hückel methods continue to appear, even though these are no longer the methods of choice for serious computations. These topics nevertheless form the basis for the way most non-theoretical chemists understand chemical processes, just as we tend to think about gas behavior as “ideal, with corrections.”



Preface to the Second Edition

The success of the first edition has warranted a second. The changes I have made reflect my perception that the book has mostly been used as a teaching text in introductory courses. Accordingly, I have removed some of the material in appendixes on mathematical details of solving matrix equations on a computer. Also I have removed computer listings for programs, since these are now commonly available through commercial channels. I have added a new chapter on MO theory of periodic systems—a subject of rapidly growing importance in theoretical chemistry and materials science and one for which chemists still have difficulty finding appropriate textbook treatments. I have augmented discussion in various chapters to give improved coverage of time-dependent phenomena and atomic term symbols and have provided better connection to scattering as well as to spectroscopy of molecular rotation and vibration. The discussion on degenerate-level perturbation theory is clearer, reflecting my own improved understanding since writing the first edition. There is also a new section on operator methods for treating angular momentum. Some teachers are strong adherents of this approach, while others prefer an approach that avoids the formalism of operator techniques. To permit both teaching methods, I have placed this material in an appendix. Because this edition is more overtly a text than a monograph, I have not attempted to replace older literature references with newer ones, except in cases where there was pedagogical benefit.

A strength of this book has been its emphasis on physical argument and analogy (as opposed to pure mathematical development). I continue to be a strong proponent of the view that true understanding comes with being able to “see” a situation so clearly that one can solve problems in one’s head. There are significantly more end-of-chapter problems, a number of them of the “by inspection” type. There are also more questions inviting students to explain their answers. I believe that thinking about such questions, and then reading explanations from the answer section, significantly enhances learning.

It is the fashion today to focus on state-of-the-art methods for just about everything. The impact of this on education has, I feel, been disastrous. Simpler examples are often needed to develop the insight that enables understanding the complexities of the latest techniques, but too often these are abandoned in the rush to get to the “cutting edge.” For this reason I continue to include a substantial treatment of simple Hückel theory. It permits students to recognize the connections between MOs and their energies and bonding properties, and it allows me to present examples and problems that have maximum transparency in later chapters on perturbation theory, group theory, qualitative MO theory, and periodic systems. I find simple Hückel theory to be educationally indispensable.

Much of the new material in this edition results from new insights I have developed in connection with research projects with graduate students. The work of all four of my students since the appearance of the first edition is represented, and I am delighted to thank Sherif Kafafi, John LaFemina, Maribel Soto, and Deb Camper for all I have learned from them. Special thanks are due to Professor Terry Carlton, of Oberlin College, who made many suggestions and corrections that have been adopted in the new edition.

Doubtless, there are new errors. I would be grateful to learn of them so that future printings of this edition can be made error-free. Students or teachers with comments, questions, or corrections are more than welcome to contact me, either by mail at the Department of Chemistry, 152 Davey Lab, The Pennsylvania State University, University Park, PA 16802, or by e-mail directed to JL3 at PSUVM.PSU.EDU.



Preface to the First Edition

My aim in this book is to present a reasonably rigorous treatment of molecular orbital theory, embracing subjects that are of practical interest to organic and inorganic as well as physical chemists. My approach here has been to rely on physical intuition as much as possible, first solving a number of specific problems in order to develop sufficient insight and familiarity to make the formal treatment of Chapter 6 more palatable. My own experience suggests that most chemists find this route the most natural.

I have assumed that the reader has at some time learned calculus and elementary physics, but I have not assumed that this material is fresh in his or her mind. Other mathematics is developed as it is needed. The book could be used as a text for undergraduate or graduate students in a half or full year course. The level of rigor of the book is somewhat adjustable. For example, Chapters 3 and 4, on the harmonic oscillator and hydrogen atom, can be truncated if one wishes to know the nature of the solutions, but not the mathematical details of how they are produced.

I have made use of appendixes for certain of the more complicated derivations or proofs. This is done in order to avoid having the development of major ideas in the text interrupted or obscured. Certain of the appendixes will interest only the more theoretically inclined student. Also, because I anticipate that some readers may wish to skip certain chapters or parts of chapters, I have occasionally repeated information so that a given chapter will be less dependent on its predecessors. This may seem inelegant at times, but most students will more readily forgive repetition of something they already know than an overly terse presentation.

I have avoided early usage of bra-ket notation. I believe that simultaneous introduction of new concepts and unfamiliar notation is poor pedagogy. Bra-ket notation is used only after the ideas have had a change to jell.

Problem solving is extremely important in acquiring an understanding of quantum chemistry. I have included a fair number of problems with hints for a few of them in Appendix 14 and answers for almost all of them in Appendix 15.¹

It is inevitable that one be selective in choosing topics for a book such as this. This book emphasizes ground state MO theory of molecules more than do most introductory texts, with rather less emphasis on spectroscopy than is usual. Angular momentum is treated at a fairly elementary level at various appropriate places in the text, but it is never given a full-blown formal development using operator commutation relations. Time-dependent phenomena are not included. Thus, scattering theory is absent,

¹In this Second Edition, these Appendixes are numbered Appendix 12 and 13.

although selection rules and the transition dipole are discussed in the chapter on time-independent perturbation theory. Valence-bond theory is completely absent. If I have succeeded in my effort to provide a clear and meaningful treatment of topics relevant to modern molecular orbital theory, it should not be difficult for an instructor to provide for excursions into related topics not covered in the text.

Over the years, many colleagues have been kind enough to read sections of the evolving manuscript and provide corrections and advice. I especially thank L. P. Gold and O. H. Crawford, who cheerfully bore the brunt of this task.

Finally, I would like to thank my father, Wesley G. Lowe, for allowing me to include his sonnet, "The Molecular Challenge."

Classical Waves and the Time-Independent Schrödinger Wave Equation

1-1 Introduction

The application of quantum-mechanical principles to chemical problems has revolutionized the field of chemistry. Today our understanding of chemical bonding, spectral phenomena, molecular reactivities, and various other fundamental chemical problems rests heavily on our knowledge of the detailed behavior of electrons in atoms and molecules. In this book we shall describe in detail some of the basic principles, methods, and results of quantum chemistry that lead to our understanding of electron behavior.

In the first few chapters we shall discuss some simple, but important, particle systems. This will allow us to introduce many basic concepts and definitions in a fairly physical way. Thus, some background will be prepared for the more formal general development of Chapter 6. In this first chapter, we review briefly some of the concepts of classical physics as well as some early indications that classical physics is not sufficient to explain all phenomena. (Those readers who are already familiar with the physics of classical waves and with early atomic physics may prefer to jump ahead to Section 1-7.)

1-2 Waves

1-2.A Traveling Waves

A very simple example of a traveling wave is provided by cracking a whip. A pulse of energy is imparted to the whipcord by a single oscillation of the handle. This results in a wave which travels down the cord, transferring the energy to the popper at the end of the whip. In Fig. 1-1, an idealization of the process is sketched. The shape of the disturbance in the whip is called the *wave profile* and is usually symbolized $\psi(x)$. The wave profile for the traveling wave in Fig. 1-1 shows where the energy is located at a given instant. It also contains the information needed to tell how much energy is being transmitted, because the height and shape of the wave reflect the vigor with which the handle was oscillated.

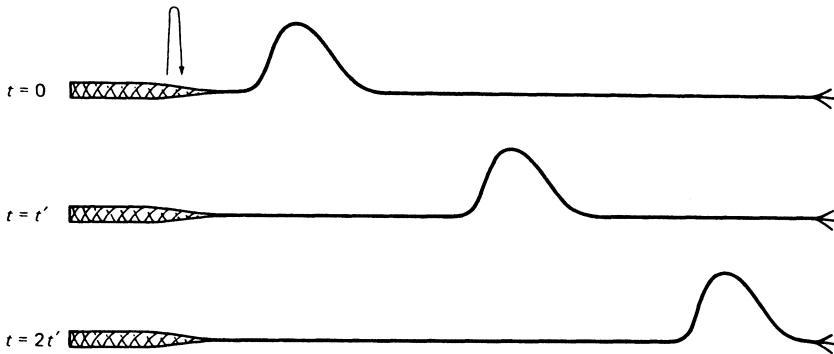


Figure 1-1 ► Cracking the whip. As time passes, the disturbance moves from left to right along the extended whip cord. Each segment of the cord oscillates up and down as the disturbance passes by, ultimately returning to its equilibrium position.

The feature common to all traveling waves in classical physics is that energy is transmitted through a medium. The medium itself undergoes no permanent displacement; it merely undergoes local oscillations as the disturbance passes through.

One of the most important kinds of wave in physics is the *harmonic* wave, for which the wave profile is a sinusoidal function. A harmonic wave, at a particular instant in time, is sketched in Fig. 1-2. The maximum displacement of the wave from the rest position is the *amplitude* of the wave, and the *wavelength* λ is the distance required to enclose one complete oscillation. Such a wave would result from a harmonic¹ oscillation at one end of a taut string. Analogous waves would be produced on the surface of a quiet pool by a vibrating bob, or in air by a vibrating tuning fork.

At the instant depicted in Fig. 1-2, the profile is described by the function

$$\psi(x) = A \sin(2\pi x/\lambda) \quad (1-1)$$

($\psi = 0$ when $x = 0$, and the argument of the sine function goes from 0 to 2π , encompassing one complete oscillation as x goes from 0 to λ .) Let us suppose that the situation in Fig. 1-2 pertains at the time $t = 0$, and let the velocity of the disturbance through the medium be c . Then, after time t , the distance traveled is ct , the profile is shifted to the right by ct and is now given by

$$\Psi(x, t) = A \sin[(2\pi/\lambda)(x - ct)] \quad (1-2)$$

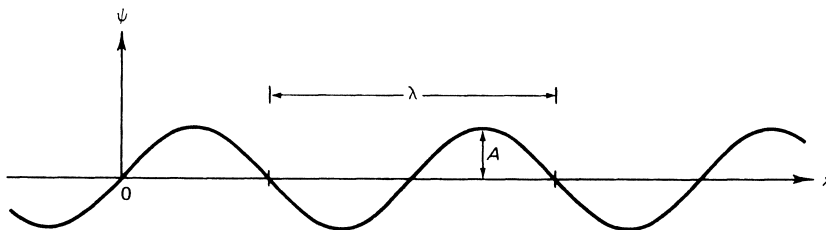


Figure 1-2 ► A harmonic wave at a particular instant in time. A is the amplitude and λ is the wavelength.

¹A harmonic oscillation is one whose equation of motion has a sine or cosine dependence on time.

A capital Ψ is used to distinguish the time-dependent function (1-2) from the time-independent function (1-1).

The *frequency* ν of a wave is the number of individual repeating wave units passing a point per unit time. For our harmonic wave, this is the distance traveled in unit time c divided by the length of a wave unit λ . Hence,

$$\nu = c/\lambda \quad (1-3)$$

Note that the wave described by the formula

$$\Psi'(x, t) = A \sin[(2\pi/\lambda)(x - ct) + \epsilon] \quad (1-4)$$

is similar to Ψ of Eq. (1-2) except for being displaced. If we compare the two waves at the same instant in time, we find Ψ' to be shifted to the left of Ψ by $\epsilon\lambda/2\pi$. If $\epsilon = \pi, 3\pi, \dots$, then Ψ' is shifted by $\lambda/2, 3\lambda/2, \dots$ and the two functions are said to be exactly out of phase. If $\epsilon = 2\pi, 4\pi, \dots$, the shift is by $\lambda, 2\lambda, \dots$, and the two waves are exactly in phase. ϵ is the *phase factor* for Ψ' relative to Ψ . Alternatively, we can compare the two waves at the same point in x , in which case the phase factor causes the two waves to be displaced from each other in time.

