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On the non-existence of parallel universes in chemistry

Richard F. W. Bader

Abstract This treatise presents thoughts on the divide that exists in chemistry between those who seek their understanding within a universe wherein the laws of physics apply and those who prefer alternative universes wherein the laws are suspended or ‘bent’ to suit preconceived ideas. The former approach is embodied in the quantum theory of atoms in molecules (QTAIM), a theory based upon the properties of a system’s observable distribution of charge. Science is experimental observation followed by appeal to theory that, upon occasion, leads to new experiments. This is the path that led to the development of the molecular structure hypothesis—that a molecule is a collection atoms with characteristic properties linked by a network of bonds that impart a structure—a concept forged in the crucible of nineteenth century experimental chemistry. One hundred and fifty years of *experimental* chemistry underlie the realization that the properties of some total system are the sum of its atomic contributions. The concept of a functional group, consisting of a single atom or a linked set of atoms, with characteristic additive properties forms the cornerstone of chemical thinking of both molecules and crystals and Dalton’s atomic hypothesis has emerged as the operational theory of chemistry. We recognize the presence of a functional group in a given system and predict its effect upon the static, reactive and spectroscopic properties of the system in terms of the characteristic properties assigned to that group. QTAM gives physical substance to the concept of a functional group.

Keywords Electron density · Atoms in molecules · Molecular structure · QTAIM

Present day chemistry

We are at a cross-roads in chemistry, wherein we face a dichotomy in two important areas: in one we must choose between physics, as embodied in the quantum theory of atoms in

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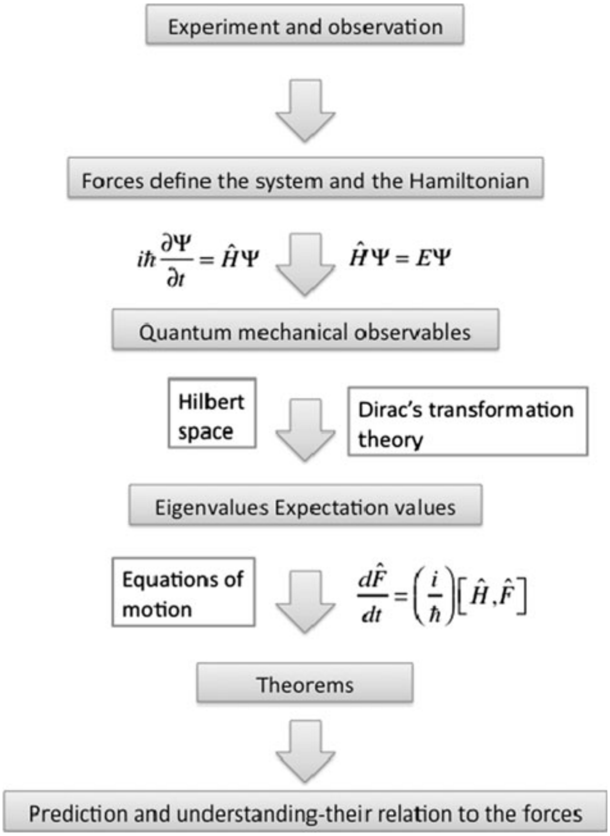
molecules (QTAIM), and those who believe the conceptual basis of chemistry to lie beyond physics, a view subscribed to by Professor Hoffmann, a Nobel Prize winner in chemistry, for example. In the other, we must choose between physics and those who challenge the laws of physics to suit their preconceived ideas. The first of these dichotomies is concisely summarized by Professor Roald Hoffmann in correspondence with the author dated December, 2007: “I also have philosophical reservations about the reductionist framework in which AIM (atoms in molecules) resides; I believe the most interesting ideas of chemistry are not reducible to physics. I think we have a fundament difference of opinion between us on this matter.” This point of view has been addressed in a recent article in Journal of Chemical Physics A (Bader 2010a). The present paper will deal primarily with the second of the dichotomies, challenging those who question the quantum theory of atoms in molecules by demonstrating that they are in effect, questioning quantum mechanics.

Theory of atoms in molecules

It was the development of QTAIM (Bader and Beddall 1972; Srebrenik and Bader 1975; Bader 1990) that bought these dichotomies to the fore. Those who deny the possible existence of a physical basis for the concepts of chemistry are placed directly at odds with QTAIM, whose very existence stems from the discovery that one finds in the observable topology of the electron density, the definitions of atoms, of the bonding between atoms and hence of molecular structure, the conceptual basis of chemistry (Bader et al. 1979a; Bader et al. 1981). By relating these concepts to the electron density, a physically measurable property, the theory provides the necessary link for their ultimate quantum definition, one that follows from the extension of a fundamental statement of physics to an atom in a molecule (Bader and Nguyen-Dang 1981; Bader 1994). Readers of this paper must be prepared to encounter the view that chemistry has been reduced to physics and that the existing language of chemistry stated in terms of models based on valence bond and molecular orbital theories and related notions such as electronegativity, resonance, Coulson’s overlap integral, nonbonded and steric interactions as well as ‘Pauli repulsions’, is to be replaced in its entirety by physics. Thus it is important to begin this treatise with a concise summary of how quantum mechanics is structured to obtain a clear understanding of the manner in which it is applied to the observations one makes on the properties of matter to obtain their fullest possible physical understanding. It is possible for a reader not well versed in the language of quantum mechanics to skip the next section and proceed directly to the discussion of its consequences for chemistry which follows.

The operational structure of quantum mechanics

The underlying structure of quantum mechanics is illustrated in Scheme 1, one that stresses that all of physics, that certainly includes chemistry, originates in experiment followed by observation, observations that are then subjected to theoretical analysis. A system is defined by its forces, the forces determining the Hamiltonian in Schrödinger’s equation. The molecular Hamiltonian that is of interest here, is expressed in terms of the potential energy operators determined by the Coulombic forces between the electrons and nuclei, each system being identified by its unique nuclear-electron potential, the ‘external potential’ of density functional theory. The resulting state vector or wave function is expressed as a linear superposition of base states spanning the Hilbert space. Dirac defines an observable to be a linear Hermitian operator expressible in terms of the dynamical



Scheme 1 The operational structure of quantum mechanics

(position and momentum) variables with a complete set of eigenfunctions, the base states that are employed in the representation of the state vector, a definition prompting the usage 'Dirac observable' (Dirac 1958). A change in representation of the state vector from one set of base states that are eigenfunctions of one particular set of commuting observables, to another, is accomplished using Dirac's transformation theory. There is a Dirac observable associated with every property and it acts on a state vector to yield eigenvalues or expectation values that may or may not be measurable. Each observable obeys a Heisenberg equation of motion and it is these equations that yield the theorems of quantum mechanics, examples being the virial theorem and the Ehrenfest and Feynman force theorems. Through these theorems, one is able to predict and understand the properties of a system and relate the values of the observables to the forces that define the system.

In 1933 Dirac published a very important paper entitled "The Lagrangian in Quantum Mechanics" publishing the paper in a new Soviet journal where it remained essentially buried for a number of years (Dirac 1933). After outlining why the Lagrangian formulation of classical mechanics should be considered more fundamental than the approach based on Hamiltonian theory, Dirac went on to say 'For these reasons it would seem desirable to take up the question of what corresponds in the quantum theory to the Lagrangian method of classical mechanics'. Spurred by this paper, Feynman and Schwinger later demonstrated how the classical action principle embodied in the Lagrangian approach to physics could be generalized to obtain its quantum analogue. Dirac's suggestion led to Feynman's path integral formulation in 1949 (Feynman 1948) and to Schwinger's principle of stationary action in 1951 (Schwinger 1951). Schwinger's reformulation of physics, which is a differential statement of Feynman's path integral, combines the principle of least action with Heisenberg's equation of motion for the quantum observables, thus providing "all of physics" in a single statement. Remarkable as this is, Schwinger's new formulation does much more; it enables the extension of quantum mechanics as outlined in Scheme 1 to an open system (Bader and Nguyen-Dang 1981; Bader 1994; Bader et al. 1978). This is a necessary step in the generalization of quantum mechanics to an atom in a molecule, the atom necessarily being an open system as it may exchange mass and momentum with its bonded neighbours. Schrödinger's equation is again obtained for the *total* system in the extension of his principle to an open system. The expectation values and associated equations of motion for each Dirac observable are defined for the open system, a bounded piece of the total system (Bader 1994). It is the extension of Schwinger's principle to an open system—a direct result of Dirac's 1933 paper—that forms the basis for QTAIM by providing the quantum mechanical description of an atom in a molecule (Bader 1990).

