QUANTUM CHEMISTRY

JOHN P. LOWE

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JOHN P. LOWE

THE PENNSYLVANIA STATE UNIVERSITY

ACADEMIC PRESS New York San Francisco London

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ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

Library of Congress Cataloging in Publication Data

Lowe, John P
Quantum chemistry.

Includes bibliographical references.
1. Quantum chemistry. I. Title.
QD462.L69 541'.28 77-6602
ISBN 0-12-457550-1

PRINTED IN THE UNITED STATES OF AMERICA

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

PREFACE

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 chance 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.

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

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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, 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."

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CHAPTER 1

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

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,

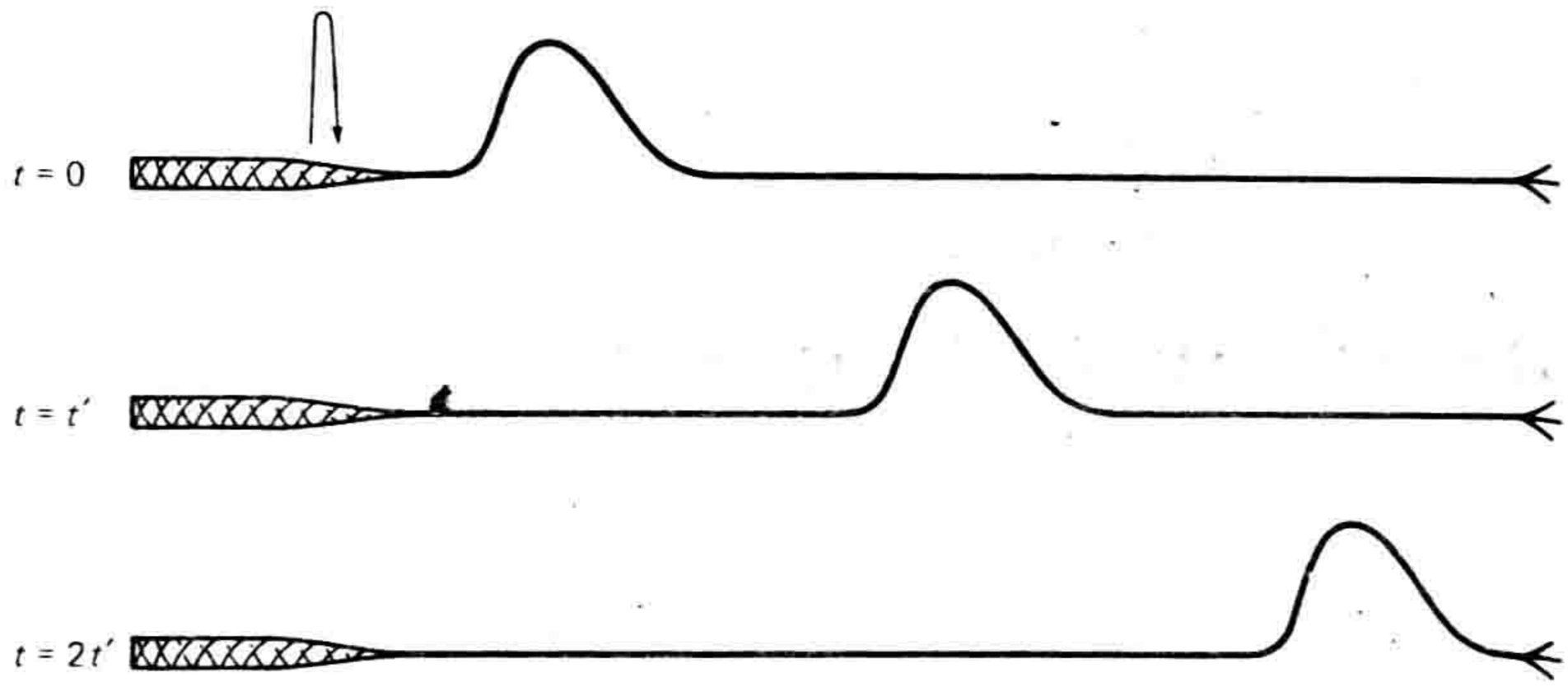

FIG. 1-1 Cracking the whip. As time passes, the disturbance moves from left to right along the extended whip cord. Each segment of the cord oscillates up and down as the disturbance passes by, ultimately returning to its equilibrium position.

because the height and shape of the wave reflect the vigor with which the handle was oscillated.

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 harmonic[1] 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.