1-2.B Standing Waves

In problems of physical interest, the medium is usually subject to constraints. For example, a string will have ends, and these may be clamped, as in a violin, so that they cannot oscillate when the disturbance reaches them. Under such circumstances, the energy pulse is unable to progress further. It cannot be absorbed by the clamping mechanism if it is perfectly rigid, and it has no choice but to travel back along the string in the opposite direction. The reflected wave is now moving into the face of the primary wave, and the motion of the string is in response to the demands placed on it by the two simultaneous waves:

$$\Psi(x, t) = \Psi_{\text{primary}}(x, t) + \Psi_{\text{reflected}}(x, t) \quad (1-5)$$

When the primary and reflected waves have the same amplitude and speed, we can write

$$\begin{aligned} \Psi(x, t) &= A \sin [(2\pi/\lambda)(x - ct)] + A \sin [(2\pi/\lambda)(x + ct)] \\ &= 2A \sin(2\pi x/\lambda) \cos(2\pi ct/\lambda) \end{aligned} \quad (1-6)$$

This formula describes a *standing wave*—a wave that does not appear to travel through the medium, but appears to vibrate “in place.” The first part of the function depends only on the x variable. Wherever the sine function vanishes, Ψ will vanish, regardless of the value of t . This means that there are places where the medium does not ever vibrate. Such places are called *nodes*. Between the nodes, $\sin(2\pi x/\lambda)$ is finite. As time passes, the cosine function oscillates between plus and minus unity. This means that Ψ oscillates between plus and minus the value of $\sin(2\pi x/\lambda)$. We say that the x -dependent part of the function gives the maximum displacement of the standing wave, and the t -dependent part governs the motion of the medium back and forth between these extremes of maximum displacement. A standing wave with a central node is shown in Fig. 1-3.

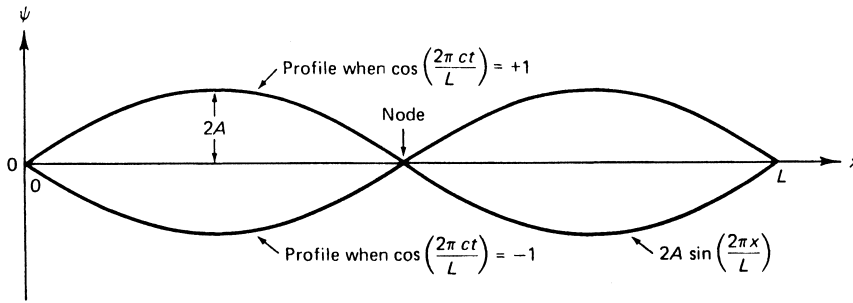


Figure 1-3 ▶ A standing wave in a string clamped at $x = 0$ and $x = L$. The wavelength λ is equal to L .

Equation (1-6) is often written as

$$\Psi(x, t) = \psi(x) \cos(\omega t) \quad (1-7)$$

where

$$\omega = 2\pi c/\lambda \quad (1-8)$$

The profile $\psi(x)$ is often called the *amplitude function* and ω is the *frequency factor*.

Let us consider how the energy is stored in the vibrating string depicted in Fig. 1-3. The string segments at the central node and at the clamped endpoints of the string do not move. Hence, their kinetic energies are zero at all times. Furthermore, since they are never displaced from their equilibrium positions, their potential energies are likewise always zero. Therefore, the total energy stored at these segments is always zero as long as the string continues to vibrate in the mode shown. The maximum kinetic and potential energies are associated with those segments located at the wave peaks and valleys (called the *antinodes*) because these segments have the greatest average velocity and displacement from the equilibrium position. A more detailed mathematical treatment would show that the total energy of any string segment is proportional to $\psi(x)^2$ (Problem 1-7).

1-3 The Classical Wave Equation

It is one thing to draw a picture of a wave and describe its properties, and quite another to predict what sort of wave will result from disturbing a particular system. To make such predictions, we must consider the physical laws that the medium must obey. One condition is that the medium must obey Newton's laws of motion. For example, any segment of string of mass m subjected to a force F must undergo an acceleration of F/m in accord with Newton's second law. In this regard, wave motion is perfectly consistent with ordinary particle motion. Another condition, however, peculiar to waves, is that each segment of the medium is "attached" to the neighboring segments so that, as it is displaced, it drags along its neighbor, which in turn drags along its neighbor,

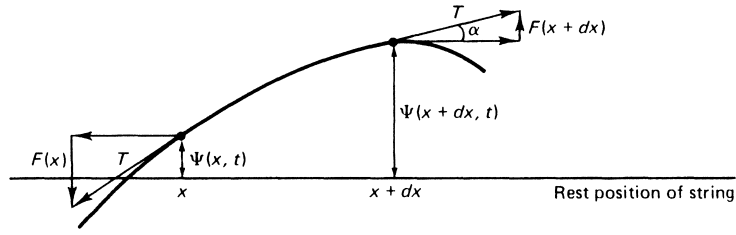


Figure 1-4 ► A segment of string under tension T . The forces at each end of the segment are decomposed into forces perpendicular and parallel to x .

etc. This provides the mechanism whereby the disturbance is propagated along the medium.²

Let us consider a string under a tensile force T . When the string is displaced from its equilibrium position, this tension is responsible for exerting a restoring force. For example, observe the string segment associated with the region x to $x + dx$ in Fig. 1-4. Note that the tension exerted at either end of this segment can be decomposed into components parallel and perpendicular to the x axis. The parallel component tends to stretch the string (which, however, we assume to be unstretchable), the perpendicular component acts to accelerate the segment toward or away from the rest position. At the right end of the segment, the perpendicular component F divided by the horizontal component gives the slope of T . However, for small deviations of the string from equilibrium (that is, for small angle α) the horizontal component is nearly equal in length to the vector T . This means that it is a good approximation to write

$$\text{slope of vector } T = F/T \quad \text{at } x + dx \quad (1-9)$$

But the slope is also given by the derivative of Ψ , and so we can write

$$F_{x+dx} = T (\partial\Psi/\partial x)_{x+dx} \quad (1-10)$$

At the other end of the segment the tensile force acts in the opposite direction, and we have

$$F_x = -T(\partial\Psi/\partial x)_x \quad (1-11)$$

The net perpendicular force on our string segment is the resultant of these two:

$$F = T [(\partial\Psi/\partial x)_{x+dx} - (\partial\Psi/\partial x)_x] \quad (1-12)$$

The difference in slope at two infinitesimally separated points, divided by dx , is by definition the second derivative of a function. Therefore,

$$F = T \partial^2\Psi/\partial x^2 dx \quad (1-13)$$

²Fluids are of relatively low viscosity, so the tendency of one segment to drag along its neighbor is weak. For this reason fluids are poor transmitters of *transverse* waves (waves in which the medium oscillates in a direction perpendicular to the direction of propagation). In *compression* waves, one segment displaces the next by pushing it. Here the requirement is that the medium possess elasticity for compression. Solids and fluids often meet this requirement well enough to transmit compression waves. The ability of rigid solids to transmit both wave types while fluids transmit only one type is the basis for using earthquake-induced waves to determine how deep the solid part of the earth's mantle extends.

Equation (1-13) gives the force on our string segment. If the string has mass m per unit length, then the segment has mass $m dx$, and Newton's equation $F = ma$ may be written

$$T \partial^2 \Psi / \partial x^2 = m \partial^2 \Psi / \partial t^2 \quad (1-14)$$

where we recall that acceleration is the second derivative of position with respect to time.

Equation (1-14) is the wave equation for motion in a string of uniform density under tension T . It should be evident that its derivation involves nothing fundamental beyond Newton's second law and the fact that the two ends of the segment are linked to each other and to a common tensile force. Generalizing this equation to waves in three-dimensional media gives

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi(x, y, z, t) = \beta \frac{\partial^2 \Psi(x, y, z, t)}{\partial t^2} \quad (1-15)$$

where β is a composite of physical quantities (analogous to m/T) for the particular system.

Returning to our string example, we have in Eq. (1-14) a *time-dependent* differential equation. Suppose we wish to limit our consideration to standing waves that can be separated into a space-dependent amplitude function and a harmonic time-dependent function. Then

$$\Psi(x, t) = \psi(x) \cos(\omega t) \quad (1-16)$$

and the differential equation becomes

$$\cos(\omega t) \frac{d^2 \psi(x)}{dx^2} = \frac{m}{T} \psi(x) \frac{d^2 \cos(\omega t)}{dt^2} = -\frac{m}{T} \psi(x) \omega^2 \cos(\omega t) \quad (1-17)$$

or, dividing by $\cos(\omega t)$,

$$d^2 \psi(x) / dx^2 = -(\omega^2 m / T) \psi(x) \quad (1-18)$$

This is the classical *time-independent* wave equation for a string.

We can see by inspection what kind of function $\psi(x)$ must be to satisfy Eq. (1-18). ψ is a function that, when twice differentiated, is reproduced with a coefficient of $-\omega^2 m / T$. One solution is

$$\psi = A \sin(\omega \sqrt{m/T} x) \quad (1-19)$$

This illustrates that Eq. (1-18) has sinusoidally varying solutions such as those discussed in Section 1-2. Comparing Eq. (1-19) with (1-1) indicates that $2\pi/\lambda = \omega \sqrt{m/T}$. Substituting this relation into Eq. (1-18) gives

$$d^2 \psi(x) / dx^2 = -(2\pi/\lambda)^2 \psi(x) \quad (1-20)$$

which is a more useful form for our purposes.

For three-dimensional systems, the classical time-independent wave equation for an isotropic and uniform medium is

$$(\partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2) \psi(x, y, z) = -(2\pi/\lambda)^2 \psi(x, y, z) \quad (1-21)$$

where λ depends on the elasticity of the medium. The combination of partial derivatives on the left-hand side of Eq. (1-21) is called the *Laplacian*, and is often given the shorthand symbol ∇^2 (del squared). This would give for Eq. (1-21)

$$\nabla^2 \psi(x, y, z) = -(2\pi/\lambda)^2 \psi(x, y, z) \quad (1-22)$$

1-4 Standing Waves in a Clamped String

We now demonstrate how Eq. (1-20) can be used to predict the nature of standing waves in a string. Suppose that the string is clamped at $x = 0$ and L . This means that the string cannot oscillate at these points. Mathematically this means that

$$\psi(0) = \psi(L) = 0 \quad (1-23)$$

Conditions such as these are called *boundary conditions*. Our question is, “What functions ψ satisfy Eq. (1-20) and also Eq. (1-23)?” We begin by trying to find the most general equation that can satisfy Eq. (1-20). We have already seen that $A \sin(2\pi x/\lambda)$ is a solution, but it is easy to show that $A \cos(2\pi x/\lambda)$ is also a solution. More general than either of these is the linear combination³

$$\psi(x) = A \sin(2\pi x/\lambda) + B \cos(2\pi x/\lambda) \quad (1-24)$$

By varying A and B , we can get different functions ψ .

There are two remarks to be made at this point. First, some readers will have noticed that other functions exist that satisfy Eq. (1-20). These are $A \exp(2\pi i x/\lambda)$ and $A \exp(-2\pi i x/\lambda)$, where $i = \sqrt{-1}$. The reason we have not included these in the general function (1-24) is that these two exponential functions are mathematically equivalent to the trigonometric functions. The relationship is

$$\exp(\pm i k x) = \cos(kx) \pm i \sin(kx). \quad (1-25)$$

This means that any trigonometric function may be expressed in terms of such exponentials and vice versa. Hence, the set of trigonometric functions and the set of exponentials is redundant, and no additional flexibility would result by including exponentials in Eq. (1-24) (see Problem 1-1). The two sets of functions are *linearly dependent*.⁴

The second remark is that for a given A and B the function described by Eq. (1-24) is a single sinusoidal wave with wavelength λ . By altering the ratio of A to B , we cause the wave to shift to the left or right with respect to the origin. If $A = 1$ and $B = 0$, the wave has a node at $x = 0$. If $A = 0$ and $B = 1$, the wave has an antinode at $x = 0$.

We now proceed by letting the boundary conditions determine the constants A and B . The condition at $x = 0$ gives

$$\psi(0) = A \sin(0) + B \cos(0) = 0 \quad (1-26)$$

³Given functions f_1, f_2, f_3, \dots . A *linear combination* of these functions is $c_1 f_1 + c_2 f_2 + c_3 f_3 + \dots$, where c_1, c_2, c_3, \dots are numbers (which need not be real).

