The Force Concept in Chemistry

Edited by

B. M. Deb
Department of Chemistry
Indian Institute of Technology
Bombay, India

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Dedication

People who met Charles Coulson during his life sometimes came away wondering who is greater: Coulson the scientist, or Coulson the man. That there has never been a simple answer to this question is itself a tribute to the rigor with which Charles Coulson developed and practiced these qualities, for it is a tragic sign of our times that the scientist in many of us far outshines the human being. There is hardly any area of applied quantum mechanics which has not been enriched by Coulson's pioneering contributions (see S. L. Altmann and E. J. Bowen, *Biographical Memoirs of Fellows of the Royal Society*, Vol. 20, pp. 75–134, December 1974). His many-sided humanitarian activities were guided by a simple principle: to understand and to serve. He had a special concern for science and social development in developing countries. Indeed, the growth of the present small body of theoretical chemists in India has been due largely to the stimulation and encouragement provided directly or indirectly by Charles Coulson. Accordingly, this book is dedicated with respect and affection to

CHARLES ALFRED COULSON (1910–1974)
SCIENTIST AND MAN

List of Contributors

R. F. W. Bader, Department of Chemistry, McMaster University, Ontario Canada

A. J. Coleman, Department of Mathematics and Statistics, Queen's University, Kingston, Canada.

K. C. Daiker, Department of Chemistry, University of New Orleans, New Orleans, Louisiana

B. M. Deb, Department of Chemistry, Indian Institute of Technology, Bombay, India

S. T. Epstein, Department of Physics, University of Wisconsin, Madison, Wisconsin

J. Goodisman, Department of Chemistry, Syracuse University, Syracuse, New York

T. Koga, Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

M. T. Marron, Department of Chemistry, University of Wisconsin-Parkside, Kenosha, Wisconsin

H. Nakatsuji, Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

P. Politzer, Department of Chemistry, University of New Orleans, New Orleans, Louisiana

P. Pulay, Department of General and Inorganic Chemistry, Eötvös Loránd University, Múzeum Körút 6-8, Budapest, Hungary

Preface

The object of this book is to draw scientists' attention to the simple but rigorous concept of electrostatic forces in molecules. This approach views chemical processes in three-dimensional space through the net forces in a molecular system, or where detailed physical insight into a chemical phenomenon is desired, through appropriately partitioned components of these net forces. The forces themselves can be derived from a knowledge of the quantum mechanical electron density, by means of the Hellmann–Feynman (H–F) theorem. Although this theorem was proposed forty years ago, a fruitful realization of its implications and potential applications had to wait until the sixties. This occurred partly because the apparent simplicity of the H–F theorem had evoked some skepticism and suspicion that too much was probably being read into too little, and partly because of the delayed availability of reliable electron densities for systems of interest. However, it must also be said that the initial disbelief at results derived from the H–F theorem did contribute significantly toward the growth of the force concept in quantum mechanics.

It has been recognized for some time that a considerable disadvantage of many highly accurate, conventional quantum-chemical calculations is the fact that simple concepts and models highly useful for chemists are extremely difficult to retrieve from the resulting maze of high-precision numbers. The difficulties are compounded by the fact that the theoretical foundations of a number of earlier concepts and pictures in current chemical use have been shown by these accurate calculations to be either nonexistent or extremely weak. But the calculations themselves could hardly provide alternative simple concepts that might be applied easily by all chemists, and so the use of earlier pictures, even if somewhat unjustified, continued unabated. As Professor C. A. Coulson once remarked, the generation of accurate numbers, whether by computation or by experiment, is a somewhat futile exercise unless these numbers can provide us with simple and useful chemical concepts: if the numbers themselves were of the essence, one might as well be interested in a telephone directory.

The force concept provides a very powerful tool for developing these much needed chemical models, which will be based on firm quantum-mechanical foundations and yet retain an essential simplicity of character. This approach

has already yielded outstanding successes in understanding chemical binding, molecular geometry, and chemical reactivity, among other subjects. These successes are due, first, to the fact that, within the Born–Oppenheimer approximation, the force is expressible merely as a balance of two opposing terms, one coming from nuclear–nuclear repulsions and the other from electron–nuclear attractions. (Interelectronic repulsions do not appear explicitly in the expression.) Secondly, the electron–nuclear attractive force is expressed in terms of the three-dimensional electron density. These two features provide a comfortable visualization of molecular behavior in three-dimensional space, a great advantage that was not accessible before. Still, the tremendous possibilities of the force concept, which also has considerable pedagogic value, have not yet been fully realized.

