

## Definition of Molecular Structure: By Choice or by Appeal to Observation?

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There are two schools of thought in chemistry: one derived from the valence bond and molecular orbital models of bonding, the other appealing directly to the measurable electron density and the quantum mechanical theorems that determine its behavior, an approach embodied in the quantum theory of atoms in molecules, QTAIM. No one questions the validity of the former approach, and indeed molecular orbital models and QTAIM play complementary roles, the models finding expression in the principles of physics. However, some orbital proponents step beyond the models to impose their personal stamp on their use in interpretive chemistry, by denying the possible existence of a physical basis for the concepts of chemistry. This places them at odds with QTAIM, whose very existence stems from the discovery in the observable topology of the electron density, the definitions of atoms, of the bonding between atoms and hence of molecular structure. Relating these concepts to the electron density provides the necessary link for their ultimate quantum definition. This paper explores in depth the possible causes of the difficulties some have in accepting the quantum basis of structure beginning with the arguments associated with the acceptance of a “bond path” as a criterion for bonding. This identification is based on the finding that *all* classical structures may be mapped onto molecular graphs consisting of bond paths linking neighboring atoms, a mapping that has no known exceptions and one that is further bolstered by the finding that there are no examples of “missing bond paths”. Difficulties arise when the quantum concept is applied to systems that are not amenable to the classical models of bonding. Thus one is faced with the recurring dilemma of science, of having to escape the constraints of a model that requires a change in the existing paradigm, a process that has been in operation since the discovery of new and novel structures necessitated the extension of the Lewis model and the octet rule. The paper reviews all facets of bonding beginning with the work of Pauling and Slater in their accounting for crystal structures, taking note of Pauling’s advocating possible bonding between large anions. Many examples of nonbonded or van der Waals interactions are considered from both points of view. The final section deals with the consequences of the realization that bonded quantum atoms that share an interatomic surface do not “overlap”. The time has come for entering students of chemistry to be taught that the electron density can be seen, touched, and measured and that the chemical structures they learn are in fact the tracings of “bonds” onto lines of maximum density that link bonded nuclei. Matter, as we perceive it, is bound by the electrostatic force of attraction between the nuclei and the electron density.

### I. Philosophical Dilemma

It is the purpose of this paper to reach a consensus regarding the dichotomous approaches to chemistry: one espoused by those who consider the fundamental concepts of chemistry to lie beyond the bounds of physics, the other, that chemical observations and hence the conceptual framework of chemistry are fully described, predicted, and accounted for by quantum mechanics, the physics governing the behavior of electrons and nuclei. The former approach is 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 fundamental difference of opinion between us on this matter.”

Of all the concepts that best illustrates these differing approaches, the concept of a bond, as opposed to the physical reality of a bond path, serves as a lightning rod of contention. Once again one can do no better than to quote R. Hoffmann, this time from the abstract of a talk presented at a symposium of the American Chemical Society on “Contemporary Aspects of Chemical Bonding”, Sept 2003: “And yet the concept of a

chem(ical) bond, so essential to chem(istry), and with a venerable history, has a life, generating controversy and incredible interest. Even if we can’t reduce it to physics ... Push the concept to its limits, accept that a bond will be a bond by some criteria, maybe not by others, respect chem(ical) tradition, have fun with the richness of something that cannot be defined clearly, and spare us the hype.” The abstract laid the groundwork for the message that a chemical bond not only lies beyond the domain of physics but also is incapable of precise physical understanding. Thus it is to the understanding of chemical bonding that we turn to face the dichotomy of approaches.

### II. Assignment of Structure on Basis of Experiment and Models of Valence

The concept of a chemical bond linking atoms evolved from our earliest attempts to account for the structures of molecules, using all of the physical information and models of valence at our disposal. The theory of valence evolved from the use of the Lewis electron pair model coupled originally with the octet rule.<sup>1</sup> These were later augmented by the molecular orbital method by Mulliken<sup>2–5</sup> and Hund<sup>6</sup> and by the valence bond model extended to include orbital hybridization, most notably



**Richard F. W. Bader** was born in Kitchener, Ontario, Canada, in 1931. He received B.Sc. and M.Sc. degrees from McMaster University, 1953 and 1955, and a Ph.D. from Massachusetts Institute of Technology in 1958 under the supervision of Professor C. G. Swain in physical organic chemistry. While at MIT, he attended the lectures on quantum mechanics given by Professor J. C. Slater. This was followed by a sabbatical year at Cambridge University under Professor Longuet-Higgins where the switch to theory was completed. In 1960 he assumed an Assistant Professorship at the University of Ottawa, leaving for an Associate Professorship at McMaster University in 1963. In the mid-1960s a collaboration was established with LMSS of Professors Mulliken and Roothaan at the University of Chicago, providing access to high quality theoretical electron density distributions that enabled their first systematic study, forming the observational basis for the theory of atoms in molecules. He remained at McMaster University until his retirement as full Professor. His research interests center on relating chemical concepts to observation and physics.

