

Preface

“The manner in which the electron density is disposed in a molecule has not received the attention its importance would seem to merit. Unlike the energy of a molecular system which requires a knowledge of the second-order density matrix for its evaluation [a] many of the observable properties of a molecule are determined in whole or in part by the simple three-dimensional electron-density distribution. In fact, these properties provide a direct measure of a wide spectrum of different moments averaged directly over the density distribution. Thus the diamagnetic susceptibility, the dipole moment, the diamagnetic contribution to the nuclear screening constant, the electric field, and the electric field gradient (as obtained from nuclear quadrupole coupling constants) provide a measure of (aside from any angular dependencies) $\langle r_i^2 \rangle$, $\langle r_i \rangle$, $\langle r_i^{-1} \rangle$, $\langle r_i^{-2} \rangle$, and $\langle r_i^{-3} \rangle$, respectively. The electric field at a nucleus due to the electron density distribution is of particular interest due to the theorem derived by Hellmann [b] and Feynman [c]. They have demonstrated that the force acting on a nucleus in a molecule is determined by the electric field at that nucleus due to the other nuclei and to the electron-density distribution.”

- a P.-O. Löwdin, *Adv. Chem. Phys.* **2**, 207 (1959)
- b J. Hellman, *Einführung in die Quantenchemie* (Detliche, Leipzig, Germany, 1937)
- c R.P. Feynman, *Phys. Rev.* **56**, 340 (1939)

Richard F.W. Bader and Glenys A. Jones (1963) [a]

It has been sixteen years since the publication of Richard Bader’s classic 1990 treatise “*Atoms in Molecules: A Quantum Theory*” [b]. The theory was founded on the recognition that the electron density plays a critical role in explaining and understanding the experimental observations of chemistry. Bader’s work is among the earliest to draw attention to the importance of the electron density in chemistry, as the opening quotation, predating the discovery of the Hohenberg–Kohn

theorem, suggests. This 1963 paper includes an early example of molecular electron density contour plots (of the ammonia molecule).

Bader's fundamental work in the sixties on molecular electron density distributions (Table 1) laid the foundations for the theory which was developed in the seventies and eighties by his research group, which became known as the theory of atoms in molecules (AIM). In more recent literature this theory is often called the quantum theory of atoms in molecules (QTAIM) in recognition of its rigorous basis in quantum mechanics [2–6]. The theory relates the concepts of chemistry, for example chemical structure, chemical bonding, transferability of functional groups, and chemical reactivity, to the topology of the underlying electron-density distribution(s). QTAIM has, in effect, moved theoretical chemistry into real three-dimensional space [7]. In Bader's words:

“the charge [electron] density provides a description of the distribution of charge throughout real space and is the bridge between the concept of state functions in Hilbert space and the physical model of matter in real space.” [2]

By defining “proper open quantum systems” as special bounded regions within a closed (whole) system, followed by the identification of these regions as “atoms in molecules”, the quantum theory of atoms in molecules brought quantum mechanics into applicability to an atom *within* a molecule. When a molecular property can be expressed in terms of a property *density*, the contribution of an atom to that molecular property can be obtained by integrating this density over the bounded volume of that atom in the molecule. In this way every atom in a molecule or crystal is characterized by a set of physical properties, each of which corresponds to a molecular property. These atomic properties, naturally, add up to those of the total molecular system and, for this reason, parallel and recover the properties of the atoms of experimental chemistry [8]. In this sense, the quantum theory of atoms in molecules is *the* quantum mechanics of atoms within molecules and crystals [9–11].

The virial theorem, which governs the relationship between the potential and kinetic energies of a molecule, occupies a prominent place in molecular quantum mechanics. This theorem has been generalized by Bader from its *global* statement (which applies to the molecule as a whole) to a *local* statement defined at every point in space [10]. In other words, the theorem has been re-written in its most general form which applies at every point of space in terms of scalar functions of space, i.e. densities. This very important generalization, known as the “local statement of the virial theorem”, Eq. (54) in Ref. [10] and Eq. (10) in Chapter 1, is, perhaps, and to the best of our knowledge, the *only* known local relationship between the energy densities and the electron density that applies everywhere in space. More precisely, the local virial theorem relates the potential energy density and the kinetic energy density distributions locally to a function of the electron density, namely, its Laplacian [2, 10]. Bader also postulated [12], and later showed [2, 13–15] that the integrated form of this theorem, discovered before its local expression, translates into a virial theorem satisfied by each atom within a molecule

Table 1 Early Publications (nineteen-sixties) on molecular electron density distributions by Professor Richard F.W. Bader.

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1. R.F.W. Bader and G.A. Jones, "The Hellmann-Feynman Theorem and Chemical Binding", *Canadian Journal of Chemistry*, **39**, (1961), 1253–1265.
 - 2.* R.F.W. Bader, "Vibrationally Induced Perturbations in Molecular Electron Distributions", *Canadian Journal of Chemistry*, **40**, (1962), 1164–1175.
 3. R.F.W. Bader and G.A. Jones, "The Electron Density Distributions in Hydride Molecules, I, The Water Molecule", *Canadian Journal of Chemistry*, **41**, (1963), 586–606.
 4. R.F.W. Bader and G.A. Jones, "The Electron Density Distribution in Hydride Molecules, II, The Ammonia Molecule", *Journal of Chemical Physics*, **38**, (1963), 2791–2802.
 5. R.F.W. Bader and G.A. Jones, "The Electron Density Distributions in Hydride Molecules, III, The Hydrogen Fluoride Molecule", *Canadian Journal of Chemistry*, **41**, (1963), 2251–2264.
 6. R.F.W. Bader, "Binding Regions in Polyatomic Molecules and Electron Density Distributions", *Journal of the American Chemical Society*, **86**, (1964), 5070–5075.
 7. R.F.W. Bader, W.H. Henneker and P.E. Cade, "Molecular Charge Distributions and Chemical Binding", *Journal of Chemical Physics*, **46**, (1967), 3341–3363.
 8. R.F.W. Bader, I. Keaveny and P.E. Cade, "Molecular Charge Distributions and Chemical Binding II. First-Row Diatomic Hydrides", *Journal of Chemical Physics*, **47**, (1967), 3381–3402.
 9. R.F.W. Bader and A.K. Chandra, "A View of Bond Formation in Terms of Molecular Charge Distributions", *Canadian Journal of Chemistry*, **46**, (1968), 953–966.
 10. R.F.W. Bader and A.D. Bandrauk, "Molecular Charge Distributions and Chemical Binding III. The Isoelectronic Series N₂, CO, BF and C₂, BeO, LiF", *Journal of Chemical Physics*, **49**, (1968), 1653–1665.
 11. R.F.W. Bader and A.D. Bandrauk, "Relaxation of the Molecular Charge Distribution and the Vibrational Force Constant", *Journal of Chemical Physics*, **49**, (1968), 1666–1675.
 12. R.F.W. Bader and H.J.T. Preston, "The Kinetic Energy of Molecular Charge Distributions and Molecular Stability", *International Journal of Quantum Chemistry*, **3**, (1969), 327–347.
 13. R.F.W. Bader, I. Keaveny and G. Runtz, "Polarizations of Atomic and Molecular Charge Distributions", *Canadian Journal of Chemistry*, **47**, (1969), 2308–2311.
 14. R.F.W. Bader, P.E. Cade, W.H. Henneker and I. Keaveny, "Molecular Charge Distributions and Chemical Binding IV. The Second-Row Diatomic Hydrides, AH", *Journal of Chemical Physics*, **50**, (1969), 5313–5333.
 15. R.F.W. Bader and J.L. Ginsburg, "Relaxations of Molecular Charge Distributions and the Vibrational Force Constants in Diatomic Hydrides", *Canadian Journal of Chemistry*, **47**, (1969), 3061–3074.
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*This paper presents an early formulation of the symmetry rules predicting the outcome of unimolecular and bimolecular reactions. Kenichi Fukui describes this paper as "the important theory of Bader" in his 1981 Nobel Lecture in the paragraph he devotes to "names which are worthy of special mention".

or an extended system (Eq. (33) of Chapter 1). This result, termed the “atomic virial theorem”, in its turn led to the definition of the energy of an atom within a larger system, for example a molecule or a crystal, i.e. an “atomic energy”. The energy of an atom in a molecule, a very desirable quantity, remained totally elusive until the discovery of the atomic virial theorem, because this energy must, for example, include contributions from the nuclear–nuclear repulsion energy, contributions which are not trivial to partition on an atom-by-atom basis (Chapters 1 and 3).

Bader’s early studies of molecular electron density distributions (Table 1) coincided with the ground-breaking formulation of modern density functional theory (DFT) [16] in 1964 and 1965 by Walter Kohn and his co-workers [17, 18]. Contemporary DFT functionals (for example those developed by Axel Becke [19–22], and Lee et al. [23]) are capable of achieving chemical accuracy and of producing electron-density maps of unprecedented quality, and rapidly.

The advent of DFT, the spectacular increase in the power of computers, and algorithmic advances all led to an explosive growth in the number of studies applying the quantum theory of atoms in molecules to a very wide range of problems (as will be seen in this book) from solid-state physics; to the science of materials; to surface science; to X-ray analyses; to organic, physical–organic, organometallic, and inorganic chemistry; and to biochemistry and drug design. Accurate calculated (and experimental) electron-density maps of larger and larger systems are now routinely computed and analyzed using the QTAIM.

