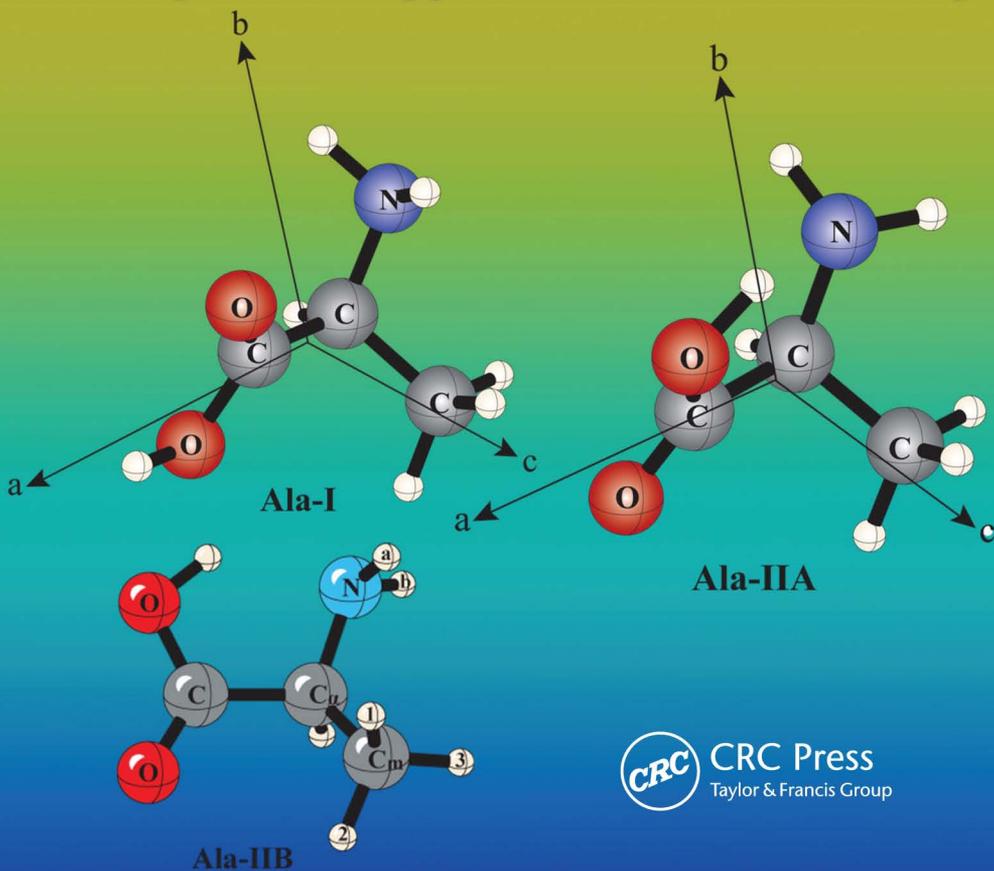


Equilibrium Molecular Structures

From Spectroscopy to Quantum Chemistry



 CRC Press
Taylor & Francis Group

Edited by Jean Demaison
James E. Boggs • Attila G. Császár
Foreword by Harry Kroto

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Contents

Foreword	vii
Editors	xi
Contributors	xiii
Introduction.....	xv
Principal Structures	xix
Chapter 1 Quantum Theory of Equilibrium Molecular Structures	1
<i>Wesley D. Allen and Attila G. Császár</i>	
Chapter 2 The Method of Least Squares	29
<i>Jean Demaison</i>	
Chapter 3 Semiexperimental Equilibrium Structures: Computational Aspects	53
<i>Juana Vázquez and John F. Stanton</i>	
Chapter 4 Spectroscopy of Polyatomic Molecules: Determination of the Rotational Constants	89
<i>Agnès Perrin, Jean Demaison, Jean-Marie Flaud, Walter J. Lafferty, and Kamil Sarka</i>	
Chapter 5 Determination of the Structural Parameters from the Inertial Moments	125
<i>Heinz Dieter Rudolph and Jean Demaison</i>	
Chapter 6 Determining Equilibrium Structures and Potential Energy Functions for Diatomic Molecules	159
<i>Robert J. Le Roy</i>	
Chapter 7 Other Spectroscopic Sources of Molecular Properties: Intermolecular Complexes as Examples	205
<i>Anthony C. Legon and Jean Demaison</i>	

Chapter 8 Structures Averaged over Nuclear Motions	233
<i>Attila G. Császár</i>	
Appendix A: Bibliographies of Equilibrium Structures	263
Appendix B: Sources for Fundamental Constants, Conversion Factors, and Atomic and Nuclear Masses	265
Author Index	267
Subject Index	275

Foreword

At some point during the education process, which resulted in my becoming a professional researcher and teacher of chemistry, I must have made some sort of subliminal intellectual jump into thinking about molecules as realizable physical objects and indeed architectural/engineering structures. I became quite comfortable, essentially thinking “unthinkingly” about objects that I had never actually “seen.” I started to take for granted that my new world was made up of networks of atoms. I do not know when my mind squeezed through this wormhole into what we now call “The Nanoworld,” but it seems to have been quite painless, and only much later did I think about this as I became aware that scientists, chemists in particular, live in an abstract world in which we have a deep atomic/molecular perspective of the material world. Neither the sizes of molecules nor the numbers of atoms in a liter of water ever seemed to be amazing. Long ago, the number 6.023×10^{23} (now apparently $6.022 \times 10^{23} - 10^{20}$ seem to have disappeared!) was permanently inscribed on a piece of paper placed in a drawer labeled Avogadro’s number in the chest of drawers of my mind. Over the years, some pieces of paper seem to have fallen down the back ending up in the wrong drawers without my knowledge or awareness of the fact—sometimes with dire consequences! In the early days, I do not remember wondering too much, about how this number had been determined, or how we “knew” the value of this number, or how the bond length of H_2 was determined to be 0.74 \AA , or indeed, what we actually meant by the term “bond length.”

While at school, I bought Fieser and Fieser’s book at the suggestion of my chemistry teacher, Harry Heaney, who left the school a little later to become, ultimately, a professor of organic chemistry, and became fascinated by organic chemistry. My memory is that Harry and his wife had two Siamese cats, called Fieser and Fieser. Another friend had two Siamese cats called Schrödinger and Heisenberg. Gradually, I became quite fluent in the abstract visual/graphic language of chemistry, drawing hexagons for benzene rings and writing symbolic schemes to describe the intricate musical chair games that bunches of atoms perform during chemical reactions. At university (Sheffield), I suddenly became completely enamored with molecular spectroscopy during an undergraduate lecture by Richard Dixon. I was introduced to the electronic spectrum of the diatomic radical AlH in which elegant branch structure indicated that the molecule could count accurately—indeed certainly better than I could.

