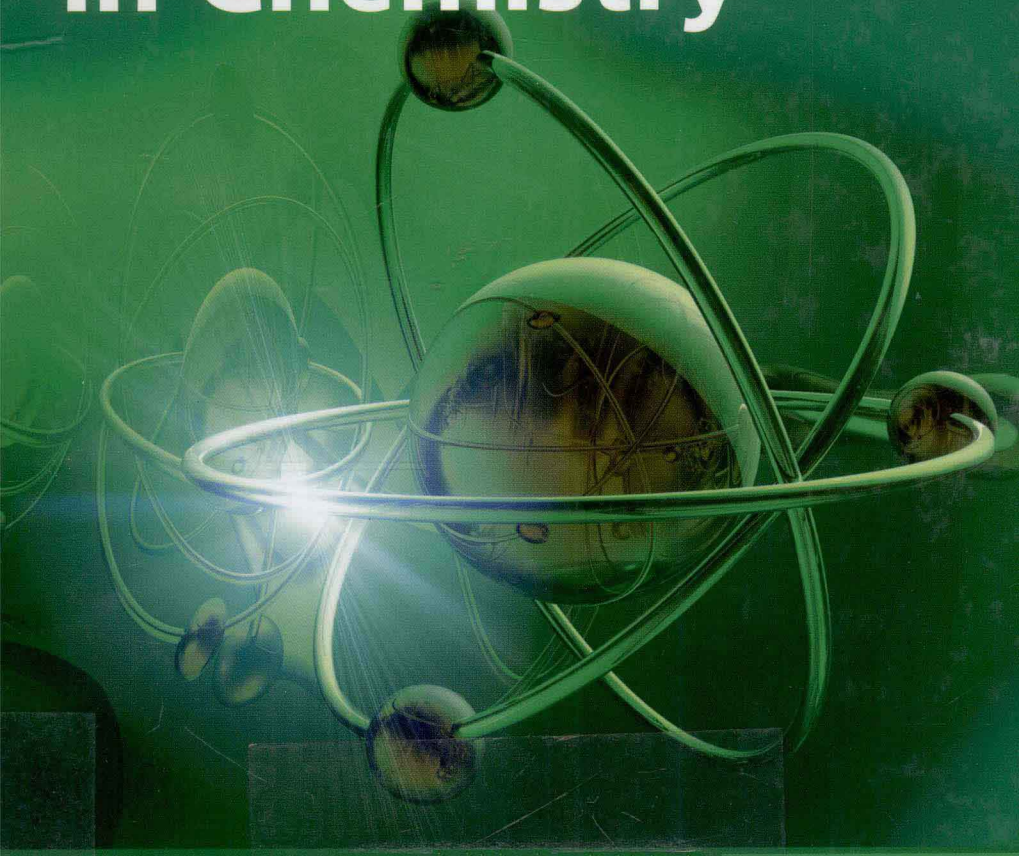
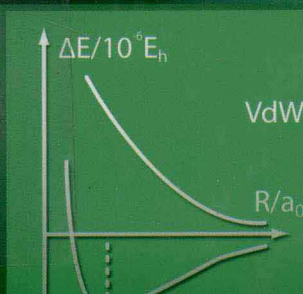
Valerio Magnasco

Models for Bonding in Chemistry



WILEY



Models for Bonding in Chemistry

Valerio Magnasco
University of Genoa, Italy

WILEY
A John Wiley and Sons, Ltd., Publication

This edition first published 2010

Registered office
John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

Library of Congress Cataloging-in-Publication Data

Magnasco, Valerio.
Models for bonding in chemistry / Valerio Magnasco.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-66702-6 (cloth) – ISBN 978-0-470-66703-3 (pbk.) 1. Chemical bonds. I. Title.
QD461.M237 2010
541'.224–dc22

2010013109

A catalogue record for this book is available from the British Library.

