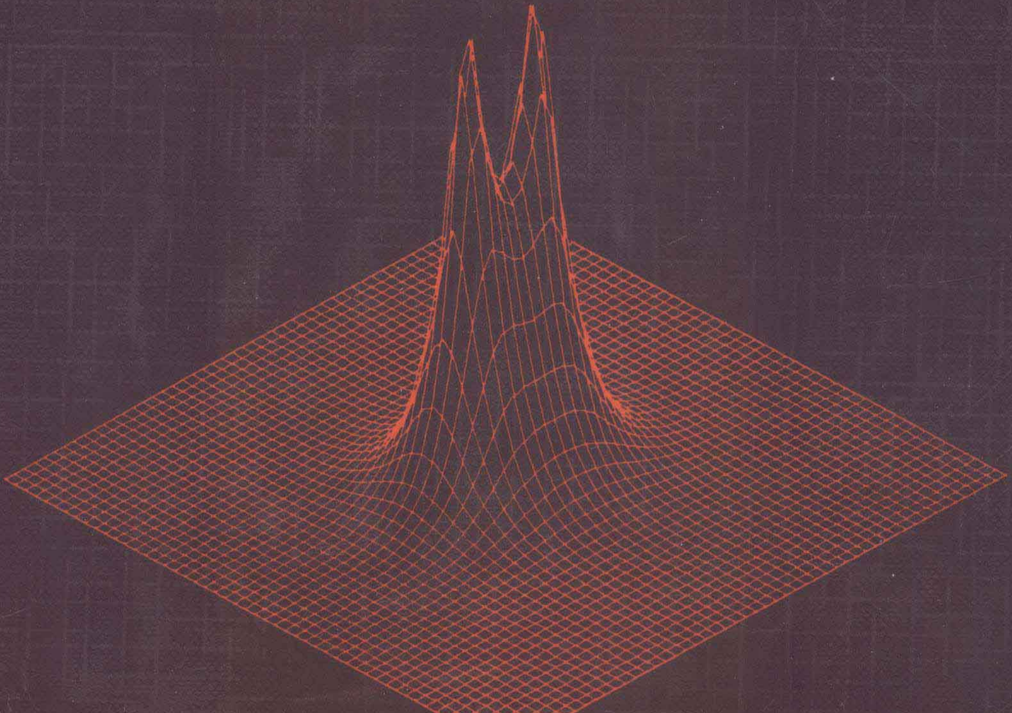
Chemical Bonding Theory

BRIAN WEBSTER



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ERRATA

Webster: *Chemical Bonding Theory*

p.30	In structure (a) of SF_4, Equational should read Equatorial.
p.46	In Equation (3.8), t should read E.
p.77	Equation (4.19) should be: $dE/dq = a + 2bq$.
p.153	In the first table, $m_s = \pm \frac{1}{2}$.

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OXFORD LONDON

EDINBURGH BOSTON MELBOURNE

To Mary

Editorial offices:
Osney Mead, Oxford OX2 0EL
25 John Street, London WC1N 2BL
23 Ainslie Place, Edinburgh EH3 6AJ
3 Cambridge Center, Suite 208
Cambridge, Massachusetts 02142, USA
107 Barry Street, Carlton
Victoria 3053, Australia

First published 1990

Set by Macmillan India Ltd, Bangalore 25
printed and bound
in Great Britain by Hartnolls Ltd,
Bodmin, Cornwall

DISTRIBUTORS
Marston Book Services Ltd
PO Box 87
Oxford OX2 0DT
(*Orders*: Tel: 0865 791155
Fax: 0865 791927
Telex: 837515)

USA
Publishers' Business Services
PO Box 447
Brookline Village
Massachusetts 02147
(*Orders*: Tel: (617) 524-7678)

Canada
Oxford University Press
70 Wynford Drive
Don Mills
Ontario M3C 1J9
(*Orders*: Tel: (416) 441-2941)

Australia
Blackwell Scientific Publications
(Australia) Pty Ltd
107 Barry Street
Carlton, Victoria 3053
(*Orders*: Tel: (03) 347-0300)

British Library
Cataloguing in Publication Data

Webster, Brian
Chemical bonding theory.
1. Chemical bonding
I. Title
541.2′24

ISBN 0-632-01619-1
ISBN 0-632-01621-3 pbk

Library of Congress
Cataloging-in-Publication Data

Webster, Brian C.
Chemical bonding theory/by Brian Webster.
p. cm.
Includes bibliographical references.
ISBN 0-632-01619-1.—ISBN 0-632-01621-3 (soft)
1. Chemical bonds. I. Title.
QD461.W38 1990
541.2′24—dc20