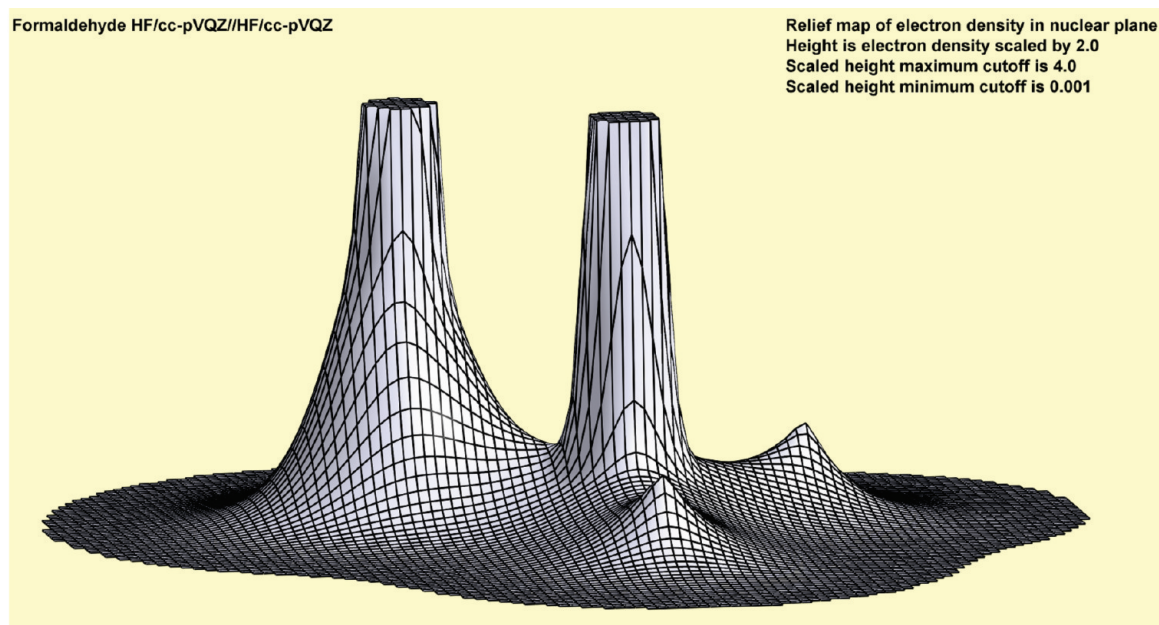
by Slater<sup>7–9</sup> and by Pauling.<sup>10–13</sup> The physical information, in addition to the interpretation of measured heats of formation, came from our ever increasing ability to determine the *geometrical* structures of molecules associated with any given atomic composition, studies that clearly necessitated an extension of the then existing models of valence. The infrared and Raman determination of the  $O_h$  structure of  $SF_6$  in 1934<sup>14,15</sup> and other molecules with an “expanded valence”, for example, resulted in the abandonment of the octet rule and the extension of the hybridization model to include other than linear, trigonal, and tetrahedral geometries. The recognition of the wide applicability of the role played by the presence of hydrogen bridges, now called hydrogen bonds in 1920 by Latimer and Rodebush<sup>16</sup> necessitated the abandonment of the Lewis notion of the chemical inertness of a closed-shell in the case of an over-riding “electrostatic” interaction.

The bridged structure assigned to the “electron deficient molecule” diborane in 1943 required the broadening of the pair concept to include three-center two-electron bonds. This extension is a good example of the failure of attempts to apply the existing ideas of bonding to a molecule that could not be accounted for in terms of electron pair bonds and of how this failure resulted in a further necessary extension to the model of bonding. The initial model, applied to an ethane-like structure, involved a hybrid structure composed of a two-electron link, a one-electron link, and a state in which there is no linkage, in an attempt to salvage the existing ideas of bonding.<sup>17</sup> Longuet-Higgins and Bell<sup>18</sup> showed that the spectral data for  $B_2H_6$  was consistent with a  $D_{2h}$  bridged structure and proposed what became accepted as a three-center two-electron bond. The examples are instructive: the discovery of new bonded structures required the extension of existing models. The structures of present day chemistry that resulted from the above synthesis of models and experiment, a process that continues to this day, will be referred to as “classical structures”.

### III. Relating Structure to the Measurable Electron Density

Hoffmanns’ belief that the concept of a “bond linking atoms” cannot be defined appears to be widespread throughout the chemical community, judging from the current literature. One might reasonably suppose that an alternative to this most important idea should be sought as a necessary step if any future advances are to be made in the theory of bonding. Any alternative definition should avoid the pitfalls presently associated with the notion of a “bond”, a result of its lack of a direct association with a particular measurable property of a molecule. This apparent dilemma was overcome in 1975 with the definition of a *bond path*,<sup>19</sup> a line of maximum electron density linking bonded pairs of atoms in an equilibrium geometry, coupled with the demonstration in 1977 that appeared to indicate that the network of classical “bonds”, however assigned, was mirrored by a corresponding network of bond paths.<sup>20</sup> This association was confirmed by further theoretical calculations of the density and, most importantly, by the topological analysis of experimentally measured electron densities.<sup>21–24</sup> Such calculations<sup>25</sup> and experiments<sup>26–29</sup> have now provided thousands of examples, demonstrating that every classical structure is but a mapping of the “bonds” onto the network of bond paths. *Every classical structure is mirrored by a molecular graph: the network of bond paths linking neighboring, that is, bonded, nuclei.* All nuances of theoretical structures are recovered in experimental density distributions, a recent example being the absence of a bond path between the boron atoms in diborane to yield the ring structure associated with the bridging hydrogen atoms.<sup>30</sup> It is important to observe that there are no examples of a bond being assigned in the absence of a corresponding bond path. Identification of structure with a network of bond paths is an efficacious step, relating structure to a measurable, physical property.

**III.1. Universality of a Bond Path.** A bond path is a consequence of the ubiquitous physical signature that the interaction of two atoms creates in the electron density.<sup>31</sup> The interaction of two atoms at any separation results in the formation of critical point (cp) in the electron density, a point where its gradient  $\nabla\rho(\mathbf{r})$  vanishes. In two dimensions it has the appearance of a saddle, as displayed for the C–O and C–H interactions in the formaldehyde molecule, Figure 1. The curvature of the density at the cp along the line connecting two nuclei is positive (the density is a minimum at the cp) while the two curvatures along mutually perpendicular lines and perpendicular to the bond path are negative (the density is a maximum at the cp). It is classified as a (3,–1) cp, a cp with a rank of 3, the signs of the three curvatures summing to –1. An *atomic interaction line* is defined by a unique pair of trajectories of the gradient of the density<sup>32</sup> of  $\nabla\rho$ . A trajectory of  $\nabla\rho$  points in the direction of maximum increase in  $\rho$  and each member of the unique pair originates at the (3,–1) cp where  $\nabla\rho = 0$  and terminates at a neighboring nucleus where the density exhibits its maximum value. This pair of trajectories demarks a line linking the nuclei along which the density is a maximum with respect to any neighboring line. 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*.<sup>25</sup> It should be remarked that one may define a *bond path operator* by having the density operator, a Dirac observable, project the density along each of the trajectories that originate at the bond cp, *making the bond path the measurable expectation value of a quantum mechanical operator*.



**Figure 1.** Relief map of the density in the plane of the nuclei for  $\text{CH}_2\text{O}$ . 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 a 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.

All interacting atoms, atoms that “touch” and thus share a common interatomic surface, are linked by an *atomic interaction line*, whether the interaction is attractive or repulsive. For interatomic separations corresponding to *motion within a bound potential well*, the forces on the nuclei are attractive and, as such, return the system to its equilibrium geometry where the forces vanish. In this situation, the atomic interaction line is designated a *bond path*. Thus, for example, the approach of two Ar atoms is initially attractive to yield a van der Waals minimum of 0.012 eV at a separation of 7.1 au and the atoms are linked by a *bond path*. The well depth is sufficient to support three vibrational quanta above the zero-point energy level. For energies in excess of this, the molecule is no longer bound and will dissociate, the atoms now being linked by an *atomic interaction line*.