ISBN 978-0-470-66702-6 (cloth) 978-0-470-66703-3 (paper)

Set in 10.5/13pt Sabon-Roman by Thomson Digital, Noida, India

Printed and bound in United Kingdom by TJ International., Padstow, Cornwall

Models for Bonding in Chemistry

To Deryk

Preface

Experimental evidence shows that molecules are not like 'liquid droplets' of electrons, but have a structure made of bonds and lone pairs directed in space. Even at its most elementary level, any successful theory of bonding in chemistry should explain why atoms are or are not bonded in molecules, the structure and shape of molecules in space and how molecules interact at long range. Even if modern molecular quantum mechanics offers the natural basis for very elaborate numerical calculations, models of bonding avoiding the more mathematical aspects of the subject in the spirit of Coulson's *Valence* are still of conceptual interest for providing an elementary description of valence and its implications for the electronic structure of molecules. This is the aim of this concise book, which grew from a series of lectures delivered by the author at the University of Genoa, based on original research work by the author and his group from the early 1990s to the present day. The book should serve as a complement to a 20-hour university lecture course in Physical and Quantum Chemistry.

The book consists of two parts, where essentially two models have been proposed, mostly requiring the solution of quadratic equations with real roots. Part 1 explains forces acting at *short range*, typical of localized or delocalized chemical bonds in molecules or solids; Part 2 explains forces acting at *long range*, between closed-shell atoms or molecules, resulting in the so-called van der Waals (VdW) molecules. An electrostatic model is further derived for H-bonded and VdW dimers, which explains in a simple way the angular shape of the dimers in terms of the first two permanent electric moments of the monomers.

The contents of the book is as follows. After a short self-contained mathematical introduction, Chapter 1 presents the essential elements of the variation approach to either total or second-order molecular energies,

the system of atomic units (au) necessary to simplify all mathematical expressions, and an introductory description of the electron distribution in molecules, with particular emphasis on the nature of the quantum mechanical exchange-overlap densities and their importance in determining the nature of chemical bonds and Pauli repulsions.

The contents of Part 1 is based on such premises. Using mostly 2×2 Hückel secular equations, Chapter 2 introduces a model of bonding in homonuclear and heteronuclear diatomics, multiple and delocalized bonds in hydrocarbons, and the stereochemistry of chemical bonds in polyatomic molecules; in a word, a model of the *strong* first-order interactions originating in the chemical bond. Hybridization effects and their importance in determining shape and charge distribution in first-row hydrides (CH_4, HF, H_2O and NH_3) are examined in some detail in Section 2.7.

In Chapter 3, the Hückel model of linear and closed polyene chains is used to explain the origin of band structure in the one-dimensional crystal, outlining the importance of the nature of the electronic bands in determining the different properties of insulators, conductors, semiconductors and superconductors.

Turning to Part 2, after a short introduction to stationary Rayleigh–Schrödinger (RS) perturbation theory and its use for the classification of long-range intermolecular forces, Chapter 4 deals with a simple two-state model of *weak* interactions, introducing the reader to an easy way of understanding second-order electric properties of molecules and VdW bonding between closed shells. The chapter ends with a short outline of the temperature-dependent Keesom interactions in polar gases.

Finally, Chapter 5 studies the structure of H-bonded dimers and the nature of the hydrogen bond, which has a strength *intermediate* between a VdW bond and a weak chemical bond. Besides a qualitative MO approach based on HOMO-LUMO charge transfer from an electron donor to an electron acceptor molecule, a quantitative electrostatic approach is presented, suggesting an electrostatic model which works even at its simplest pictorial level.

A list of alphabetically ordered references, and author and subject indices complete the book.

The book is dedicated to the memory of my old friend and colleague Deryk Wynn Davies, who died on 27 February 2008. I wish to thank my colleagues Gian Franco Musso and Giuseppe Figari for useful discussions on different topics of this subject, Paolo Lazzeretti and Stefano Pelloni for

some calculations using the SYSMO programme at the University of Modena and Reggio, and my son Mario who prepared the drawings on the computer. Finally, I acknowledge the support of the Italian Ministry for Education University and Research (MIUR) and the University of Genoa.

Valerio Magnasco
Genoa, 20 December 2009

Contents

1

Mathematical Foundations

In physics and chemistry it is not possible to develop any useful model of matter without a basic knowledge of some elementary mathematics. This involves use of some elements of linear algebra, such as the solution of algebraic equations (at least quadratic), the solution of systems of linear equations, and a few elements on matrices and determinants.