⁴If one member of a set of functions (f_1, f_2, f_3, \dots) can be expressed as a linear combination of the remaining functions (i.e., if $f_1 = c_2 f_2 + c_3 f_3 + \dots$), the set of functions is said to be linearly dependent. Otherwise, they are linearly independent.

However, since $\sin(0) = 0$ and $\cos(0) = 1$, this gives

$$B = 0 \quad (1-27)$$

Therefore, our first boundary condition forces B to be zero and leaves us with

$$\psi(x) = A \sin(2\pi x/\lambda) \quad (1-28)$$

Our second boundary condition, at $x = L$, gives

$$\psi(L) = A \sin(2\pi L/\lambda) = 0 \quad (1-29)$$

One solution is provided by setting A equal to zero. This gives $\psi = 0$, which corresponds to no wave at all in the string. This is possible, but not very interesting. The other possibility is for $2\pi L/\lambda$ to be equal to $0, \pm\pi, \pm2\pi, \dots, \pm n\pi, \dots$ since the sine function vanishes then. This gives the relation

$$2\pi L/\lambda = n\pi, \quad n = 0, \pm 1, \pm 2, \dots \quad (1-30)$$

or

$$\lambda = 2L/n, \quad n = 0, \pm 1, \pm 2, \dots \quad (1-31)$$

Substituting this expression for λ into Eq. (1-28) gives

$$\psi(x) = A \sin(n\pi x/L), \quad n = 0, \pm 1, \pm 2, \dots \quad (1-32)$$

Some of these solutions are sketched in Fig. 1-5. The solution for $n = 0$ is again the uninteresting $\psi = 0$ case. Furthermore, since $\sin(-x)$ equals $-\sin(x)$, it is clear that the set of functions produced by positive integers n is not physically different from the set produced by negative n , so we may arbitrarily restrict our attention to solutions with positive n . (The two sets are linearly dependent.) The constant A is still undetermined. It affects the amplitude of the wave. To determine A would require knowing how much energy is stored in the wave, that is, how hard the string was plucked.

It is evident that there are an infinite number of acceptable solutions, each one corresponding to a different number of half-waves fitting between 0 and L . But an even larger infinity of waves has been excluded by the boundary conditions—namely, all waves having wavelengths not divisible into $2L$ an integral number of times. The result

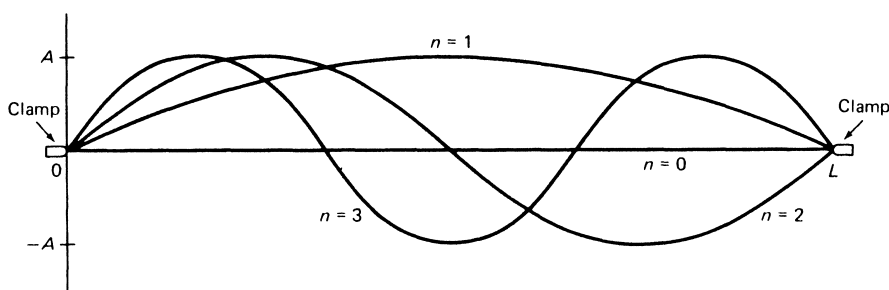


Figure 1-5 ► Solutions for the time-independent wave equation in one dimension with boundary conditions $\psi(0) = \psi(L) = 0$.

of applying boundary conditions has been to restrict the allowed wavelengths to certain discrete values. As we shall see, this behavior is closely related to the quantization of energies in quantum mechanics.

The example worked out above is an extremely simple one. Nevertheless, it demonstrates how a differential equation and boundary conditions are used to define the allowed states for a system. One could have arrived at solutions for this case by simple physical argument, but this is usually not possible in more complicated cases. The differential equation provides a systematic approach for finding solutions when physical intuition is not enough.

1-5 Light as an Electromagnetic Wave

Suppose a charged particle is caused to oscillate harmonically on the z axis. If there is another charged particle some distance away and initially at rest in the xy plane, this second particle will commence oscillating harmonically too. Thus, energy is being transferred from the first particle to the second, which indicates that there is an oscillating electric field emanating from the first particle. We can plot the magnitude of this electric field at a given instant as it would be felt by a series of imaginary test charges stationed along a line emanating from the source and perpendicular to the axis of vibration (Fig. 1-6).

If there are some magnetic compasses in the neighborhood of the oscillating charge, these will be found to swing back and forth in response to the disturbance. This means that an oscillating *magnetic* field is produced by the charge too. Varying the placement of the compasses will show that this field oscillates in a plane perpendicular to the axis of vibration of the charged particle. The combined electric and magnetic fields traveling along one ray in the xy plane appear in Fig. 1-7.

The changes in electric and magnetic fields propagate outward with a characteristic velocity c , and are describable as a traveling wave, called an electromagnetic wave. Its frequency ν is the same as the oscillation frequency of the vibrating charge. Its wavelength is $\lambda = c/\nu$. Visible light, infrared radiation, radio waves, microwaves, ultraviolet radiation, X rays, and γ rays are all forms of electromagnetic radiation, their only difference being their frequencies ν . We shall continue the discussion in the context of light, understanding that it applies to all forms of electromagnetic radiation.

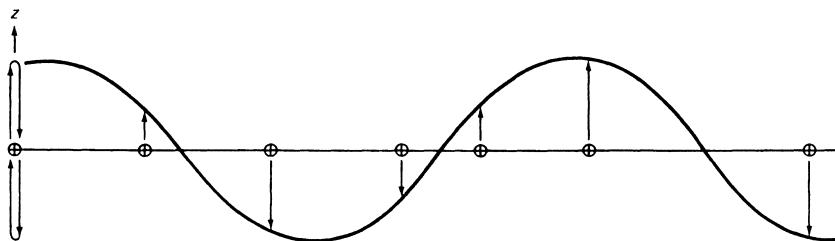


Figure 1-6 ► A harmonic electric-field wave emanating from a vibrating electric charge. The wave magnitude is proportional to the force felt by the test charges. The charges are only imaginary; if they actually existed, they would possess mass and under acceleration would absorb energy from the wave, causing it to attenuate.

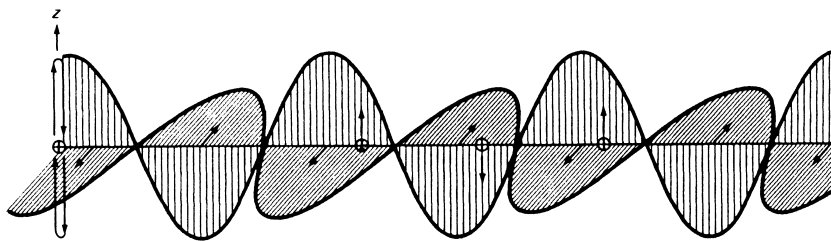


Figure 1-7 ► A harmonic electromagnetic field produced by an oscillating electric charge. The arrows without attached charges show the direction in which the north pole of a magnet would be attracted. The magnetic field is oriented perpendicular to the electric field.

If a beam of light is produced so that the orientation of the electric field wave is always in the same plane, the light is said to be plane (or linearly) polarized. The plane-polarized light shown in Fig. 1-7 is said to be z polarized. If the plane of orientation of the electric field wave rotates clockwise or counterclockwise about the axis of travel (i.e., if the electric field wave “corkscrews” through space), the light is said to be right or left circularly polarized. If the light is a composite of waves having random field orientations so that there is no resultant orientation, the light is unpolarized.

Experiments with light in the nineteenth century and earlier were consistent with the view that light is a wave phenomenon. One of the more obvious experimental verifications of this is provided by the interference pattern produced when light from a point source is allowed to pass through a pair of slits and then to fall on a screen. The resulting interference patterns are understandable only in terms of the constructive and destructive interference of waves. The differential equations of Maxwell, which provided the connection between electromagnetic radiation and the basic laws of physics, also indicated that light is a wave.

But there remained several problems that prevented physicists from closing the book on this subject. One was the inability of classical physical theory to explain the intensity and wavelength characteristics of light emitted by a glowing “blackbody.” This problem was studied by Planck, who was forced to conclude that the vibrating charged particles producing the light can exist only in certain discrete (separated) energy states. We shall not discuss this problem. Another problem had to do with the interpretation of a phenomenon discovered in the late 1800s, called the *photoelectric effect*.

1-6 The Photoelectric Effect

This phenomenon occurs when the exposure of some material to light causes it to eject electrons. Many metals do this quite readily. A simple apparatus that could be used to study this behavior is drawn schematically in Fig. 1-8. Incident light strikes the metal dish in the evacuated chamber. If electrons are ejected, some of them will strike the collecting wire, giving rise to a deflection of the galvanometer. In this apparatus, one can vary the potential difference between the metal dish and the collecting wire, and also the intensity and frequency of the incident light.

Suppose that the potential difference is set at zero and a current is detected when light of a certain intensity and frequency strikes the dish. This means that electrons

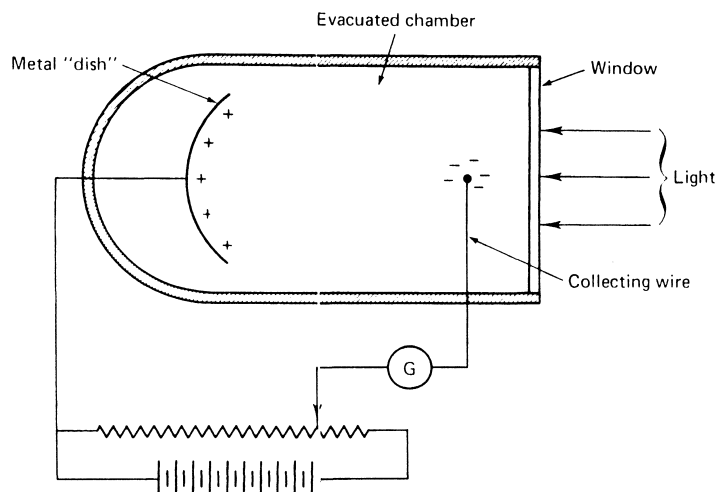


Figure 1-8 ► A phototube.

are being emitted from the dish with finite kinetic energy, enabling them to travel to the wire. If a retarding potential is now applied, electrons that are emitted with only a small kinetic energy will have insufficient energy to overcome the retarding potential and will not travel to the wire. Hence, the current being detected will decrease. The retarding potential can be increased gradually until finally even the most energetic photoelectrons cannot make it to the collecting wire. This enables one to calculate the maximum kinetic energy for photoelectrons produced by the incident light on the metal in question.

The observations from experiments of this sort can be summarized as follows:

1. Below a certain cutoff frequency of incident light, no photoelectrons are ejected, no matter how intense the light.
2. Above the cutoff frequency, the number of photoelectrons is directly proportional to the intensity of the light.
3. As the frequency of the incident light is increased, the maximum kinetic energy of the photoelectrons increases.
4. In cases where the radiation intensity is extremely low (but frequency is above the cutoff value) photoelectrons are emitted from the metal without any time lag.

Some of these results are summarized graphically in Fig. 1-9. Apparently, the kinetic energy of the photoelectron is given by

$$\text{kinetic energy} = h(\nu - \nu_0) \quad (1-33)$$

where h is a constant. The cutoff frequency ν_0 depends on the metal being studied (and also its temperature), but the slope h is the same for all substances.

We can also write the kinetic energy as

$$\text{kinetic energy} = \text{energy of light} - \text{energy needed to escape surface} \quad (1-34)$$

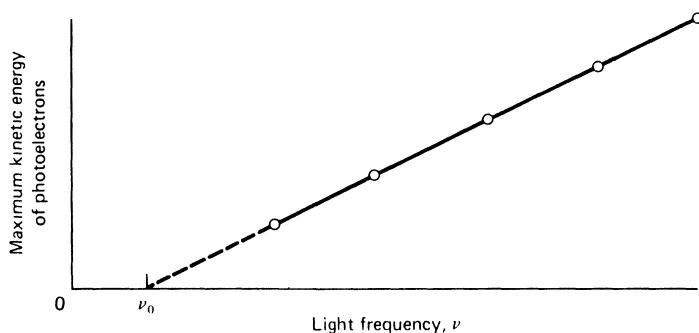


Figure 1-9 ► Maximum kinetic energy of photoelectrons as a function of incident light frequency, where ν_0 is the minimum frequency for which photoelectrons are ejected from the metal in the absence of any retarding or accelerating potential.