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:<sup>33</sup> “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”.

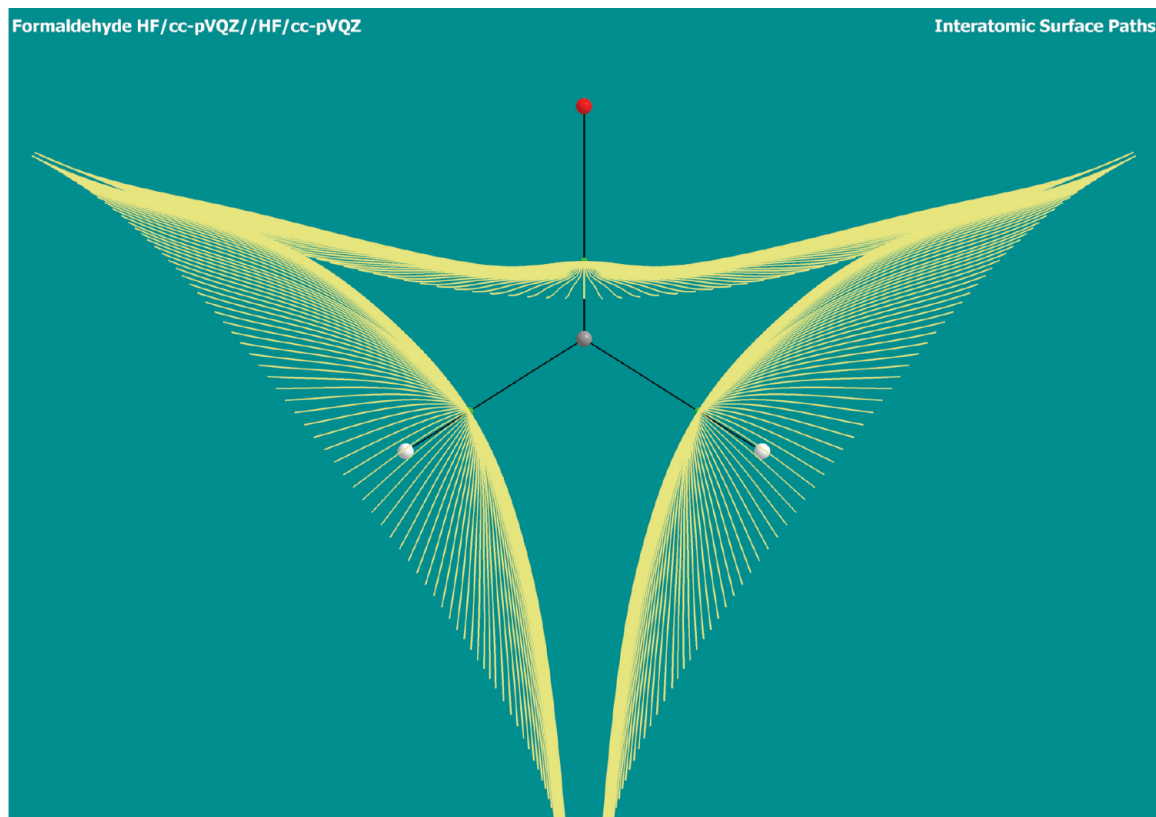
The belief in the credo of science, that what one observes is determined by the properties of the system one is observing, provides an immediate counter argument to this statement; to wit, “that chemistry has done so well precisely because the models of bonding coupled with experimental observation were 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”. In a relatively short time this association was confirmed by the topological analysis of experimentally measured electron densities. It is well to recall at this point that there is no example of a “bond” being assigned in the absence of a mirror image in the 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.

The bond paths shown in Figure 1 are found only to link pairs of atoms that are considered to be bonded to one another in the classical structure. Fritz London was the first to draw attention to this property of the density, and he did so in 1928 on the basis of the electron density distributions he calculated for the ground state and the repulsive triplet state of the hydrogen molecule using the Heitler–London wave functions determined in the previous year.<sup>34</sup> These were the first calculated representations of molecular electron density distributions and they have recently been reproduced by the author.<sup>35</sup> On the basis of these displays London made the astute observation: “*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*”, a prediction borne out by the display of the density shown in Figure 1. London was the first to define a bond path as a “bridge of density” linking bonded atoms (atoms forming a valence) and to foresee its role in the prediction and understanding of chemical bonding. The presence of the same “bridge of density” provides a vindication of Lewis’ homopolar electron pair bond; the postulated presence an electron pair bond is given physical realization in the presence of a “bridge of density”.<sup>36</sup>

**III.2. Atoms Linked by Bond Paths.** One cannot have bonding “between atoms” without first defining the atoms and the formation of a (3,−1) cp fulfills this condition. The two negative curvatures at the cp define a set of trajectories of  $\nabla\rho$ , all of which terminate at the cp, and define an interatomic surface. This is illustrated in Figure 2 for the trajectories that define the interatomic surfaces denoting the boundaries of the atoms bonded to one another in the formaldehyde molecule.





**Figure 2.** Interatomic surfaces defining the basins of the H, C, and O atoms. A surface is defined by the set of trajectories of the gradient of the density,  $\nabla\rho(\mathbf{r})$ , which *terminate* at the bond critical point. Also shown are the bond paths defined by the pairs of trajectories that *originate* at the bond critical point and terminate at the adjacent nuclei. The shapes of the surfaces are characteristic for each atomic interaction.

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  $\nabla\rho$ . It is this “zero-flux” property of the interatomic surfaces, expressed in eq 1, which serves as the quantum boundary condition for an atom in a molecule.<sup>37,38</sup>

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \text{ for all points } \mathbf{r} \text{ on the interatomic surface} \quad (1)$$