1.1 MATRICES AND SYSTEMS OF LINEAR EQUATIONS

We start from matrices, limiting ourselves to the case of a *square matrix* of order two, namely a matrix involving two rows and two columns. Let us denote this matrix by the boldface capital letter **A**:

$$\mathbf{A} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \tag{1.1}$$

Models for Bonding in Chemistry Valerio Magnasco

where A_{ij} is a number called the *ij*th *element* of matrix **A**. The elements A_{ii} $(j = i)$ are called diagonal elements. We are interested mostly in *symmetric* matrices, for which $A_{21} = A_{12}$. If $A_{21} = A_{12} = 0$, the matrix is *diagonal*. Properties of a square matrix **A** are its *trace*(tr $\mathbf{A} = A_{11} + A_{22}$), the sum of its diagonal elements, and its *determinant*, denoted by $|\mathbf{A}| = \det \mathbf{A}$, a number that can be evaluated from its elements by the rule:

$$|\mathbf{A}| = A_{11}A_{22} - A_{12}A_{21} \tag{1.2}$$

Two 2×2 matrices can be multiplied rows by columns by the rule:

$$\mathbf{AB} = \mathbf{C} \tag{1.3}$$

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} B_{11} & B_{12} \\ B_{21} & B_{22} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{pmatrix} \tag{1.4}$$

the elements of the product matrix **C** being:

$$\begin{cases} C_{11} = A_{11}B_{11} + A_{12}B_{21}, & C_{12} = A_{11}B_{12} + A_{12}B_{22}, \\ C_{21} = A_{21}B_{11} + A_{22}B_{21}, & C_{22} = A_{21}B_{12} + A_{22}B_{22}. \end{cases} \tag{1.5}$$

So, we are led to the *matrix multiplication rule:*

$$C_{ij} = \sum_{\kappa=1}^{2} A_{i\kappa}B_{\kappa j} \tag{1.6}$$

If matrix **B** is a simple number a, Equation (1.6) shows that *all* elements of matrix **A** must be multiplied by this number. Instead, for $a|\mathbf{A}|$, we have from Equation (1.2):

$$a|\mathbf{A}| = a(A_{11}A_{22} - A_{12}A_{21}) = \begin{vmatrix} aA_{11} & aA_{12} \\ A_{21} & A_{22} \end{vmatrix} = \begin{vmatrix} aA_{11} & A_{12} \\ aA_{21} & A_{22} \end{vmatrix}, \tag{1.7}$$

so that, multiplying a determinant by a number is equivalent to multiplying just *one* row (or *one* column) by that number.

We can have also *rectangular* matrices, where the number of rows is different from the number of columns. Particularly important is the 2×1 *column vector* **c**:

$$\mathbf{c} = \begin{pmatrix} c_{11} \\ c_{21} \end{pmatrix} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \tag{1.8}$$

or the 1×2 *row vector* $\tilde{\mathbf{c}}$:

$$\tilde{\mathbf{c}} = (c_{11} \quad c_{12}) = (c_1 \quad c_2) \tag{1.9}$$

where the tilde $\tilde{}$ means interchanging columns by rows or vice versa (the *transposed* matrix).

The linear *inhomogeneous* system:

$$\begin{cases} A_{11}c_1 + A_{12}c_2 = b_1 \\ A_{21}c_1 + A_{22}c_2 = b_2 \end{cases} \tag{1.10}$$

can be easily rewritten in matrix form using matrix multiplication rule (1.3) as:

$$\mathbf{Ac} = \mathbf{b} \tag{1.11}$$

where $\mathbf{c}$ and $\mathbf{b}$ are 2×1 column vectors.

Equation (1.10) is a system of two algebraic equations linear in the *unknowns* c_1 and c_2, the elements of matrix $\mathbf{A}$ being the *coefficients* of the linear combination. Particular importance has the case where $\mathbf{b}$ is proportional to $\mathbf{c}$ through a number λ:

$$\mathbf{Ac} = \lambda\mathbf{c} \tag{1.12}$$

which is known as the *eigenvalue equation* for matrix $\mathbf{A}$. λ is called an *eigenvalue* and $\mathbf{c}$ an *eigenvector* of the square matrix $\mathbf{A}$. Equation (1.12) is equally well written as the *homogeneous* system:

$$(\mathbf{A}-\lambda\mathbf{1})\mathbf{c} = \mathbf{0} \tag{1.13}$$

where $\mathbf{1}$ is the 2×2 diagonal matrix having 1 along the diagonal, called the *identity* matrix, and $\mathbf{0}$ is the zero vector matrix, a 2×1 column of zeros. Written explicitly, the homogeneous system (Equation 1.13) is:

$$\begin{cases} (A_{11}-\lambda)c_1 + A_{12}c_2 = 0 \\ A_{21}c_1 + (A_{22}-\lambda)c_2 = 0 \end{cases} \tag{1.14}$$