The last quantity in Eq. (1-34) is often referred to as the *work function* W of the metal. Equating Eq. (1-33) with (1-34) gives

$$\text{energy of light} - W = h\nu - h\nu_0 \quad (1-35)$$

The material-dependent term W is identified with the material-dependent term $h\nu_0$, yielding

$$\text{energy of light} \equiv E = h\nu \quad (1-36)$$

where the value of h has been determined to be 6.626176×10^{-34} J sec. (See Appendix 10 for units and conversion factors.)

Physicists found it difficult to reconcile these observations with the classical electromagnetic field theory of light. For example, if light of a certain frequency and intensity causes emission of electrons having a certain maximum kinetic energy, one would expect increased light *intensity* (corresponding classically to a greater electromagnetic field amplitude and hence greater energy density) to produce photoelectrons of higher kinetic energy. However, it only produces more photoelectrons and does not affect their energies. Again, if light is a wave, the energy is distributed over the entire wavefront and this means that a low light intensity would impart energy at a very low rate to an area of surface occupied by one atom. One can calculate that it would take years for an individual atom to collect sufficient energy to eject an electron under such conditions. No such induction period is observed.

An explanation for these results was suggested in 1905 by Einstein, who proposed that the incident light be viewed as being comprised of discrete units of energy. Each such unit, or *photon*, would have an associated energy of $h\nu$, where ν is the frequency of the oscillating emitter. Increasing the intensity of the light would correspond to increasing the number of photons, whereas increasing the frequency of the light would increase the energy of the photons. If we envision each emitted photoelectron as resulting from a photon striking the surface of the metal, it is quite easy to see that Einstein's proposal accords with observation. But it creates a new problem: If we are to visualize light as a stream of photons, how can we explain the wave properties of light, such as the double-slit diffraction pattern? What is the physical meaning of the electromagnetic wave?

Essentially, the problem is that, in the classical view, the square of the electromagnetic wave at any point in space is a measure of the energy density at that point. Now the square of the electromagnetic wave is a continuous and smoothly varying function, and if energy is continuous and infinitely divisible, there is no problem with this theory. But if the energy cannot be divided into amounts smaller than a photon—if it has a particulate rather than a continuous nature—then the classical interpretation cannot apply, for it is not possible to produce a smoothly varying energy distribution from energy *particles* any more than it is possible to produce, at the microscopic level, a smooth density distribution in gas made from atoms of matter. Einstein suggested that the square of the electromagnetic wave at some point (that is, the sum of the squares of the electric and magnetic field magnitudes) be taken as the *probability density* for finding a photon in the volume element around that point. The greater the square of the wave in some region, the greater is the probability for finding the photon in that region. Thus, the classical notion of energy having a definite and smoothly varying distribution is replaced by the idea of a smoothly varying probability density for finding an atomistic packet of energy.

Let us explore this probabilistic interpretation within the context of the two-slit interference experiment. We know that the pattern of light and darkness observed on the screen agrees with the classical picture of interference of waves. Suppose we carry out the experiment in the usual way, except we use a light source (of frequency ν) so weak that only $h\nu$ units of energy per second pass through the apparatus and strike the screen. According to the classical picture, this tiny amount of energy should strike the screen in a delocalized manner, producing an extremely faint image of the entire diffraction pattern. Over a period of many seconds, this pattern could be accumulated (on a photographic plate, say) and would become more intense. According to Einstein's view, our experiment corresponds to transmission of one photon per second and each photon strikes the screen at a localized point. Each photon strikes a new spot (not to imply the same spot cannot be struck more than once) and, over a long period of time, they build up the observed diffraction pattern. If we wish to state in advance where the next photon will appear, we are unable to do so. The best we can do is to say that the next photon is more likely to strike in one area than in another, the relative probabilities being quantitatively described by the square of the electromagnetic wave.

The interpretation of electromagnetic waves as probability waves often leaves one with some feelings of unreality. If the wave only tells us relative probabilities for finding a photon at one point or another, one is entitled to ask whether the wave has "physical reality," or if it is merely a mathematical device which allows us to analyze photon distribution, the photons being the "physical reality." We will defer discussion of this question until a later section on electron diffraction.

EXAMPLE 1-1 A retarding potential of 2.38 volts just suffices to stop photoelectrons emitted from potassium by light of frequency $1.13 \times 10^{15} \text{ s}^{-1}$. What is the work function, W , of potassium?

SOLUTION ► $E_{\text{light}} = h\nu = W + KE_{\text{electron}}, W = h\nu - KE_{\text{electron}} = (4.136 \times 10^{-15} \text{ eV s}) (1.13 \times 10^{15} \text{ s}^{-1}) - 2.38 \text{ eV} = 4.67 \text{ eV} - 2.38 \text{ eV} = 2.29 \text{ eV}$ [Note convenience of using h in units of eV s for this problem. See Appendix 10 for data.] ◀

EXAMPLE 1-2 Spectroscopists often express ΔE for a transition between states in wavenumbers, e.g., m^{-1} , or cm^{-1} , rather than in energy units like J or eV. (Usually cm^{-1} is favored, so we will proceed with that choice.)

- What is the physical meaning of the term wavenumber?
- What is the connection between wavenumber and energy?
- What wavenumber applies to an energy of 1.000 J? of 1.000 eV?

SOLUTION ▶ a) Wavenumber is the number of waves that fit into a unit of distance (usually of one centimeter). It is sometimes symbolized $\tilde{\nu}$. $\tilde{\nu} = 1/\lambda$, where λ is the wavelength in centimeters. b) Wavenumber characterizes the light that has photons of the designated energy. $E = h\nu = hc/\lambda = hc\tilde{\nu}$. (where c is given in cm/s). c) $E = 1.000 \text{ J} = hc\tilde{\nu}$; $\tilde{\nu} = 1.000 \text{ J}/hc = 1.000 \text{ J}/[(6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^{10} \text{ cm/s})] = 5.034 \times 10^{22} \text{ cm}^{-1}$. Clearly, this is light of an extremely short wavelength since more than 10^{22} wavelengths fit into 1 cm. For 1.000 eV, the above equation is repeated using h in eV s. This gives $\tilde{\nu} = 8065 \text{ cm}^{-1}$. ◀

1-7 The Wave Nature of Matter

Evidently light has wave and particle aspects, and we can describe it in terms of photons, which are associated with waves of frequency $\nu = E/h$. Now photons are rather peculiar particles in that they have zero rest mass. In fact, they can exist only when traveling at the speed of light. The more normal particles in our experience have nonzero rest masses and can exist at any velocity up to the speed-of-light limit. Are there also waves associated with such normal particles?

Imagine a particle having a finite rest mass that somehow can be made lighter and lighter, approaching zero in a continuous way. It seems reasonable that the existence of a wave associated with the motion of the particle should become more and more apparent, rather than the wave coming into existence abruptly when $m = 0$. De Broglie proposed that all material particles are associated with waves, which he called “matter waves,” but that the existence of these waves is likely to be observable only in the behaviors of extremely light particles.

De Broglie’s relation can be reached as follows. Einstein’s relation for photons is

$$E = h\nu \quad (1-37)$$

But a photon carrying energy E has a relativistic mass given by

$$E = mc^2 \quad (1-38)$$

Equating these two equations gives

$$E = mc^2 = h\nu = hc/\lambda \quad (1-39)$$

or

$$mc = h/\lambda \quad (1-40)$$

A normal particle, with nonzero rest mass, travels at a velocity v . If we regard Eq. (1-40) as merely the high-velocity limit of a more general expression, we arrive at an equation relating particle momentum p and associated wavelength λ :

$$mv = p = h/\lambda \quad (1-41)$$

or

$$\lambda = h/p \quad (1-42)$$

Here, m refers to the rest mass of the particle plus the relativistic correction, but the latter is usually negligible in comparison to the former.

This relation, proposed by de Broglie in 1922, was demonstrated to be correct shortly thereafter when Davisson and Germer showed that a beam of electrons impinging on a nickel target produced the scattering patterns one expects from interfering waves. These “electron waves” were observed to have wavelengths related to electron momentum in just the manner proposed by de Broglie.

Equation (1-42) relates the de Broglie wavelength λ of a matter wave to the momentum p of the particle. A higher momentum corresponds to a shorter wavelength. Since

$$\text{kinetic energy } T = mv^2 = (1/2m)(m^2v^2) = p^2/2m \quad (1-43)$$

it follows that

$$p = \sqrt{2mT} \quad (1-44)$$

Furthermore, Since $E = T + V$, where E is the total energy and V is the potential energy, we can rewrite the de Broglie wavelength as

$$\lambda = \frac{h}{\sqrt{2m(E - V)}} \quad (1-45)$$

Equation (1-45) is useful for understanding the way in which λ will change for a particle moving with constant total energy in a varying potential. For example, if the particle enters a region where its potential energy increases (e.g., an electron approaches a negatively charged plate), $E - V$ decreases and λ increases (i.e., the particle slows down, so its momentum decreases and its associated wavelength increases). We shall see examples of this behavior in future chapters.

Observe that if $E \geq V$, λ as given by Eq. (1-45) is real. However, if $E < V$, λ becomes imaginary. Classically, we never encounter such a situation, but we will find it is necessary to consider this possibility in quantum mechanics.

EXAMPLE 1-3 A He^{2+} ion is accelerated from rest through a voltage drop of 1.000 kilovolts. What is its final deBroglie wavelength? Would the wavelike properties be very apparent?

SOLUTION ► Since a charge of two electronic units has passed through a voltage drop of 1.000×10^3 volts, the final kinetic energy of the ion is 2.000×10^3 eV. To calculate λ , we first

convert from eV to joules: $KE \equiv p^2/2m = (2.000 \times 10^3 \text{ eV})(1.60219 \times 10^{-19} \text{ J/eV}) = 3.204 \times 10^{-16} \text{ J}$. $m_{He} = (4.003 \text{ g/mol})(10^{-3} \text{ kg/g})(1 \text{ mol}/6.022 \times 10^{23} \text{ atoms}) = 6.65 \times 10^{-27} \text{ kg}$; $p = \sqrt{2m_{He} \cdot KE} = [2(6.65 \times 10^{-27} \text{ kg})(3.204 \times 10^{-16} \text{ J})]^{1/2} = 2.1 \times 10^{-21} \text{ kg m/s}$. $\lambda = h/p = (6.626 \times 10^{-34} \text{ Js})/(2.1 \times 10^{-21} \text{ kg m/s}) = 3.2 \times 10^{-13} \text{ m} = 0.32 \text{ pm}$. This wavelength is on the order of 1% of the radius of a hydrogen atom—too short to produce observable interference results when interacting with atom-size scatterers. For most purposes, we can treat this ion as simply a high-speed particle. ◀

1-8 A Diffraction Experiment with Electrons

In order to gain a better understanding of the meaning of matter waves, we now consider a set of simple experiments. Suppose that we have a source of a beam of monoenergetic electrons and a pair of slits, as indicated schematically in Fig. 1-10. Any electron arriving at the phosphorescent screen produces a flash of light, just as in a television set. For the moment we ignore the light source near the slits (assume that it is turned off) and inquire as to the nature of the image on the phosphorescent screen when the electron beam is directed at the slits. The observation, consistent with the observations of Davisson and Germer already mentioned, is that there are alternating bands of light and dark, indicating that the electron beam is being diffracted by the slits. Furthermore, the distance separating the bands is consistent with the de Broglie wavelength corresponding to the energy of the electrons. The variation in light intensity observed on the screen is depicted in Fig. 1-11a.