Spectroscopy is arguably the most fundamental of the experimental physical sciences. After all, we obtain most of our knowledge through our eyes and it is via the quest for an in-depth understanding of what light is, and what it can tell us, that almost all our deeper understanding of the universe has been obtained. Answers to these questions about light have led to many of our greatest discoveries, not least our present description of the way almost everything works both on a macroscopic and on a microscopic scale. In the deceptively simple question of why objects possess color at all—such an everyday experience that probably almost no one thinks

it odd—lies the seed for the development of arguably our most profound and far-reaching theory—quantum mechanics.

I decided to do research on the spectra of small free radicals produced, detected, and studied by flash photolysis—the technique pioneered by George Porter who was then professor of physical chemistry at Sheffield University. In 1964, I went to the National Research Council (NRC) in Ottawa where Gerhard Herzberg, Alec Douglas, and their colleagues, such as Cec Costain, had created the legendary Mecca of Spectroscopy. While at NRC, I discovered microwave spectroscopy in Cec Costain's group and from that moment, the future direction of my career as a researcher was sealed. I gained a very high degree of satisfaction from making measurements at high resolution on the rotational spectra of small molecules and in particular from the ability to fit the frequency patterns with theory to the high degree of accuracy that this form of spectroscopy offered. Great intellectual satisfaction comes from knowing that the parameters deduced—such as bond lengths, dipole moments, quadrupole and centrifugal distortion parameters—are well-determined quantities both numerically and in a physically descriptive sense. Some sort of deep understanding seems to develop as one gains more-and-more familiarity with quantum mechanical (mathematical) approaches to spectroscopic analyses that add a quantitative perspective to the (subliminal?) classical descriptions needed to convince oneself that one really knows what is going on. I was to learn later that such levels of satisfying certitude of knowledge are a rarity in many other branches of science and in almost all aspects of life in general. It gives one a very clear view of how the scientific mindset develops and what makes science different from all other professions and within the sciences, a clear vision of what it means to really “know” something.

The equations of Kraitchman [1] and the further development of their application in the r_s substitution approach to isotopic substitution data in the 1960s by my former supervisor Cec Costain [2] resulted in a wealth of accurate structural information on small to moderate size molecules from rotational microwave measurements. Jim Watson took these ideas a step further in his development of the r_m method [3]. At Sussex, in 1974, my colleague David Walton and I put together a project for an undergraduate researcher, Andrew Alexander, to synthesize some long(ish) chain species starting with HC_5N and study their spectra—infrared and NMR as well as microwave [4]. This study was to lead to the discovery of long carbon chain molecules in interstellar space and stars [5] and ultimately the experiment that uncovered the existence of the C_{60} molecule.

I sometimes feel that as other scientists casually bandy about bond lengths, our exploits as spectroscopists are not appreciated—the hard work that is needed to obtain those simple but accurate numbers and the efforts needed to determine the molecular architectures as well as the deep understanding of the dynamic factors involved. Indeed, it took quite a significant amount of research before an understanding of what the experimentally obtained numbers really mean was gradually achieved. In particular, the realization that different techniques yield different values for the “bond lengths,” for example, the average value of r is obtained by electron diffraction and this can differ significantly from the average values or $1/r^2$ for a particular vibrational state, which is obtained from rotational spectra [6]. Alas, it

seems it is the particular lot of the molecular rotational microwave spectroscopy community to be so little appreciated! I sometimes feel that we should forbid the use of our structural data by scientists who do not appreciate us in a way parallel to the way I feel about “creationists,” who I suggest should be deprived of the benefits of the medications that have been developed on the basis of a clear understanding of Darwinian evolution.

Microwave measurements can reveal many important molecular properties. Internal rotation can give barrier heights, centrifugal distortion parameters can be analyzed to extract vibrational force-field data, and splittings due to the quadrupole moments can yield bond electron-density properties. Arguably, Jim Watson made the major final denouement in his classic paper on the vibration-rotation Hamiltonian—or “the Watsonian”—in which some issues involved in the Wilson–Howard Hamiltonian formulation were finally resolved [7]. Early on in my career I had wondered about the spectrum of acetylene studied by Ingold and King [8] and the way in which shape changes might affect the spectrum—in this case from linear to trans bent in the excited state. Later, I started to learn about quasi-linearity and quasi-planarity. Our present understanding of this phenomenon was due to the groundbreaking work of, among others, Richard Dixon [9] and Jon Hougen, and Phil Bunker and John Johns [10]. At Sussex, we obtained a truly delightful spectrum that afforded us great intellectual pleasure as well as a uniquely satisfying insight into the meaning of “quasi-linearity.” This was to be found in the microwave spectrum of NCNCS which Mike King and Barry Landsberg studied [11]. As the angle bending vibration of this V-shaped molecule increases, the spectroscopic pattern observed at low ν_{bend} changes to that of a linear one at ca. $\nu_{\text{bend}} = 4$, where the bending amplitude is so large that when averaged over the A axis it appears roughly linear. Brenda Winnewisser et al. have taken the study of this beautiful system to a further fascinating level of even deeper understanding in their elegant study of quantum monodromy [12].

As we now trek deeper into the twenty-first century, numerous ingenious researchers have resolved many fundamental theoretical spectroscopic problems. Molecular spectroscopy itself has become less of an intrinsic art form, but more of a powerful tool to uncover the ever more fascinating secrets of complex molecular behavior, and has become worthy of fundamental study in its own right. The compendium assembled in this monograph is one that helps a new generation of scientists, interested in understanding the deeper aspects of molecular behavior, to understand this fascinating subject. Even so, it is a fairly advanced textbook that even expert practitioners will find absorbing as it contains much of value as the articles deal with our state-of-the-art understanding of, among other things: *ab initio*, Born–Oppenheimer, equilibrium, adiabatic and vibrationally averaged structures; Coriolis, Fermi, and other interactions; variational approaches as well as conformations of complexes and so on.