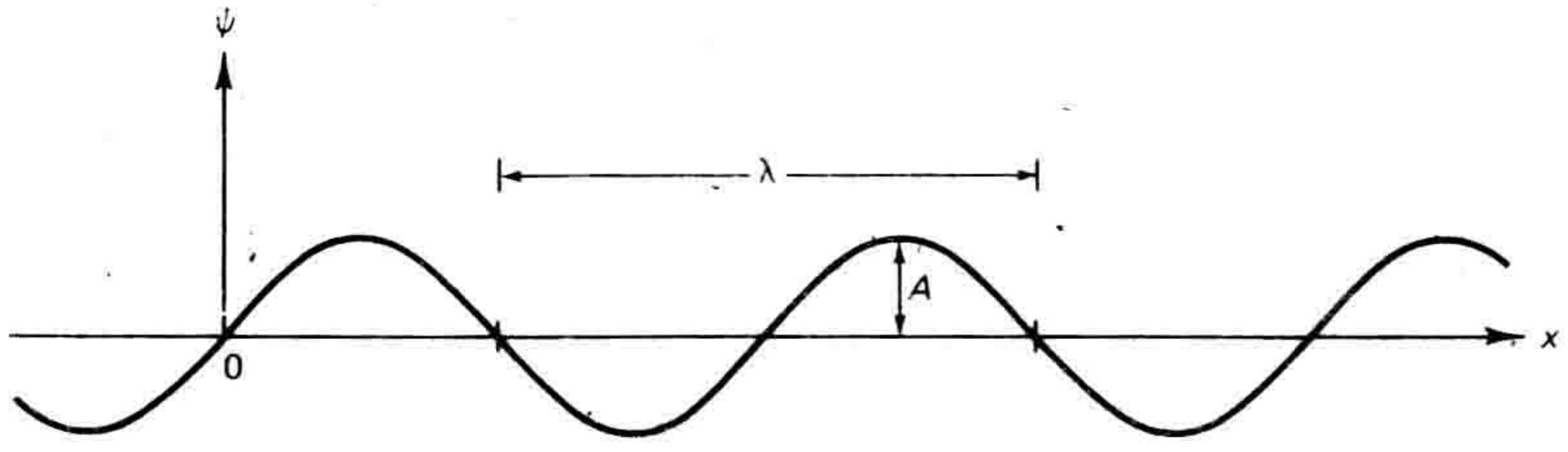

FIG. 1-2 A harmonic wave at a particular instant in time. A is the amplitude and λ is the wavelength.

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

$$\psi(x) = A \sin(2\pi x/\lambda) \tag{1-1}$$

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

($\psi = 0$ 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

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

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,

$$\nu = c/\lambda \tag{1-3}$$

Note that the wave described by the formula

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

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 $\epsilon = \pi, 3\pi, \ldots$, then Ψ' is shifted by $\lambda/2, 3\lambda/2, \ldots$ and the two functions are said to be exactly out of phase. If $\epsilon = 2\pi, 4\pi, \ldots$, the shift is by $\lambda, 2\lambda, \ldots$, 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.

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:

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

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

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

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.