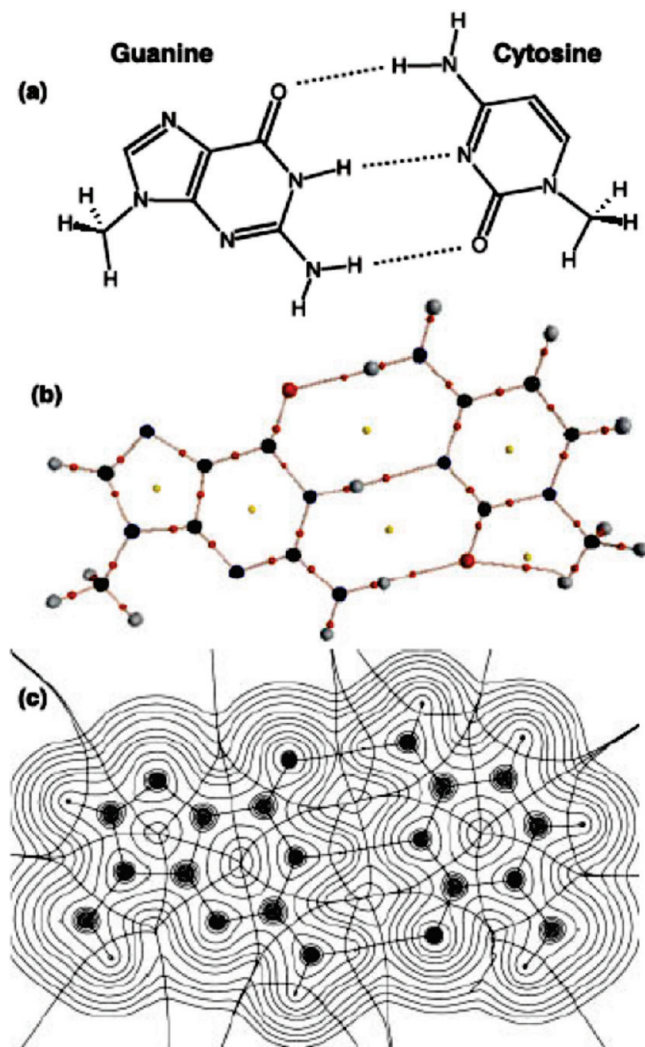
A region of space encompassed by a zero-flux surface or a connected set of such surfaces is a *proper open system*, one whose properties are defined and predicted by quantum mechanics.<sup>39</sup> Thus quantum mechanics predicts all properties not only for the molecule but also for each of its constituent atoms, recovering the experimentally measured values for atomic properties in series of molecules that exhibit “additivity schemes”.<sup>25,40</sup> While the quantum definition is based upon the variational derivation of the physics of an open system from a fundamental statement of physics,<sup>39</sup> a heuristic proof of the zero-flux surface defining a spatial region subject to the theorems of quantum mechanics is open to anyone possessing knowledge of Schrödinger’s equation.<sup>41</sup>

Atoms in a molecule are clearly open systems and their physics reflects this, their properties including a contribution from the flux in property currents across their interatomic surfaces. *Thus the definitions of a bond path and hence molecular structure are inseparable from the quantum mechanical definition of an atom as a proper open system*, both of which are defined by the topological behavior associated with the ubiquitous presence of a (3,−1) critical point. 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. This association of a chemical structure with a molecular graph, the latter being determined by the pairs of atoms that share an interatomic surface, is illustrated in Figure 3 for the pairing of the guanine and cytosine bases in a structural unit of DNA. The molecular graph in (b) extracts the essential structural information from the fuller description of the atomic interactions given in (c), in precisely the manner in which the same information is summarized by the classical structure (a). There is a clear mapping of the classical structure, including the dotted lines employed to denote the presence of hydrogen bonds, with the bonding determined by the topology of the electron density, a determination of structure that transcends all models.

#### IV. Why is the Topological Definition of Structure Rejected by Some?

The recovery of all classical structures by corresponding molecular graphs, both in theoretically and particularly in experimentally determined densities, would appear to vindicate the association of structure with the topology of the density. 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,



**Figure 3.** Representations of the molecular structure of the guanine-cytosine base pair: (a) classical structure; (b) structure defined by the bond paths that originate at the intervening bond critical points denoted by the small red dots, ring critical points being denoted by yellow dots; (c) contour map of  $\rho(\mathbf{r})$  overlaid with the bond path and intersection of the interatomic surface associated with each bond critical point. The classical structure is recovered in its entirety in the topology of the electron density.

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 occasioned by the observation of “novel structures”, 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.

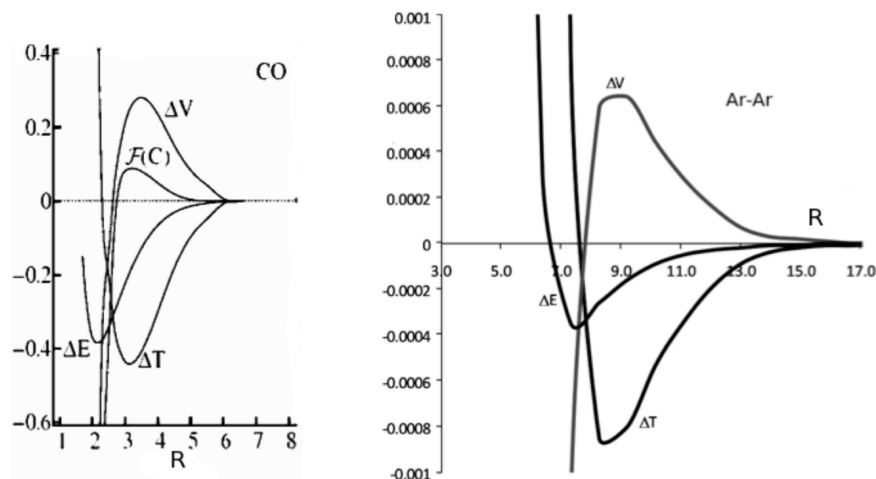
**IV.1. Example of the Density Explaining and Correcting the Failure of a Model.** A pertinent example of this is provided by the VSEPR model of molecular geometry which successfully accounts for the geometries of molecules based on arguments of presumed preferred geometrical arrangements of electron pairs in the vicinity of a central nucleus.<sup>42</sup> A physical basis for the VSEPR model is provided by the observation that the patterns of local charge concentrations (CCs) defined by  $L(\mathbf{r})$ , the negative of the Laplacian of  $\rho(\mathbf{r})$ , are in remarkable correspondence with the numbers, the relative magnitudes, and arrangements of electron pairs assumed in the VSEPR model.<sup>43,44</sup> It is found, however, that