Chemical Bonding Theory

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Preface

The principal objective of this book is to instruct beginners in modern views of the chemical bond. When Nevil Sidgwick had completed his fine description of the electronic theory of valence, in 1927, he had to admit that the development of the theory of wave mechanics necessitates a fundamental change in our views of atomic structure. The implication was that the emergence of wave mechanics could alter all previous views of valence. Sidgwick, however, could no more bring himself to discard these views of the chemical bond than can the chemist of the present day. We still choose to describe the electronic structure of molecules in terms of bond pairs of electrons and, where appropriate, assign lone pairs of electrons to atoms in molecules. Whether this practice is allowed by any quantum mechanical condition does not worry many chemists too much.

The wave equation for atoms and molecules can now be solved readily by using computer packages which run even on personal computers. Studies of large molecules can be tackled on a dedicated mini-computer and for persons with access to a vector processor main-frame computer, highly advanced and accurate calculations are possible. The development of molecular orbital methods has resulted in a great enlightenment of the nature of chemical bonding. Bonding theory courses often do not reflect these advances and treat only bonding rules and pictorial orbital theory. Other courses in this subject enthusiastically assume that the beginner will grasp the required elements of quantum mechanics and group theory as they are led through the details of semiempirical and ab initio molecular orbital calculations. In this book I have attempted to combine both approaches but keeping to an elementary level. We possess a sound chemical way to chemical bonding which derives from Gilbert Lewis and Linus Pauling. This book keeps to this tradition but incorporates the results of ab initio molecular orbital calculations to show the modern description of chemical bonding.

I have taught bonding theory to beginners and advanced students, at Glasgow, for over 20 years. This book stems from that experience. Much of the material has been tested in lectures, workshop sessions, and tutorials. Beginners in bonding theory often, in my experience, find they are soon overcome by wave equations and group theory before they have even had a chance to master writing a Lewis formula for a polyatomic molecule. Of course, I well recognize the importance of a good grounding in formal quantum mechanics and group theory for the chemist but it is a question of timing. Many students have told me of the difficulties they find in bonding theory courses and textbooks. Here I have attempted to answer some of their questions.

The book is divided into four parts. These parts cover valence rules and molecular shape, atomic orbitals and atomic properties, molecular orbitals and molecular structure for diatomic molecules, and polyatomic molecules. This last part treats orbital symmetry, complex ions, and molecular attractions. The key features of the text are as follows:

- Learning outcomes are given at the beginning of each part so that students know exactly what skills they should have acquired on completion of that part.
- The SI system of units is used throughout the text and is complemented, where required, by atomic units which are often used in atomic and molecular calculations.
- The key mathematical equations are highlighted by grey tints and quantities are expressed in the style 'quantity/unit'.
- Key words and concepts are set in *italic* type.
- Examples with solutions are given at appropriate points to illustrate the use of an equation or chemical idea.
- All of the mathematical illustrations derive from a solution of the wave equation by an ab initio molecular orbital method or are based on the relevant equation.
- A wide selection of chemical structures are illustrated which are based on experimental data.
- A summary is given for each chapter highlighting the key points.
- Each chapter ends with a selection of problems which are mixed with respect to difficulty.
- The recommended readings for each chapter are taken mainly from the *Journal of Chemical Education* which is widely available to students.
- A full list of about 100 references is provided giving a start to any student wishing to track the development of bonding theory from its origins.
- A data section provides values for fundamental constants and other physical data required in the problems.

Instructors could find it helpful, for classes of moderate ability and for which time is restricted, to use this book taking only Chapters 1, 2, 3, 5 and 7. This selection will provide a short course in bonding theory at an elementary level having no spectroscopic component and requiring little mathematical skill. In general the other chapters develop some topics in bonding theory and spectroscopy which require simple algebraic skills. Group theory is not included in the book but this does not mean there is a lack of symmetry-related ideas. Indeed one objective of the book is to lay a foundation to facilitate the introduction of symmetry operations in a higher level course. There is no direct use of Hamiltonian operators or quantum mechanical methods because at the level of this text I think they will only obscure the views presented. Many students, however, could be stimulated to enquire into the means by which the solutions to the wave equation are obtained and proceed to a higher level course in quantum mechanics.