This book sets down in detail the theoretical machinery developed so far within the force concept. It then deals in depth with numerous applications of the concept to investigate molecular phenomena. The topics covered range from the H–F theorem to works which have been inspired directly or indirectly by the theorem, as well as other works related to the force concept. The presentation is at a level which should generally be comprehensible to a graduate student in chemistry or physics who has been exposed to quantum mechanics at the undergraduate level. Throughout the book, emphasis has been upon highlighting how new concepts and insights spring from the force concept, and how the reader can apply these concepts in dealing with molecular (and solid state) behavior. Considerable effort has been made to include all relevant work done so far in this area, thus making the book as comprehensive and exhaustive as possible. The editor would be very grateful to have his attention drawn to any omission of related work.

The idea for this book arose from the unexpected and very gratifying response, from all over the world, to a review article by the editor on the force concept.* Those people who showed an interest included mathematicians, physicists, chemists, biologists, geologists, medical researchers, chemical engineers, materials scientists, among others. While it is too much to expect that the present book would be of service to all these people, it is the editor's fond hope that this expectation may be realized at least in part.

The organization of the book is described below.

In Chapter 1, Epstein provides a thorough and elegant account of the general H–F theorem, and various other related theorems such as the electrostatic and time-dependent H–F theorems, integral and integrated H–F theorems, etc. Since the form of the force operator (the derivative of the Hamiltonian) depends on the choice of coordinate system, the effects of coordinate transformations on the general and electrostatic H–F theorems are discussed. Conditions under which optimal variational wavefunctions satisfy the various theorems are then examined;

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these conditions may be regarded as virtues to be acquired by such approximate wavefunctions. The relation between perturbation theory and the H–F theorems, which is important for the treatment of, e.g., long-range intermolecular forces, as well as the connection between the H–F theorem and hypervirial theorems has also been dealt with. Finally, it is also possible to define a regional H–F theorem where the integration is performed over a subspace of the total space. (The implications of such quantum subspaces are brought out in Chapter 2). Chapter 1 thus lays down most of the theoretical foundations for the whole book.

Applications of the various H–F theorems to chemical problems begin with Chapter 2. In this chapter, Bader presents a rigorous and comprehensive discussion of chemical binding based on the properties of molecular electronic charge distributions, and the forces which these distributions exert on the nuclei. Chemical binding is examined in detail through density difference maps, which represent pictorially the redistribution of charge accompanying the formation of a chemical bond. A partitioning of the electron–nuclear attractive force vis-à-vis the density difference map reveals that in covalent binding the nuclei are bound by the electron density shared between them, while in ionic binding the nuclei are bound by the electron density localized about a single nucleus, thereby confirming the old hypothesis of G. N. Lewis. A combined use of the virial and electrostatic H–F theorems enables one to derive certain general constraints that might be placed on the signs and relative magnitudes of the changes in kinetic and potential energy over the complete range of internuclear distances involved in molecule formation. Bader discusses in considerable detail the changes in kinetic energy accompanying the formation of a molecule, and points to the existence of local regions of space in which the kinetic energy attains rather low values. The locations of these regions in different systems may be predicted from the charge distributions depicted in density difference maps. Finally, Bader highlights the role of the charge density in quantum mechanics, and discusses some very interesting properties of quantum subspaces.

From the theories of chemical binding it is but one step to enquire about the relative spatial arrangements of the bound atoms in a molecule. It is well known that many physical, chemical, and biological properties of substances can be correlated with their characteristic molecular shapes. Unfortunately, the broad problem of molecular geometry has defied solution for a long time. Nakatsuji and Koga open Chapter 3 with a brief discussion on several earlier models of molecular geometry, and then proceed to give an exhaustive account of the various phenomena governing molecular geometry, based on two force models. Of these two models, one is more pictorial, employing the HOMO (highest occupied molecular orbital) postulate, and provides a consistent qualitative view of all static aspects of molecular geometry. The other model is more quantitative in character, and can also deal with dynamic changes in molecular geometry occurring during chemical reactions, as well as with long-range intermolecular forces (see Chapter 7). In all such discussions the paramount importance of the three-

dimensional electron density becomes quite obvious. The origin of the internal force which favors or disfavors the passage of a molecule from one configuration to another lies in the relaxation of the electron cloud during such processes. Obviously, the stretching and bending force constants of molecules (see Chapter 5) can be interpreted on the basis of such relaxation processes, some features of which have been described by Nakatsuji and Koga.