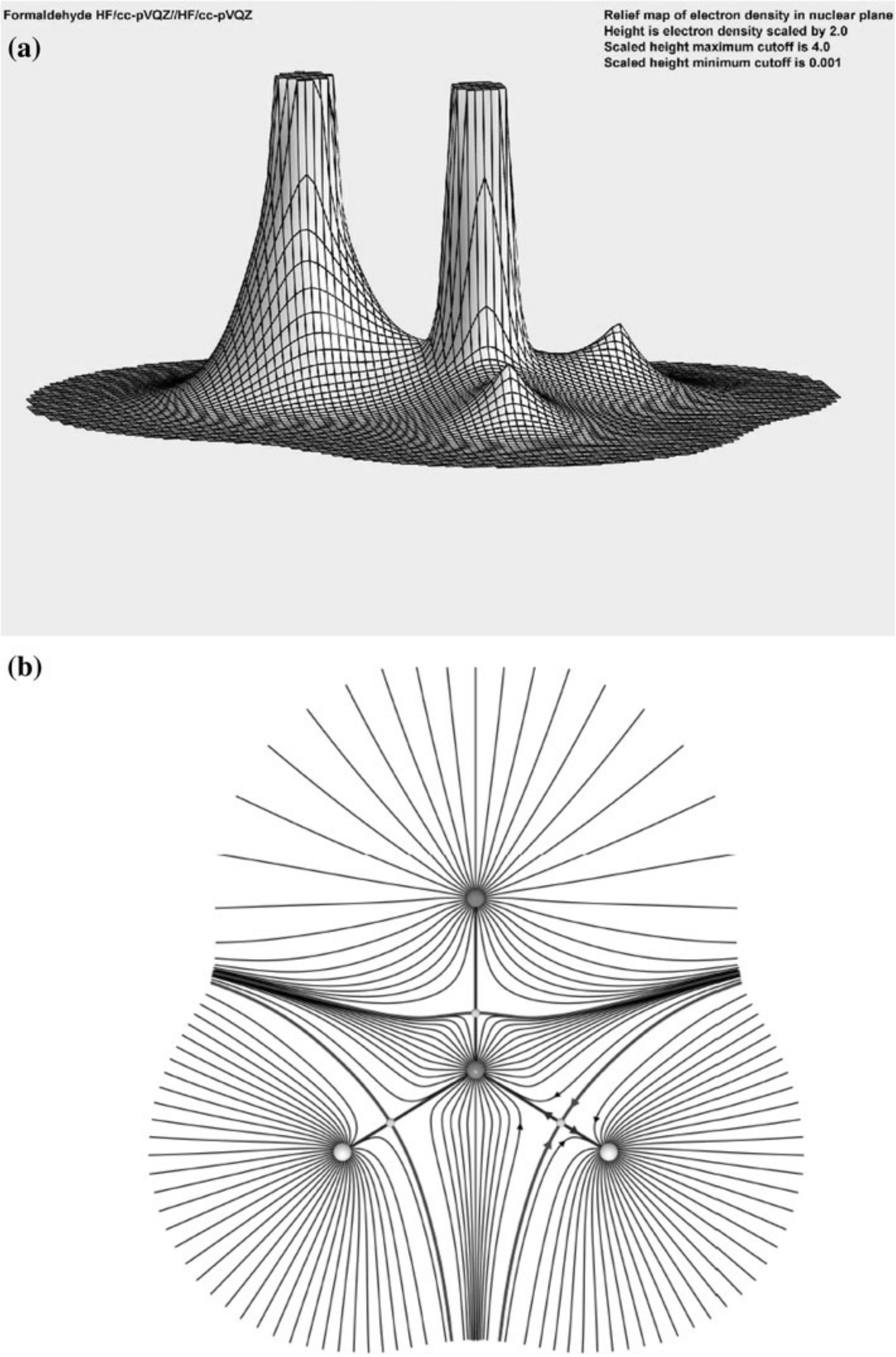
Definition of an atom in a molecule

It is over two hundred years since Dalton proposed his atomic theory based on the observations of relative combining weights of the elements and the prediction of the law of multiple proportions (Dalton 1808). The vindication of Dalton's assumptions had to await 100 years for Rutherford to propose his nuclear model of the atom, thereby validating Dalton's assumed constancy in the atom's mass and the retention of its chemical identity throughout chemical change. It is Rutherford's nuclear model that gives rise to the atomic concept in chemistry, a consequence of the dominance of the nuclear–electron (n–e) attractive force resulting from the point-like nuclei attracting the relatively diffuse spatial distribution of electronic charge described by the experimentally measureable electron density, $\rho(\mathbf{r})$ (Coppens 1997; Tsirelson and Ozerov 1996). Because of the dominance of this force, which acts in opposition to the electron–electron (e–e) and the nuclear–nuclear (n–n) forces of repulsion, $\rho(\mathbf{r})$ exhibits local maxima at the positions of the nuclei and each atom is stamped by its own chemical identity. This all important property of the electron density is illustrated by its portrayal for the formaldehyde molecule CH_2O in Fig. 1a.

The electron density

The spatial distribution of electronic charge in the field of the nuclei and its flow in the presence of external fields are the physical manifestations of the forces operative in matter

Fig. 1 **a** A relief map of the density in the plane of the nuclei for CH_2O. The nuclear maxima in the density at O and C have been terminated at 4 au (atomic units) and the map boundary at $\rho = 0.001$ au. Note the presence of 'saddles' in the density between bonded atoms. The presence of maxima in the density at the positions of the nuclei is the dominant topological feature of the electron density and is responsible for the atomic form of matter. **b** A map of the trajectories traced out by the gradient vectors of $\rho(\mathbf{r})$ in the field of the nuclei in CH_2O. Members of the infinite set of trajectories terminating at each nucleus, as indicated by the *arrow heads* on two such pairs, define the atomic basins. The (3,−1) or bond cps are denoted by *dots* located between the nuclei. Two members of the infinite set defining the interatomic surface between each pair of bonded nuclei that terminate at each such cp are appear in the plane of the figure, as indicated for one such pair between C and one H, by *arrow heads*. The same cp serves as the origin for the unique pair of trajectories that originate there and terminate at the neighbouring nuclei defining the bond path, as indicated by *arrow heads* for the same C|H pair of atoms. This behaviour is universal ►


Formaldehyde HF/cc-pVQZ//HF/cc-pVQZ
(a)
Relief map of electron density in nuclear plane
Height is electron density scaled by 2.0
Scaled height maximum cutoff is 4.0
Scaled height minimum cutoff is 0.001
(b)

and they determine the form of matter in real space. It therefore should come as no surprise that the electronic charge and current distributions serve as the carriers of physical information, the topology of the electron density $\rho(\mathbf{r})$ reflecting and encoding the concepts of atoms, bonds, structure, and structural stability, the current $\mathbf{j}(\mathbf{r})$ providing an understanding of the magnetic properties of matter. Their use in a theory of atoms in molecules enables one to link the language of chemistry with that of physics. The electron density provides a physical model of matter, one in which point-like nuclei are embedded in a relatively diffuse, spatial distribution of negative charge—the density of electronic charge—a distribution that is static for a system in a stationary state and one that changes in a continuous manner during any adiabatic change, i.e., one that does not involve a change in the electronic state of the system.

The electron density in a stationary state is not a probability distribution, an interpretation that is inconsistent with the role $\rho(\mathbf{r})$ plays in the determination of the properties where electrical moments are obtained by averaging the appropriate operator over the static charge distribution. More important, the probabilistic interpretation is inconsistent with the measurement of the electron density by the *elastic scattering* of X-rays from crystals, since no excited states are involved in the scattering process, as required by the Born probabilistic postulate (Coppens 1997).

The electron density was defined by Schrödinger in his fourth and final paper published in 1926 and, aside from including electron spin, is the accepted definition of $\rho(\mathbf{r})$, the expression given in Eq. (1) in terms of a many-electron wave function ψ (Schrödinger 1926),

$$\rho(\mathbf{r}) = N \int d\tau' \psi^* \psi \tag{1}$$

The symbol $N \int d\tau'$ implies a summation over spins followed by integration of the product $\psi^* \psi$ over the coordinates of all N electrons but one, whose position $\mathbf{r}$ is fixed at a point in space, an integration procedure that is followed throughout QTAIM to obtain density distributions for all properties. Schrödinger, in the same paper, defined the current density $\mathbf{j}(\mathbf{r})$ describing the flow of $\rho(\mathbf{r})$ and the equation of continuity linking them. This aspect of the theory, including the Born postulate, has been recently discussed (Bader 2010b).

Topology of the density

The dominance of the n–e attractive force enables the extension of quantum mechanics to an atom in a molecule by imposing on the density a universal topological property that serves as the quantum boundary condition for an open system. This is a much reviewed topic (Bader 1990) and only the major points are summarized here, the conciseness of the summary being made possible by the very dominance of the n–e force. The topology of $\rho(\mathbf{r})$ is brought to the fore in terms of its gradient vector field, the field generated by the paths traced out by the trajectories of the gradient vector $\nabla\rho(\mathbf{r})$. A trajectory of $\nabla\rho(\mathbf{r})$ points in the direction of maximum increase in $\rho(\mathbf{r})$ and hence all of the trajectories of $\nabla\rho(\mathbf{r})$ in the vicinity of a given nucleus terminate at the nucleus and as a consequence, space is exhaustively partitioned into mononuclear regions. An atom is defined as the union of the nucleus and its associated basin, the region of space traversed by the set of trajectories that terminate at the nucleus, the nucleus acting as an attractor in the gradient vector field. This property of the density is illustrated by the map shown in Fig. 1b.

The interaction of two atoms at any separation results in the formation of a critical point (cp) in the electron density, a point where its gradient vanishes, $\nabla\rho(\mathbf{r}) = \mathbf{0}$. In two-dimensions the cp has the appearance of a saddle, as displayed for the C–O and C–H interactions in the formaldehyde molecule, Fig. 1(a). The curvature of the density at the cp along the line connecting two nuclei is positive—the density is a minimum along this line at the cp and the trajectories originate at the cp, while the two curvatures on axes perpendicular to it are negative and the trajectories terminate there, since the density is a maximum at the cp in these directions. It is classified as a (3,−1) cp, a cp with a rank of three, the signs of the three curvatures summing to −1. The behaviour of the trajectories associated with a (3,−1) cp are illustrated in Fig. 1b.

It is also clear from Fig. 1b that each atomic basin is bounded by an infinite set of trajectories that terminate at a (3,−1) cp that constitute the definition of an interatomic surface. The sets of trajectories that define the interatomic surfaces of the atoms bonded to one another in the formaldehyde molecule are displayed in three-dimensions in Fig. 2. The interatomic surfaces are surfaces of zero-flux in $\nabla\rho$, that is, they exhibit the important property of not being crossed by any trajectories of $\nabla\rho$. (The reader is asked to recall that $\nabla\rho(\mathbf{r}) = \mathbf{0}$ at a critical point.) It is this 'zero-flux' property of the interatomic surfaces expressed in Eq. (2), which serves as the quantum boundary condition for an atom A in a molecule,

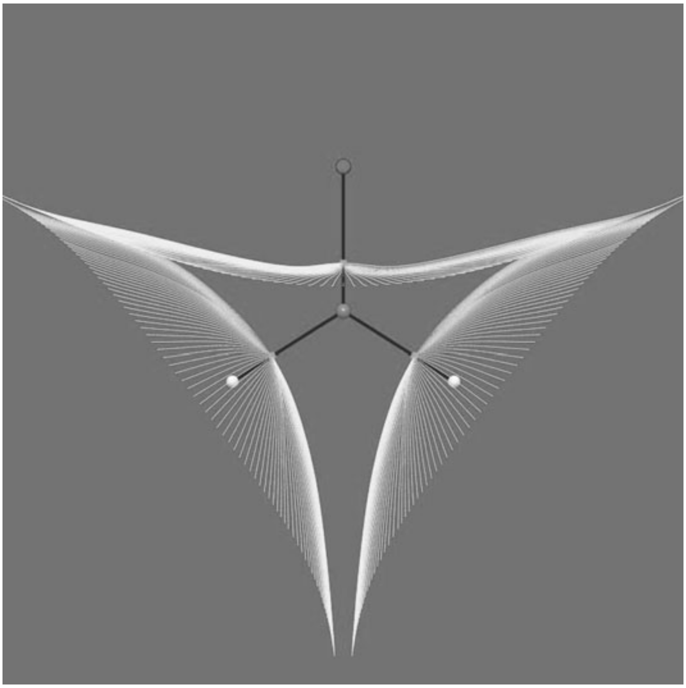


Fig. 2 A three-dimensional display of the interatomic surfaces defining the basins of the H, C and O atoms that are defined by the sets of trajectories that *terminate* at each bond critical point. The bond paths defined by the pairs of trajectories that *originate* at the bond critical point and terminate at the adjacent nuclei are also indicated. The shapes of the surfaces are characteristic for each atomic interaction

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})=0 \quad \text{for all points } \mathbf{r} \text{ on the surface } S(A;\mathbf{r}) \tag{2}$$

with $\mathbf{n}(\mathbf{r})$ denoting a unit vector normal to the surface S(A;**r**) at the point **r**. Thus one has the important result that regions of space containing a single nucleus are bounded by surfaces through which there is a 'zero-flux' in the gradient vector field of the density. As demonstrated in "Time to choose between single- and multi-universes", it is this topological property of the *measurable* density $\rho(\mathbf{r})$ that enables the extension of quantum mechanics to an open system—to an atom in a molecule. Atoms are real (Matta and Bader 2006). They exist in real space with definable properties whose additive contributions determine the measurable properties of every system.

Definition of molecular structure

Figure 1b demonstrates that the (3,−1) cp serving as the terminus for the trajectories that define an atomic surface, also serves as the origin for a pair of trajectories that terminate at the neighbouring nuclei. They define a line along which the density is a maximum with respect to any neighbouring line; they define an *atomic interaction line*. It is important to recall that this is a consequence of the ubiquitous physical signature that the interaction of two atoms creates in the electron density, the formation of a (3,−1) cp. One each, of this unique pair terminates at the neighbouring nucleus where the density exhibits its maximum value. In an equilibrium geometry or one in which attractive forces act on the nuclei so as to draw them together, such a line is called a bond path and the associated cp is termed a bond cp (Coulson and Buckingham 1975; Runtz et al. 1977). When encountering statements that a bond path is found to link atoms in 'clearly repulsive situations', the reader is asked to keep this proviso of the absence of any definable repulsive physical force in mind. Any repulsive forces invoked in such criticisms are necessarily fictitious, being undefined by quantum mechanics. It is difficult to account for the persistence of such unfounded criticisms in any branch of science, but as demonstrated in this treatise, they are common throughout interpretive chemistry wherein undefined 'Pauli, exchange, steric or non-bonded' forces of repulsion are commonly invoked.

The linked set of bond paths defines a molecular structure, as shown in Fig. 1b (Bader 1990; Bader et al. 1981). A scalar field in R^3 exhibits four possible 'stable' critical points which, labeled by their rank and signature, are: (3,−3) denoting a nuclear position; (3,−1) a bond critical point; (3,+1) a ring cp, whose presence denotes the existence of bonded ring of atoms; (3,+3) a cage cp, whose presence denotes the existence of a region of space bounded by at least two rings (Collard and Hall 1977). A molecular structure defined in this manner recovers all known 'classical' (i.e, textbook) chemical structures that are obtained by linking atoms with lines representing chemical bonds. There are no exceptions to be found in either experimentally measured or theoretically determined densities (Bader 1990) a topic recently reviewed (Bader 2010a). Equally important, there are no cases wherein a bond is postulated in the absence of a bond path. Figure 3 displays molecular graphs for metal carbonyl and cyclopentadienyl complexes, the latter displaying both ring and cage structures (Cortés-Guzmán and Bader 2005).

It is the definition of the atom that is of paramount importance. The presence of the bond path is but a useful way of depicting and summarizing which pairs of atoms share an interatomic surface. That this shorthand notation mimics the way in which the same information is conveyed by the classical structures that evolved from experimental chemistry is surely one of the most powerful of all the physical vindications of the zero-flux boundary condition.

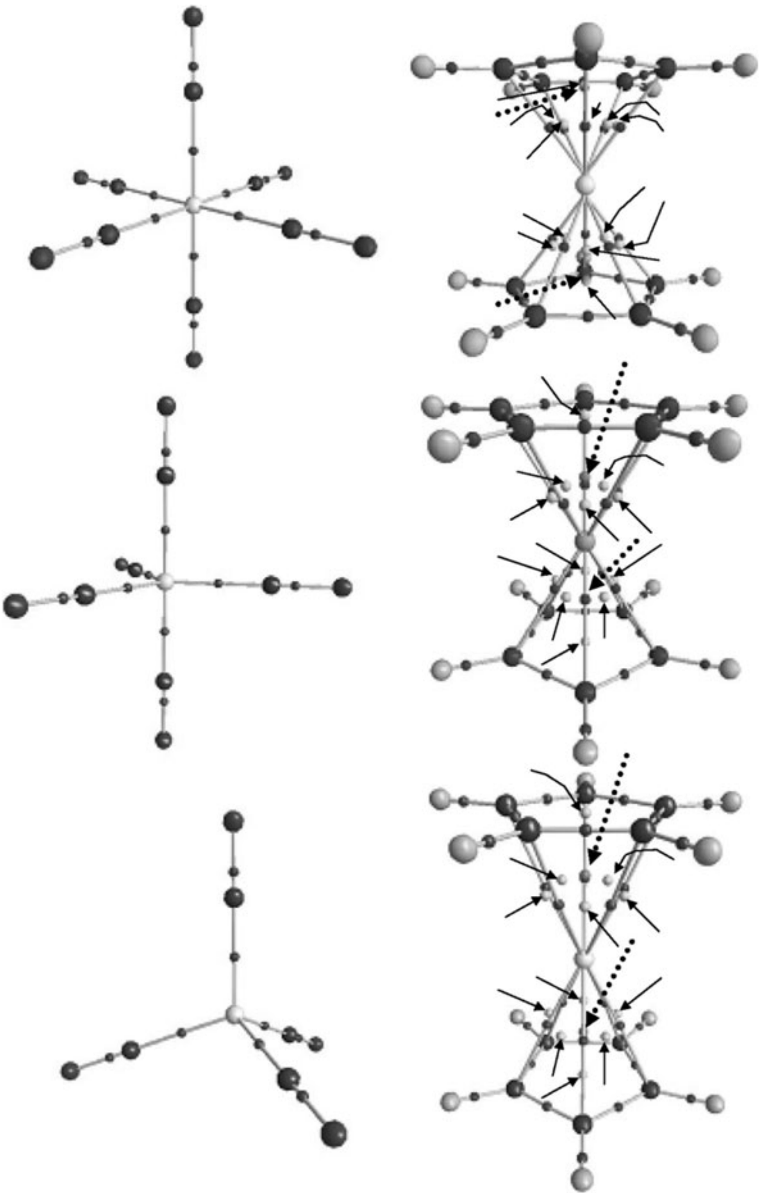


Fig. 3 Molecular graphs of the carbonyl complexes of Cr, Fe and Ni in descending order on the left, and of the metallocenes of Fe, Al^+ and Ge on the right. The scheme for identifying the critical points in the metallocenes is as follows; the (3,−1) or bond cps are denoted by *dots*; (3,+1) or ring cps are denoted by *straight arrows*; (3,+3) or cage cps by a *dotted arrow*. The nuclear maxima, denoted by *larger spheres*. The alternating bond and ring cps resulting from the bonding of M to the carbons in the metallocenes denote a ring of almost constant density and a corresponding delocalization of the bonding density over the ring surfaces

It is at this point, where one has arrived at a physical mapping of molecular structure onto an observable topological feature of the electron density, that reference should be made once again to a recent statement by Hoffmann: “Chemistry has done more than well in creating a universe of structure and function on the molecular level with just this “imperfectly defined” concept of a chemical bond. Or maybe it has done so well precisely because the concept is flexible and fuzzy.” This statement is made in a paper entitled ‘A bonding quandary—a demonstration that scientists are not born with logic’ (Alvarez et al. 2009).

The belief in the credo of science, that what one observes is determined by the properties of the system one is observing, provides an immediate counter argument to this statement; to wit, ‘that chemistry has done so well precisely because the models of bonding coupled with experimental observation were in effect achieving a successful one-to-one mapping of ‘chemical bonds’ onto an observable physical property of a molecule—that bonded atoms are linked by lines of maximum electron density. Thus the mapping of a ‘classical molecular structure’ onto a molecular graph, whose existence is predicted by theoretical studies of the electron density, is complete and confirmed by observation. Chemistry does not advance through ‘fuzzy thinking’, but rather by observation followed by appeal to theory. There is a clear, *logical* connection between the concept of a bond and an observable bond path. One may in fact, define a *bond path operator* as a Dirac observable by having the density operator project the density along each of the trajectories that originate at the bond critical point and terminate at the neighbouring nuclei. Thus the bond path is the *measured* consequence of the action of a quantum mechanical observable (Bader 2009a).

The reductionist approach afforded by QTAIM offers a clear solution to the myriad of personal views and models of bonding. As has been amply demonstrated by appeal to physics, the presence of a bond path linking a pair of atoms fulfills the sufficient and necessary conditions that the atoms are bonded to one another (Bader 1990; Bader et al. 2007; Cortés-Guzmán and Bader 2005; Hernández-Trujillo et al. 2007). This definition, which necessarily applies to quantum mechanical densities, transcends all bonding schemes and categories and provides a unified physical understanding of atomic interactions. One assumes such unification to be a primary goal of any physical theory.

As nuclei execute spatial motions, the density may undergo catastrophic, discontinuous changes, causing a change in the molecular structure. These topological changes and the ensuing changes in structure are all predicted and quantified using the mathematics of qualitative dynamics and one obtains a complete theory not only of molecular structure, but of structural stability (Palis and Smale 1968; Thom 1975), as well. A reader interested in obtaining a clear understanding of the ‘making and breaking of chemical bonds’ is referred to the monographs dealing with this aspect of the theory (Bader et al. 1979b, 1981). The existence of fluxional molecules and their readily interchangeable possible structures are readily predicted and accounted for by the nuclear induced relative motions of critical points in close proximity (Brown et al. 2009; Salinas-Olvera et al. 2008).

Where do valence bond and molecular orbital theories fit in Scheme 1

With this introduction to QTAIM, we turn to the question of where valence bond and molecular orbital theories fit in the general scheme of quantum mechanics. These theories provide different starting points for obtaining approximate solutions to Schrödinger’s equation and thus they enter Scheme 1 immediately following the identification of the Coulombic forces acting in a molecular system. This relegates them to the determination of the wave function for its use in determining the expectation values and equations of motion for the observables that determine the measured properties. This is the procedure recommended by Schrödinger in his fourth paper in 1926, wherein he derived the expressions for the electron density, the vector current density and the equation of continuity connecting them (Schrödinger 1926). In this paper he specifically warns against the use of the wave function for other than the determination of the electron and current densities whose use he championed in the understanding the properties of matter. The wave function is of course, essential to the determination of the eigen- and expectation values of observables and their subsequent use in the theorems of quantum mechanics, the path followed in QTAIM, but his advice that one avoid using ψ directly in the interpretation of physical observations and instead relegate it to the purpose of determining expectation values, including the density $\rho(\mathbf{r})$, was not followed resulting in a delay in relating the chemical concepts of atoms and bonding to a system's charge distribution.

The role of molecular orbital theory extends beyond providing approximate wave functions. It is indispensable to the understanding of many-electron systems. Orbitals are one-electron states that are used to construct Slater determinants that span the Hilbert space or a truncated portion of it, determinants that are used to approximate the wave function of a many-electron system. Molecular orbital (MO) theory, Hartree–Fock and beyond, and more recently, orbital-based density functional theory (Kohn and Sham 1965), are the procedures presently used to obtain approximate wave functions. Most importantly, MO theory provides the prediction, ordering and classification of many-electron states in terms of the component one-electron states, as developed in the early papers of Mulliken (1928, 1930, 1931 and Hund (1927), work that provides the link with experimental spectroscopy, as admirably illustrated by Herzberg (1950). Changes in the occupations of the Hartree–Fock canonical orbitals may be directly associated with the generation of particular ionized or excited states. Molecular orbital theory enables one to determine the energy ordering of transition densities that may be usefully approximated by the product of orbitals undergoing a change in occupation for use in symmetry rules based on the second-order Jahn–Teller effect (Bader 1960, 1962). This paper presents an orbital correlation diagram from reactants to transition state to products that demonstrates how in an allowed reaction, a new low-lying excited state is generated as a consequence of the non-crossing rule for orbitals of the same symmetry, creating a transition density that facilitates the motion of the system over the energy barrier) or on the conservation of orbital symmetry (Woodward and Hoffmann 1970). The eminently useful predictive models that come from MO theory exemplify its proper use: the prediction of a molecule's electronic structure by the successive occupation of the orbitals.

One finds statements to the effect that QTAIM requires that one give up mo theory, which are of course, untrue. Molecular orbital theory is a branch of quantum mechanics and all its predictions may be reformulated in terms of atomic contributions using QTAIM. All physically sound models derived from orbital arguments, those that relate to measurable properties, are recovered by the physics of an atom in a molecule. These include the hybridization model as applied to atomic stability (Bader et al. 1990; Wiberg et al. 1987), homoaromatic conjugation (Bader et al. 1983; Cremer et al. 1995), 'resonance' (Bader 1998) and strain energies (Wiberg et al. 1987; Cortés-Guzmán and Bader 2004), NMR deshielding of an aromatic proton (Keith and Bader 1996), confirmation of the presence of the Chatt-Duncanson model of $d\pi - p\pi^*$ back-bonding in the quadrupolar polarization of the ligand density (Cortés-Guzmán and Bader 2005) and the predictions of frontier orbital theory (Bader et al. 2004), to cite a few examples. One is not asked to give up orbital models, but rather to relate them more directly to the underlying physics.

An excellent example of QTAIM replacing orbital models that fell short of accounting for the physics (Ditchfield 1974; Kutzelnigg 1980) is its determination of the current density induced by an external magnetic field. QTAIM overcomes the so-called 'gauge origin' problem by bypassing orbitals and proceeding directly to the observable physics, the determination of the induced current. This is achieved by the extension of the idea of assigning a gauge origin an atom at a time (Keith and Bader 1992), to its limit of using a continuous set of gauge transformations (CGST) (Keith and Bader 1993) to obtain for the first time displays of the induced current that satisfies the necessary condition for the conservation of electronic charge—that the divergence of the current vanish. The CSGT method provided the first representations of the induced current that could be topologically analyzed (Keith and Bader 1993) (the reader is referred to the resulting beautiful, published displays of the current including the induced ring current in benzene) that give visualization to all of the magnetic properties associated with the induced current (Bader and Keith 1993; Keith and Bader 1996).

Why were the electron and current densities overlooked?

The recovery of all classical structures by corresponding molecular graphs, in both theoretically and particularly in experimentally determined densities, would appear to vindicate the association of structure with the topology of the density (Bader 2010a). The acceptance is however, not universal for reasons that are historically understandable in terms of past examples of observation requiring the extension or modification of existing models requiring a change in the existing paradigms. Relating structure to a topological property of the electron density necessarily broadens the scope of the concept of structure, extending it beyond the models that were used in its development. Just as the models of valence were expanded to meet the new requirements of structure that accompanied the increasing ability to experimentally determine the observation of 'novel structures' such as the O_h structure of SF_6 requiring the relinquishment of the octet rule by the extension of the hybridization model, the acceptance of closed-shell bonding in hydrogen bonding, and the introduction of three-centre two-electron bonding—so the topology of the density reveals the presence of bond paths in situations where they were similarly not predicted by the Lewis model or its extensions. Such a finding should be anticipated, as all models provide but an incomplete picture of the underlying physics, a situation encountered throughout science. The following introduction to the mechanics of bonding will demonstrate that all bonding, whether it be intra- or inter-molecular, has a common physical origin, one that does not allow for the exclusion of any measured molecular interactions.

Historically, one can trace the shunning of the density in favor of the wave function in the period following the advent of Schrödinger's 'wave equation' in 1926 (Schrödinger 1926) to a paper that appeared the following year by Heitler and London (1927) wherein they applied the wave equation to the hydrogen diatomic molecule and demonstrated that quantum mechanics could account for 'covalent' bonding, as opposed to ionic bonding, which at the time was readily explained in terms of electrostatics. The Heitler–London (H–L) paper expressed the wave function for H_2 as a combination of two atomic-like terms: a(1)b(2) assigning electrons 1 and 2 to atoms 'a' and 'b' and the term a(2)b(1) where the electronic positions are exchanged between the atoms. This process was likened to quantum mechanical resonance [although H–L went to some lengths in their paper to counter this analogy (Bader 2009b)] and the interpretation of bonding in terms of the wave function and 'resonance' were to dominate theory from that moment on to the present day, as exemplified in the recent statement: 'which showed that the bond energy in H_2 is due to resonance between the electrons as they exchange positions between the two atoms' (Shaik 2007). London noted in 1928 that the physical consequence of 'resonance' was the accumulation of density between the nuclei (London 1928), something that all wave functions that account for bonding predict, and bonding is not uniquely linked to 'resonance'. Schrödinger's advice that one relegate the use of the of the wavefunction to the determination of the electron and current densities to avoid using ψ directly in the interpretation of physical observations (Schrödinger 1926) was not followed and experimental chemistry is presently explained using empirical concepts, many of which do not relate directly to any measureable property nor to quantum mechanical theorems.

It is surprisingly little known that the fundamental role of the density in understanding chemical bonding was first pointed out by London in 1928 in a companion paper to the one he co-authored with Heitler giving the quantum mechanical description of homo-polar bonding (London 1928). London gave contour diagrams of the density distributions associated with the symmetric and antisymmetric solutions to the Heitler–London (H–L) equations. His diagrams which give the first calculated representations of $\rho(\mathbf{r})$, have been recently reproduced (Bader 2009b). London, in describing the symmetric ground state density notes that as the two atomic densities draw closer they tend to become one in opposition to that obtained for the antisymmetric excited state where they are clearly pushed outward, as if they would separate if possible. Thus he states: “With the help of these figures, one can imagine how in complicated molecules the atoms which form a valence are connected by such a bridge of $\psi^*\psi$-density, while all remaining atoms stay separate.” His figure for the symmetric state clearly illustrates the build-up of density between the nuclei, a situation commented on by Feynman: “In a H_2 molecule for example … the (H–L) symmetrical solution can easily permit charge concentration between the nuclei and hence it is the only solution which is symmetrical that leads to strong attraction, and the formation of a molecule, as is well known.” London was the first to define a bond path as a ‘bridge of density’ and to postulate its physical significance in the understanding of bonding. Unfortunately, this paper went unheeded (and remained so for 80 years) and instead the chemical community embraced the ‘mysterious wave function’ and its associated ‘resonance’. It has in fact been stated by a proponent of this view that the bonding process is too complicated to be understood by the average chemist, the concept of a wave function being “too abstract and too elusive” for chemists to grasp! (Frenking 2003).

Quantum definition of an atom in a molecule

The characterization of bonding in terms of the electron density began with the study of the densities obtained from the near Hartree–Fock wave functions obtained at the Mulliken-Roothaan Laboratory of Molecular Structure and Spectra (LMSS) at the university of Chicago beginning in the 1960s (Cade and Huo 1973, 1975; Cade and Wahl 1974). One need only view the molecular densities and their density difference or ‘bond density’ maps with the accompanying discussions of the Feynman forces to understand the conclusion that the density held the key to the understanding of chemical bonding (Bader et al. 1967a, b; Bader and Bandrauk 1968; Cade et al. 1969) as exemplified by contrasting the density difference maps for N_2 and LiF, Fig. 4 (Bader et al. 1967a; Bader 1970, 2010, 2010). The study of the LMSS densities provided the first exhaustive, systematic study of molecular charge distributions and they set the stage for the development of the theory of atoms in molecules, the result of a crucial observation regarding the paralleling behaviour of the electronic and kinetic energy densities (Bader and Beddall 1972). The kinetic energy is determined by the expectation value of a one-electron operator and it can be expressed as a density distribution in real space. This is most usefully done in terms of its positive definite form $G(\mathbf{r}) = {}^1\!/_2\hbar^2\nabla\psi \cdot \nabla\psi$ as introduced and studied in 1969 and discussed in the Supplementary Material (Bader and Preston 1969). In many-electron systems, a contour map of G($\mathbf{r}$) resembles a corresponding map for $\rho(\mathbf{r})$, with maxima at the positions of the nuclei.

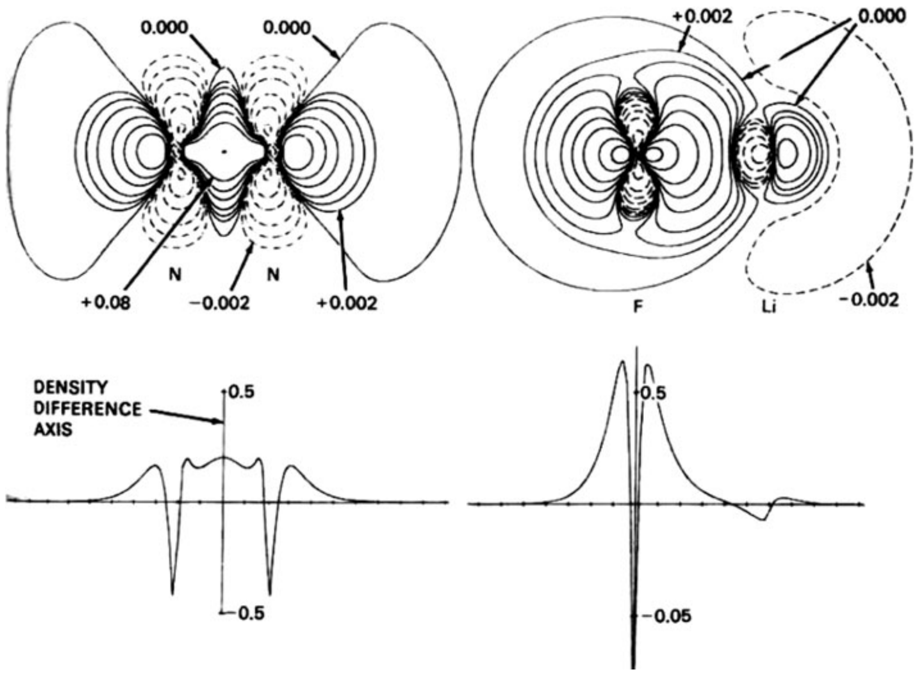


Fig. 4 Density difference maps for ground states LiF and N_2 calculated from separated atoms in their proper valence states, i.e, the states that the atoms dissociate into. The atoms are bound by the density shared by both nuclei in the binding region of N_2 and by the density localized on the F atom in LiF with atomic charges q(X) ± 0.94e. Note that both atomic distributions in LiF are polarized in a direction opposite to the transfer of electron density, as required to balance the Feynman forces on the nuclei and account for the dipole moment being reduced from the spherical ion value of eR = 7.3 debyes (assuming q(X) ± 0.94e) debyes to 7.1 debyes

In 1972 the electron density $\rho(\mathbf{r})$ and the kinetic energy density $G(\mathbf{r})$, were found to be equally transferable over open systems bounded by zero-flux surfaces, Eq. (2), a surface found to maximize the transferability of their charge density (Bader and Beddall 1972). Equally important was the accompanying observation underlying the concept of a functional group: that atoms or linked groupings of atoms, bounded by zero-flux surfaces, can exhibit characteristic forms and properties in spite of gross changes in their immediate neighbours. This paralleling behaviour of $\rho(\mathbf{r})$ and $G(\mathbf{r})$ was the crucial *observation* that led to the theory of atoms in molecules, as deduced from the following chain of reasoning. The virial theorem for a system governed by Coulombic forces states that the total energy of a molecule in electrostatic equilibrium (no Feynman forces acting on the nuclei) equals the negative of the average kinetic energy of the electrons, $E = -T$. If the virial theorem exists for an atom Ω molecule—that is, for a region of space bounded by a zero-flux surface—one could use this theorem to define $E(\Omega)$, the energy of an atom in a molecule, as $E(\Omega) = -T(\Omega)$. Since $T(\Omega)$ is additive, the same additivity applies to $E(\Omega)$ and the energy of a molecule would be given by the sum of its atomic contributions, $E = \Sigma_{\Omega} E(\Omega)$. The existence of the atomic virial theorem was proven a few years later in 1975 for an open system bounded by a zero-flux surface (Srebrenik and Bader 1975) by an extension of Schrödinger's original derivation of the 'wave equation' (Schrödinger 1926). It provides a unique physical partitioning into atomic contributions of all of the electrostatic interactions, both repulsive and attractive, between the nuclei and the electrons.

The identification of E(Ω) with—T(Ω) has a number of important consequences. A statement of the virial theorem for the topological atom predicts that when the form of an atom in real space remains unchanged on transfer, so does its contribution to the total energy. That is, based on these *observations*, the energy of an atom and thus its other properties, would be transferable to the same extent as is its charge distribution. The identification $E(\Omega) = -T(\Omega)$ satisfies in a single stroke the two essential requirements of the atoms of 'conceptual chemistry'—additivity and transferability of properties. It is common sense that two identical pieces of matter must possess identical properties and consequently, two atoms possessing identical charge distributions, that is, atoms indistinguishable in real space, must exhibit identical properties (Bader 1990). Atoms in molecules resulted from a mapping of chemical concepts onto the observed properties of the density.

Thus QTAIM enables one to determine the expectation values of all observables for an atom in a molecule, as for example the Cr atom in the molecule $Cr(CO)_6$ shown in Fig. 5, bounded by its six 'zero-flux' surfaces whose molecular graph is shown in Fig. 3. In all cases where atomic or group properties are found to be experimentally additive; heats of formation—including measured strain and 'resonance' energies; magnetic susceptibilities, including aromatic exaltation; polarizabilities, infrared atomic polar tensors, volumes etc.,

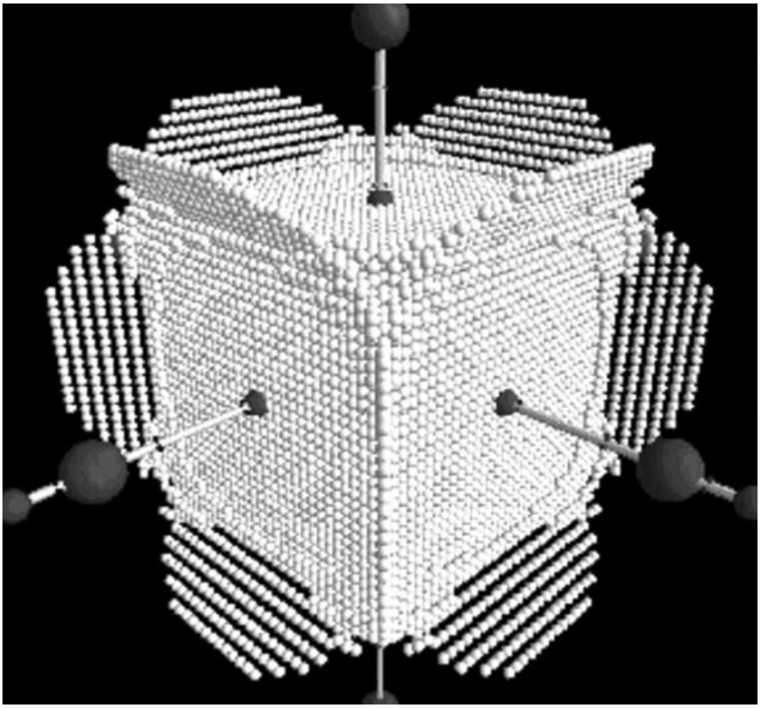


Fig. 5 Three of the six surfaces bounding a Cr atom in $Cr(CO)_6$, a molecule with D_{6h} symmetry, are shown. All of the properties of this enclosed region are defined by quantum mechanics and they make additive contributions to the properties of the complex. It is shown that the principal source of bonding in $Cr(CO)_6$ is the electrostatic interaction of the Cr atom density with the nuclei of the ligands. The bond cps are denoted by the *black dots* embedded in each surface, there being one bond cp in each Cr|C surface. Also shown are the bond paths originating at each of these bond critical points and linking a carbon nucleus, denoted by a *black ball*, and the further bond path linking each C to an oxygen atom

the group contributions determined by the physics of an open system agree with the experimental values (Matta and Bader 2006; Bader 1998; Cortés-Guzmán and Bader 2004). The charge on an atom in a molecule is the quantum expectation value of the number operator, a Dirac observable (Bader and Matta 2004). An atomic charge is in many cases measurable and it, together with its change, contribute to numerous measurable properties: to all molecular moments, to molecular polarizabilities, to intensities of electronic, infrared and Raman absorption intensities and to the polarization of a dielectric. What other test is there of a theory? It is useful here to quote Hans Bethe; "In science, you know when you know" (Bethe and March 18 2005).

All of the nuances of chemical models are recovered by QTAIM including, via the atomic partitioning of the exchange density, a physical measure of the localization/delocalization of electrons (Bader and Stephens 1975; Bader and Heard 1999), a property mirrored in real space by the topology exhibited in the Laplacian of the electron density, the quantity $\nabla^2\rho(\mathbf{r})$. The Laplacian of a scalar function such as the density, determines where the function is locally concentrated, $\nabla^2\rho(\mathbf{r}) < 0$, and locally depleted, $\nabla^2\rho(\mathbf{r}) > 0$ and the topology of the function $\mathrm{L(r)} = -\nabla^2\rho(\mathbf{r})$ recovers in its three-dimensional display of the regions of local charge concentration and depletion, the Lewis electron pair model (Bader et al. 1984, 1989). It is now recognized for example, that the Laplacian recovers all aspects of the valence-shell electron pair repulsion model (VSEPR) of molecular geometry (Gillespie 1972), including as well, an accounting of its failures (Bytheway et al. 1995; Gillespie et al. 1996). The Laplacian predicts and accounts for the intermolecular interactions found in condensed phases by the alignment of a charge concentration, a Lewis base, with a region of charge depletion, a Lewis acid (Tsirelson et al. 1995; Gibbs et al. 2009; Scherer et al. 2000; Bui et al. 2009). The molecular complementary predicted by the topology of the Laplacian is the embodiment of Emil Fischer's 'lock and key' model of the enzyme-substrate interaction, one that can now be displayed using EVolVis, a program that provides a three-dimensional display of a molecule's reactive surface defined by the Laplacian distribution (MacDougall and Henze 2001).

Time to choose between single- and multi-universes

I believe in the existence of a single universe, one in which the laws of physics apply. I do not believe in the existence of parallel universes wherein the laws are either ignored or 'bent' to accommodate personal points of view. Two prime examples of broadly accepted models that require the acceptance of alternative universes are one; the argument that the kinetic energy must decrease in the energy change associated with bond formation (Ruedenberg 1962; Feinberg and Ruedenberg 1971; Ruedenberg and Schmidt 2009; Kutzelnigg 1973; Goddard and Wilson 1972) and two; the use of energy decomposition schemes (EDA) in the understanding of structure and chemical reactions (Morokuma 1977). These models stem from neither physics nor observation but from imaginary steps envisaged in the minds of their proponents and require a universe in which the Ehrenfest, Feynman and virial theorems, in addition to the Pauli principle are suspended.

It is important to distinguish schemes such as this from *models*, which as normally done, spring from attempts to organize and explain *observations*, a most noble and useful cause. Good models are ultimately related to physics and this brings forth the strongest argument against the use of imagined schemes; they refer to a universe in which the laws of physics are suspended and thus they cannot be related to any observation nor used to make any predictions, the ultimate goal of science.

Feynman, Ehrenfest and virial theorems and the electrostatic basis of bonding

Ascribing bonding to ‘resonance’ removes one from the realm of the physics of definable forces—the force exerted on the nuclei, as given by Feynman’s electrostatic theorem (Feynman 1939) and the Ehrenfest force exerted on the electrons (Ehrenfest 1927; Bader and De-Cai 2005). These are the only forces operative in bonding and they are never invoked in present day discussions. All electrostatic interpretations are held suspect when in fact, the potential energy operator in the Hamiltonian consists of the electrostatic interactions between the electrons and the nuclei. The sole attractive interaction in the Hamiltonian, and hence the term responsible for chemical bonding, is the electrostatic interaction between the nuclei and the electrons (the dominant n–e interaction that determines the topology of the density) that, since it is a one-electron operator, can be recast in terms of the electron density. This attractive force acts in opposition to the repulsions between the electrons (e–e) and between the point-like nuclei (n–n). While the repulsion between the electrons is a two-electron contribution, that through the Pauli exclusion principle leads to its breakdown into a classical-like Coulomb contribution and the purely quantum mechanical exchange energy, it is describable in terms of electrostatic repulsions using the Ehrenfest theorem which determines the forces acting on the electron density.

Feynman’s and Ehrenfest’s theorems are unified by Slater’s virial theorem (Slater 1933) which relates the electronic kinetic energy to the total and potential energies. The viral is obtained by scalar multiplication of the Ehrenfest force acting at a point by the position vector **r**, transforming the force into a potential energy. It is the virial of the Ehrenfest force acting on the electrons that includes as well the virial of any residual Feynman forces acting on the nuclei that determines a system’s virial, its potential energy. Thus through the Ehrenfest and Feynman theorems, one has the tools that are needed to describe the forces acting in a molecule and through the virial theorem, to relate these forces to the molecule’s energy and its kinetic and potential contributions. Slater was the first to make extensive use of these theorems in discussions of chemical bonding (Slater 1933; Slater 1963). He viewed the virial and Feynman theorems as being the two most powerful theorems applicable to molecules and solids. Unfortunately, the first two of these theorems are ignored and the third is contravened in many present-day discussions of chemistry.

Full discussions of the role these three theorems play in providing a physical understanding of bonding stated ion terms of the observable electron density are to be found elsewhere (Bader 2010a; Bader 1990; Bader et al. 2007). The Feynman, Ehrenfest and virial theorems all lead to the identical cause of chemical bonding: the result of lowering the potential energy of the molecule resulting from the accumulation of electron density between the nuclei. It is difficult to understand how such a view can be questioned in the face of the *observation* that every ‘bond’ in a classical molecular structure is mirrored by a bond path whose presence denotes an accumulation of density, a ‘bridge’ of density in London’s words, linking the bonded nuclei, an observation verified many times over in the quantum theory of atoms in molecules.

Criticisms of Feynman’s theorem and the virial theorem

The two most maligned theorems of theoretical chemistry and the two most important for the understanding of chemical bonding, are Feynman’s electrostatic theorem and the virial theorem. The criticisms of Feynman’s theorem, apparently surprised him when he first learned of the controversy that had erupted among chemists, a result of some stating that ‘the theorem was too simple to be true’ (Gleick 1992). It has been stated that the Feynman theorem offers no information regarding dV/dR and dT/dR (Feinberg and Ruedenberg 1971). This statement is at variance with the unified picture of bonding afforded by the viral theorem. It has been demonstrated on numerous occasions (Bader 1990, 2010; Bader et al. 2007) that the Feynman force and the kinetic and potential energies are all interdetermined, noting in particular that the Feynman force F(R) and its derivative dF(R)/dR, completely determine the behaviour of both T and V over the entire range of internuclear separations. Feynman's electrostatic theorem could well be considered as the cornerstone for the construction of a quantum mechanical theory of bonding.

One finds many references to and discussions of a model of bonding ascribed to Hellmann (1937, 1937) based on the premise that the kinetic energy is decreased on bond formation. The reading of his 1937 Russian treatise (the indispensible work of the translators being thanked in the Acknowledgement) makes clear that he did not unequivocally support what became known as 'Hellmann's model of bonding' as demonstrated by a reading of the relevant portions of his book, a review summarized in the Supplementary Material. Hellmann's scientific career and contributions are reviewed by Schwarz together with a number of German and Russian scientists (Schwarz et al. 1903).

A recent quotation from a paper by Ruedenberg and Schmidt summarizes the present interpretation of Hellmann's point of view (Ruedenberg and Schmidt 2009): "Hellmann … was convinced that covalent bonding resulted from a lowering of the kinetic energy due to the increase in volume available to the electron in the molecule, i.e, to delocalization." Ruedenberg and Schmidt (RS) (Ruedenberg and Schmidt 2009) dispute the understanding that bonding is a result of the accumulation of electron density between the nuclei, a view summarized in Ruedenberg's statement: "The ubiquitous statement that overlap accumulation of electrons in a bond leads to a lowering of the potential energy is based upon 'fallacious' reasoning" (Ruedenberg 1962). (meaning 'deceptive' according to Oxford Universal Dictionary) This statement is at odds with Slater (Slater 1933, 1963), RS commenting that "Slater on the other hand observed that, by virtue of the rigorous virial theorem, it is in fact the potential energy that decreases upon bond formation whereas the kinetic energy increases."

It is interesting to compare Slater's 1933 view on the behaviour of the kinetic energy on bonding which, like those based on Hellmann's model, is also based upon the model of overlapping atomic orbitals (Slater 1933). After properly accounting for its initial decrease at large separations, a result of attractive forces acting on the nuclei, he notes that the kinetic energy begins to rise on closer approach because the electrons are forced into a smaller space as a result of the overlapping of the atomic orbitals, the decrease in volume bring proportional to the overlap integral S of the orbital model. This argument sounds more plausible than Hellmann' claiming a doubling in available volume as two 'potential boxes' are joined together on bonding. It is in direct opposition to the view of Schwarz et al. (1903) who 'bring Hellmann's model up to date' by replacing his boxes with orbitals leading them to state that overlapping orbitals increase the volume available to the electrons. This leads one to inquire 'what happened to the orbital overlap integral?' which is proportional to the decrease in volume as orbitals overlap. One may obtain a direct answer to the change in volume encountered in passing from two isolated H atoms to the H_2 molecule by using the 0.001 au isodensity surface that determines the van der Waals volume (Bader et al. 1987). The van der Walls volume occupied by two isolated H atoms is 200 au compared to 119 au for the H_2 molecule. Thus formation of H_2 results in a nearly two-fold decrease in volume as opposed to the doubling assumed by Hellmann. The delocalization of electrons is a well-defined physical property quantitatively determined by the integration of the quantum mechanical exchange density over the atomic basins (Fradera et al. 1999). Ascribing a decrease in T to an increase in available volume or to ‘electron sharing’ in some imaginary process are, respectfully, wrong and unnecessary, a point of view made clear in the Supplementary material.

Those who employ Hellmann’s model (Ruedenberg 1962; Kutzelnigg 1973; Ruedenberg and Schmidt 2009) break the bonding energy into steps that reflect their personal view of how bonding should be understood. Central to these is the ‘interference density’ that arises from electron ‘sharing’ obtained by allowing 1s orbitals on two centres to overlap. The ‘sharing term’ raises the potential energy by transferring density from the regions of the nuclei to the bonding region and *simultaneously lowers the kinetic energy*, steps that are followed by orbital contraction bringing the changes back in V and T in line with the virial theorem by decreasing V and increasing T (Ruedenberg and Schmidt 2009). A plot of the ‘interference density’ for H_2^+ shows a “*charge shift* corresponding to a *charge accumulation in the bond* at the expense of *charge depletion near the nuclei”*. This is precisely the change in density that *does occur* for large separations in the formation of H_2 as can be seen by the striking similarity of their Fig. 5 with that shown for a separation of 6 au in the density difference maps depicting the formation of the H_2 molecule (Bader 1970), a figure that has recently been reproduced (Bader 2010a). These maps, that portray the actual change in density occurring on bond formation, show that at large separations the density of each atom is polarized in the direction of the other and thus, as pointed out by Feynman in 1939 (Feynman 1939), dispersion forces are not caused by ‘oscillating dipoles but rather are a result “the attraction of each nucleus for the distorted charge distribution of its own electrons that give the attractive $1/R^7$ force”. The charge rearrangement at R = 6 au is indeed that associated with an initial decrease in T that accompanies the initial approach of all neutral species, as first demonstrated by Slater in his 1933 derivation of the virial theorem (Slater 1933). However, the decrease occurs only in the presence of attractive Feynman forces acting on the nuclei, as required by F(R) and dF(R)/dR in conjunction with the virial theorem. Such a decrease cannot occur at R_e, as postulated by Ruedenberg, wherein the Feynman force F(R) vanishes. Thus to postulate a decrease in T at R_e requires that one enter a universe wherein physics does not apply and the beauty of the unification of the forces responsible for bonding afforded by the virial theorem is lost.

Criticisms of the topological definition of structure

The advent of the topological theory of chemical bonding in terms of the measureable electron density makes possible the extension of the theory of bonding to all atomic interactions, since all interactions leave the same signature in the density; the formation of a bond cp and its associated bond path. The extension of this definition of molecular structure to situations not consistent with the Lewis model has led to criticisms and misunderstandings of the underlying physics. This situation has recently been discussed at length in a paper covering all aspect of bonding (Bader 2010a), from that between anions in ionic crystals to the observed bonding and its associated bond path in the helium dimer (Luo et al. 1993; Schöllkopf and Toennies 1994).

Criticisms of the theory have occurred particularly in the realm of what are classically described as ‘nonbonded interactions’, although one finds it difficult to understand the rationale behind this term as such interactions are invoked to account for the linking (bonding) of molecules in condensed states. It apparently has its roots in the refusal of some to consider such interactions as being the result of the presence of intermolecular ‘bonds’. Instead, one finds statements to the effect that atoms that touch necessarily repel one another (by Pauli or steric repulsions) and yet are simultaneously bound by van der walls R^{-6} forces (Poater et al. 2006) in some cases admitting to the presence of hydrogen bonds. Here surely, is a prime example of applying the ‘reductionism’ approach; in the replacement of the plethora of models of nonbonded interactions through observation and physics that is made possible by QTAIM.

First and foremost is the understanding that all bonded interactions—all interactions that bind one atom to another thus requiring a force to separate them—have a common underlying physical basis and are universal in character. The pertinent theorems—Feynman’s, Ehrenfest’s and the virial—are all interconnected, and none should be considered in isolation of the others. Thus Feynman’s theorem demonstrates that the Feynman force F(R) along with dF(R)/dR, determine the behaviour of the total energy E(R), of the kinetic T(R) and of the potential energy V(R) changes involved in the formation of any bonded interaction as predicted by the virial theorem over the entire range of internuclear separations R. The universal behaviour of these energies has been documented for all interactions—van der Waals, ‘nonbonded interactions’, metallic, covalent, followed by all degrees of polarity, down to the ionic limit, a classification based on experimental observation (Bader 2010a; Bader et al. 2007). There are no exceptions. How could there be? Even Slater emphasized that there is no fundamental distinction in the bonding mechanism operative in the measured extremes of van der Waals and covalent bonding (Slater 1972).

Invoking the universality of bonding has led to the making of what can only be described as fatuous statements, as exemplified recently; “It (QTAIM) maintains that *all* possible facets of bonding are considered, however, dismissing the chemically relevant differences between ‘ionic, polar, covalent, H-bonding and van der Waals nonbonding and other interactions” (Wang et al. 2010). These are the *very* examples whose characteristic signatures were displayed to demonstrate the universal character of atomic interactions (Cortés-Guzmán and Bader 2005; Bader et al. 2007; Hernández-Trujillo et al. 2007; Bader and De-Cai 2005). It has been repeatedly pointed out that while all interactions are subject to the same laws of physics, they differ one from another in the manner in which the electron density is distributed and shared over the atomic basins, as made evident for example, in Fig. 4 (Bader 1990; Bader 2010a, b; Bader et al. 2007).

In point of fact, the characterization of bonding afforded by QTAIM (Bader and Essén 1984) is now the most widely employed of all such measures. This began with the ability to detect and measure the properties of bond critical points in crystal structures, now a routine procedure in accurate X-ray diffraction measurements of $\rho(\mathbf{r})$ (Coppens 2005; Spackman 1998; Gatti 2005). The usefulness of these measures in the characterization of atomic interactions is enhanced by the local statement of the atomic virial theorem given in Eq. (3), applied to the indicated quantities at the bond cp,

$$(\hbar^2/4m)\nabla^2\rho_b(\mathbf{r}) = 2G_b(\mathbf{r}) + \mathcal{V}_b(\mathbf{r}) \tag{3}$$

$G_b(\mathbf{r})$ is the positive definite form of the kinetic energy density and $\mathcal{V}_b(\mathbf{r})$ is the virial field, the electronic potential energy density defined as the local virial of the Ehrenfest force. Thus tabulations of the values of the density $\rho_b(\mathbf{r})$, its Laplacian $\nabla^2\rho_b(\mathbf{r})$ along with the energy densities $G_b(\mathbf{r})$ and $\mathcal{V}_b(\mathbf{r})$ are routinely reported. Their wide use is illustrated by its recent adoption by Shaik and co-workers in the classification of the different valence bond structures that participate in the co-called ‘charge-shift’ model of chemical bonding (Zhang et al. 2009).

The local virial theorem provides the physics underlying the use of the Laplacian in understanding Lewis acid–base reactions as previously discussed in “Quantum definition of an atom in a molecule” (Bader et al. 1984). A negative value for $\nabla^2\rho(\mathbf{r})$, denotes a local charge concentration in $L(\mathbf{r})$, indicating a region where $\mathcal{V}(\mathbf{r})$ overrides the kinetic energy accounting for the role of nonbonded charge concentrations as sites of nucleophilic activity or Lewis bases. Contra-wise, minima in L(**r**), that is, regions of charge depletion, denote sites that perform as Lewis acids and the approach of reactants is determined by the alignment of the charge concentrations on one reactant with the complement of charge depletions on the other.

Among the greatest protestations against the association of a bond path with a bonded interaction are those arising from the publication of an article which reported the presence of bond paths between essentially neutral, bonded hydrogen atoms (Matta et al. 2003). Bond paths linking two bonded hydrogen atoms bearing identical or similarly small atomic charges were reported between the *ortho*-hydrogens in planar biphenyl, between the hydrogens bonded to 1–4 carbons in phenanthrene and other angular polybenzenoids and between the methyl hydrogens in molecules corseted with tertiary-*tetra*-butyl groups. It is shown that each such H–H interaction, rather than denoting the presence of 'nonbonded steric repulsions' (Bickelhaupt and Baerends 2003), makes a stabilizing contribution in an amount up to 10 kcal/mol to the energy of the molecule in which it occurs. The quantum theory of atoms in molecules demonstrates that while the approach of two bonded hydrogen atoms to a separation less than the sum of their van der Waals radii in attaining the planar structure of biphenyl for example, does result in an increase in the repulsive contributions to their energies, these changes are dominated by an increase in the magnitude of the attractive interaction of the protons that follows from the accumulation of electron density between them and the net result is a stabilizing change in the energy. It is pointed out that H–H interactions must be ubiquitous, their stabilization energies contributing to the sublimation energies of hydrocarbon molecular crystals, as well as solid hydrogen. Indeed, H–H bonding is now an experimentally established property of many crystalline structures (Wolstenholme and Cameron 2006; Matta 2006).

All of these physical arguments are dismissed by those who reside in an alternative universe where physics does not apply. The counter arguments are presented in terms of arbitrarily chosen non-physical reference states that violate the laws of physics. The Pauli principle in particular is violated in the case of frequently employed energy decomposition analysis, EDA (Poater et al. 2006; Wang et al. 2010; Bickelhaupt and Baerends 2003) This criticism is aptly summarized by Morokuma himself whose EDA analysis provides the basis to these approaches: "There is no unique choice for the intermediate wave functions, and they do not correspond to reality (e.g., 'not all' satisfy the Pauli principle!)" (Morokuma 1971). The 'Pauli repulsions' in EDA that are held responsible for any 'steric repulsion', arise by imposing antisymmetry on an initial simple product wave function of arbitrarily chosen fragments that are prepared in the geometries they possess in the product molecule, in effect correcting for the improper overlap obtained by the superposition of the fragment densities. Thus one obtains 'Pauli repulsions' by first violating the Pauli principle and then imposing it! These arguments have been responded to in full (Bader 2006a; Hernández-Trujillo et al. 2007).

Epilogue

It is the accepted practice in science that when one does not agree with the statements or conclusions obtained from a theory, one has the choice of disproving the theory or demonstrating that its predictions do not coincide with observation, either choice ensuring the truth of the other. The theory has never been disproven (Bader 2001, 2002, 2006b). Its greatest strength—it's derivation from the quantum action principle (Schwinger 1951), a principle that some consider to be the real foundation of quantum mechanics and thus of physical theory (Gell-Mann 1989)—may also be its greatest drawback in its gaining general acceptance, as the underlying physics is unfamiliar to many. Still this offers no excuse for anyone to dismiss the theory as it has been demonstrated that it is straightforward to develop the theory of an atom in a molecule—the extension of quantum mechanics to an open system—by deriving the necessary equations of motion from Schrödinger's equation, followed by a comparison of the predicted properties with experiment to determine the correct (zero-flux) boundary condition (Bader 2007). While less fundamental than the variational derivation of the quantum theory of atoms in molecules, this heuristic approach makes the quantum mechanics of an atom in a molecule accessible to 'everyman' possessing knowledge of Schrödinger's equation and most importantly, it demonstrates the rooting of the physics of an open system in experiment. A readable account of the development of the theory from its observational beginning is available (Bader 2005).

The paralleling behaviour of the density and energies for an open system is perhaps the most important of the observations made in the development of QTAIM. It has led to the establishment of a new empirical theorem for the electron density: the electron density of an atom in a molecule or a crystal determines its additive contribution to all properties of the total system, its transferability being determined by a paralleling degree of transferability in the atom's virial field (Bader 2008). This theorem is essential for the recovery of the concept of a functional group from quantum mechanics. It may be taken as the open system analogue of the theorem of Hohenberg and Kohn (HK), that the ground state density of a closed system determines the wave function and its energy (Hohenberg and Kohn 1964). The HK theorem, that the electron density is a unique functional of the external potential, applies to a closed system with a fixed number of electrons. Transferability of the electron density of an atom between two systems, necessary to account for the fundamental role of a functional group with characteristic properties in chemistry on the other hand, is a problem in the physics of an open system. Consider the density distributions of the pentane, hexane and octane molecules shown in Fig. 6. The H–K theorem dictates that they have different densities because they have different external potentials. A chemist however, knows that the

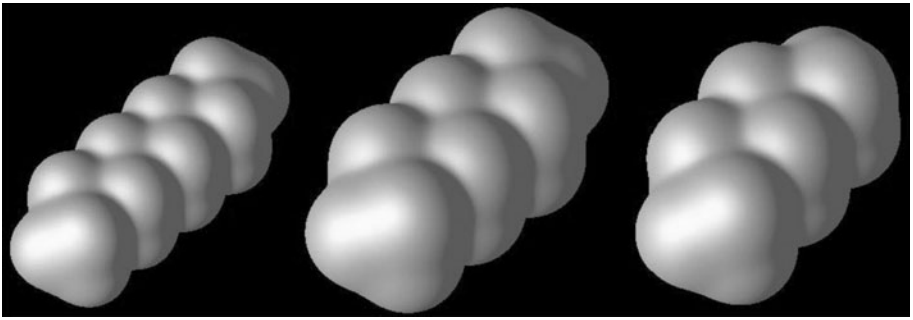


Fig. 6 Maps of the 0.001 au density envelopes of the pentane, hexane and octane molecules. The methyl and methylene groups are clearly discernible, a consequence of the C|C interatomic surfaces intersecting the density envelope. Note that the density distributions of equivalent groups are transferable between the molecules, insuring the transfer of the properties of the group, the hydrocarbons being the earliest examples of 'additivity of group properties' in chemistry. No one viewing this picture can deny the existence of atoms in molecules nor question the role of the electron density as the vehicle for the transmission of chemical information

methyl and methylene groups make additive, transferable contributions to the molecular properties in this series of molecules (Bader 1990). The diagram makes clear that corresponding groups have identifiable, transferable electron densities in spite of differing external potentials and that the densities of the groups determine their properties, a property verified many times over from both theory and experiment (Bader 2008, 2010; Matta and Bader 2003; Cortés-Guzmán and Bader 2003; Benabicha et al. 2000; Flaig et al. 2002; Kingsforf-Adaboh et al. 2002; Flaig et al. 1998; Scheins et al. 2004; Bader and Bayles 2000; Bader et al. 1994; Bader and Cortés-Guzmán 2009). No one viewing this picture can question the existence of atoms in molecules nor the role of the electron density in determining their chemistry.

The universe in which we live is more exciting and demanding of our abilities than any that one might care to invent. Most of it remains to be explored, in particular, that portion wherein chemistry resides. The purpose of QTAIM is straightforward: to propose that one maximally embrace observation and physics in the understanding of chemistry, an understanding that has grown from the finding of chemical concepts in the topology of the electron density. It is a goal that is approached more closely each day, as more and more workers apply QTAIM in their research, research that covers all facets of the study of matter at the atomic level.

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