In writing this book I have been continuously aware of my good fortune in having had tutors who pursued their vocation with a clarity of vision, inspiration, and purpose it is difficult to find now. To these teachers I owe a significant debt. They include Dr Leslie Sutton FRS and Dr Luigi Venanzi, when at Magdalen College, Oxford. Both introduced me to the application of quantum mechanics and group theory in chemistry at a time when the new ligand field theory was being applied to interpret the physical properties of transition metal complexes. Interestingly, Leslie had been educated at Lincoln College, Oxford, where the Chemistry Fellow was Nevil Sidgwick. Afterwards, Leslie proceeded to the USA to the laboratory of Linus Pauling. Professor Charles Coulson FRS, who possessed a remarkable gift for intuitive thought on chemical bonding, guided me with rigour into molecular orbital theory at the Mathematical Institute. He was a forceful proponent of molecular orbital ideas following his early training in Cambridge from John Lennard-Jones. It was Lennard-Jones, when at the University of Bristol, England, in 1929, together with Friederich Hund in Germany, and Robert Mulliken in the USA who were the principal originators of the molecular orbital approach to chemical bonding.

Later, at Glasgow, Professor Durward Cruickshank FRS led me to appreciate the beauty of crystal structures and the importance of accurate molecular calculations. I have also learnt from several gifted postgraduate research students it has been my privilege to guide. The computer graphics in this book derive from some of our research activities. In general, the ab initio results were obtained using a computer package known as ATMOL. These results were then treated in ancillary programs devised by ourselves and, in particular, by Dr Maria Ramos, University of Oporto, Portugal. My colleagues in Glasgow have also assisted me by their searching discussions on chemical bonding and spectroscopy. I have also benefited from the study of many excellent papers, review articles and textbooks, some of which are listed in the References. Of all the general books I have read James Huheey's, *Inorganic Chemistry* (Third Edition, 1983, Harper & Row) was highly enjoyable and the first place I looked to check an inorganic fact.

Every effort has been made to acknowledge all source material and to obtain permission from copyright holders when required. In the event of any question arising as to the source of any material, we will be pleased to include the relevant acknowledgement in the next printing.

My sincere thanks are due to Professor John Winn, Dartmouth College, New Hampshire, for his careful reading of the draft of the book and many constructive comments. At Blackwell Scientific Publications, Navin Sullivan has given me much encouragement. The book production has benefited from the skills of Edward Wates and Emmie Williamson; Dr Kaveh Bazargan has used his holographic expertise to produce the accomplished artwork of this book. Finally a special note of thanks is due to Mary, an Alpine lover and a physics teacher who knows SI units perfectly.

In my lectures on bonding theory I try to speak to each member of the class as if a discussion were taking place just with that person and myself, although the lecture theatre is sometimes packed. In this book I have attempted to maintain this type of discussion with you, the reader, although you are not present in the lecture theatre. If you find this book illuminating, or otherwise, please send me a note to let me know.

BRIAN WEBSTER
Bearsden, 1989

Contents

Part 3. Diatomic Molecules

Part 4. Polyatomic Molecules

Addenda

Part 1. Electron Pairs and the Shape of Molecules

Bonding theory concerns the distribution of electrons about nuclei and the manner in which this electronic charge distribution determines the shape and physical properties of a molecule. Mathematical procedures are well advanced for the calculation of the electronic structure of molecules. Chemists, however, often use a few simple rules, based upon models of electronic structure, to describe chemical bonding. We begin our study by learning some of these rules. Later we will enquire whether the results of modern calculations support the rules.

On completion of Part 1 you should be able to:

1 Write a Lewis formula for a molecule.

2 Interpret the bonding in some transition-metal complexes.

3 Understand the concept of aromaticity.

4 Predict the shape of molecules having a central atom using the valence-shell electron-pair repulsion rules.

5 Apply a critical valence-electron number rule to predict the shape of a small polyatomic molecule.

You will also have started in your mind a collection of molecules containing both classic and contemporary items.

1 Valence Rules

1.1 Introduction

On Friday 22 March 1885 William Ramsay extracted a gas from the mineral cleveite. This gas was identified with a species known previously only on the sun, so it was called helium, after Helios. Ramsay also removed molecular oxygen O_2 and carbon dioxide CO_2 from a sample of air and 'fixed' the N_2 in air by reaction with hot magnesium. From this residual gas he obtained an element, present in air at 1/125th by volume, which did not react with Mg. This new element was most unreactive and was aptly named argon, which means 'lazy'. Other companion elements, neon, krypton and xenon, were discovered later; the family was completed when it was found that the white metal, radium, emits α particles to produce the gas we now call radon. Both α particles and the noble gases were to play a crucial role in unravelling the structure of atoms. We begin by looking briefly at the use of α particles in probing the atomic nucleus.