Evidently, the electrons in this experiment are displaying wave behavior. Does this mean that the electrons are spread out like waves when they are detected at the screen? We test this by reducing our beam intensity to let only one electron per second through the apparatus and observe that each electron gives a localized pinpoint of light, the entire diffraction pattern building up gradually by the accumulation of many points. Thus, the square of de Broglie's matter wave has the same kind of statistical significance that Einstein proposed for electromagnetic waves and photons, and the electrons really are localized particles, at least when they are detected at the screen.

However, if they are really particles, it is hard to see how they can be diffracted. Consider what happens when slit b is closed. Then all the electrons striking the screen must have come through slit a . We observe the result to be a single area of light on the screen (Fig. 1-11b). Closing slit a and opening b gives a similar (but displaced)

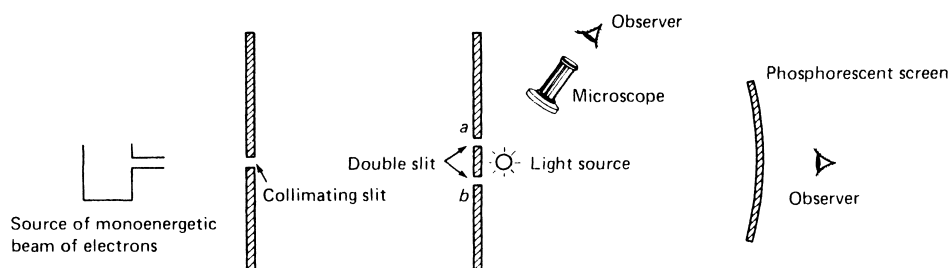


Figure 1-10 ▶ The electron source produces a beam of electrons, some of which pass through slits a and/or b to be detected as flashes of light on the phosphorescent screen.

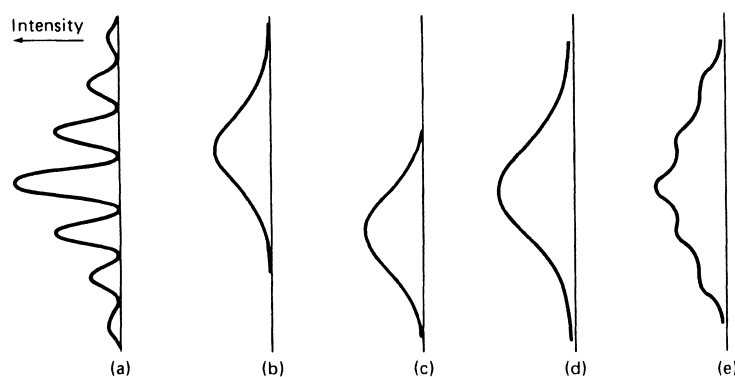


Figure 1-11 ► Light intensity at phosphorescent screen under various conditions: (a) a and b open, light off; (b) a open, b closed, light off; (c) a closed, b open, light off; (d) a and b open, light on, λ short; (e) a and b open, light on, λ longer.

light area, as shown in Fig. 1-11c. These patterns are just what we would expect for particles. Now, with both slits open, we expect half the particles to pass through slit a and half through slit b , the resulting pattern being the *sum* of the results just described. Instead we obtain the diffraction pattern (Fig. 1-11a). How can this happen? It seems that, somehow, an electron passing through the apparatus can sense whether one or both slits are open, even though as a particle it can explore only one slit or the other. One might suppose that we are seeing the result of simultaneous traversal of the two slits by two electrons, the path of each electron being affected by the presence of an electron in the other slit. This would explain how an electron passing through slit a would “know” whether slit b was open or closed. But the fact that the pattern builds up even when electrons pass through at the rate of one per second indicates that this argument will not do. Could an electron be coming through both slits at once?

To test this question, we need to have detailed information about the positions of the electrons as they pass through the slits. We can get such data by turning on the light source and aiming a microscope at the slits. Then photons will bounce off each electron as it passes the slits and will be observed through the microscope. The observer thus can tell through which slit each electron has passed, and also record its final position on the phosphorescent screen. In this experiment, it is necessary to use light having a wavelength short in comparison to the interslit distance; otherwise the microscope cannot resolve a flash well enough to tell which slit it is nearest. When this experiment is performed, we indeed detect each electron as coming through one slit or the other, and not both, but we also find that the diffraction pattern on the screen has been lost and that we have the broad, featureless distribution shown in Fig. 1-11d, which is basically the sum of the single-slit experiments. What has happened is that the photons from our light source, in bouncing off the electrons as they emerge from the slits, have affected the momenta of the electrons and changed their paths from what they were in the absence of light. We can try to counteract this by using photons with lower momentum; but this means using photons of lower E , hence longer λ . As a result, the images of the electrons in the microscope get broader, and it becomes more and more ambiguous as to which slit a given electron has passed through or that it really passed through only one slit. As we become more and more uncertain about the path

of each electron as it moves past the slits, the accumulating diffraction pattern becomes more and more pronounced (Fig. 1-11e). (Since this is a “thought experiment,” we can ignore the inconvenient fact that our “light” source must produce X rays or γ rays in order to have a wavelength short in comparison to the appropriate interslit distance.)

This conceptual experiment illustrates a basic feature of microscopic systems—we cannot measure properties of the system without affecting the future development of the system in a nontrivial way. The system with the light turned off is significantly different from the system with the light turned on (with short λ), and so the electrons arrive at the screen with different distributions. No matter how cleverly one devises the experiment, there is some minimum necessary disturbance involved in any measurement. In this example with the light off, the problem is that we know the momentum of each electron quite accurately (since the beam is monoenergetic and collimated), but we do not know anything about the way the electrons traverse the slits. With the light on, we obtain information about electron position just beyond the slits but we change the momentum of each electron in an unknown way. The measurement of particle position leads to loss of knowledge about particle momentum. This is an example of the *uncertainty principle* of Heisenberg, who stated that the product of the simultaneous uncertainties in “conjugate variables,” a and b , can never be smaller than the value of Planck’s constant h divided by 4π :

$$\Delta a \cdot \Delta b \geq h/4\pi \quad (1-46)$$

Here, Δa is a measure of the uncertainty in the variable a , etc. (The easiest way to recognize conjugate variables is to note that their dimensions must multiply to joule seconds. Linear momentum and linear position satisfies this requirement. Two other important pairs of conjugate variables are energy–time and angular momentum–angular position.) In this example with the light off, our uncertainty in momentum is small and our uncertainty in position is unacceptably large, since we cannot say which slit each electron traverses. With the light on, we reduce our uncertainty in position to an acceptable size, but subsequent to the position of each electron being observed, we have much greater uncertainty in momentum.

Thus, we see that the appearance of an electron (or a photon) as a particle or a wave depends on our experiment. Because *any* observation on so small a particle involves a significant perturbation of its state, it is proper to think of the electron plus apparatus as a single system. The question, “Is the electron a particle or a wave?” becomes meaningful only when the apparatus is defined on which we plan a measurement. In some experiments, the apparatus and electrons interact in a way suggestive of the electron being a wave, in others, a particle. The question, “What is the electron when were not looking?,” cannot be answered experimentally, since an experiment is a “look” at the electron. In recent years experiments of this sort have been carried out using single atoms.⁵

EXAMPLE 1-4 The lifetime of an excited state of a molecule is 2×10^{-9} s. What is the uncertainty in its energy in J? In cm^{-1} ? How would this manifest itself experimentally?

⁵See F. Flam [1].

SOLUTION ► The Heisenberg uncertainty principle gives, for minimum uncertainty $\Delta E \cdot \Delta t = h/4\pi$. $\Delta E = (6.626 \times 10^{-34} \text{ J s}) / [(4\pi)(2 \times 10^{-9} \text{ s})] = 2.6 \times 10^{-26} \text{ J} (2.6 \times 10^{-26} \text{ J}) (5.03 \times 10^{22} \text{ cm}^{-1} \text{ J}^{-1}) = 0.001 \text{ cm}^{-1}$ (See Appendix 10 for data.) Larger uncertainty in E shows up as greater line-width in emission spectra. ◀

1-9 Schrödinger's Time-Independent Wave Equation

Earlier we saw that we needed a wave equation in order to solve for the standing waves pertaining to a particular classical system and its set of boundary conditions. The same need exists for a wave equation to solve for matter waves. Schrödinger obtained such an equation by taking the classical time-independent wave equation and substituting de Broglie's relation for λ . Thus, if

$$\nabla^2 \psi = -(2\pi/\lambda)^2 \psi \quad (1-47)$$

and

$$\lambda = \frac{h}{\sqrt{2m(E - V)}} \quad (1-48)$$

then

$$\left[-(h^2/8\pi^2 m) \nabla^2 + V(x, y, z) \right] \psi(x, y, z) = E \psi(x, y, z) \quad (1-49)$$

Equation (1-49) is Schrödinger's time-independent wave equation for a single particle of mass m moving in the three-dimensional potential field V .

In classical mechanics we have separate equations for wave motion and particle motion, whereas in quantum mechanics, in which the distinction between particles and waves is not clear-cut, we have a single equation—the Schrödinger equation. We have seen that the link between the Schrödinger equation and the classical *wave* equation is the de Broglie relation. Let us now compare Schrödinger's equation with the classical equation for *particle* motion.

Classically, for a particle moving in three dimensions, the total energy is the sum of kinetic and potential energies:

$$(1/2m)(p_x^2 + p_y^2 + p_z^2) + V = E \quad (1-50)$$

where p_x is the momentum in the x coordinate, etc. We have just seen that the analogous Schrödinger equation is [writing out Eq. (1-49)]

$$\left[\frac{-h^2}{8\pi^2 m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x, y, z) \right] \psi(x, y, z) = E \psi(x, y, z) \quad (1-51)$$

It is easily seen that Eq. (1-50) is linked to the quantity in brackets of Eq. (1-51) by a relation associating classical momentum with a partial differential operator:

$$p_x \longleftrightarrow (h/2\pi i)(\partial/\partial x) \quad (1-52)$$

and similarly for p_y and p_z . The relations (1-52) will be seen later to be an important postulate in a formal development of quantum mechanics.

The left-hand side of Eq. (1-50) is called the *hamiltonian* for the system. For this reason the operator in square brackets on the LHS of Eq. (1-51) is called the *hamiltonian operator*⁶ H . For a given system, we shall see that the construction of H is not difficult. The difficulty comes in solving Schrödinger's equation, often written as

$$H\psi = E\psi \quad (1-53)$$

The classical and quantum-mechanical wave equations that we have discussed are members of a special class of equations called *eigenvalue equations*. Such equations have the format

$$\text{Op } f = cf \quad (1-54)$$

where Op is an operator, f is a function, and c is a constant. Thus, eigenvalue equations have the property that operating on a function regenerates the same function times a constant. The function f that satisfies Eq. (1-54) is called an *eigenfunction* of the operator. The constant c is called the *eigenvalue* associated with the eigenfunction f . Often, an operator will have a large number of eigenfunctions and eigenvalues of interest associated with it, and so an index is necessary to keep them sorted, viz.

$$\text{Op } f_i = c_i f_i \quad (1-55)$$

We have already seen an example of this sort of equation, Eq. (1-19) being an eigenfunction for Eq. (1-18), with eigenvalue $-\omega^2 m/T$.

The solutions ψ for Schrödinger's equation (1-53), are referred to as eigenfunctions, wavefunctions, or state functions.

EXAMPLE 1-5 a) Show that $\sin(3.63x)$ is not an eigenfunction of the operator d/dx .
 b) Show that $\exp(-3.63ix)$ is an eigenfunction of the operator d/dx . What is its eigenvalue?
 c) Show that $\frac{1}{\pi} \sin(3.63x)$ is an eigenfunction of the operator $((-h^2/8\pi^2m)d^2/dx^2)$. What is its eigenvalue?

SOLUTION ► a) $\frac{d}{dx} \sin(3.63x) = 3.63 \cos(3.63x) \neq \text{constant times } \sin(3.63x)$.

b) $\frac{d}{dx} \exp(-3.63ix) = -3.63i \exp(-3.63ix) = \text{constant times } \exp(-3.63ix)$. Eigenvalue = $-3.63i$.

c) $((-h^2/8\pi^2m)d^2/dx^2) \frac{1}{\pi} \sin(3.63x) = (-h^2/8\pi^2m)(1/\pi)(3.63) \frac{d}{dx} \cos(3.63x)$
 $= [(3.63)^2 h^2/8\pi^2m] \cdot (1/\pi) \sin(3.63x)$
 $= \text{constant times } (1/\pi) \sin(3.63x)$.