geometries of molecules containing a metal atom can differ from those of the analogous main group molecule and thus are not in accord with the VSEPR model. For example, whereas  $\text{CO}_2$  and  $\text{NO}_2^+$  are linear and in accord with the model,  $\text{CaF}_2$ ,  $\text{BaH}_2$ ,  $\text{TiO}_2$ ,  $\text{VO}_2^+$ , and  $\text{CrO}_2^+$  are bent in clear violation of the VSEPR model.<sup>45,46</sup> Since  $L(\mathbf{r})$  is a physical property of a system and model independent, its topology should differ between that for main group molecules and those containing a metal atom to account for their differing geometries, and this is indeed the case. In the latter cases it is found that the outer core of the metal (with the shells of the core density defined by  $L(\mathbf{r})$ ) is polarized to create CCs that unlike their adjacency to the ligands in main group molecules, are diagonally opposed to the positions of the ligands, giving rise to ligand-opposed CCs.<sup>45</sup> This fundamental difference in the topology of  $L(\mathbf{r})$  between main group molecules and their analogous metal molecules accounts for their differing geometries, the ligand-opposed topology of  $L(\mathbf{r})$  appearing in all cases where the VSEPR model fails, accounting as well, for the differing chemistry of the transition metals from their main group counterparts. It should be noted that the topology of  $L(\mathbf{r})$  is determined by the physics of the pair density. In all cases,  $L(\mathbf{r})$  is homeomorphic with the topology of the Laplacian of the conditional pair density.<sup>47</sup> It thus provides a mapping of the essential aspects of electron pairing determined by the pair density determined in six-dimensional space onto the three-dimensional space of the electron density. *Thus while models can fail, the failure is predicted and accounted for when the underlying physical basis of the model is known.* Correspondingly, models of structure can be extended to cases hitherto not encompassed by the models when so indicated by the topology of the density, the underlying physical basis for the definition of structure.

**IV.2. Uncoupling the Notion of a Lewis “Bond” from the Concept of a Bond Path.** A particular source of disagreement over the use of a bond path to denote the presence of a bonded interaction between atoms is the inability of some to dissociate the concept of a “bond”, particularly in the Lewis sense, from the presence of a bond path.<sup>35</sup> The problems associated with such an identification were anticipated from the beginning of the theory, leading to the following statement in the treatise *Atoms in Molecules: A Quantum 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.”<sup>25</sup>

This distinction is not one of semantics, but of physics. A bond path is a measurable property of a system that, following on the theorems of quantum mechanics, denotes a bonded interaction, while a “bond” is neither measurable nor susceptible to theoretical definition and means different things to different people. 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.<sup>48,49</sup> *This definition, which necessarily applies to quantum mechanical densities, transcends all bonding schemes and categories and provides a unified physical understanding of atomic interactions.* Indeed, bond critical point data are widely used and increasingly so, in the characterization of bonding throughout all facets of chemistry,<sup>50</sup> using both experimental and theoretical densities.<sup>25,51</sup>

The concept of a bond is, in the minds of some, inseparable from the Lewis model and hence from its limitations. Until that time when the topological definition of structure and its physical



**Figure 4.** (a) Variation with internuclear separation  $R$  in the changes with respect to the separated atoms in the total energy  $E$ , the kinetic energy  $T$ , the potential energy  $V$  in au =  $e^2/a_0$ , and the Ehrenfest force on the C atom,  $\mathcal{F}(C)$ , in the ground state of CO in au =  $e^2/a_0^2$  plotted on the vertical axis. (b) Same variations in  $E$ ,  $T$ , and  $V$  for the approach of two ground state argon atoms. The forms displayed in these plots for  $E$ ,  $T$ , and  $V$  are universal.

basis are universally accepted, it is best to distinguish between a “bond” and “bonding”, the latter denoted by a bond path.

## V. Dealing with Common Misconceptions

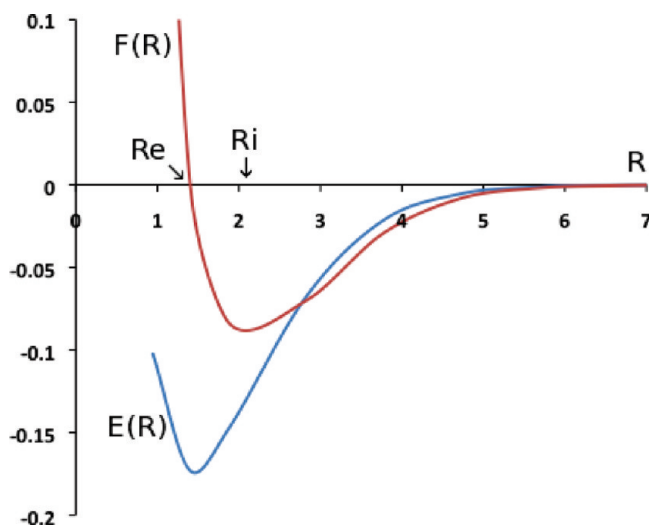
**V.1. Theorems Governing Chemical Bonding.** All of the criticisms put forth regarding the identification of bonding with the presence of a bond path are a result of a lack of understanding of the underlying physics, or the refusal of some to accept the extension of quantum mechanics to an atom in a molecule. For that reason this section begins with a review of the Ehrenfest, Feynman, and virial theorems.<sup>25</sup> *The Ehrenfest force acting on the electrons*<sup>52,53</sup> and *the Feynman force exerted on the nuclei*<sup>54</sup> are the only forces involved in chemical bonding. The molecular virial theorem<sup>55</sup> relates the virial of the Ehrenfest force acting on the electrons to their kinetic energy, the molecular virial including in addition to the total potential energy of the system, a contribution from the virial of the Feynman forces acting on the nuclei. 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 in the manner promulgated by Slater.<sup>56</sup>

All of the essential physics contained in these three theorems is contained in their application to a diatomic molecule. Figure 4 displays the changes, with respect to the separated atoms, in the total energy  $E$ , the kinetic energy  $T$ , and the potential energy  $V$  (with  $E = T + V$ ), as a function of the separation  $R$  between the nuclei for the molecules, CO and Ar<sub>2</sub>. The wave function for CO is from a highly correlated calculation with a large basis set<sup>57</sup> and that for Ar<sub>2</sub> from a new calculation, QCISD(Full)/6-311++(3df), giving  $R_e = 7.3$  (7.1) and  $D_e = 3.5 \times 10^{-4}$  ( $4.5 \times 10^{-4}$ ) in au, experimental values in brackets. The behavior displayed in these curves is typical of *all atomic interactions* even though CO and Ar<sub>2</sub> shown here supposedly exhibit disparate bonding mechanisms.<sup>58–60</sup>

Slater’s molecular virial theorem<sup>55</sup> written for a diatomic molecule may be expressed as

$$T = E - R(dE/dR) = -E + RF(R) \quad (2)$$

The quantity  $F(R) = -(dE/dR)$ , is the Feynman force on a nucleus at some separation  $R$ : attractive for  $R > R_e$ , the



**Figure 5.** Variation in au in the total energy  $E(R)$  and the Feynman force  $F(R)$  on a nucleus in a diatomic molecule versus internuclear separation  $R$  in au.  $R_e$  is the minimum energy separation where  $F(R) = 0$  and  $R_i$  is the inflection point in the  $E(R)$  curve where  $F(R)$  attains its maximum attractive value.

equilibrium separation, and repulsive for  $R < R_e$ . In the case of the separated atoms and at  $R_e$  where  $E(R)$  attains its minimum value,  $F(R) = 0$ . Thus in these cases  $T = -E$  and one may recast eq 2 in terms of the changes in the energies relative to their values at infinite separation to give the relation between  $\Delta E$  and the kinetic energy  $\Delta T$

$$\Delta T = -\Delta E + RF(R) \quad (3)$$

and the potential energy  $\Delta V$ .

$$\Delta V = 2\Delta E - RF(R) \quad (4)$$

**V.1.1. Feynman Force.** Figure 5 displays the Feynman force  $F(R)$  acting on a nucleus in a diatomic molecule as a function of  $R$ , illustrating its relationship to  $E(R)$ . The  $F(R)$  curve is universal in form for a bound state, being attractive up to its vanishing at  $R_e$ , beyond which it is repulsive. The force attains its maximally attractive value at  $R_i$ , the inflection point in  $E(R)$ .



The energy  $E(R)$  is the potential energy curve for motion of the nuclei, since it involves only the coordinates of the nuclei and the Feynman force is thus the negative derivative of a potential energy with respect to a nuclear coordinate. The bonding energy of a diatomic molecule is, therefore, given by the integration of the  $F(R)$  curve from infinity up to  $R_e$ , the area lying between the  $F(R)$  curve and the  $R$  axis.

$$\text{bonding energy} = \int_{\infty}^{R_e} F(R) dr \quad (5)$$

The deeper this minimum in  $F(R)$ , the larger is the integrated area and the larger is the bonding energy. Thus knowledge of the force on a nucleus as a function of  $R$  is sufficient to determine the energy of interaction. It was demonstrated early on that simple empirical LCAO approximations to the density give estimates of bonding energies superior to what was then obtained from molecular orbital calculations.<sup>61</sup>

It is the Feynman force that determines the motion of a molecule on a potential energy surface and whose vanishing determines the minimum energy geometries and the geometries of transition states. The beauty of Feynman's electrostatic theorem lies in its demonstration that the force on a nucleus is the simple resultant of the electrostatic force of repulsion exerted by the other nuclei and the force of attraction exerted by each and every element of the electron density. *It is this force and this force alone that determines whether a given nucleus experiences an attractive, a repulsive or a vanishing force in any given geometry.*

**V.1.2. Ehrenfest Force.** The Ehrenfest force, on the other hand, determines the force acting on an atom, as obtained by the integration of the force it exerts on an element of the electron density over the atomic basin. It is determined by the negative gradient of the total potential energy operator with respect to the coordinates of an electron and then averaged over the entire molecular charge distribution to yield the force as a density in real space. Thus, like the Feynman force, it is the result of an attractive and a repulsive force: the force of attraction exerted by the nuclei and the repulsive force exerted by the electron distribution. While both the Feynman and Ehrenfest forces are determined by gradients of a potential energy, the Ehrenfest force in a stationary state is necessarily balanced at every point in space by an equal and opposite "quantum force" expressed in terms of the gradient of the quantum stress tensor. The Ehrenfest force on atom  $\Omega$ , denoted by  $\mathcal{F}(\Omega)$ , is balanced by an equal and opposite force exerted on its surface  $S(\mathbf{r})$ , expressed in terms of the stress tensor  $\sigma(\mathbf{r})$ , as given in eq 6

$$\mathcal{F}(\Omega) = - \oint dS(\mathbf{r}) \sigma(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = \mathcal{J}(\Omega) \quad (6)$$

The stress tensor has the dimensions of an energy density or, equivalently, of force per unit area, and thus when integrated over an atomic surface, it yields the force exerted on the atom by its surroundings. The vanishing of the Ehrenfest force in no way detracts from its usefulness, as one can determine its direction at a point in space or over an atomic basin. In a diatomic molecule A|B sharing a surface  $S(\text{A|B})$ , the surface integral for A,  $\mathcal{J}(\text{A})$ , is equal and opposite to that for B, as  $\mathbf{n}(\text{A};\mathbf{r})$ , the outwardly directed normal to the surface  $= -\mathbf{n}(\text{B};\mathbf{r})$ . Thus  $\mathcal{J}(\text{A}) = -\mathcal{J}(\text{B})$  and if the force on atom A draws it toward atom B, then B is similarly attracted toward atom A. The Ehrenfest force on an atom is dominated either by the repulsion of the neighbor's electrons or by the attraction of its nuclei.

The resultant force, as are all questions of bonding, is couched in the language of simple electrostatics.

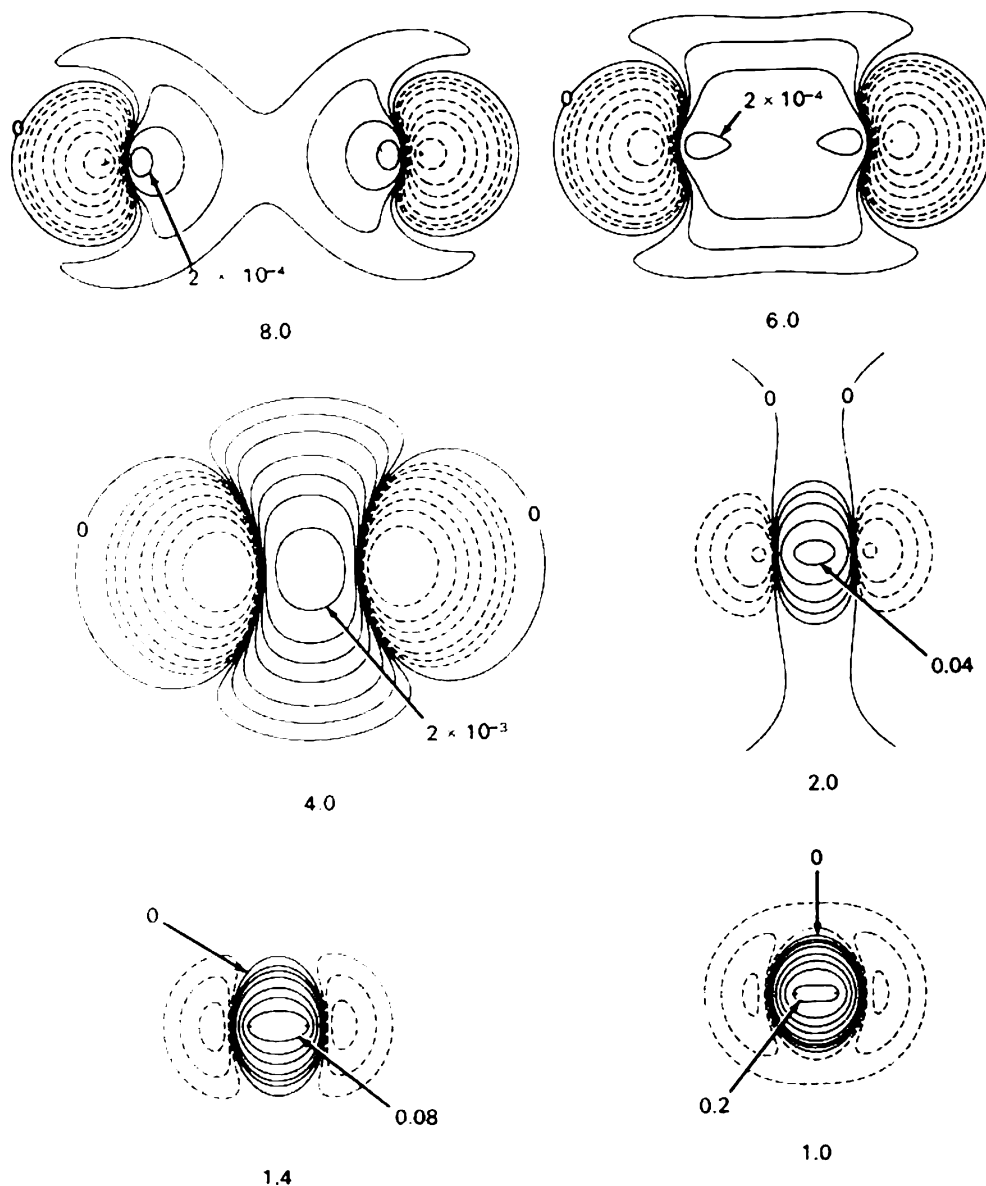
The behavior of the Ehrenfest force is also general and of the form illustrated by the curve giving the Ehrenfest force acting on the carbon atom in the CO molecule shown in Figure 4. It is repulsive for large separations but becomes increasingly attractive for decreasing separations, beginning at values in excess of  $R_e$ . This is the expected behavior as it is the virial of the atomic Ehrenfest force that determines the potential energy of an atom in a molecule and this energy is stabilizing in a bound state.

### V.1.3. Unification of the Forces by the Virial Theorem.

What at first might be surprising in terms of the oft quoted statement of the virial theorem, that the kinetic energy must increase on bonding by an amount equal to the decrease in energy, is the apparent reversal in the stabilizing-destabilizing roles of the kinetic and potential energies displayed in Figure 4, with the potential energy initially increasing and the kinetic energy decreasing, as the atoms approach from infinity. This behavior is, however, readily understandable by relating the behavior of  $\Delta T$  and  $\Delta V$  through eqs 3 and 4, to the changes in the Feynman force on the nuclei  $F(R)$ , and hence to changes in the density as displayed for example, in the density difference maps  $\Delta\rho(\mathbf{r})$  for the approach of two H atoms shown in Figure 6.

The virial of a force, the quantity  $RF(R)$  in eqs 3 and 4, is negative and stabilizing when the Feynman force is attractive,  $RF(R) < 0$ . *It is only in the presence of an attractive force where  $RF(R) < 0$  that  $\Delta T$  and  $\Delta V$  can change sign:  $\Delta T < 0$  when  $|RF(R)| > -\Delta E$  and  $\Delta T = 0$  when  $|RF(R)| = -\Delta E$ ;  $\Delta V > 0$  when  $-RF(R) > 2|\Delta E|$  and  $\Delta V = 0$  when  $2|\Delta E| = -RF(R)$ .* Thus  $\Delta V$  becomes negative before  $\Delta T$  becomes positive. When the Feynman force is repulsive,  $RF(R) > 0$  and  $\Delta T > 0$  and  $\Delta V < 0$ .

The behavior in the range  $\Delta T < 0$  and  $\Delta V > 0$  is understandable in terms of the changes in the electron density that accompany the initial approach of the atoms as shown for  $R = 8$  and 6 au in Figure 6. Density is removed from the immediate vicinities of both nuclei where  $V(\mathbf{r})$  is maximally negative and  $T(\mathbf{r})$  is maximally positive and accumulated in a diffuse distribution in the binding region resulting in the relaxation of the gradients in  $\rho$  and thus further reducing  $T$ . Thus  $V$  is increased,  $T$  is decreased, and the density accumulation in the binding region and its removal from the antibinding regions results in an attractive Feynman force on the nuclei. Each nucleus is attracted by its own *inwardly polarized density* and the resulting "boot strap" force is, as explained by Feynman, the origin of the initial  $1/R^6$  long-range attraction between neutral atoms. Thus the initial decrease in  $T$  is a result of the creation of attractive Feynman forces on the nuclei *resulting from the accumulation of density in the bonded region (Slater's overlap density)* the essential first step in bond formation and one that continues up to the equilibrium separation where  $\Delta E = -\Delta T$  as seen from the maps in Figure 6, the value of  $\rho_b$  increasing to 0.273 au at  $R_e$ . The map for  $R = 2.0 = R_i$ , the point where the attractive force on a proton is of maximum magnitude, shows that the boundaries between the region of density increase in the binding region and decrease in the antibinding regions, passing through the nuclei. The continuing approach of the atoms to values of  $R < R_i$ , causes density to be increasingly accumulated in the antibinding regions, leading to a reduction in the magnitude of the attractive Feynman force and to its eventual reversal in sign for values of  $R < R_e$ . All of this physics is clearly visible and understandable from the displays of  $\Delta\rho(\mathbf{r})$  given in Figure 6.