The nature of α particles proved puzzling for some years until it was established first, that such particles have a positive electrical charge and secondly, that α particles are identical with the nuclei of helium atoms. Guided by the ideas of Ernest Rutherford, Hans Geiger and Ernest Marsden proceeded to show that every atom contains a central nucleus having a positive electrical charge. Using a collimated beam of α particles emitted from a radon source, they observed that α particles could pass through wafer-thin metal foils of gold, silver and copper. Occasionally an α particle was observed to turn back in its tracks: 'it was', wrote Rutherford, 'as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you'. Rutherford reasoned that contrary to the accepted belief the positive charge of an atom is confined to a very small region which he called the nucleus. Most α particles can pierce metal foil without encountering a nucleus. However, when such an event does occur the force between the incoming α particle and a gold nucleus is so great as to reverse the path of the particle. On the basis of Coulomb's law, Rutherford devised a formula to account for these scattering events. Geiger and Marsden then applied this formula to measure the electrical charge on an atomic nucleus.

The natural unit of electrical charge is the charge carried by an electron, symbolized e. An electron has a charge of $-e$. The positive charge of a nucleus derives from the number of protons in the nucleus. Each proton has a charge of $+e$ exactly opposite to that of an electron. The number of protons in a nucleus defines the *atomic number*, symbolized Z. A gold nucleus with $Z = 79$ has an electrical charge of $+79e$.

For most chemical purposes a nucleus is a spherical region, containing a number of protons and, except for H, a number of neutrons which have zero electrical charge. The sum of the number of protons and neutrons defines A, the *mass number* of a nucleus. These facts are given in the symbol ${}^{A}_{Z}X$ for nuclei of the element X, as ${}^{4}_{2}He$ for helium nuclei which are α particles, or ${}^{197}_{79}Au$ for nuclei in gold foil. For radon ${}^{222}_{86}Rn$ with 136 neutrons we have a nucleus which is fragile. Radon nuclei disintegrate naturally with emission of α particles ^4_2He, just like their parent nuclei of radium $^{226}_{88}Ra$.

Electrons surround the nucleus of an atom and their negative charge neutralizes the positive nuclear charge to yield a neutral species. The electrons tend to distribute themselves into spherical shells with the nucleus at the center. Roughly, the radius of an atom is the distance from the nucleus to the outermost electronic shell. Consequently, atoms are much larger than the nuclei they contain.

Naturally, the mass of a nucleus depends upon its mass number: however, all nuclei are observed to have about the same density. With the density given by the ratio, mass/volume, this observation implies that the volume of a nucleus is roughly proportional to A. You know that the volume of a sphere is $(4/3)\pi r^3$, where r is the radius, so the radius of a spherical nucleus varies as $A^{1/3}$. To gauge the radius of a nucleus, r_{nuc}/pm, we can use the empirical relation

$$r_{\text{nuc}} = 1.2 \times 10^{-3} A^{1/3} \tag{1.1}$$

We find a helium nucleus has a radius of 0.02 pm (1 pm = 10^{-12} m), and a gold nucleus a radius of 0.07 pm. Atoms in metallic gold have a radius of 144 pm; therefore, they are about 2000 times larger than gold nuclei. We can now begin to understand how most α particles can penetrate gold foil but a few α particles are deflected back. The gold target facing an incoming α particle presents plenty of space for the particle to pass through the metal without having a close encounter with a nucleus.

Coulomb's law states that the force of repulsion F/N between two like electrical charges Q_1/C and Q_2/C varies inversely with the square of their distance R/m apart as

$$F = \frac{Q_1 Q_2}{(4\pi\varepsilon_0)R^2} \tag{1.2}$$

Rutherford assumed that Coulomb's law applies for the interaction between two positive charges $+Z_1 e$ and $+Z_2 e$, when the force of repulsion is given by

$$F = \frac{Z_1 Z_2 e^2}{(4\pi\varepsilon_0)R^2} \tag{1.3}$$

Values for ε_0, the permittivity of vacuum, and e, the magnitude of the electronic charge, are given in the data section. When R is expressed in pm, we find

$$F = 2.307 \times 10^{-4} \frac{Z_1 Z_2}{R^2} \tag{1.4}$$

Thus if an α particle passes at a distance of 144 pm from a nucleus in gold foil we find it experiences a negligible force of about 20 millionths of a newton; but for a near collision, with the α particle 0.03 pm from a nucleus, a force of 1000 N repels the α particle. For comparison, if we could switch a force field of 1000 N across a paper tissue for 1 s, we could see a 20 kg projectile approaching the paper surface with a velocity 25 m s^{-1} turned back along its path, with an equal and opposite velocity, just as in Rutherford's analogy. One of our objectives later is to understand how the repulsive forces between nuclei are counteracted by the attractive forces of electrons towards nuclei in the creation of molecules.