The theory has also benefited significantly from parallel advances in accurate X-ray crystallography. The development of multipolar refinement techniques, pioneered by Hansen and Coppens [24–26], coupled with low-temperature data collection and ever-more sensitive CCD detectors, has enabled crystallographers, for the first time, to obtain high-resolution experimental electron-density maps of quality sufficient to capture the fine details of the electron density in the bonding regions between atoms. Nowadays, crystallographers rely routinely on QTAIM to decode the wealth of chemical information contained in accurate experimental electron-density maps, bringing crystallography and chemical theory closer than ever before (see, for example, Refs [25–28] and the literature cited therein).

Bader’s landmark book [2], which includes (but is more than) an authoritative review of the theory up to 1990, sets forth the development and principles of this theory and explains how the atoms of experiment arise naturally from the laws of quantum mechanics. Since 1990 the field of QTAIM has grown dramatically both conceptually and in terms of the volume of publications and citations, a growth that has been reflected in several reviews (see, for example, Refs [3–6, 25–30]). In 1996, a special issue of the *Canadian Journal of Chemistry* was dedicated to Richard Bader on the occasion of his 65th birthday [31]. The objective of this book is to cover the developments in this field since the publication of Bader’s book.

QTAIM is rigorous, beautiful, and powerful. It provides a unifying thread of physical insight in chemistry, which explains its popularity. The breadth of QTAIM and its applications renders a comprehensive treatment of all its ramifi-

cations impossible in a book of this size. We have therefore *sampled* research in QTAIM by extending invitations to a necessarily incomplete group of world-leading researchers to review their respective contributions to the field. This has resulted in a volume written by fifty authors representing thirteen countries in five different continents (a list of contributors is given below). Despite this impressive list of contributors, we could not possibly have invited all the leaders of the field, unavoidable omissions for which we do apologize. These omissions, however, do not diminish the value of the phenomenal cross-section and depth of current fundamental and applied research in QTAIM that has been captured in this book.

As the editors of this book it is with considerable humility that we start with our own introductory chapter. The *only* reason for this choice is to facilitate the reading of the remainder of the book by introducing the basic concepts and terminology. The order of the other parts and chapters is purely and exclusively based on what we think is their logical order. All chapters, including our own, have been carefully refereed by at least three independent reviewers and were all revised and corrected before final acceptance.

The book is divided into five parts. The introductory chapter is followed by Part II which concentrates on the fundamental advances in the theory itself. Part II reviews the rapid development in the applications of the QTAIM to periodic systems (solid state and surfaces). Part III focuses on developments resulting from the synergy between experimental highly accurate X-ray crystallography and the QTAIM, with particular emphasis on the electron density of large biological molecules. Part VI deals with the wide diversity of applications of the QTAIM in organic, physical organic, and organometallic chemistry, and reviews the characterization of conventional and non-conventional chemical bonding. Part V reports on important developments in the use of QTAIM in the modeling of biological molecules and drug design.

We would like to thank each one of the authors individually for his or her invaluable contribution to this volume, and we thank Professor Axel D. Becke for writing the Foreword. We are much indebted to our publisher, Wiley-VCH, and its staff for their continual support, professionalism, and invaluable help, with special thanks to Nele Denzau, Dr. Tim Kersebohm, Dr. Romy Kirsten, Claudia Nussbeck, Dr. Martin Ottmar, Dr. Gudrun Walter, and Dr. Waltraud Wüst. We are particularly grateful for the care, rigor, and effort of our peer-reviewers (many of whom are also among the authors of chapters in this book): Professor Richard F.W. Bader, Dr. Miguel Blanco, Professor Curt M. Breneman, Dr. Clémence Corminboeuf, Professor Katherine V. Darvesh, Dr. Jason R. Dwyer, Dr. Carlo Gatti, Professor Kathleen M. Gough, Professor Sławomir J. Grabowski, Professor George L. Heard, Professor Jesús Hernández-Trujillo, Dr. Sian T. Howard, Professor Claude Lecomte, Professor Victor Luaña, Professor Peter Luger, Dr. Piero Macchi, Professor Preston J. MacDougall, Professor Louis J. Massa, Professor Angel Martín Pendás, Dr. James A. Platts, Dr. Paul L.A. Popelier, Dr. Kathy N. Robertson, Professor Bernard Silvi, Professor Vladimir G. Tsirelson, and Dr. Elizabeth A. Zhurova – we thank them all.

It is with delight that we dedicate this work to Professor Richard F.W. Bader on the occasion of his 75th birthday.

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Chérif F. Matta and Russell J. Boyd

References

- 1 R.F.W. Bader, G.A. Jones; The electron density distribution in hydride molecules. The ammonia molecule. *J. Chem. Phys.* **1963**, *38*, 2791–2802.
- 2 R.F.W. Bader; *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.
- 3 R.F.W. Bader; The quantum mechanical basis of conceptual chemistry. *Monatsh. Chem.* **2005**, *136*, 819–854.
- 4 R.F.W. Bader; 1997 Polanyi Award Lecture: Why are there atoms in chemistry? *Can. J. Chem.* **1998**, *76*, 973–988.
- 5 R.F.W. Bader, in: P.v.-R. Schleyer (Ed.); *Encyclopedia of Computational Chemistry*; John Wiley and Sons: Chichester, UK, 1998, pp 64–86.
- 6 P.L.A. Popelier; *Atoms in Molecules: An Introduction*; Prentice Hall: London, 2000.
- 7 R.F.W. Bader, P.L.A. Popelier, T.A. Keith; Theoretical definition of a functional group and the molecular orbital paradigm. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 620–631.
- 8 C.F. Matta, R.F.W. Bader; An experimentalist's reply to "What is an atom in a molecule?"; *J. Phys. Chem. A* **2006**, *110*, 6365–6371.
- 9 R.F.W. Bader; Principle of stationary action and the definition of a proper open system. *Phys. Rev. B* **1994**, *49*, 13348–13356.
- 10 R.F.W. Bader; Quantum topology of molecular charge distributions. III. The mechanics of an atom in a molecule. *J. Chem. Phys.* **1980**, *73*, 2871–2883.
- 11 P.F. Zou, R.F.W. Bader; Variational principle and path integrals for atoms in molecules. *Int. J. Quantum Chem.* **1992**, *43*, 677–699.
- 12 R.F.W. Bader, P.M. Beddall; Virial field relationship for molecular charge distributions and the spatial partitioning of molecular properties. *J. Chem. Phys.* **1972**, *56*, 3320–3328.
- 13 R.F.W. Bader, P.M. Beddall, J. Jr. Peslak; Theoretical development of a virial relationship for spatially defined fragments of molecular systems. *J. Chem. Phys.* **1973**, *58*, 557–566.
- 14 S. Srebrenik, R.F.W. Bader; Towards the development of the quantum mechanics of a subspace. *J. Chem. Phys.* **1975**, *63*, 3945–3961.
- 15 S. Srebrenik, R.F.W. Bader, T.T. Nguyen-Dang; Subspace quantum mechanics and the variational principle. *J. Chem. Phys.* **1978**, *68*, 3667–3679.
- 16 R.G. Parr, W. Yang; *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.
- 17 P. Hohenberg, W. Kohn; Inhomogeneous electron gas. *Phys. Rev. B* **1964**, *136*, 864–871.
- 18 W. Kohn, L.J. Sham; Self consistent equations including exchange and correlation effects. *Phys. Rev. A* **1965**, *140 (4A)*, 1133–1138.
- 19 A. Becke; Density-functional thermochemistry.1. The effect of the exchange-only gradient correction. *J. Chem. Phys.* **1992**, *96*, 2155–2160.
- 20 A. Becke; Density-functional thermochemistry.2. The effect of the Perdew-Wang generalized-gradient correlation correction. *J. Chem. Phys.* **1992**, *97*, 9173–9177.
- 21 A. Becke; A new mixing of Hartree-Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- 22 A. Becke; Density-functional thermochemistry.3. The role of exact

- exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- 23** C. Lee, W. Yang, R. Parr; Development of the Colle–Salvetti correlation-energy formula into a functional of the electron-density. *Phys. Rev. B* **1988**, *37*, 785–789.
- 24** N.K. Hansen, P. Coppens; Testing aspherical atom refinement on small molecules data sets. *Acta Cryst.* **1978**, *A34*, 909–921.
- 25** P. Coppens; *X-ray Charge Densities and Chemical Bonding*; Oxford University Press, Inc.: New York, 1997.
- 26** T.S. Koritsanszky, P. Coppens; Chemical applications of X-ray charge-density analysis. *Chem. Rev.* **2001**, *101*, 1583–1628.
- 27** C. Gatti; Chemical bonding in crystals: New directions. *Z. Kristallogr.* **2005**, *220*, 399–457.
- 28** P. Macchi, A. Angelo Sironi; Chemical bonding in transition metal carbonyl clusters: Complementary analysis of theoretical and experimental electron densities. *Coord. Chem. Rev.* **2003**, *238–239*, 383–412.
- 29** R.F.W. Bader; Can there be more than a single definition of an atom in a molecule? *Can. J. Chem.* **1999**, *77*, 86–93.
- 30** R.J. Gillespie, P.L.A. Popelier; *Molecular Geometry and Chemical Bonding: From Lewis to Electron Densities*; Oxford University Press: New York, 2001.
- 31** R.J. Boyd, R.A. McLelland, N.H. Werstiuk (Guest Editors); *Can. J. Chem.* (Special issue dedicated to Professor Richard F.W. Bader) **1996**, *74*(6).