Elementary algebra then says that the system of equations (1.14) has acceptable solutions if and only if the determinant of the coefficients vanishes, namely if:

$$|\mathbf{A}-\lambda\mathbf{1}| = \begin{vmatrix} A_{11}-\lambda & A_{12} \\ A_{21} & A_{22}-\lambda \end{vmatrix} = 0 \tag{1.15}$$

Equation (1.15) is known as the *secular equation* for matrix $\mathbf{A}$. If we expand the determinant according to the rule of Equation (1.2), we obtain

for a symmetric matrix **A**:

$$(A_{11}-\lambda)(A_{22}-\lambda)-A_{12}{}^2 = 0 \tag{1.16}$$

giving the *quadratic* equation in λ:

$$\lambda^2-(A_{11}+A_{22})\lambda+A_{11}A_{22}-A_{12}{}^2 = 0 \tag{1.17}$$

which has the two *real*[1] solutions (the eigenvalues, the roots of the equation):

$$\begin{cases} \lambda_1 = \dfrac{A_{11}+A_{22}}{2} + \dfrac{\Delta}{2} \\ \lambda_2 = \dfrac{A_{11}+A_{22}}{2} - \dfrac{\Delta}{2} \end{cases} \tag{1.18}$$

where Δ is the *positive* quantity:

$$\Delta = \left[(A_{22}-A_{11})^2+4A_{12}{}^2\right]^{1/2} > 0 \tag{1.19}$$

Inserting each root in turn in the homogeneous system (Equation 1.14), we obtain the corresponding solutions (the eigenvectors, our unknowns):

$$\begin{cases} c_{11} = \left(\dfrac{\Delta+(A_{22}-A_{11})}{2\Delta}\right)^{1/2}, & c_{21} = \left(\dfrac{\Delta-(A_{22}-A_{11})}{2\Delta}\right)^{1/2} \\ c_{12} = -\left(\dfrac{\Delta-(A_{22}-A_{11})}{2\Delta}\right)^{1/2}, & c_{22} = \left(\dfrac{\Delta+(A_{22}-A_{11})}{2\Delta}\right)^{1/2} \end{cases} \tag{1.20}$$

where the second index (a column index, shown in bold type in Equations 1.20) specifies the eigenvalue to which the eigenvector refers. All such results can be collected in the 2×2 square matrices:

$$\Lambda = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}, \quad \mathbf{C} = (\,\mathbf{c}_1 \quad \mathbf{c}_2\,) = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} \tag{1.21}$$

the first being the diagonal matrix of the eigenvalues (the *roots* of our secular equation 1.17), the second the row matrix of the eigenvectors (the *unknowns* of the homogeneous system 1.14). Matrix multiplication rule shows that:

$$\tilde{\mathbf{C}}\mathbf{A}\mathbf{C} = \Lambda, \quad \tilde{\mathbf{C}}\mathbf{C} = \mathbf{C}\tilde{\mathbf{C}} = \mathbf{1} \tag{1.22}$$

[1]This is a mathematical property of real symmetric matrices.