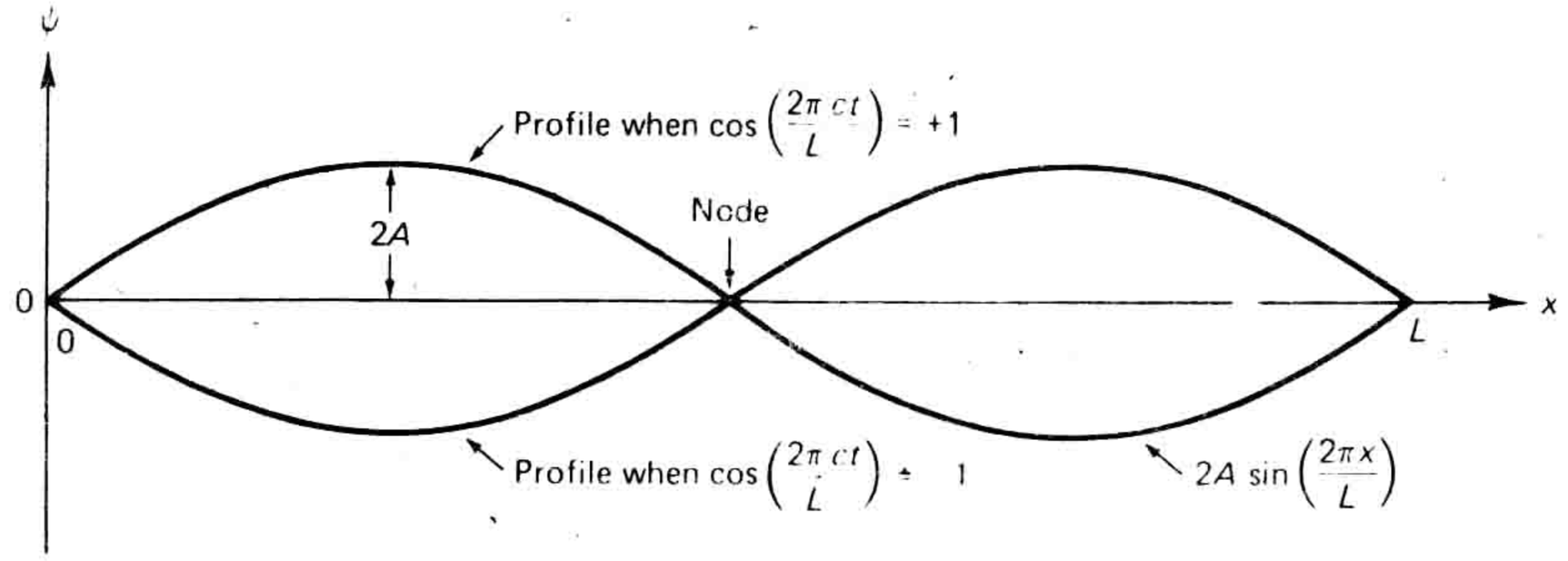

FIG. 1-3 A standing wave in a string clamped at $x = 0$ and $x = L$. The wavelength λ is equal to L.

Equation (1-6) is often written as

$$\Psi(x, t) = \psi(x)\cos(\omega t) \tag{1-7}$$

where

$$\omega = 2\pi c/\lambda \tag{1-8}$$

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, 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

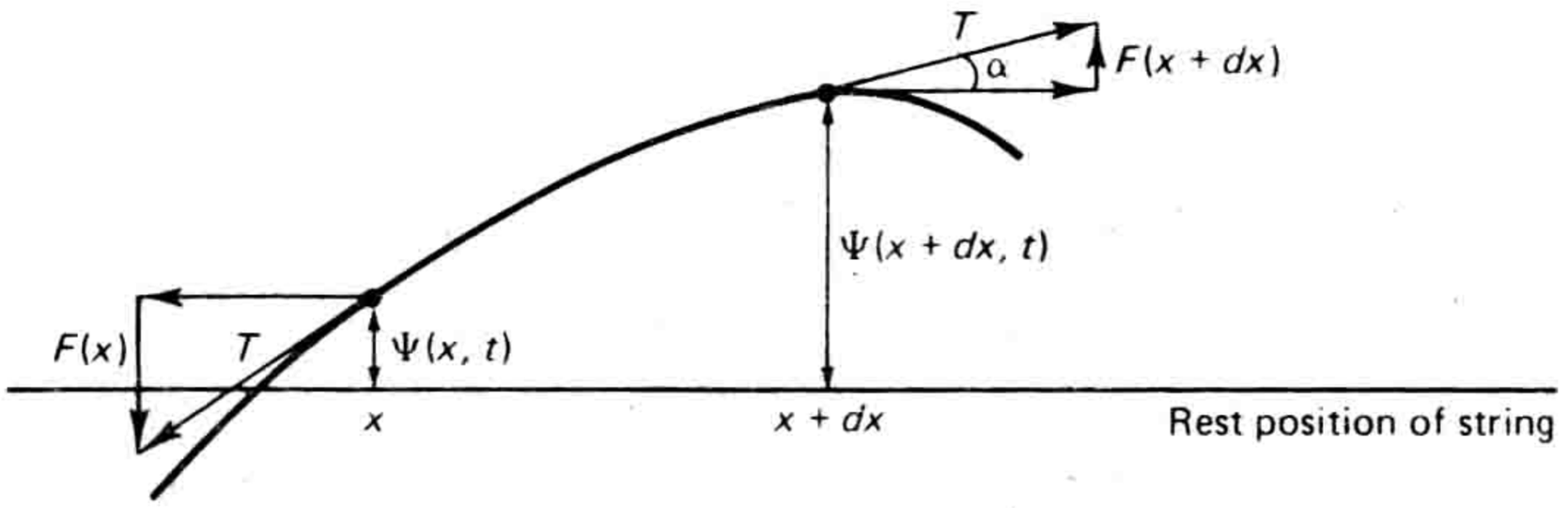

FIG. 1-4 A segment of string under tension T. The forces at each end of the segment are decomposed into forces perpendicular and parallel to x.

[2] Fluids 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.

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