Of course, there is now a new twenty-first century buzzword—“nanotechnology” or as I prefer to call it, N&N (not to be confused with M&M!) or nanoscience and nanotechnology. There is much confusion in the mind of the public as to what N&N actually is. However, as it deals with molecules and atomic aggregates at nanoscale dimensions, it is really only a new name for chemistry with a twenty-first century “bottom-up” perspective. Our molecule C_{60} is, as it happens, almost exactly 1 nm

in diameter, or to be more accurate, the center-to-center distance of C_{60} molecules in a crystal is 1 nm (to an accuracy of ca. 1%). C_{60} has become something of an iconic symbol representing N&N and therefore I cannot help feeling a bit like Monsier Jourdain in Molière's *Bourgeois Gentilhomme* (MJ—Monsieur Jourdain, PM—Philosophy Master):

- MJ *I wish to write to my lady.*
 PM *Then without doubt it is verse you will need.*
 MJ *No. Not verse.*
 PM *Do you want only prose then?*
 MJ *No—neither.*
 PM *It must be one or the other.*
 MJ *Why?*
 PM *Everything that is not prose is verse and everything that is not verse is prose.*
 MJ *And when one speaks—what is that then?*
 PM *Prose.*
 MJ *Well by my faith! For more than forty years I have been speaking prose without knowing anything about it.*

My response is (preferably in London Cockney vernacular):

“Cor blimey, guv ... I'm a spectroscopist so I must have been a nanotechnologist all my life!”

Harold Kroto

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Editors

Jean Demaison is a former Research Director at CNRS, University of Lille I. The research for his PhD, which he received in 1972, was performed in Freiburg and Nancy in the field of microwave spectroscopy. He was invited to be a Professor at the Universities of Ulm, Louvain-La-Neuve, and Brussels. In 2008, he received the International Barbara Mez-Starck prize for outstanding contribution in the field of structural chemistry. He has published over 300 papers in research journals and contributed to 17 books.

Professor Attila G. Császár is the head of the Laboratory of Molecular Spectroscopy at Eötvös University of Budapest, Hungary. He received his PhD in 1985 in theoretical chemistry at the same place. His research interests include computational molecular spectroscopy, structure determinations of small molecules, ab initio thermochemistry, and electronic structure theory. He has published more than 150 papers in these fields, mostly in leading international journals.

James E. Boggs is Professor Emeritus at the University of Texas at Austin. His PhD was received from the University of Michigan after working on the Manhattan District Project. He has spent sabbaticals at Harvard, Berkeley, and the University of Oslo. Dr. Boggs has published over 325 papers, mostly on microwave spectroscopy and applications of quantum theory. He organized the first 23 biennial meetings of the Austin Symposium on Molecular Structure. In 2010, he received the International Barbara Mez-Starck prize for outstanding contributions in structural chemistry. He has been chosen as a Fellow of the American Chemical Society.

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Introduction

James E. Boggs

In 1861 [1], the famous Russian chemist Aleksandr Mikhailovich Butlerov (1828–1886) used the term “chemical structure” for perhaps the first time in a modern sense. He argued as we argue today that molecular structure is perhaps the most basic information about a substance and it has very strong ties to most macroscopic physical and chemical properties.

The study of molecular structures has been hampered by the fact that every experimental method applies its own definition of “structure” and thus structural results corresponding to different sources are usually significantly different. For example, the distance between maxima in the electron density distribution as measured by X-ray diffraction is very different from the distance corresponding to the minima in the vibrational potential energy surface as measured by quantum chemical computations or the various vibrational averages of that distance as measured by different methods of molecular spectroscopy. The sophisticated protocols that have been developed to account for these differences, and render intercomparisons and the use of combined experimental and computational techniques possible, is the subject of this advanced textbook.

Most of our notions about structure arise from within the Born–Oppenheimer approximation. The potential energy surfaces that result from this venerable approximation are one of the most useful and ubiquitous paradigms in descriptive chemistry. They give rise to our notions of activation energies and transition states for chemical reactions, force constants to which the strength of various bonds can be related, and most important for the topic of this textbook, the equilibrium structure (r_e). The latter is defined by the geometry that the nuclei adopt when in a minimum on the potential energy surface. None of these common concepts “exists” in the context of more rigorous theory—they are in a sense artifacts of the Born–Oppenheimer approximation. However, forming the central paradigm of molecular structure and chemical dynamics, the Born–Oppenheimer approximation is a very good one, and knowing what the r_e structures really “are” is desirable.

This book is novel in several ways. To the best of our knowledge, the subject matter of equilibrium molecular structures has never before been treated in a book in a manner that provides balance between quantum theory and experiment. Another novel aspect of this textbook is that the editors have endeavored to bring together a number of distinguished educators and practitioners in this branch of science to write chapters on their own fields of expertise, starting with the basic elements and proceeding to the latest advances and current best practices. Reading the book may be compared to sitting in on a series of lectures by some of the best experts in the world on the subjects they address. This is a book on molecular structure, but it does not describe the instruments or details of the experimental methods that are used in

determining the structure. Rather, it describes the theory involved in determining, and converting measured or computed data into the most accurate and best understood molecular structures possible from the available data set. This step is of vital importance in chemistry where most of the significant information in a structure is contained in differences of structural parameters amounting to less, often considerably less than one percent.

The book is not only intended to be a textbook suitable for advanced undergraduate or graduate courses but is also sufficiently complete for interested readers and active workers in the area who would like to learn about certain aspects of the field with which they are not familiar. As Linus Pauling pointed out in 1939 in the preface of his famous book, *The Nature of the Chemical Bond*, [2] “the ideas involved in modern structural chemistry are no more difficult and require for their understanding no more, or a little more, mathematical preparation than the familiar concepts of chemistry.” Thus, while most chapters of our textbook do make extensive use of mathematics, it is never beyond the scope of a student who is in the last half of an undergraduate program in chemistry or physics. In keeping with its purpose to be used as a textbook, the chapters contain several examples and exercises, some given with solutions and some without. Each chapter is provided with a table of contents and an overall index is given at the end of the book. Important references are given in case the reader wants to look at the original presentation of the information discussed.

The book is organized in the following way:

Chapter 1 deals with quantum chemistry, introduces the concept of potential energy surfaces on which the idea of equilibrium molecular structures is built. It also discusses the quantum chemical computation of structures and anharmonic force fields, the two central quantities of this book.