We usually say that the first of Equations (1.22) expresses the *diagonalization* of the symmetric matrix **A** through a transformation with the complete matrix of its eigenvectors, while the second equations express the *normalization* of the coefficients (i.e., the resulting vectors are chosen to have modulus 1).[2]

Equations (18–20) simplify noticeably in the case $A_{22} = A_{11} = \alpha$. Then, putting $A_{12} = A_{21} = \beta$, we obtain:

$$\begin{cases} \lambda_1 = \alpha + \beta, \quad \lambda_2 = \alpha - \beta \\ \mathbf{c}_1 = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}, \quad \mathbf{c}_2 = \begin{pmatrix} -1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \end{cases} \tag{1.23}$$

Occasionally, we shall need to solve the so called *pseudosecular equation* for the symmetric matrix **A** arising from the *pseudoeigenvalue equation*:

$$\mathbf{Ac} = \lambda \mathbf{Sc} \Rightarrow |\mathbf{A} - \lambda \mathbf{S}| = \begin{vmatrix} A_{11} - \lambda & A_{12} - \lambda S \\ A_{21} - \lambda S & A_{22} - \lambda \end{vmatrix} = 0 \tag{1.24}$$

where **S** is the *overlap matrix*:

$$\mathbf{S} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} = \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \tag{1.25}$$

Solution of Equation (1.24) then gives:

$$\begin{cases} \lambda_1 = \dfrac{A_{11} + A_{22} - 2A_{12}S}{2(1-S^2)} - \dfrac{\Delta}{2(1-S^2)} \\ \lambda_2 = \dfrac{A_{11} + A_{22} - 2A_{12}S}{2(1-S^2)} + \dfrac{\Delta}{2(1-S^2)} \end{cases} \tag{1.26}$$

$$\Delta = \left[(A_{22} - A_{11})^2 + 4(A_{12} - A_{11}S)(A_{12} - A_{22}S) \right]^{1/2} > 0 \tag{1.27}$$

The eigenvectors corresponding to the roots (Equations 1.26) are rather complicated (Magnasco, 2007), so we shall content ourselves here by giving only the results for $A_{22} = A_{11} = \alpha$ and $A_{21} = A_{12} = \beta$:

[2]The length of the vectors. A matrix satisfying the second of Equations (1.22) is said to be an *orthogonal* matrix.

$$\begin{cases} \lambda_1 = \dfrac{\alpha+\beta}{1+S}, & c_{11} = (2+2S)^{-1/2}, \quad c_{21} = (2+2S)^{-1/2} \\ \lambda_2 = \dfrac{\alpha-\beta}{1-S}, & c_{12} = -(2-2S)^{-1/2}, \quad c_{22} = (2-2S)^{-1/2} \end{cases} \tag{1.28}$$

under these assumptions, these are the elements of the square matrices Λ and **C** (Equations 1.21). Matrix multiplication shows that these matrices satisfy the generalization of Equations (1.22):

$$\tilde{\mathbf{C}}\mathbf{A}\mathbf{C} = \Lambda, \quad \tilde{\mathbf{C}}\mathbf{S}\mathbf{C} = \mathbf{C}\mathbf{S}\tilde{\mathbf{C}} = \mathbf{1} \tag{1.29}$$

so that matrices **A** and **S** are simultaneously diagonalized under the transformation with the orthogonal matrix **C**.

All previous results can be extended to square symmetric matrices of order N, in which case the solution of the corresponding secular equations must be found by numerical methods, unless use can be made of symmetry arguments.

1.2 PROPERTIES OF EIGENVALUES AND EIGENVECTORS

It is of interest to stress some properties hidden in the eigenvalues $(\lambda_1 \quad \lambda_2)$ and eigenvectors $\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$, (Equations 1.23), of the symmetric matrix **A** of order 2 with $A_{22} = A_{11} = \alpha$ and $A_{21} = A_{12} = \beta$.

In fact, Equation (1.17) can be written:

$$(\lambda_1-\lambda)(\lambda_2-\lambda) = \lambda_1\lambda_2-(\lambda_1+\lambda_2)\lambda+\lambda^2 = 0 \tag{1.30}$$

so that:

$$\lambda_1\lambda_2 = A_{11}A_{22}-A_{12}{}^2 = \alpha^2-\beta^2 = \det \mathbf{A} \tag{1.31}$$

$$\lambda_1+\lambda_2 = A_{11}+A_{22} = 2\alpha = \operatorname{tr} \mathbf{A} \tag{1.32}$$

In Equation (1.17), therefore, the coefficient of λ^0, the determinant of matrix **A**, is expressible as the *product* of the two eigenvalues; the coefficient of λ, the trace of matrix **A**, is expressible as the *sum* of the two eigenvalues.

From the eigenvectors of Equations (1.23) we can construct the two square symmetric matrices of order 2: