Bond Paths Are Not Chemical Bonds

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Received: July 5, 2009; Revised Manuscript Received: August 14, 2009

This account takes to task papers that criticize the definition of a bond path as a criterion for the bonding between the atoms it links by mistakenly identifying it with a chemical bond. It is argued that the notion of a chemical bond is too restrictive to account for the physics underlying the broad spectrum of interactions between atoms and molecules that determine the properties of matter. A bond path on the other hand, as well as being accessible to experimental verification and subject to the theorems of quantum mechanics, is applicable to any and all of the interactions that account for the properties of matter. It is shown that one may define *a bond path operator as a Dirac observable, making the bond path the measurable expectation value of a quantum mechanical operator.* Particular attention is given to van der Waals interactions that traditionally are assumed to represent attractive interactions that are distinct from chemical bonding. They are assumed by some to act in concert with Pauli repulsions to account for the existence of condensed states of molecules. It is such dichotomies of interpretation that are resolved by the experimental detection of bond paths and the delineation of their properties in molecular crystals. Specific criticisms of the stabilization afforded by the presence of bond paths derived from spectroscopic measurements performed on dideuteriophenanthrene are shown to be physically unsound. The concept of a bond path as a "bridge of density" linking bonded atoms was introduced by London in 1928 following the definition of the electron density by Schrödinger in 1926. These papers marked the beginning of the theory of atoms in molecules linked by bond paths.

1. Bad Grammar and Bad Physics

Papers continue to appear criticizing the quantum theory of atoms in molecules (QTAIM) based on improper physics and bad grammar. This paper addresses criticisms that have recently appeared in papers by Grimme et al.[1] and Merino et al.,[2,3] but the problems addressed here are general.

1.1. Bad Grammar.

We begin with the bad grammar. The papers by Grimme et al. and Merino et al., as do many other papers critical of bond paths,[4−7] state that a bond path defined by the topology of the electron density denotes a bond. Reference to the 1990 book "Atoms in Molecules: a Quantum Theory" makes clear that such an identification is not made in the theory: "It is to be stressed that a bond path is not to be understood as representing a 'bond'. The presence of a bond path linking a pair of nuclei implies that the corresponding atoms are bonded to one another."[8] *This distinction is not one of semantics, but of physics.*

All papers identifying a bond path with a bond begin with a discussion of the lack of an unambiguous definition of a chemical bond. The opening discussion by Grimme et al. for example, contains the statement that "a precise and unambiguous definition of when a chemical bond exists between atoms is difficult", a statement that few would question. In contrast, a bond path is well-defined both in theory and in experiment, its presence verifiable by observation of the electron density, a now commonplace occurrence.[9,10] We return to a more detailed discussion of the physics later. At this point we treat the question of grammar.

The word "bond" is a *noun* that according to the *Oxford Universal Dictionary*, 1955, implies "a restraining force or a uniting tie". The word "bonded" on the other hand is a *participial adjective*, "a word that partakes of the notion of a verb (to bond in this case) and an adjective: a derivative of a verb which has the function and construction of an adjective (qualifying a noun) while retaining some of those of the verb - a verbal adjective." One could not ask for a more apt description of the concept of a bond path; a line of maximum density that denotes that the atoms it links are bonded to one another. A bond path is a measurable property of a system[11] that, following on the theorems of quantum mechanics, denotes a bonded interaction,[12] while a "bond" is neither measurable nor susceptible to theoretical definition. Imprecise language is a sign of imprecise thinking and one can think of no more apt example of this than the identification of a bond path with a chemical bond, a step clearly indicating either careless grammar or ignorance of the underlying theory.

1.2. Bad Physics.

More on language, this time the language of physics. Grimme et al. state "that no quantum mechanical 'bond operator' exists that would provide the desired answer ... as a conventional expectation value."[1] Dirac defines a quantum observable as a linear Hermitian operator that possesses a complete set of eigenfunctions.[13] Its eigenvalues or expectation values may or may not be *measurable*. Eigenvalues of the Hamiltonian operator, for example, are not measurable; only energy differences are. The density operator $\hat{\rho}(\mathbf{r}) = \Sigma_i \delta(\hat{\mathbf{r}}_i - \mathbf{r})$ on the other hand is a Dirac observable whose expectation values are measurable.[14] One may 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 neighboring nuclei. Thus the bond path is the *measured* consequence of the action of a quantum mechanical observable and thus satisfies a further requirement of Grimme et al.: "chemical bonding must have an effect on *measurable* properties of the system."[1] Why do the authors choose to discredit a definition of *bonding* that satisfies their own criterion of physical relevance? Their statement that "As long as no conclusive experimental evidence for their 'reality' is presented, we suggest to abandon the term

10.1021/jp906341r CCC: $40.75

hydrogen−hydrogen bonding in cases ... where they are subjected to conventional van der Waals interactions" cannot be justified. This statement is wrong on two counts. First, H−H bond paths have been observed experimentally. Matta[15] and Wolstenholme and Matta[16] review the overwhelming experimental evidence from X-ray diffraction studies of the existence of inter- and intramolecular H−H bonded interactions. Second, it follows the fallacy of suggesting that van der Waals bonding must in some manner be distinguished from chemical bonding, a topic refuted in detail below in terms of the physics of interacting atoms.

A recent extreme example of the misidentification of a bond path with a chemical bond is provided by the work of Cerpa et al.[2] They pose the question: "Is the existence of a bond path a sufficient condition that proves the two atoms are connected by a bond in the chemical sense of the word?" and then proceed to look for bond paths in examples where the "number of gradient paths terminating at an atom is chemically meaningless." It is difficult to fathom why this question is posed in the face of the known physics of a bond path and the underlying theory that states that it is not to be so identified. This is known as "setting up a straw man". The only point disproven by their finding of 60 bond paths terminating at an Ar atom in $Ar@C_{60}$ is their own mistaken one of identifying a bond path with a chemical bond! What the authors fail to point out is that bond paths provide valuable structural information by indicating which atoms interact in any given system. Thus in a companion paper,[3] they find each He atom in $He_2@C_{20}H_{20}$ to be dicoordinated in the D_{3d} structure, pentacoordinated in D_{5d}, and tricoordinated in the D_{2h} structure. Thus the formation of bond paths is selective, but the authors give no critical point information to enable one to ascertain the reasons for the selectivity and they make no effort to follow up on this interesting observation, choosing instead to state that the observed bond paths are a function of molecular symmetry and not indicative of the "presence of a chemical bond between atoms'" How symmetry alone can account for two-, five-, and three-coordination within a cage composed of 20 atoms is not explained. The encased atom in an adamantane cage, for example, interacts only with the methine carbon atoms and the accompanying analysis of the critical point and atomic properties including the degree of charge transfer, clarify this observation.[17]

2. Why Go from Bonds to Bonding?

2.1. Limitations of the Concept of a Chemical Bond. The paper by Cerpa et al.[2] does raise an important point. The notion of a chemical bond is both limited and dominated by the pair concept of Lewis. The Lewis model is unable to account for the bonding in metals and necessitates the presence of ionic interactions in an ionic crystal, as well as in hydrogen bonding, for example. Bond formation between closed-shell neutral atoms is forbidden in the Lewis model and in simple molecular orbital theory. Attractive closed-shell interactions are accepted only with the stipulation that the atoms be held together by weak, nondirectional van der Waals forces that are not considered chemical bonds, thus relegating interactions between molecules in condensed phases to the realm of (nonbonded) van der Waals interactions. That van der Waals interactions are not to be considered chemical bonds is a frequently expressed view, as exemplified the statement: "... but most chemists will have no difficulty in distinguishing between a molecule and a weakly bound aggregate such as a noble gas dimer which is held together by weak van der Waals forces." This statement appears in an otherwise well-reasoned accounting of the bonding in inclusion complexes of rare gas dimers in C_{60}.[7]

Thus the notion of a chemical bond is too restrictive and is ill-suited to account for the physics underlying the spectrum of interactions between atoms and molecules that determine the properties of matter. What is needed is a definition of bonding rather than of a bond, one that can describe the complete range of bonded interactions that account for the properties of all matter. Such is the role fulfilled by a bond path. A recent illustrative example of its universal character is given by the finding that the properties of the bond critical points linking the Ni atoms in Ni metal are virtually the same as those in the mineral heazlewoodite Ni_3S_2. NiNi bond paths radiate throughout Ni metal and the metallic Ni_3S_2 structures as continuous networks whereas vaesite NiS_2, another Ni-sulphide mineral, an insulator at low temperatures and a doped semiconductor at higher temperatures, lacks Ni−Ni bond paths. Electron transport in Ni metal and Ni_3S_2 is pictured as occurring along the bond paths, which behave as networks of atomic size wires that radiate in a contiguous circuit throughout the two structures.[18]

2.2. Interacting Atoms Are Bonded to One Another. 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.[12] *This definition transcends all bonding schemes and categories and provides a unified physical understanding of atomic interactions.* It is based upon the theorems of quantum mechanics that govern the interactions between atoms. There are only two forces operative in chemistry, the Feynman force exerted on the nuclei and the Ehrenfest force exerted on the electrons. The virial theorem relates the virial of the Ehrenfest force to the kinetic energy of the electrons, the virial including a contribution from the virial of the Feynman forces acting on the nuclei.[19] Thus, through the Ehrenfest and Feynman theorems, one has the tools that are needed to describe the forces acting in any system and, through the virial theorem, to relate these forces to the system's energy and its potential and kinetic contributions.[20] This is the physics underlying all bonded interactions, and when combined with the properties of the electron and energy densities at a bond critical point, it provides one with a classification scheme that establishes trends and the distinguishing features of atomic interactions over the entire spectrum of bonding.[21,22] It is widely employed in the analysis of experimental densities[15,16,10,23−35] and has an ever widening range of application as exemplified by its recent novel use in establishing a classification scheme based on the covalent, ionic, and resonance components of valence bond theory.[36] Anyone possessed with knowledge of Schrödinger's equation may derive QTAIM and its theorems without knowledge of its derivation from Schwinger's principle of stationary action,[37] making the theory accessible to all.[38]

Many applications of the bond critical point analysis apply to bond paths observed in systems where van der Waals interactions were previously invoked. Experimentally, "van der Waals interactions" are revealed as directed bond paths in measured densities, their directional properties being essential to the understanding of crystal and mineral structures. The first example of this was in the explanation of the layered structure of solid chlorine that could not be accounted for in terms of nondirectional van der Waals interactions.[39] This work and the study of the experimental and theoretical densities of crystalline N_4S_4 by Scherer et al.[40] provided early examples of the use of the "lock and key" analogy in the prediction of directed intermolecular interactions provided by the alignment of charge concentrations with charge depletions, as defined by the Laplacian of the electron density. Gibbs et al. have employed the same "lock and key" properties of the Laplacian of the density to account for the presence of the directed bond paths found for the weak intermolecular interactions in the structures of molecular solids in a paper entitled "Role of directed van der Waals bonded interactions in the determination of structures of molecular arsenate solids".[41] They state that their study provides a new basis for the understanding of the structures of the arsenates and call for a reappraisal of the concept of van der Waals bonded interactions in terms of their directed, rather than isotropic, character.

A point of particular contention is H−H bonding: the finding of bond paths linking essentially neutral, similarly charged hydrogen atoms in situations where they were assumed to be subject to "Pauli repulsions", the ortho hydrogens in the planar geometry of biphenyl, for example.[42] An experimental study directly related to H−H bonding is that of Wolstenholme and Cameron.[43] Their X-ray determinations of electron densities were carried out on crystal structures chosen to enable a comparative study of the weak interactions in $C-H^{\delta+}\cdots{}^{\delta+}H-C$, $C-H\cdots O$, and $C-H\cdots C_\pi$ systems. This study resulted in the establishment of similarities and differences in the correlations of these weak interactions and to a better understanding of H−H interactions in particular. Matta,[15] in addition to reviewing the experimental and theoretical papers on H−H bonding, contrasts the characteristics of H−H bonding with those for dihydrogen bonding,[44] an interaction that binds two H atoms, one bearing a partial negative charge, the other a partial positive charge, thereby emulating a normal hydrogen bonded interaction. The bonded interaction between two H atoms will cover the entire spectrum of charge separation. Who is to judge at which point the charge separation falls to a value where the "electrostatic description" fails and the atoms are no longer bonded? Now, of course, all bonding is electrostatic in origin, the molecular Hamiltonian consisting of the attractive and repulsive interactions between the electrons and nuclei, the electron−nuclear interaction being the only attractive force in chemistry.[20,45]

The above are but recent examples of previous work[46] that have led to an increased understanding of crystal structures afforded by the observation of bond paths associated with weak interactions. From the comments of Grimme et al., one must conclude that they suggest that there are van der Waals forces of attraction between the ortho hydrogens in phenanthrene that are linked by a bond path,[42] but at the same time they are repelled by Pauli forces. Strange as this conclusion might sound, it is one advocated by Poater et al.:[4] that nonbonded interactions in molecular solids are subject to Pauli repulsions because of the impossibility of forming an electron pair bond and the stability of the crystal is due to the presence of weak dispersion forces. Recognizing the presence of a bond path in such situations as an indication that the atoms of neighboring molecules are bonded to one another, thereby making the interactions both measurable and open to physical interpretation, is surely preferable to invoking the action of unknown forces of repulsion acting in concert with isotropic "nonbonded" forces of attraction.

Slater emphasized that there is no fundamental distinction between van der Waals binding and covalent binding,[47] a view recently illustrated by the homeomorphic displays of the changes in the total, kinetic, and potential energies with internuclear separation for homopolar, polar, and van der Waals interactions, displays that illustrate that all interactions exhibit a common underlying quantum mechanism.[20] Feynman, in his paper on the electrostatic explanation of chemical bonding,[48] drew specific attention to the point that van der Waals attractive forces are not the result of "the interactions between oscillating dipoles" but arise from the accumulation of electron density between the nuclei, fulfilling the universal requirement for all chemical bonding and simultaneously, the physical requirement for the presence of a bond path.

3. A Spectroscopic Based Criticism of H−H Bonding

We next consider the specific criticism leveled against QTAIM in the paper by Grimme et al. entitled "When do interacting atoms form a chemical bond? Spectroscopic measurements and theoretical analyses of dideuteriophenanthrene."[1] The paper questions the conclusion that the ortho hydrogen atoms in phenanthrene, which are linked by a bond path in the equilibrium geometry where no forces act on the nuclei, are bonded to one another.[42] The authors employ deuterium substitution of the ortho hydrogens to decouple the associated symmetric (S) and antisymmetric (AS) C−D vibrations from the remainder of the molecule and employ a two-state model to determine the interaction constant $k = d^2E/dr_1\,dr_2$, where E is the total energy and r_1 and r_2 are the C−D stretching coordinates. The interaction constant k determines the magnitude and direction of the splitting between the S and AS modes, the force constants being given by $k_s = k_{11} + k$ for the S mode and $k_a = k_{11} - k$ for the AS mode. One observes the S frequency to exceed the AS frequency indicating that the interaction constant $k > 0$.

The authors incorrectly interpret the positive sign for k as indicating "that the short H···H distance of about 2.0 Å in phenanthrene corresponds to the repulsive part of the H−H interaction potential which already contradicts the conclusions from AIM." Now, of course, k does not determine a curvature of the potential energy surface (a force constant) that is associated with any nuclear motion and thus it does not determine an associated force. One must be very clear about this. The force acting on a nucleus in a molecule is the Feynman electrostatic force, which is determined by the negative gradient of the potential energy, and the force constant is obtained by taking the gradient of the force in an equilibrium geometry. All potential constants are determined by the charge distribution and its variation with nuclear coordinates.[49] There are forces exerted on the protons upon displacement in both the S and AS modes as given by $-k_sQ_s$ and $-k_aQ_a$, respectively, but there is no motion of the protons that is governed by the interaction constant k and thus no corresponding or definable force. *There is no curvature of the potential energy surface corresponding to k and no coordinate associated with it in the quadratic expansion of the potential energy function, and thus there is no associated or definable force.*

What a positive interaction constant does imply is that the lowest lying transition density for displacement of the nuclei is of b_1 symmetry, a statement determined by the use of the Herzberg−Teller Hamiltonian—the second-order expansion of the Hamiltonian in terms of the normal coordinates—in conjunction with second-order perturbation theory.[50] The electron density thus undergoes its most favorable relaxation when the nuclei are displaced in a b_1 vibration, this same procedure yielding the first symmetry rule governing chemical reactions.[51]

What one can do is calculate the properties of the potential energy surface associated with the vibrational mode that is primarily the symmetric stretch of the ortho hydrogens and from this determine the forces acting on the two protons.[52] At equilibrium these forces are, of course, zero. The symmetrical increase in the two ortho C−H lengths *decreases* the separation between the protons and the resulting force is repulsive, pushing the protons back toward their equilibrium positions. The symmetrical compression increases their separation and there is an attractive force drawing them back to their equilibrium positions. *These are the forces anticipated for the lengthening and shortening of the distance between a pair of atoms linked by a bond path.* These quantum mechanical calculations override the results obtained by Grimme et al. employing empirical force field calculations.[1]

Actually, this entire discussion is unnecessary. As spectroscopists, the authors are aware that the forces exerted on the nuclei are the Feynman electrostatic forces determined by the gradients of the potential energy (PE) function and, for a molecule in an equilibrium geometry or residing in a many-dimensional minimum on the PE surface, all such forces vanish. The H−H bond paths, as are all bond paths, are defined for a system in electrostatic equilibrium or residing in the attractive part of the PE surface. Thus there are no Feynman forces acting on the protons in the equilibrium geometry of phenanthrene and *there are no other forces associated with motion on a PE surface, the surface governing the nuclear motions of chemistry.* Their statement that their results "are in complete agreement with the traditional view of this H−H interaction as steric (Pauli) repulsion" as given by Poater et al.[53] aligns them with those who believe that chemistry lies beyond the theorems and understanding of physics. They are of course welcome hold this view, but they should refrain from using nonphysical arguments to criticize observations and conclusions based upon physics. After reaffirming their belief in "conventional van der Waals interactions" and their use in place of hydrogen−hydrogen bonding, they conclude their paper with the admonishing statement "and all theoretical energy partitioning schemes should be applied with great care."[1] Now this statement certainly applies to their supported view of Pauli repulsions in H−H bonding reported by Bickelhaupt et al.[53] obtained from an arbitrary energy partitioning scheme that violates quantum mechanics and in particular the Pauli principle,[54] but it does not apply to an analysis obtained from the quantum mechanics of an open system employed in the description of H−H bonding. If they question any part of the QTAIM atomic energies that are obtained as quantum expectation values of the kinetic energy operator in conjunction with the virial theorem for an open system, they must be specific and state which theorems are in error and disprove them.

The authors make one final statement indicating an incomplete knowledge of the quantum mechanics underlying QTAIM: "The resulting (atomic) energy changes are well-defined in AIM but represent only local quantities that must need not be interpreted in a conventional sense as bond energies." Because of the atomic virial theorem, the energy of an atom in a molecule may indeed be determined by an integration of the kinetic energy density over the basin of the atom, $E(\mathrm{A}) = -T(\mathrm{A})$. However, the same theorem relates the energy to the atom's viral (the atom's potential energy) $E(\mathrm{A}) = V(\mathrm{A})/2$, a quantity determined by the interaction of every element of density in the atomic basin with all of the nuclei in the molecule and with the average distribution of the electrons over the entire molecule, the virial field. *The virial field, because it includes all contributions to the potential exerted at a point in space, is the most short-range possible description of the potential interactions in a many-electron system.* It is the transferable nature of the viral field that is responsible for the concept of a functional group in chemistry and for the theorem that the density of an atom in a molecule determines all of its properties.[55] The quantum definition of the energy of an atom in a molecule must include its interaction with the entire system. A bond energy is no more precisely defined than is a bond, but its need is obviated by QTAIM, which offers among other possible analyses of the interactions between atoms,[20,45,56] the definition of the contribution to the energy of formation arising from the formation of an interatomic surface and its associated bond path.[17] When applied to the formation of H−H bond paths and as illustrated in the paper introducing H−H bonding,[42] it measures precisely the contribution to the energy of the molecule arising from the formation of the H−H bond path, the open system counterpart of a "bond energy". The authors choose to ignore the comprehensive discussion of the energy of H−H bonding presented in terms of the quantum mechanics of an open system.

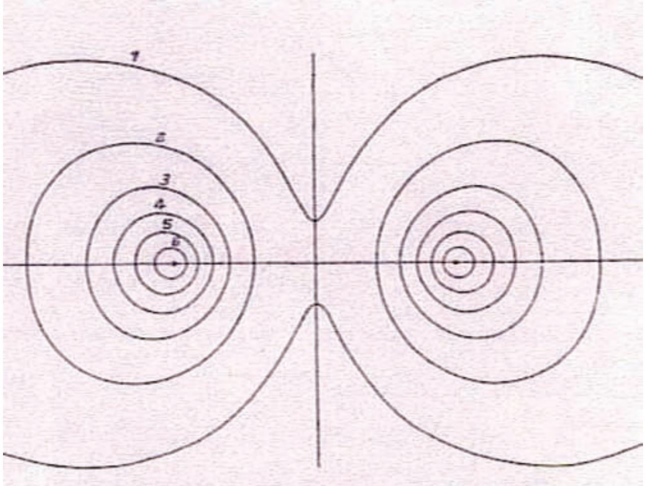
4. A Finale on the Physical Significance of the Density

It is surprisingly little known that the fundamental role of the density in understanding chemical bonding was first pointed out by London in a companion paper[57] to the one he coauthored with Heitler giving the quantum mechanical description of homopolar bonding.[58] London gave contour diagrams of the densities associated with the antisymmetric and symmetric solutions to the Heitler−London (H−L) equations, the first displays of molecular density distributions. He obtained the densities by integrating $\Psi^*\Psi(\mathbf{r}_1,\mathbf{r}_2)$ over the coordinates of one of the electrons, employing the definition of the density $\rho(\mathbf{r})$ provided by Schrödinger in the preceding year, a paper that included the definition of the current density $\mathbf{j}(\mathbf{r})$ and the continuity equation relating them.[59] Schrödinger went to considerable lengths to distance himself from any attempts to use Ψ in a way other than to obtain $\Psi^*\Psi$, stating his hope that the density and its current would prove useful in the understanding of the properties of matter.

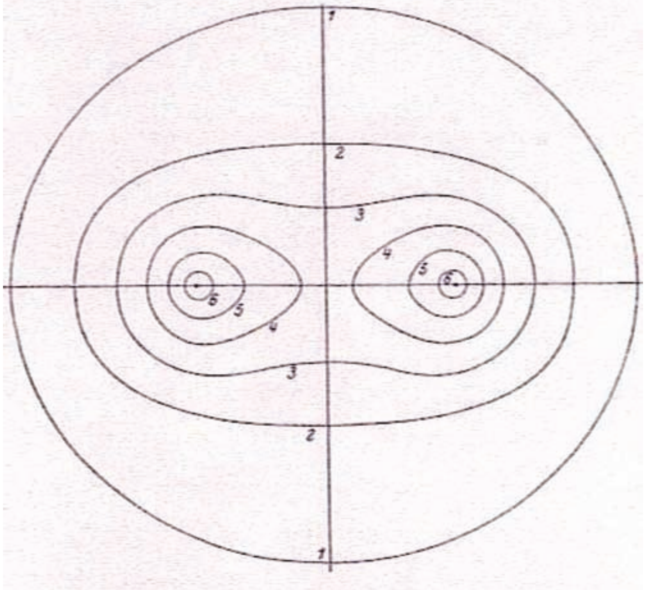
London, in describing the antisymmetric and symmetric density distributions that are reproduced here in Figure 1, states: "We see that the densities (in his Figure 2 for the antisymmetric solution) are clearly pushed outward, as if they would separate if possible. If we would bring the nuclei ... closer together, the strangling of the density between the atoms would increase"; "In opposition to Fig. 2, (his) Fig. 3 which gives the density for the symmetric solution, shows the two atoms which are in a state of homo-polar binding. Here the two densities seem to draw closer and become one. *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 3 clearly illustrates the buildup 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."[48] 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. This, to my knowledge, has never been referred to in the vast literature springing from the H−L papers, literature that stresses the "resonance" interpretation of homopolar bonding, the exchange of the positions of the electrons between the two atoms. This interpretation was disowned by H−L, as shown by a careful reading of their paper[60] and one that places chemical bonding beyond the realm of definable physical forces.

It is informative to read the acknowledgment given by London in his 1928 paper: "I would like to thank Prof. Schrödinger for the continual deep interest with which he supervised my work", "interest" that surely included discussions of the electron density.

Figure 2 displays isodensity surfaces of the pentane and hexane molecules with clearly defined methyl and methylene



Density distribution for elastic reflection.



Density distribution for homo-polar reflection.

Figure 1. Electron density distributions for the hydrogen molecule given by London in 1928[57] calculated from the Heitler−London wave functions. His Figure 2 is for the antisymmetric function, the lowest excited (triplet) state, and his Figure 3 is for the symmetric ground state density. Reprinted with kind permission of Springer Science+Business Media. Copyright 1928.

Figure 2. The 0.001 au density envelopes of the pentane and hexane molecules. The methyl and methylene groups are clearly discernible, a consequence of the C|C interatomic surfaces intersecting the density envelope. The unique hydrogen atom of a methyl group is directed upward in the terminal methyl group of pentane, while in hexane the pair of identical hydrogen atoms occupies this position. 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.

functional groups, a consequence of their C|C interatomic surfaces intersecting the density envelope. The diagram illustrates the distance traveled in the study of the electron density since its introduction by Schrödinger in 1926. It is good to remember that the derivation of the theory of an atom in a molecule was initially obtained by generalizing Schrödinger's derivation of his "wave equation" presented in the first[61] of his four 1926 papers to a system with finite spatial boundaries.[62] The theorem of Hohenberg and Kohn, showing the interdependence between the density and the external potential, while of great theoretical significance, does not account for the concept of a functional group in chemistry. The theorem, which applies to a *closed isolated system*, states that molecules with different external potentials possess different electron densities, as indeed evidenced in Figure 2.[63] However, a chemist knows that the methyl and methylene groups in this series of molecules make additive, transferable contributions to the molecular properties. It is thus apparent that corresponding chemical groups, defined as *open systems by the zero-flux boundary condition*, have transferable electron densities *in spite of their differing external potentials* and that the densities determine their properties. This figure is a limiting example illustrating the primary dictum of QTAIM: that the density of an atom in a molecule determines its contribution to the energy and to all other properties of the total system.[55]

Acknowledgment. The author expresses his thanks to the following people for their suggestions and comments: Dr. C. F. Matta, Dr. J. Hernández-Trujillo, Dr. F. Cortés-Guzmàn, Dr. D. Wolstenholme, and particularly Dr. T. Keith for performing the AIMALL calculations on a symmetrical mode of phenanthrene.

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JP906341R