Eigenvalue = $(3.63)^2 h^2/8\pi^2m$. ◀

⁶An *operator* is a symbol telling us to carry out a certain mathematical operation. Thus, d/dx is a differential operator telling us to differentiate anything following it with respect to x . The function $1/x$ may be viewed as a multiplicative operator. Any function on which it operates gets multiplied by $1/x$.

1-10 Conditions on ψ

We have already indicated that the square of the electromagnetic wave is interpreted as the probability density function for finding photons at various places in space. We now attribute an analogous meaning to ψ^2 for *matter* waves. Thus, in a one-dimensional problem (for example, a particle constrained to move on a line), the probability that the particle will be found in the interval dx around the point x_1 is taken to be $\psi^2(x_1) dx$. If ψ is a complex function, then the *absolute square*, $|\psi|^2 \equiv \psi^* \psi$ is used instead of ψ^2 .⁷ This makes it mathematically impossible for the average mass distribution to be negative in any region.

If an eigenfunction ψ has been found for Eq. (1-53), it is easy to see that $c\psi$ will also be an eigenfunction, for any constant c . This is due to the fact that a multiplicative constant commutes⁸ with the operator H , that is,

$$H(c\psi) = cH\psi = cE\psi = E(c\psi) \quad (1-56)$$

The equality of the first and last terms is a statement of the fact that $c\psi$ is an eigenfunction of H . The question of which constant to use for the wavefunction is resolved by appeal to the probability interpretation of $|\psi|^2$. For a particle moving on the x axis, the probability that the particle is between $x = -\infty$ and $x = +\infty$ is unity, that is, a certainty. This probability is also equal to the sum of the probabilities for finding the particle in each and every infinitesimal interval along x , so this sum (an integral) must equal unity:

$$c^*c \int_{-\infty}^{+\infty} \psi^*(x)\psi(x) dx = 1 \quad (1-57)$$

If the selection of the constant multiplier c is made so that Eq. (1-57) is satisfied, the wavefunction $\psi' = c\psi$ is said to be *normalized*. For a three-dimensional function, $c\psi(x, y, z)$, the normalization requirement is

$$c^*c \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \psi^*(x, y, z)\psi(x, y, z) dx dy dz \equiv |c|^2 \int_{\text{all space}} |\psi|^2 dv = 1 \quad (1-58)$$

As a result of our physical interpretation of $|\psi|^2$ plus the fact that ψ must be an eigenfunction of the hamiltonian operator H , we can reach some general conclusions about what sort of mathematical properties ψ can or cannot have.

First, we require that ψ be a *single-valued* function because we want $|\psi|^2$ to give an unambiguous probability for finding a particle in a given region (see Fig. 1-12). Also, we reject functions that are infinite in any region of space because such an infinity will always be infinitely greater than any finite region, and $|\psi|^2$ will be useless as a measure of comparative probabilities.⁹ In order for $H\psi$ to be defined everywhere, it is necessary that the second derivative of ψ be defined everywhere. This requires that the first derivative of ψ be *piecewise continuous* and that ψ itself be *continuous* as in Fig. 1d. (We shall see an example of this shortly.)

⁷If $f = u + iv$, then f^* , the complex conjugate of f , is given by $u - iv$, where u and v are real functions.

⁸ a and b are said to *commute* if $ab = ba$.

⁹There are cases, particularly in relativistic treatments, where ψ is infinite at single points of zero measure, so that $|\psi|^2 dx$ remains finite. Normally we do not encounter such situations in quantum chemistry.

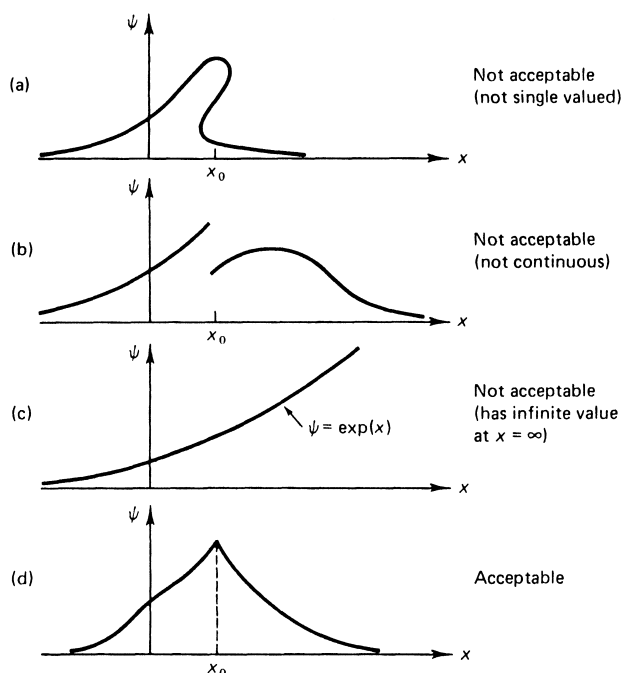


Figure 1-12 ► (a) ψ is triple valued at x_0 . (b) ψ is discontinuous at x_0 . (c) ψ grows without limit as x approaches $+\infty$ (i.e., ψ “blows up,” or “explodes”). (d) ψ is continuous and has a “cusp” at x_0 . Hence, first derivative of ψ is discontinuous at x_0 and is only piecewise continuous. This does not prevent ψ from being acceptable.

Functions that are single-valued, continuous, nowhere infinite, and have piecewise continuous first derivatives will be referred to as *acceptable* functions. The meanings of these terms are illustrated by some sample functions in Fig. 1-12.

In most cases, there is one more general restriction we place on ψ , namely, that it be a normalizable function. This means that the integral of $|\psi|^2$ over all space must not be equal to zero or infinity. A function satisfying this condition is said to be *square-integrable*.

1-11 Some Insight into the Schrödinger Equation

There is a fairly simple way to view the physical meaning of the Schrödinger equation (1-49). The equation essentially states that E in $H\psi = E\psi$ depends on two things, V and the second derivatives of ψ . Since V is the potential energy, the second derivatives of ψ must be related to the kinetic energy. Now the second derivative of ψ with respect to a given direction is a measure of the rate of change of slope (i.e., the curvature, or “wiggleness”) of ψ in that direction. Hence, we see that a more wiggly wavefunction leads, through the Schrödinger equation, to a higher kinetic energy. This is in accord with the spirit of de Broglie’s relation, since a shorter wavelength function is a more wiggly function. But the Schrödinger equation is more generally applicable because we can take second derivatives of any acceptable function, whereas wavelength is defined

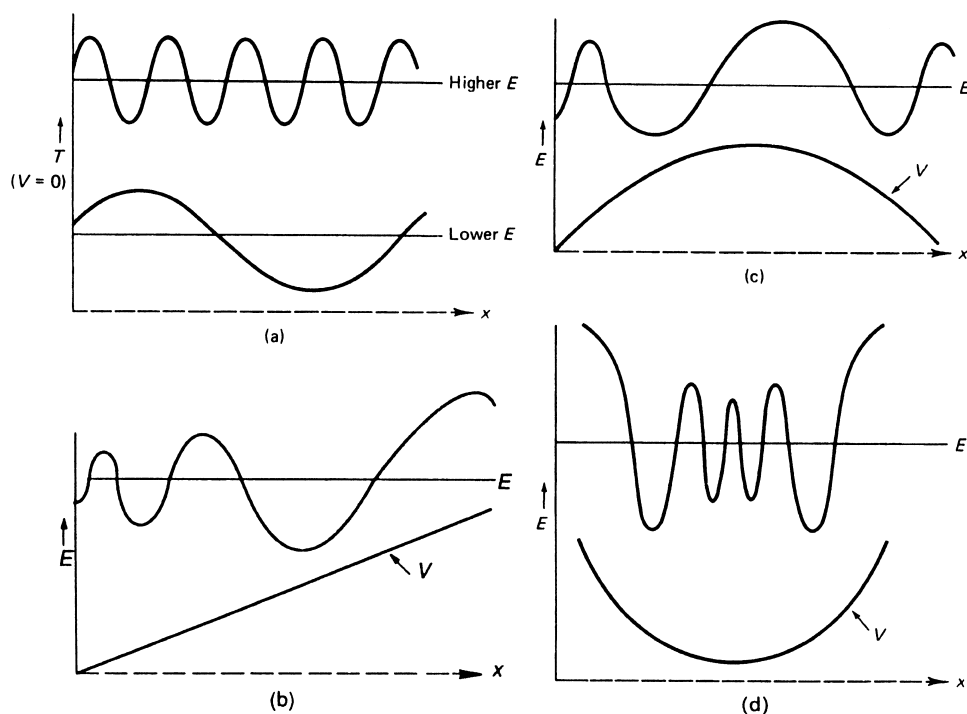


Figure 1-13 ► (a) Since $V = 0$, $E = T$. For higher T , ψ is more wiggly, which means that λ is shorter. (Since ψ is periodic for a free particle, λ is defined.) (b) As V increases from left to right, ψ becomes less wiggly. (c)–(d) ψ is most wiggly where V is lowest and T is greatest.

only for periodic functions. Since E is a constant, the solutions of the Schrödinger equation must be more wiggly in regions where V is low and less wiggly where V is high. Examples for some one-dimensional cases are shown in Fig. 1-13.

In the next chapter we use some fairly simple examples to illustrate the ideas that we have already introduced and to bring out some additional points.

1-12 Summary

In closing this chapter, we collect and summarize the major points to be used in future discussions.

1. Associated with any particle is a wavefunction having wavelength related to particle momentum by $\lambda = h/p = h/\sqrt{2m(E - V)}$.
2. The wavefunction has the following physical meaning; its absolute square is proportional to the probability density for finding the particle. If the wavefunction is normalized, its square is *equal* to the probability density.
3. The wavefunctions ψ for time-independent states are eigenfunctions of Schrödinger's equation, which can be constructed from the classical wave equation by requiring $\lambda = h/\sqrt{2m(E - V)}$, or from the classical particle equation by replacing p_k with $(h/2\pi i)\partial/\partial k$, $k = x, y, z$.

4. For ψ to be acceptable, it must be single-valued, continuous, nowhere infinite, with a piecewise continuous first derivative. For most situations, we also require ψ to be square-integrable.
5. The wavefunction for a particle in a varying potential oscillates most rapidly where V is low, giving a high T in this region. The low V plus high T equals E . In another region, where V is high, the wavefunction oscillates more slowly, giving a low T , which, with the high V , equals the same E as in the first region.

1-12.A Problems¹⁰

- 1-1. Express $A \cos(kx) + B \sin(kx) + C \exp(ikx) + D \exp(-ikx)$ purely in terms of $\cos(kx)$ and $\sin(kx)$.
- 1-2. Repeat the standing-wave-in-a-string problem worked out in Section 1-4, but clamp the string at $x = +L/2$ and $-L/2$ instead of at 0 and L .
- 1-3. Find the condition that must be satisfied by α and β in order that $\psi(x) = A \sin(\alpha x) + B \cos(\beta x)$ satisfy Eq. (1-20).
- 1-4. The apparatus sketched in Fig. 1-8 is used with a dish plated with zinc and also with a dish plated with cesium. The wavelengths of the incident light and the corresponding retarding potentials needed to just prevent the photoelectrons from reaching the collecting wire are given in Table P1-4. Plot incident light frequency versus retarding potential for these two metals. Evaluate their work functions (in eV) and the proportionality constant h (in eV s).

TABLE P1-4 ►

$\lambda(\text{Å})$	Retarding potential (V)	
	Cs	Zn
6000	0.167	—
3000	2.235	0.435
2000	4.302	2.502
1500	6.369	1.567
1200	8.436	6.636

- 1-5. Calculate the de Broglie wavelength in nanometers for each of the following:
 - a) An electron that has been accelerated from rest through a potential change of 500 V.
 - b) A bullet weighing 5 gm and traveling at 400 m s^{-1} .
- 1-6. Arguing from Eq. (1-7), what is the time needed for a standing wave to go through one complete cycle?

¹⁰Hints for a few problems may be found in Appendix 12 and answers for almost all of them appear in Appendix 13.

1-7. The equation for a standing wave in a string has the form

$$\Psi(x, t) = \psi(x) \cos(\omega t)$$

- Calculate the time-averaged potential energy (PE) for this motion. [*Hint:* Use $PE = -\int F d\Psi$; $F = ma$; $a = \partial^2\Psi/\partial t^2$.]
- Calculate the time-averaged kinetic energy (KE) for this motion. [*Hint:* Use $KE = 1/2mv^2$ and $v = \partial\Psi/\partial t$.]
- Show that this harmonically vibrating string stores its energy *on the average* half as kinetic and half as potential energy, and that $E(x)_{av} \propto \psi^2(x)$.

1-8. Indicate which of the following functions are “acceptable.” If one is not, give a reason.

- $\psi = x$
- $\psi = x^2$
- $\psi = \sin x$
- $\psi = \exp(-x)$
- $\psi = \exp(-x^2)$

1-9. An acceptable function is never infinite. Does this mean that an acceptable function must be square integrable? If you think these are not the same, try to find an example of a function (other than zero) that is never infinite but is not square integrable.

1-10. Explain why the fact that $\sin(x) = -\sin(-x)$ means that we can restrict Eq. (1-32) to nonnegative n without loss of physical content.

1-11. Which of the following are eigenfunctions for d/dx ?

- x^2
- $\exp(-3.4x^2)$
- 37
- $\exp(x)$
- $\sin(ax)$
- $\cos(4x) + i \sin(4x)$

1-12. Calculate the minimum de Broglie wavelength for a photoelectron that is produced when light of wavelength 140.0 nm strikes zinc metal. (Workfunction of zinc = 3.63 eV.)

Multiple Choice Questions

(Intended to be answered without use of pencil and paper.)

1. A particle satisfying the time-independent Schrödinger equation must have

- an eigenfunction that is normalized.
- a potential energy that is independent of location.
- a de Broglie wavelength that is independent of location.

- d) a total energy that is independent of location.
e) None of the above is a true statement.
2. When one operates with d^2/dx^2 on the function $6 \sin(4x)$, one finds that
- the function is an eigenfunction with eigenvalue -96 .
 - the function is an eigenfunction with eigenvalue 16 .
 - the function is an eigenfunction with eigenvalue -16 .
 - the function is not an eigenfunction.
 - None of the above is a true statement.
3. Which one of the following concepts did Einstein propose in order to explain the photoelectric effect?
- A particle of rest mass m and velocity v has an associated wavelength λ given by $\lambda = h/mv$.
 - Doubling the intensity of light doubles the energy of each photon.
 - Increasing the wavelength of light increases the energy of each photon.
 - The photoelectron is a particle.
 - None of the above is a concept proposed by Einstein to explain the photoelectric effect.
4. Light of frequency ν strikes a metal and causes photoelectrons to be emitted having maximum kinetic energy of $0.90 h\nu$. From this we can say that
- light of frequency $\nu/2$ will not produce any photoelectrons.
 - light of frequency 2ν will produce photoelectrons having maximum kinetic energy of $1.80 h\nu$.
 - doubling the intensity of light of frequency ν will produce photoelectrons having maximum kinetic energy of $1.80 h\nu$.
 - the work function of the metal is $0.90 h\nu$.
 - None of the above statements is correct.
5. The reason for normalizing a wavefunction ψ is
- to guarantee that ψ is square-integrable.
 - to make $\psi^*\psi$ equal to the probability distribution function for the particle.
 - to make ψ an eigenfunction for the Hamiltonian operator.
 - to make ψ satisfy the boundary conditions for the problem.
 - to make ψ display the proper symmetry characteristics.

Reference

- [1] F. Flam, *Making Waves with Interfering Atoms. Physics Today*, 921–922 (1991).

Quantum Mechanics of Some Simple Systems

2-1 The Particle in a One-Dimensional “Box”

Imagine that a particle of mass m is free to move along the x axis between $x = 0$ and $x = L$, with no change in potential (set $V = 0$ for $0 < x < L$). At $x = 0$ and L and at all points beyond these limits the particle encounters an infinitely repulsive barrier ($V = \infty$ for $x \leq 0, x \geq L$). The situation is illustrated in Fig. 2-1. Because of the shape of this potential, this problem is often referred to as a *particle in a square well* or a *particle in a box* problem. It is well to bear in mind, however, that the situation is really like that of a particle confined to movement along a finite length of wire.

When the potential is discontinuous, as it is here, it is convenient to write a wave equation for each region. For the two regions beyond the ends of the box

$$\frac{-h^2}{8\pi^2m} \frac{d^2\psi}{dx^2} + \infty\psi = E\psi, \quad x \leq 0, x \geq L \quad (2-1)$$

Within the box, ψ must satisfy the equation

$$\frac{-h^2}{8\pi^2m} \frac{d^2\psi}{dx^2} = E\psi, \quad 0 < x < L \quad (2-2)$$

It should be realized that E must take on the same values for both of these equations; the eigenvalue E pertains to the entire range of the particle and is not influenced by divisions we make for mathematical convenience.

Let us examine Eq. (2-1) first. Suppose that, at some point within the infinite barrier, say $x = L + dx$, ψ is finite. Then the second term on the left-hand side of Eq. (2-1) will be infinite. If the first term on the left-hand side is finite or zero, it follows immediately that E is infinite at the point $L + dx$ (and hence everywhere in the system). Is it possible that a solution exists such that E is finite? One possibility is that $\psi = 0$ at all points where $V = \infty$. The other possibility is that the first term on the left-hand side of Eq. (2-1) can be made to cancel the infinite second term. This might happen if the second derivative of the wavefunction is infinite at all points where $V = \infty$ and $\psi \neq 0$. For the second derivative to be infinite, the first derivative must be discontinuous, and so ψ itself must be nonsmooth (i.e., it must have a sharp corner; see Fig. 2-2). Thus, we see that it may be possible to obtain a finite value for both E and ψ at $x = L + dx$, provided that ψ is nonsmooth there. But what about the next point, $x = L + 2dx$, and all the other points outside the box? If we try to use the same device, we end up with the requirement that ψ be nonsmooth at every point where $V = \infty$. A function that is

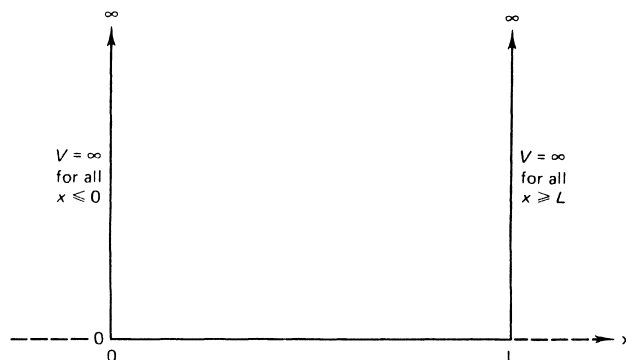


Figure 2-1 ► The potential felt by a particle as a function of its x coordinate.

continuous but which has a point-wise discontinuous first derivative is a contradiction in terms (i.e., a continuous f cannot be 100% corners. To have recognizable corners, we must have some (continuous) edges. We say that the first derivative of ψ must be *piecewise continuous*.) Hence, if $V = \infty$ at a single point, we might find a solution ψ which is finite at that point, with finite energy. If $V = \infty$ over a finite range of connected points, however, either E for the system is infinite, and ψ is finite over this region or E is not infinite (but is indeterminate) and ψ is zero over this region.

We are not concerned with particles of infinite energy, and so we will say that the solution to Eq. (2-1) is $\psi = 0$.¹

Turning now to Eq. (2-2) we ask what solutions ψ exist in the box having associated eigenvalues E that are finite and positive. Any function that, when twice differentiated, yields a negative constant times the selfsame function is a possible candidate for ψ . Such functions are $\sin(kx)$, $\cos(kx)$, and $\exp(\pm ikx)$. But these functions are not all independent since, as we noted in Chapter 1,

$$\exp(\pm ikx) = \cos(kx) \pm i \sin(kx) \quad (2-3)$$

We thus are free to express ψ in terms of $\exp(\pm ikx)$ or else in terms of $\sin(kx)$ and $\cos(kx)$. We choose the latter because of their greater familiarity, although the final answer must be independent of this choice.

The most general form for the solution is

$$\psi(x) = A \sin(kx) + B \cos(kx) \quad (2-4)$$

where A , B , and k remain to be determined. As we have already shown, ψ is zero at $x \leq 0$, $x \geq L$ and so we have as boundary conditions

$$\psi(0) = 0 \quad (2-5)$$

$$\psi(L) = 0 \quad (2-6)$$

Mathematically, this is precisely the same problem we have already solved in Chapter 1 for the standing waves in a clamped string. The solutions are

$$\begin{aligned} \psi(x) &= A \sin(n\pi x/L), \quad n = 1, 2, \dots, \quad 0 < x < L \\ \psi(x) &= 0, \quad x \leq 0, x \geq L \end{aligned} \quad (2-7)$$

¹Thus, the particle never gets into these regions. It is meaningless to talk of the energy of the particle in such regions, and our earlier statement that E must be identical in Eqs. (2-1) and (2-2) must be modified; E is constant in all regions where ψ is finite.

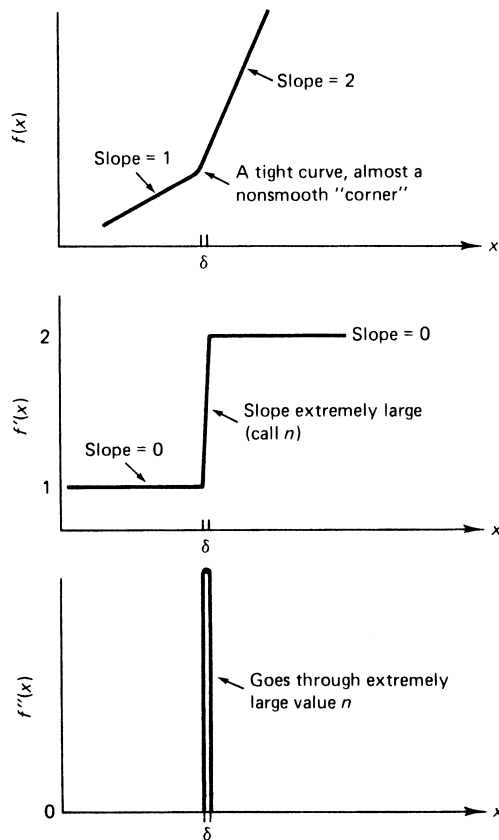


Figure 2-2 ► As the function $f(x)$ approaches being nonsmooth, δ approaches zero (the width of one point) and n approaches infinity.

One difference between Eq. (2-7) and the string solutions is that we have rejected the $n = 0$ solution in Eq. (2-7). For the string, this solution was for no vibration at all—a physically realizable circumstance. For the particle-in-a-box problem, this solution is rejected because it is not square-integrable. (It gives $\psi = 0$, which means *no* particle on the x axis, contradicting our starting premise. One could also reject this solution for the classical case since it means no energy in the string, which might contradict a starting premise depending on how the problem is worded.)

Let us check to be sure these functions satisfy Schrödinger’s equation:

$$\begin{aligned}
 H\psi(x) &= \frac{-\hbar^2}{8\pi^2m} \frac{d^2[A \sin(n\pi x/L)]}{dx^2} \\
 &= \frac{-\hbar^2}{8\pi^2m} \left[-A \frac{n^2\pi^2}{L^2} \sin\left(\frac{n\pi x}{L}\right) \right] \\
 &= \frac{n^2\hbar^2}{8mL^2} \left[A \sin\left(\frac{n\pi x}{L}\right) \right] = E\psi(x) \qquad (2-8)
 \end{aligned}$$

This shows that the functions (2-7) are indeed eigenfunctions of H . We note in passing that these functions are acceptable in the sense of Chapter 1.

The only remaining parameter is the constant A . We set this to make the probability of finding the particle in the well equal to unity:

$$\int_0^L \psi^2(x) dx = A^2 \int_0^L \sin^2(n\pi x/L) dx = 1 \quad (2-9)$$

This leads to (Problem 2-2)

$$A = \sqrt{2/L} \quad (2-10)$$

which completes the solving of Schrödinger's time-independent equation for the problem. Our results are the normalized eigenfunctions

$$\psi_n(x) = \sqrt{(2/L)} \sin(n\pi x/L), \quad n = 1, 2, 3, \dots \quad (2-11)$$

and the corresponding eigenvalues, from Eq. (2-8),

$$E_n = n^2 h^2 / 8mL^2, \quad n = 1, 2, 3, \dots \quad (2-12)$$

Each different value of n corresponds to a different stationary state of this system.

2-2 Detailed Examination of Particle-in-a-Box Solutions

Having solved the Schrödinger equation for the particle in the infinitely deep square-well potential, we now examine the results in more detail.

2-2.A Energies

The most obvious feature of the energies is that, as we move through the allowed states ($n = 1, 2, 3, \dots$), E skips from one discrete, well-separated value to another (1, 4, 9 in units of $h^2/8mL^2$). Thus, the particle can have only certain discrete energies—the energy is *quantized*. This situation is normally indicated by sketching the allowed *energy levels* as horizontal lines superimposed on the potential energy sketch, as in Fig. 2-3a. The fact that each energy level is a horizontal line emphasizes the fact that E is a constant and is the same regardless of the x coordinate of the particle. For this reason, E is called a *constant of motion*. The dependence of E on n^2 is displayed in the increased spacing between levels with increasing n in Fig. 2-3a. The number n is called a *quantum number*.

We note also that E is proportional to L^{-2} . This means that the more tightly a particle is confined, the greater is the spacing between the allowed energy levels. Alternatively, as the box is made wider, the separation between energies decreases and, in the limit of an infinitely wide box, disappears entirely. Thus, we associate quantized energies with spatial confinement.

For some systems, the degree of confinement of a particle depends on its total energy. For example, a pendulum swings over a longer trajectory if it has higher energy. The potential energy for a pendulum is given by $V = \frac{1}{2}kx^2$ and is given in Fig. 2-3b. If one solves the Schrödinger equation for this system (see Chapter 3), one finds that the energies are proportional to n rather than n^2 . We can rationalize this by thinking of

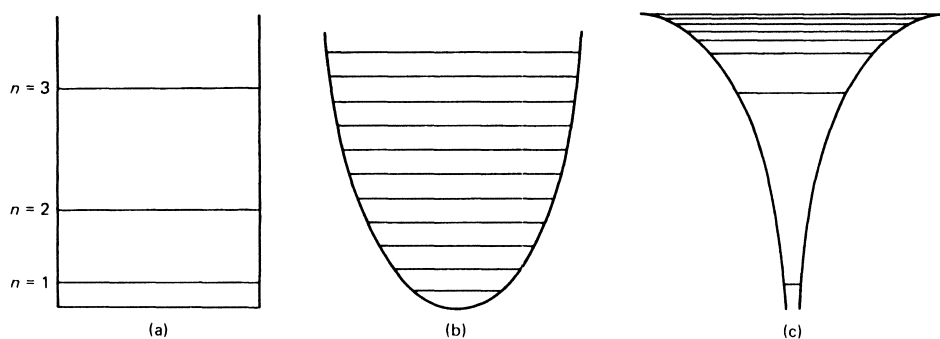


Figure 2-3 ► Allowed energies for a particle in various one-dimensional potentials. (a) “box” with infinite walls. (b) quadratic potential, $V = \frac{1}{2}kx^2$. (c) $V = -1/|x|$. Tendency for higher levels in (b) and (c) not to diverge as in (a) is due to larger “effective box size” for higher energies in (b) and (c).

the particle as occupying successively bigger boxes as we go to higher energies. This counteracts the n^2 increase in energy levels found for constant box width. For the potential $V = -1/|x|$ (which is the one-dimensional analog of a hydrogen atom) E varies as $1/n^2$ (Fig. 2-3c), and this is also consistent with the effective increase in L with increasing E .

The energy is proportional to $1/m$. This means that the separation between allowed energy levels decreases as m increases. Ultimately, for a macroscopic object, m is so large that the levels are too closely spaced to be distinguished from the continuum of levels expected in classical mechanics. This is an example of the *correspondence principle*, which, in its most general form, states that the predictions of quantum mechanics must pass smoothly into those of classical mechanics whenever we progress in a continuous way from the microscopic to the macroscopic realm.

Notice that the lowest possible energy for this system occurs for $n = 1$ and is $E = h^2/8mL^2$. This remarkable result means that a constrained particle (i.e., L not infinite) can never have an energy of zero. Evidently, the particle continues to move about in the region 0 to L , even at a temperature of absolute zero. For this reason, $h^2/8mL^2$ is called the *zero-point energy* for this system. In general, a finite zero-point energy occurs in any system having a restriction for motion in any coordinate. (Note that *finite* here means *not equal to zero*.)

It is possible to show that, for $L \neq \infty$, our particle in a box would have to violate the Heisenberg uncertainty principle to achieve an energy of zero. For, suppose the energy is precisely zero. Then the momentum must be precisely zero too. (In this system, all energy of the particle is kinetic since $V = 0$ in the box.) If the momentum p_x is *precisely* zero, however, our *uncertainty* in the value of the momentum Δp_x is also zero. If Δp_x is zero, the uncertainty principle [Eq. (2-46)] requires that the uncertainty in position Δx be infinite. But we know that the particle is between $x = 0$ and $x = L$. Hence, our uncertainty is on the order of L , not infinity, and the uncertainty principle is not satisfied. However, when $L = \infty$ (the particle is unconstrained), it is possible for the uncertainty principle to be satisfied simultaneously with having $E = 0$, and this is in satisfying accord with the fact that $E = h^2/8mL^2$ goes to zero as L approaches infinity.

Finally, we note that each separate value of n leads to a different energy. Thus, no two states have the same energy, and the states are said to be *nondegenerate* with respect to energy.

EXAMPLE 2-1 Consider an electron in a one-dimensional box of length 258 pm.
 a) What is the zero-point energy (*ZPE*) for this system? For a mole of such systems?
 b) What electronic speed classically corresponds to this *ZPE*? Compare to the speed of light.

SOLUTION ▶ a) $ZPE = E_{lowest} = E_{n=1}$

$$= 1^2 h^2 / 8mL^2 = \frac{(1)^2 (6.626 \times 10^{-34} \text{ J s})^2}{8(9.11 \times 10^{-31} \text{ kg})(258 \times 10^{-12} \text{ m})^2}$$

$$= 9.05 \times 10^{-19} \text{ J};$$

Per mole, this equals

$$(9.05 \times 10^{-19} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ kJ}/10^3 \text{ J}) = 54.5 \text{ kJ mol}^{-1}$$

b) E is all kinetic energy since $V = 0$ in the box, so $E = mv^2/2$. Hence,

$$v = \left[\frac{2E}{m} \right]^{1/2} = \left[\frac{2(9.05 \times 10^{-19} \text{ J})}{9.11 \times 10^{-31} \text{ kg}} \right]^{1/2} = 1.41 \times 10^6 \text{ m s}^{-1}$$

Compared to the speed of light, this is $\frac{1.41 \times 10^6 \text{ m s}^{-1}}{2.998 \times 10^8 \text{ m s}^{-1}} = 0.0047$, or about 0.5% of the speed of light. ◀

2-2.B Wavefunctions

We turn now to the eigenfunctions (2-11) for this problem. These are typically displayed by superimposing them on the energy levels as shown in Fig. 2-4 for the three lowest-energy wavefunctions. (It should be recognized that the energy units of the vertical axis do *not* pertain to the amplitudes of the wavefunctions.)

It is apparent from Fig. 2-4 that the allowed wavefunctions for this system could have been produced merely by placing an integral number of half sine waves in the

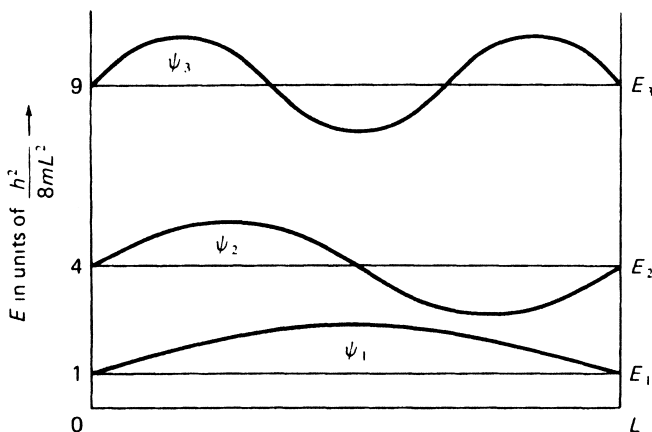


Figure 2-4 ▶ The eigenfunctions corresponding to $n = 1, 2, 3$, plotted on the corresponding energy levels. The energy units of the ordinate do not refer to the wavefunctions ψ . Each wavefunction has a zero value wherever it intersects its own energy level, and a maximum value of $\sqrt{2}/L$.

range $0-L$. The resulting wavelengths would then yield the energy of each state through application of de Broglie's relation (1-42). Thus, by inspection of Fig. 2-4, the allowed wavelengths are

$$\lambda = 2L/n, \quad n = 1, 2, 3, \dots \quad (2-13)$$

Therefore

$$p = h/\lambda = nh/2L \quad (2-14)$$

and

$$E = p^2/2m = n^2h^2/8mL^2 \quad (2-15)$$

in agreement with Eq. (2-12). As pointed out in Section 1-11, the wavefunctions having higher kinetic energy oscillate more rapidly. (Here $V = 0$, and E is all kinetic energy.)

Let us now consider the physical meaning of the eigenfunctions ψ . According to our earlier discussion, ψ^2 summarizes the results of many determinations of the position of the particle. Suppose that we had a particle-in-a-box system that we had somehow prepared in such a way that we knew it to be in the state with $n = 1$. We can imagine some sort of experiment, such as flashing a powerful γ -ray flashbulb and taking an instantaneous photograph, which tells us where the particle was at the instant of the flash. Now, suppose we wish to determine the position of the particle again. We want this second determination to be for the $n = 1$ state also, but we cannot use our original system for this because we have "spoiled" it by our first measurement process. Hitting the particle with one or more γ -ray photons has knocked it into some other state, and we do not even know which one. Therefore, we must either reprepare our system, or else use a separate system whose preparation is identical to that of the first system. In general we shall assume that we have an inexhaustible supply of identically prepared systems. Therefore, we take a second photograph (on our second system) using the same photographic plate. Then we photograph a third system, a fourth, etc., until we have amassed a large number of images of the particle on the film. The distribution of these images is given by ψ_1^2 . (Since ψ is always a real function for this system, we do not need to bother with $\psi^*\psi$.) Other states, like ψ_2, ψ_3 , will lead to different distributions of images. The results for the several states are depicted in Fig. 2-5. It is obvious that the probability for finding the particle near the center of the box is predicted to be much larger for the $n = 1$ than the $n = 2$ state.

The probability for finding the particle at the midpoint of the "wire" in the $n = 2$ state approaches zero in the limit of our measurement becoming precise enough to observe a single point. This troubles many students at first encounter because they worry about how the particle can get from one side of the box to the other in the $n = 2$ state. In fact, this question can be raised for any state whose wavefunction has any nodes. However, our discussion in the preceding paragraph shows that this question, like the question, "Is an electron a particle or a wave when we are not looking?" has no meaningful answer because no experiment can be conceived that would answer it. To test whether or not the particle does travel from one side of the box to the other, we would have to prepare the system in the $n = 2$ state and measure the position of the particle enough times so that we either (a) always find it on the same side (requires many measurements for confidence), or (b) find it on different sides (requires at least two measurements).