Chapter 2 describes the method of least squares that is commonly used to calculate a structure from the moments of inertia. The dangers posed by the problem of ill-conditioning and the presence of outliers and leverage points are discussed in detail and some remedies are proposed.

Chapter 3 discusses certain uses of perturbation theory in the study of molecular structures as well as computational aspects related to the study of so-called semiexperimental equilibrium structures.

Chapter 4 deals with the determination of moments of inertia from experimental spectra. The resonances, which make difficult the determination of reliable equilibrium constants, are discussed in detail.

Chapter 5 derives the relationship between moments of inertia and structural parameters and discusses the different methods permitting derivation of the structure. Empirical structures which are obtained from ground-state moments of inertia and which are assumed to be a good approximation of the equilibrium structure are also presented.

Chapter 6 deals with the determination of the potential of a diatomic molecule. Semiclassical methods as well as quantum mechanical methods are discussed and the Born–Oppenheimer breakdown effects are also treated here.

Chapter 7 presents complementary sources of information, which can be used for at least partial structure analysis with particular emphasis on the structure of molecular complexes.

Chapter 8 defines temperature-dependent position and distance averages and how they can be computed in addition to equilibrium molecular structures, bridging the gap between usual quantum theory and experiment.

The table Principal Structure, which can be found on the inside cover and after the Introduction, gathers the structures that are discussed in the book and that are encountered in the literature. The book is accompanied by a CD that presents further examples and exercises and additional information on the methods that are discussed in the main text as well as more technical material.

The editors and the authors are grateful to Therese Huet for reading Chapter 7, to Francois Rohart for reading Chapter 2, and to Harald Møllendal for reading most of the chapters.

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Principal Structures

Symbol	Definition	Section
Equilibrium structures		
r_e^{BO}	Born–Oppenheimer equilibrium structure: Corresponds to a minimum of the potential energy hypersurface defined within the Born–Oppenheimer separation of electronic and nuclear motion and determined by techniques of electronic structure theory.	1.1
r_e^{ad}	Adiabatic equilibrium structure: Mass-dependent equilibrium structure corresponds to the adiabatic potential energy hypersurface obtained after adding a small, first-order, so-called diagonal Born–Oppenheimer correction (DBOC) to r_e^{BO} .	1.6
r_e^{SE}	Semiexperimental equilibrium structure: Determined from a fit of the structural parameters to the equilibrium moments of inertia, obtained from the experimental effective, ground-state rotational constants corrected by the rovibrational contribution calculated using a cubic force field usually determined first principles (ab initio).	3.3
r_e^{exp}	Experimental equilibrium structure: Obtained from a fit of the structural parameters to the experimental equilibrium moments of inertia.	4.3
Average structures		
Position averages		
$r_z = r_{\alpha,0}$	Zero-point average structure: A temperature-independent average structure belonging to the average nuclear positions in the ground vibrational state.	8.1
$r_{\alpha,T}$	r_{α} -structure: Distance between the nuclear positions averaged at a given temperature T assuming thermal equilibrium.	8.1
Distance (and angle) averages		
$r_{g,T}$	Mean (average) internuclear distance (angle): Average internuclear distance (angle), related to the expectation value $\langle r \rangle$, at temperature T assuming thermal equilibrium (“g” stands for center of gravity of the distance distribution function).	8.1
$r_{a,T}$	Inverse internuclear distance (angle): Average related to electron scattering intensities.	8.1
$\langle r^2 \rangle_T^{1/2}$	Root-mean-square (rms) internuclear distance (angle): Related to the expectation value $\langle r^2 \rangle$, at temperature T assuming thermal equilibrium.	8.1
$\langle r^{-2} \rangle_T^{-1/2}$	Effective internuclear distance (angle): Related to the expectation value $\langle r^{-2} \rangle$, at temperature T assuming thermal equilibrium.	8.1
$\langle r^3 \rangle_T^{1/3}$	Cubic internuclear distance (angle): Related to the expectation value $\langle r^3 \rangle$, at temperature T assuming thermal equilibrium.	8.1
$\langle r^{-3} \rangle^{-1/3}$	Inverse cubic: Average, appears in dipolar coupling constants.	8.1, 7.5

(Continued)

Symbol	Definition	Section
Mass-dependent structures		
r_m	Mass-dependent structure: Obtained from a fit of the structural parameters to the mass-dependent moments of inertia $I_m = 2I_s - I_0$, where I_s are the substitution moments of inertia that are calculated from the substitution coordinates r_s , and I_0 the ground-state moments of inertia. Generally no better than r_s .	5.5.1
r_c	Improvement of the r_m structure by using complementary sets of isotopologues.	5.5.2
r_m^p	r_m^p structure: Since the rovibrational contributions e^0 vary less within a set of isotopologues than the inertial moments I^0 , scaling of the inertial moments of all isotopologues by an appropriate common factor $(2\rho_g - 1)$ (for each principal axis g) calculated for the parent, and then submitting the scaled inertial moments to a least-squares fit to obtain the bond coordinates.	5.5.3
$r_m^{(1)}, r_m^{(2)}$	Mass-dependent structure: Based on the different dependence of inertial moments and their rovibrational contributions on the atomic masses (of one and half degrees). Models the rovibrational contributions by the (least possible number of) parameters: c_g (for each principal axis g), multiplied by the square root of the inertial moment of the individual isotopologue $\sqrt{I_g}$, and d_g (for $r_m^{(2)}$ only), multiplied by an isotopologue-dependent, but g -independent mass factor. Least-squares fitting to obtain bond coordinates and rovibrational parameters. The Laurie contraction of a X-H bond upon deuteration is modeled ($r_m^{(1L)}, r_m^{(2L)}$) by an additional parameter δ_H . Refined models $r_m^{(1r)}, r_m^{(2r)}$ assume that the rovibrational effects depend more on the overall shape or contour of the molecule (equal for all isotopologues) than on the principal axis systems whose orientations within the molecular shapes differ among the isotopologues.	5.5.4
Empirical structures		
r_0	Effective structure: Least-squares fitting of experimental ground-state inertial moments I^0 of a set of isotopologues to obtain bond coordinates, neglecting rovibrational contributions e^0 completely, can be realized in practice by means of different sets of observables: $r_0(I)$, $r_0(P)$, $r_0(B)$, and also $r_0(I, \Delta I)$, $r_0(P, \Delta P)$, where the moments of only the parent and the moment differences between parent and isotopologues are used.	5.3
r_s	Substitution structure: Aimed at obtaining Cartesian coordinates of individual atom, numerically dominated by inertial moment difference ΔI upon substitution, no least-squares used, though expandable on sets of several isotopologues (substituted atoms) by least-squares fitting: r_s -fit (determined via the Kraitchman equations).	5.4
r_s variants: $r_{\Delta I}, r_{\Delta P}$	ps-Kr ("pseudo-Kraitchman") structure: Attempts to compensate rovibrational contributions by least-squares, fitting exclusively differences of moments between parent and isotopologues ΔI^0 or ΔP^0 to obtain bond coordinates, realized by $r(\Delta I)$, $r(\Delta P)$.	5.3.2