The modern Periodic Table given in the data section places the noble gases in Group 18. This position reflects their electronic structure with the electrons of each noble atom producing a complete electronic shell about the nucleus. With He, two electrons fill the shell, but subsequent noble atoms have filled shells with eight and 18 electrons until with Rn there is a 32-electron shell. We have then the electronic shell structures,

Noble gas	Shell structure	Z
He	2	2
Ne	2–8	10
Ar	2–8–8	18
Kr	2–8–18–8	36
Xe	2–8–18–18–8	54
Rn	2–8–18–32–18–8	86

The atoms lying between these noble gases have incomplete electronic shells, electrons being added, one by one, moving along the rows of the Periodic Table. Another objective is to account for the shell structure of atoms by an orbital model of electronic structure. However we can see at once from this simple description that the outermost shell of a noble gas fills with eight electrons; this fact has strongly influenced thinking about chemical bonds.

1.2 The eight electron rule

Valence is the combining capacity of an atom. Describing a new series of organic compounds containing metals, Frankland wrote, in 1852, ‘No matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms’. Phosphorus for example is attributed combining powers of three and five. This idea was contested by Kekule who considered valence to be a fixed property. He formulated phosphorus pentachloride as a molecular compound $PCl_3 \cdot Cl_2$ in keeping with its thermal decomposition liberating Cl_2. After the preparation of thermally stable PF_5 by Thorpe, in 1877, it became evident that a variable valence is exhibited by phosphorus, a property which is likely to be common to other elements. The sulfur atom linked to two hydrogen atoms in hydrogen sulfide H_2S is divalent but is hexavalent in SF_6, sulfur hexafluoride.

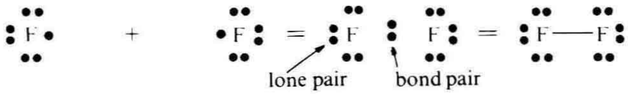
‘The cardinal phenomenon of all chemistry is the electron pair bond’, wrote Gilbert Lewis in 1916, when he published a chemical model for the electronic structure of atoms and molecules. Noting the differing valencies of atoms, Lewis deduced that the nucleus of an atom is centered within a core of inner electrons, beyond which there is an outer electronic shell. This outer shell contains the electrons involved in linking atoms together. The electrons in this shell are called *valence electrons* and the shell is called the *valence shell.*

When atoms combine they share valence electrons. A single chemical bond consists of a pair of shared electrons. These bonding electron pairs are localized between the nuclei linked in the molecule. Lewis deduced that an atom in a molecule likes to complete its valence shell with eight electrons. *An atom shares sufficient valence electrons to fill the valence shell of each atom in the molecule.* This is the *eight electron rule.* In application of this rule, bonding pairs are counted as common to each atom linked by the bond. The remaining valence electrons of each atom are arranged in pairs. They are nonbonding electrons named *lone pairs.* The valence electrons of an atom divide then into two types—bond pairs, and lone pairs of electrons:

↗ **bond pairs**
Valence electrons
↘ **lone pairs**
ATOM MOLECULE

Let us view the core of inner electrons in Lewis's model to be a complete shell similar in electronic structure to a noble gas. To evaluate the number of valence electrons for an atom with $Z < 18$, take the atomic number of the element and subtract the atomic number of the preceding noble gas, He, Ne, or Ar. Thus, for F, $Z = 9$, He with $Z = 2$ is the noble gas preceding F in the Periodic Table, so F has seven valence electrons. We shall learn later how to treat other atoms when we study electronic configurations.

Two F atoms combine producing molecular fluorine F_2. By sharing one pair of electrons each F fills its valence shell to satisfy the eight electron rule. There remain six valence electrons at each atom. These are arranged as three lone pairs in the Lewis formula with a dot '•' representing a valence electron:



We can see here a clue to Lewis's model. By filling the valence shell using electron pairs to make the bond we step from an electronic structure like a noble gas for the atom's core, to an electronic structure for the atom in the molecule similar to the next noble gas. Each atom in a molecule strives, it seems, to have an electronic structure like a noble element, as if in some way this confers a stability upon the molecule against dissociation into atomic fragments.

Example 1.1

What is the Lewis formula for: (1) molecular nitrogen N_2, (2) sulfur monoxide SO, (3) the interhalogen ClF?

1 N_2: we proceed in the following steps:
(a) The noble gas preceding N (7) is He (2).
(b) N has $7 - 2 = 5$ valence electrons.