As Epstein explains in Chapter 1, the forces can be integrated to give energies and energy differences. However, here a problem arises, in that (except in some special cases) the resulting energy quantities are generally less accurate than the corresponding quantities obtained by a variational or perturbational calculation. Further, with the integral H-F theorem, for example, the value of the integral may sometimes depend on the choice of the path of integration. Indeed, by a careful choice of path one can obtain an energy difference superior to that given by the difference in expectation values! These and other related issues are discussed at length by Marron in Chapter 4, where he also explains how one can obtain useful physical insights into the mechanisms of internal motions.

The topics of chemical binding, molecular geometry, internal motions, and force constants are all intricately linked. The last-mentioned topic forms the subject matter of Chapter 5. Here Goodisman analyzes various ways of calculating and interpreting force constants of diatomic and polyatomic molecules. There are certain practical advantages in calculating force constants from forces over the conventional double differentiation of the energy, although the vexing question of accuracy again crops up here. However, there are situations where even wavefunctions of less than Hartree-Fock accuracy can provide good estimates of stretching and bending force constants via forces.

By means of the three-dimensional electron density one can define the electrostatic potential at any point in the space around a molecule; the negative derivative of the potential, multiplied by the charge, gives the force at any point in the three-dimensional space. Like the H-F force, the electrostatic potential is given by a balance of two opposing contributions, one a nuclear–nuclear repulsion term and the other an electron–nuclear attraction term. Using a number of interesting examples, which include nucleic acid bases as well as drug–receptor interactions, Politzer and Daiker explain in Chapter 6 how the electrostatic potential in large molecules serves as an attractive guide to their reactivity. For example, it can reveal the regions in a molecule that are most susceptible to electrophilic attack and provide a measure of their relative reactivities toward electrophiles. Politzer and Daiker also discuss other force approaches to chemical reactivity.

Chapter 7 gathers together a number of other interesting applications of the H-F theorem to atomic and molecular physics, solid state physics, statistical thermodynamics, etc. Topics as diverse as the calculation of three-center force integrals, inner-shell binding energies (ESCA), binding energy of biexcitons, relativistic and nonrelativistic classical analogs of the H-F theorem, the stress

concept as a generalization of the force concept, etc., are discussed. Chapter 7 also includes an account of the long-range forces between atoms in their ground and excited or ionized states, as well as intermolecular forces in other systems. Feynman's original conjecture about the origin of the van der Waals attraction between molecules is verified.

All these applications of the force concept repeatedly highlight the role of the three-dimensional electron density, indicating that a great deal of chemistry can be dealt with simply in three-dimensional space. Since it is generally believed that all information of physical significance about a system is encoded in the single-particle and two-particle reduced density matrices, quantum mechanists have been trying for some time to devise algorithms for direct calculation of these density matrices, i.e., without first calculating the wavefunction. Unfortunately, these efforts have been beset with a very serious problem, that of N-representability of the 1-matrix and 2-matrix. In Chapter 8, Coleman provides an erudite account of these efforts and indicates how close we are now to this goal. He summarizes the basic properties of the 1- and the 2-matrix, and reviews the efforts to solve what is denoted as the ensemble N-representability problem, after which he includes a discussion of the numerical results achieved so far.

The final chapter concerns itself with the direct analytical evaluation of energy gradients ("exact" forces). Its author and main protagonist Pulay points out that direct analytical evaluation, wherever applicable, is computationally superior to numerical determination of gradients from calculated energy values. Further, with approximate wavefunctions the error in the "exact" force is always of second order in the error parameter, unlike the H-F forces. Pulay looks into the calculation of energy gradients from various types of SCF wavefunctions, and discusses in detail the determination of molecular geometries, saddle points on potential energy surfaces, and different types of force constants via these "exact," or non-H-F forces.