1 Quantum Theory of Equilibrium Molecular Structures

Wesley D. Allen and Attila G. Császár

CONTENTS

1.1	Concept of the Potential Energy Surface.....	1
1.2	Interplay of Electronic and Nuclear Contributions to the Potential Energy Surface	5
1.3	Optimization Algorithms.....	11
1.4	Anharmonic Molecular Force Fields.....	14
1.5	A Hierarchy of Electronic Structure Methods.....	17
1.5.1	Physically Correct Wave Functions	20
1.5.2	One-Particle Basis Sets.....	22
1.6	Pursuit of the Ab Initio Limit.....	25
	References and Suggested Reading	28

1.1 CONCEPT OF THE POTENTIAL ENERGY SURFACE

Molecular quantum mechanics, as embodied in the time-independent Schrödinger equation $\hat{H}\Psi = E\Psi$, is the physical foundation of chemistry. For systems containing atoms no heavier than Ar, highly accurate results are obtained from the standard nonrelativistic Hamiltonian involving only Coulombic interactions:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{\nabla_{\alpha}^2}{M_{\alpha}} - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 r_{\alpha\beta}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_i \sum_{j > i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (1.1)$$

in which Greek (α and β) indices refer to nuclei with masses M_{α} and charges Z_{α} , and Latin (i and j) indices refer to electrons with mass m_e and charge e , while the corresponding interparticle distances are denoted by $r_{\alpha\beta}$, $r_{i\alpha}$, and r_{ij} . The Laplacian operator for each particle takes the simple form $\Delta \equiv \nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ in rectilinear Cartesian coordinates but generally is considerably more complicated if curvilinear internal coordinates are used.

The five operators in order of appearance in Equation 1.1 represent nuclear kinetic energy (\hat{T}_N), electronic kinetic energy (\hat{T}_e), nuclear–nuclear repulsion (\hat{V}_{NN}), electron–nuclear attraction (\hat{V}_{eN}), and electron–electron repulsion (\hat{V}_{ee}). Because exact, analytic solutions to the Schrödinger equation built on \hat{H} are not possible for many-particle systems, effective approximation methods must be employed. The development of algorithms for such methods has been one of the main goals of modern computational quantum chemistry. Rigorous approaches that do not resort to empirical parameterization and only invoke the fundamental constants are termed *ab initio* (from the beginning) or first-principles methods.

Nuclear and electronic motions in molecular systems have greatly different time-scales and a wide separation in classical velocities (at least three orders of magnitude) that has profound consequences for chemistry. Because electrons are much lighter than nuclei ($m_e/m_H \approx 1/1836$), they move much more vigorously. In effect, the light, fast electrons adjust instantaneously to the motions of the slow, heavy nuclei. Therefore, the nuclear and electronic degrees of freedom can be separated adiabatically, as in the highly accurate Born–Oppenheimer (BO) approximation,* whereby the electronic part of the Schrödinger equation is solved repeatedly with nuclei clamped at various positions. The purely electronic equation is

$$\hat{H}_e \Psi_e(\mathbf{r}_i; \mathbf{r}_\alpha) = E_e(\mathbf{r}_\alpha) \Psi_e(\mathbf{r}_i; \mathbf{r}_\alpha) \quad (1.2)$$

in which the electronic Hamiltonian is $\hat{H}_e = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{eN}$, and the nuclear coordinates \mathbf{r}_α are fixed parameters. Adding the nuclear–nuclear repulsion energy to the electronic energy eigenvalues $E_e(\mathbf{r}_\alpha)$ that depend parametrically on the nuclear positions yields a potential energy surface (PES) for nuclear motion,

$$V(\mathbf{r}_\alpha) = E_e(\mathbf{r}_\alpha) + V_{NN}(\mathbf{r}_\alpha) \quad (1.3)$$

The nuclear Schrödinger equation resulting from the BO approximation is

$$[\hat{T}_N + V(\mathbf{r}_\alpha)] \Psi_N(\mathbf{r}_\alpha) = E_N \Psi_N(\mathbf{r}_\alpha) \quad (1.4)$$

This equation can be solved for the vibrational-rotational states that occur within a given electronic state. Derivatives of the electronic wave function with respect to the nuclear coordinates, namely $\nabla_\alpha \Psi_e$ and $\nabla_\alpha^2 \Psi_e$, are neglected in the BO approximation and are usually very small.

The PESs $V(\mathbf{r}_\alpha)$, illustrated by a model function in Figure 1.1, are fundamental to most modern branches of chemistry, especially spectroscopy and kinetics. The topography of the surface $V(\mathbf{r}_\alpha)$ constitutes the basis for ascribing geometric structures to

* The BO separation of electronic and nuclear degrees of freedom was introduced in Born, M., and J. R. Oppenheimer. 1927. *Ann Phys* 84:457. However, a better, more contemporary and accessible reference is Born, M., and K. Huang. 1954. *Dynamical Theory of Crystal Lattices*, appendix VIII. London: Oxford University Press.

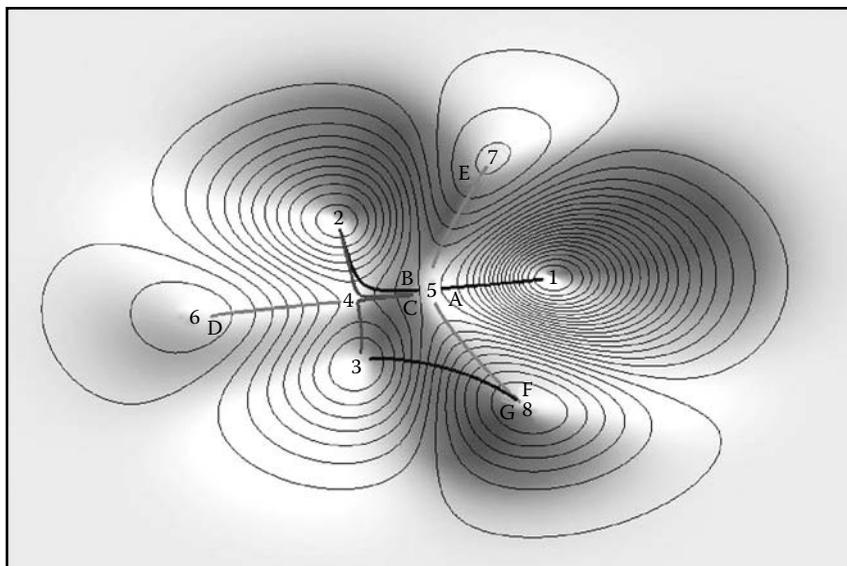


FIGURE 1.1 A two-dimensional model of a molecular potential energy surface and characteristic features and paths on it: points (**1**, **2**, **3**) are local minima; (**4**, **5**) are transition states (first-order saddle points); and (**6**, **7**, **8**) are second-order saddle points that appear as local maxima in this cross section of the PES. Paths A and B comprise the intrinsic reaction path of steepest descent that connects reactant **1** to product **2** via transition state **5**. Path C starts at a valley-ridge inflection point; small perturbations about such a point can cause a bifurcation of steepest descent paths and instability in the final products, in this case either **2** or **3**. Paths D, E, and F are gradient extremum paths descending from points **6**, **7**, and **8**, respectively, along ridges to minimize the steepness of the route. Path G is a corresponding steepest descent path that starts out coincident with F but falls off the ridge into the basin of minimum **3**.

molecules.* The local minima occurring on this multidimensional PES correspond to the equilibrium (r_e) structures of molecules, on which virtually all chemical intuition is built. Accordingly, it is the BO approximation that allows equilibrium structures to be defined as special points among the instantaneous configurations (geometries) that nuclei may exhibit. Depictions of static molecular frameworks are pervasively used to describe and understand chemical phenomena, and the implicit assumption therein is that the nuclei are localized in potential energy wells centered about the corresponding r_e structures and execute only small-amplitude vibrations away from their equilibrium positions. Without the BO separation of nuclear and electronic motions, the traditional concept of molecular structure would be lost, and only a murky quantum soup of delocalized particles would exist.

* As indicated by the notation $V(\mathbf{r}_n)$, PESs are inherently hypersurfaces for all molecules larger than triatomics, involving $3N - 6$ internal degrees of freedom for a nonlinear N -atomic molecule. Even in the case of a nonlinear triatomic molecule, a four-dimensional plot (V vs. three degrees of freedom) would be required to fully represent the potential energy function.

The variation of the total energy of the chemical system as a function of the internal coordinates of the constituent nuclei is described by PESs. Internal coordinates describe the vibrations of N -atomic molecules, and thus their number is $6(5)$ less than the total number ($3N$) of Cartesian variables for nonlinear (linear) molecules. Because an equilibrium structure is a local minimum of the corresponding PES, the associated quadratic force constant matrix must be positive definite.*

In the conventional BO separation of nuclear and electronic motions, the resulting PES is isotope independent, because the masses of the nuclei are assumed to be infinitely heavy. For example, the BO PESs of molecules containing deuterium (D) instead of hydrogen (H) are identical. By means of first-order perturbation theory (PT), the diagonal Born—Oppenheimer correction (DBOC) may be used to relax this strict assumption somewhat while keeping the concept of a PES intact. Appending the DBOC to $V(\mathbf{r}_\alpha)$ gives rise to adiabatic PESs (APESs) that are dependent on the masses of the nuclei and are slightly different for a series of isotopologues or isotopomers.†

It is important to realize that many PESs exist for any given molecule, each corresponding to a different electronic state solution of Equation 1.2. Of course, the most fundamental PESs and r_e structures are those of ground electronic states. Nevertheless, well-defined r_e structures are also generally exhibited for the PESs of excited electronic states. Frequently, the r_e structures of excited states are markedly different from those of ground states, as in the case of CO_2 , for which bent equilibrium structures are found for the lowest excited states. Equilibrium structures are most useful for interpretive purposes if the PESs of excited electronic states are well separated and not highly coupled, but their mathematical basis is retained even if such circumstances are not met. In special cases where nonadiabatic nuclear–electronic interactions occur, as in the Jahn–Teller or Renner–Teller effects,‡ multiple PESs that are strongly coupled must be considered simultaneously to understand the motion of the nuclei. However, to maintain focus, we are concerned neither with such cases where multiple electronic states are coupled nor with the evaluation of nonadiabatic coupling matrix elements.

Much of contemporary experimental physical chemistry, through spectroscopic, scattering, and kinetic studies, is directed toward the elucidation of salient features of potential energy hypersurfaces (Figure 1.1). One can obtain details of the PES most easily, including structural and spectroscopic signatures of its minima, from an analysis of well-resolved vibrational-rotational (often abbreviated as rovibrational) spectra or from scattering experiments. When characterization of local minima of

* A square matrix is called “positive definite” if all of its eigenvalues are larger than zero. A square matrix is called “positive semidefinite” if all of its eigenvalues are nonnegative.

† According to the International Union of Pure and Applied Chemistry (IUPAC), *isotopologues* are molecular entities that differ only in isotopic composition (number of isotopic substitutions), for example, CH_4 , CH_3D , and CH_2D_2 . On the other hand, an *isotopomer*, where the term comes from the contraction of “isotopic isomer,” refers to an isomer having the same number of each isotopic atom in a molecule but differing in positions.

‡ The interested reader can find details about the Renner–Teller and Jahn–Teller effects, related to degeneracies forced by symmetry at linear and nonlinear molecular geometries, respectively, in part 4 of the book Jensen, P., and P. R. Bunker, eds. 2000. *Computational Molecular Spectroscopy*. Chichester: Wiley.

the PES is the goal, the best spectroscopic techniques possess several advantages over scattering measurements: (1) they can provide results of higher intrinsic accuracy and (2) there is less need to average over the usually somewhat loosely defined experimental conditions. Generally, experiments, through well-defined modeling approaches, yield parameters, including molecular structures, in more or less local representations of potential surfaces.