The editor is deeply appreciative of the enthusiastic participation of all the other authors of this book, and their great patience when the work was passing through difficult phases. If this book has any merits, it is because of their efforts to provide accounts of their areas which would be as comprehensive and readable as possible. If the book has any defects, in spite of its rich material, the editor assumes responsibility for them. This effort to produce the first book on the force concept in chemistry has received warm encouragement from many scientists in India and the world at large. Limitations of space prevent listing their names, but the editor is very grateful for their kindness. It is a pleasure to thank Dr. (Mrs.) Geeta Mahajan, Dr. (Mrs.) Anjuli Bamzai, Mr. S. K. Ghosh and Mr. G. B. Pattanaik for their help in various ways, and the editor's colleagues at I.I.T. Bombay for their encouragement and support. Finally, words of gratitude are hardly adequate for the efforts of the one particular individual who, besides

helping with the author index, nursed her husband through continued ill health and kept him on his feet during the course of this project. Without her this book might not have been possible.

B. M. Deb
Editor

Acknowledgments

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1
The Hellmann-Feynman Theorem*

Saul T. Epstein

Department of Physics
University of Wisconsin
Madison, Wisconsin

Contents

1-1. INTRODUCTION

The electrostatic Hellmann–Feynman theorem will play an important role in many of the chapters of this book. Our major task in this first chapter is therefore to provide a reasonably precise and thorough introduction to that theorem. The method we will use will be to view the electrostatic theorem as "simply" a special case of a more general theorem—the Hellmann–Feynman (H–F) theorem. Our reasons for this approach are twofold. First, a more general point of view presumably enhances appreciation of special cases; and, second, many other special cases of the general theorem are also of interest (see Section 1-5). At the end of our discussion we will also include some brief comments on other general theorems of a related sort, and on some other matters as well.

We will be concerned with the normalizable (i.e., bound-state) eigenfunctions and corresponding eigenvalues of a Hamiltonian H. At first we will confine attention to the ideal situation in which we have an exact eigenfunction and eigenvalue; later we will turn to the more practical situation in which we have only approximations to these quantities.

1-2. STATEMENT OF THE HELLMANN–FEYNMAN THEOREM

Let ψ be a normalizable eigenfunction of H with eigenvalue E, thus

$$H\psi = E\psi \tag{1-1}$$

and let σ be a real parameter in H. Then the theorem[1] states that

$$\frac{\partial E}{\partial \sigma} = \frac{\left\langle \psi \left| \frac{\partial H}{\partial \sigma} \right| \psi \right\rangle}{\langle \psi | \psi \rangle}. \tag{1-2}$$

Below we offer three "different" proofs of this theorem.[2] It is true that one would do; however, each proof is instructive in its own way.

1-3. THREE PROOFS OF THE HELLMANN–FEYNMAN THEOREM

1-3-1. First Proof (94, 95)

In this first proof we simply appeal to well-known results (the second and third proofs are more self-contained). Namely, suppose that we change the parameter in H from σ to $\sigma + \delta \sigma$. Then H will change by δH, where

$$\delta H = \frac{\partial H}{\partial \sigma} \delta \sigma + O((\delta \sigma)^2), \tag{1-3}$$

whence, from first-order perturbation theory,[3] the energy will change by

$$\delta E = \frac{\left\langle \psi \left| \frac{\partial H}{\partial \sigma} \right| \psi \right\rangle}{\langle \psi | \psi \rangle} \delta \sigma + O((\delta \sigma)^2). \tag{1-4}$$

If now we divide both sides of (1-4) by $\delta \sigma$, and then let $\delta \sigma$ tend to zero, we evidently arrive at (1-2).[4]   Q.E.D.

1-3-2. Second Proof (25, 39)

Here we first differentiate the identity

$$\langle \psi | H - E | \psi \rangle = 0 \tag{1-5}$$

with respect to σ to find

$$\left\langle \frac{\partial \psi}{\partial \sigma} \middle| H - E \middle| \psi \right\rangle + \left\langle \psi \left| \frac{\partial H}{\partial \sigma} - \frac{\partial E}{\partial \sigma} \right| \psi \right\rangle + \left\langle \psi \middle| H - E \middle| \frac{\partial \psi}{\partial \sigma} \right\rangle = 0. \tag{1-6}$$

However[5]

$$(H - E)|\psi\rangle = 0 \quad \text{and} \quad \langle \psi|(H - E) = 0, \tag{1-7}$$