Much of modern quantum chemistry is also aimed at mapping out given portions or the whole of potential energy hypersurfaces of molecular species or reactive (scattering) systems by computational, rather than experimental, means. The availability of analytic gradients and higher derivative methods in standard electronic structure programs,* for reasons discussed in Sections 1.3 and 1.4, has substantially increased the utility of quantum chemistry for the exploration of PESs. For structural studies, the PES is needed mostly in the vicinity of a minimum. Therefore, techniques based on power series expansions around a single stationary point can be highly useful. Indeed, locating r_e structures and evaluating attendant (anharmonic) force fields based on series expansions of rather large molecules is now commonplace in quantum chemistry.

1.2 INTERPLAY OF ELECTRONIC AND NUCLEAR CONTRIBUTIONS TO THE POTENTIAL ENERGY SURFACE

Equilibrium structures, transition states, and other stationary points of chemical systems occur when the gradient of the PES with respect to nuclear coordinates is zero. Force fields for molecular vibrations are constituted by the higher-order derivatives of the PES at these stationary points. According to Equation 1.3, all derivatives of the PES can be decomposed into electronic energy [$E_e(\mathbf{r}_\alpha)$] and nuclear–nuclear repulsion [$V_{\text{NN}}(\mathbf{r}_\alpha)$] terms. Both of these contributions are large and almost always of opposite signs. Thus, it is the interplay of these competing terms that determine the positions of equilibrium structures and the strength and sign of the force constants for molecular vibrations. The V_{NN} contribution and its derivatives can be calculated exactly by simple algebraic expressions involving Coulombic terms, whereas the E_e contribution and its derivatives can be determined only approximately by means of computationally intensive electronic structure theory. This situation creates an imbalance of errors that must be appreciated to understand the effects that govern the accuracy of ab initio theoretical predictions of structures and force fields.

The N_2 and F_2 diatomic molecules provide paradigms for the interplay of the E_e and V_{NN} contributions to molecular PESs. Experimental potential energy curves [$V_{\text{RKR}}(r)$] for N_2 and F_2 (Figure 1.2) can be extracted from rovibrational spectroscopic data by means of the Rydberg–Klein–Rees (RKR) inversion technique. In particular, the classical turning points for each quantized vibrational level are known from RKR inversion up to vibrational quantum numbers $v = 22$ and $v = 23$ for N_2 and F_2 , respectively. Details of the RKR method are available in the related literature and Chapter 6 of this book. For comparison to experiment, we also consider the potential

* Yamaguchi, Y., Y. Osamura, J. D. Goddard, and H. F. Schaefer III. 1994. *A New Dimension to Quantum Chemistry: Derivative Methods in Ab Initio Molecular Electronic Structure Theory*. New York: Oxford University Press.

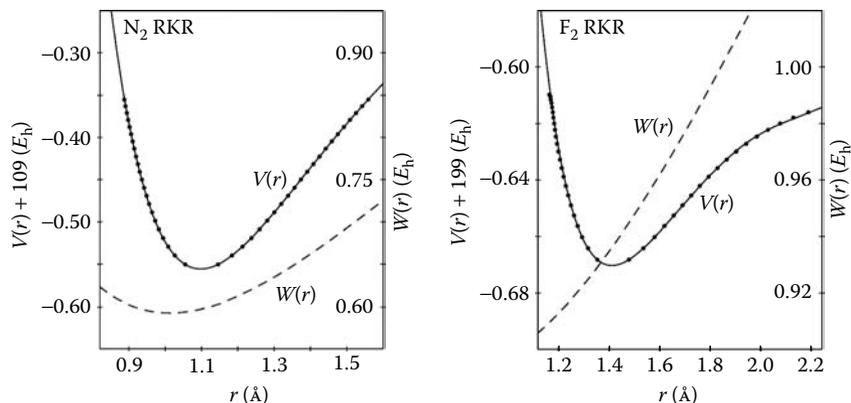


FIGURE 1.2 Rydberg–Klein–Rees (RKR) potential energy curves of N₂ and F₂ and the corresponding functions $W(r) = V_{\text{RHF}}(r) - V_{\text{RKR}}(r)$.

energy curves obtained from a beginning level of ab initio electronic structure theory, namely, the restricted Hartree–Fock (RHF) method with a Gaussian double- ζ plus polarization (DZP) basis set.* In Figure 1.2, the difference function $W(r) = V_{\text{RHF}}(r) - V_{\text{RKR}}(r)$ is plotted alongside $V_{\text{RKR}}(r)$ for N₂ and F₂, showing the variation of the magnitude of the electron correlation energy with bond distance.

Robust analytical representations[†] of both the RKR and RHF potential curves allow derivatives of $V(r)$ and hence $E_e(r) = V(r) - V_{\text{NN}}(r)$ to be determined analytically through fourth order as a function of the bond distance for our diatomic paradigms. Thus, at any specified point within a given range, the RHF/DZP[‡] theoretical predictions for the potential energy derivatives of various orders can be compared to “exact experimental” values. Specific numerical comparisons are made in Tables 1.1 and 1.2 at the distinct equilibrium bond distances of the RHF and RKR curves. In addition, the RKR derivative functions are plotted in Figure 1.3, and the corresponding RHF curves are virtually indistinguishable on the scale of the plots. The N₂ and F₂ examples are chosen not only because accurate experimental data are available but also because they exhibit very different levels of agreement between theoretical and experimental equilibrium structures. In particular, for N₂ the RHF/DZP equilibrium distance is 0.015 Å too short, within typical ranges of error, whereas for F₂ this difference is 0.077 Å, which is very large even for this introductory level of electronic structure theory.

The ab initio and experimental data for N₂ and F₂ in Tables 1.1 and 1.2 clearly demonstrate that the $E_e(r)$ and $V_{\text{NN}}(r)$ derivatives are sizable at all orders and opposite in sign. The E_e and V_{NN} contributions to the gradient obviously cancel each

* See Section 1.5 for a description of Gaussian basis sets and electronic structure methods.

[†] For a detailed account, see Allen, W. D., and A. G. Császár. 1993. *J Chem Phys* 98:2983.

[‡] In ab initio electronic structure theory, it is customary to employ the notation “level/basis,” where “level” denotes a particular wave function method and “basis” a particular one-particle basis set (see Figure 1.5).

TABLE 1.1

A Comparison of RHF/DZP Theoretical and RKR Experimental Data for the Electronic (E_e), Nuclear–Nuclear Repulsion (V_{NN}), and Total (V) Energies of N_2 and Their Geometric Derivatives through Fourth Order^a

	At $r_e(\text{RHF/DZP}) = 1.082707 \text{ \AA}$			At $r_e(\text{Expt}) = 1.097685 \text{ \AA}$		
	RHF/DZP	RKR	Percentage Error	RHF/DZP	RKR	Percentage Error
$E_e(N_2)$	-132.907896	-133.503919	-0.45	-132.580357	-133.177747	-0.45
E'_e	96.437	96.074	0.38	94.255	93.823	0.46
E''_e	-147.88	-152.54	-3.1	-143.55	-148.01	-3.0
E'''_e	294.1	308.4	-4.6	283.9	297.6	-4.6
E''''_e	-692.1	-733.8	-5.7	-665.5	-704.9	-5.6
$V_{NN}(N_2)$	23.948932	23.948932	0	23.622147	23.622147	0
V'_{NN}	-96.437	-96.437	0	-93.823	-93.823	0
V''_{NN}	178.14	178.14	0	170.95	170.95	0
V'''_{NN}	-493.6	-493.6	0	-467.2	-467.2	0
V''''_{NN}	1823.6	1823.6	0	1702.5	1702.5	0
$V(N_2)$	-108.958964	-109.554988	-0.54	-108.958210	-109.555600	-0.55
V'	0.00	-0.3632	-	0.4315	0.00	-
V''	30.26	25.60	18.2	27.40	22.94	19.4
V'''	-199.5	-185.2	7.7	-183.3	-169.6	8.1
V''''	1131.4	1089.8	3.8	1037.0	997.6	3.9

^a All energies are given in hartrees, whereas all derivatives correspond to energies measured in attojoules and distances in \AA . The percentage errors are given as $100(\text{RHF/RKR} - 1)$. The RKR data are based on Lofthus, A., and P. H. Krupenie. 1977. *J Phys Chem Ref Data* 6:113.

other completely at equilibrium. What is less appreciated is that the cancellation is almost as great for the quadratic force constants. For the higher-order force constants, the derivatives of V_{NN} become increasingly dominant. To be precise, for N_2 at the experimental geometry the ratios are $E'_e/V'_{NN} = -1.00$, $E''_e/V''_{NN} = -0.87$, $E'''_e/V'''_{NN} = -0.63$, and $E''''_e/V''''_{NN} = -0.38$, whereas in the F_2 case these ratios are -1.00 , -0.96 , -0.87 , and -0.74 , respectively. Figure 1.3 shows that this behavior is not restricted to the experimental bond distance alone, because the $V(r)$ derivative curves shift away from the r axis as the order of the derivative is increased as a consequence of the growing importance of the V_{NN} contributions. In brief, the higher-order bond stretching derivatives depend strongly on core–core nuclear repulsions, and the cancellation of the E_e and V_N derivative terms decreases substantially in higher order.

The accuracy of the RHF/DZP electronic energy derivatives of both N_2 and F_2 is remarkably good for such a modest level of theory. The errors in the $E_e(r)$ derivatives through fourth order are under 6% for both molecules over bond-length intervals of at least 0.5 \AA surrounding r_e . However, the theoretical values for the second derivatives

TABLE 1.2

A Comparison of RHF/DZP Theoretical and RKR Experimental Data for the Electronic (E_e), Nuclear–Nuclear Repulsion (V_{NN}), and Total (V) Energies of F_2 and Their Geometric Derivatives through Fourth Order^a

	At $r_e(\text{RHF/DZP}) = 1.334980 \text{ \AA}$			At $r_e(\text{Expt}) = 1.411930 \text{ \AA}$		
	RHF/DZP	RKR	Percentage Error	RHF/DZP	RKR	Percentage Error
$E_e(F_2)$	-230.847255	-231.773494	-0.40	-229.092257	-230.027524	-0.41
E'_e	104.859	104.371	0.47	94.277	93.741	0.57
E''_e	-148.28	-148.88	-0.4	-127.42	-128.08	-0.5
E'''_e	298.1	296.8	0.4	245.9	245.7	0.08
E''''_e	-755.4	-745.8	1.3	-604.6	-588.0	2.8
$V_{NN}(F_2)$	32.107853	32.107853	0	30.357979	30.357979	0
V'_{NN}	-104.859	-104.859	0	-93.741	-93.741	0
V''_{NN}	157.094	157.094	0	132.784	132.784	0
V'''_{NN}	-353.03	-353.03	0	-282.13	-282.13	0
V''''_{NN}	1057.8	1057.8	0	799.3	799.3	0
$V(F_2)$	-198.739402	-199.665641	-0.46	-198.734278	-199.669545	-0.47
V'	0.00	-0.4873	-	0.5365	0.00	-
V''	8.818	8.217	7.3	5.365	4.703	14.1
V'''	-54.95	-56.24	-2.3	-36.18	-36.39	-0.6
V''''	302.3	311.9	-3.1	194.7	211.3	-7.9

^a All energies are given in hartree, whereas all derivatives correspond to energies measured in attojoules and distances in Å. The percentage errors are given as $100(\text{RHF/RKR} - 1)$. The RKR data are based on Colbourn, E. A., M. Dagenais, A. E. Douglas, and J. W. Raymond. 1976. *Can J Phys* 54:1343.

of $V(r)$ are much less accurate than those of $E_e(r)$ —a disparity that becomes smaller for higher-order derivatives. Because the errors in the $E_e(r)$ derivatives are comparable at all orders, the fact that the V'' predictions are much poorer than the V''' and V'''' results is a direct consequence of the cancellation of nuclear repulsion and electronic energy effects. As a specific example, the theoretical E''_e value for N_2 is in error by only 3.0% at the experimental r_e distance, but the corresponding discrepancy for V'' is 19.4% (see Table 1.1). In contrast, E_e'''' and V'''' for N_2 are predicted by the RHF/DZP method with comparable accuracies of 5.6% and 3.9%, respectively.

It must be recognized that slight inaccuracies in the evaluation of $E'_e(r)$ by theoretical methods may lead to substantial errors in the value of $V'(r)$. This is the reason correlation effects (see Section 1.5) are prominent in computing gradients and, consequently, equilibrium structures. In this sense, it is fundamentally more difficult to determine accurate r_e parameters by electronic structure techniques than force constants (especially higher-order ones). The case of F_2 demonstrates the situation