**Figure 6.** Density difference plots for the formation of ground state  $\text{H}_2$  calculated from a correlated wave function. The interatomic separation is listed under each figure in au. The solid and dashed contours increase or decrease respectively from the zero contour in the order  $\pm 2 \times 10^{-n}$  and  $\pm 4 \times 10^{-n}$ ,  $\pm 8 \times 10^{-n}$  au for decreasing values of  $n$ . The maps for  $R = 8, 6$ , and  $4$  au begin with  $n = 5$  and those for  $2.0, 1.4$ , and  $1.0$  au begin with  $3$ . Note the inward polarization of the atomic densities at large separations as predicted by Feynman. At  $R = 2$  au, the inflection point in the  $E(R)$  curve, the boundary of the charge accumulation in the binding region passes through the nuclei and  $F(R)$  is a maximum. For  $R < 2$  au, density is increasingly placed in the antibinding regions.<sup>108</sup> The equilibrium separation is  $1.4$  au.

One may combine the virial and Feynman theorems through the use of eqs 2 and 3 to obtain differential statements for  $dT(R)$  and  $dV(R)$ . These expressions yield constraints on the signs of the slopes  $dT(R)/dR$  and  $dV(R)/dR$ , which are seen from Figure 4 to change sign with decreasing  $R$ . The derivation of these equations and their full discussion have been given previously,<sup>25,62</sup> only their principal consequences are summarized here.<sup>25</sup> The derivatives are determined by two contributions,  $F(R)$  and  $R dF(R)/dR$ . For large values of  $R$  lying in the range  $\infty > R > R_i$ , the two terms differ in sign with  $F(R) < 0$  and  $R dF(R)/dR > 0$ . For large  $R$ , the latter term will dominate with the result that  $T$  must decrease and  $V$  increase upon the initial approach of two neutral atoms (or the approach of one neutral and one charged atom).

At  $R = R_i$ ,  $F(R)$  is maximally attractive, Figure 5, occurring at  $\sim 2$  au for  $\text{H}_2$ , Figure 6. Thus,  $dF(R)/dR = 0$  and the signs of the derivatives are uniquely determined with  $dT/dR < 0$  and  $dV/dR > 0$ , requiring that  $T$  must increase and  $V$  decrease upon

further approach of the atoms, changes that actually take effect for  $R > R_i$ . In summary, the virial theorem relates the changes in  $E$ ,  $T$ , and  $V$  to the forces exerted on the nuclei over the entire range of internuclear separations:  $T(R)$ ,  $V(R)$ , and  $F(R)$  are all interdetermined, the behavior of each being an inescapable consequence of the others. The result that the kinetic energy  $T$  can decrease only in the presence of attractive Feynman forces, calls into question models that ascribe bonding to a decrease in  $T$  at the equilibrium geometry where  $F(R)$  vanishes.

**V.2. Forces Acting in Ionic Crystals.** The Lewis model does not apply to an ionic crystal, and structures are assigned on the basis of linking neighboring anions and cations, regardless of how many “bonds” this might require, a number that certainly exceeds any assignment on the basis of electron pair bonds. Bonds are thus assigned a “fractional bond order”, one-sixth for the links in sodium chloride, for example. This procedure becomes impractical for crystals with other than simple structures. Witness for example, the number of anion–cation bonds



thus generated in a halide peroxide crystal,  $\text{AMX}_3$ , wherein the cation  $\text{A}^+$  alone has 12 neighboring halide ions. A topological analysis of the electron density should prove useful in clarifying and understanding the range of structural parameters they exhibit and this was indeed shown to be the case.<sup>63</sup> In addition to the topology of the crystal density recovering the anticipated anion–cation interactions, such as six bond paths to each  $\text{M}^{2+}$  ion, six to each  $\text{F}^-$  ion, and twelve bond paths linking the  $\text{A}^+$  and  $\text{F}^-$  ions, perovskite structures with  $\text{X} = \text{Cl}^-$  and  $\text{I}^-$  exhibit eight bond paths linking the anions. The presence of bond paths linking anions was an early source of contention in accepting the presence of a bond path as indicative of bonding,<sup>64</sup> notwithstanding the suggestion by Pauling<sup>65</sup> who postulated the presence of  $\text{X}-\text{X}$  bonds in  $\text{LiCl}$ ,  $\text{LiBr}$ , and  $\text{LiI}$  as a way of explaining the anomalous sequence in their geometries.

The finding of  $\text{X}-\text{X}$  bond paths provides an ideal case for distinguishing between the Feynman force exerted on a nucleus and the Ehrenfest force acting on the atom. A crystal resides in an equilibrium geometry in which the Feynman forces acting on the nuclei vanish. Any displacement of an ion from its equilibrium geometry results in the creation of an attractive Feynman restoring force returning it to its equilibrium position and the crystal is energetically stable. There are no Feynman forces, attractive or repulsive, acting on the nuclei in the equilibrium geometry.

The electrons on neighboring ions do indeed repel one another, but these repulsions contribute to the Ehrenfest force exerted on the *atom* and play no direct role in determining the force on a *nucleus*. Recalling that the virial of the Ehrenfest force determines an atom's potential and total energies and that the crystal is energetically stable, it is clear that these repulsive forces are more than compensated for by the attractive forces exerted on the density by the nuclei of the neighboring ions. Thus the Ehrenfest force acting on anion in a crystal is attractive across each of the interatomic surfaces it shares with its neighbors, which may include other anions. All of the ions in the crystal are bound by an attractive Ehrenfest force and every atom contributes to the lowering of the energy of the crystal.

A simple example of  $\text{X}-\text{X}$  bonding is found (as postulated by Pauling<sup>65</sup>) in  $\text{LiI}$ . Each  $\text{Li}^+$  ion is linked to  $\text{I}^-$  ions by six bond paths to give the anticipated classical structure for  $\text{LiI}$ . In addition, however, each  $\text{I}^-$  ion is linked to 12 neighboring  $\text{I}^-$  ions and is thus 18 coordinated.<sup>66</sup> Crystal symmetry dictates the cps that denote the presence of the 6-fold coordination of  $\text{Li}^+$  are bond cps, but the cp that is identified as a bond cp in  $\text{LiI}$  is not required by crystal symmetry to be a bond cp and is not so in many alkali halides. Instead, its bonding character is reserved primarily for crystals containing anions such as  $\text{I}^-$  and  $\text{Br}^-$  and  $\text{Cl}^-$  with diffuse outer density distributions, although bond paths can be found between  $\text{F}^-$  ions when the cation is small, as in  $\text{LiF}$ .<sup>64</sup> As noted above, the perovskite structures containing these same ions also exhibit  $\text{X}-\text{X}$  bond paths. In the case of a cation with a large ionic radius, such as  $\text{Cs}^+$  in conjunction with the presence of a small anion such as  $\text{F}^-$ , it is possible to find bond paths linking the cations as well.<sup>63</sup>

The outer density of large ions is relatively diffuse and the crystal achieves extra stability through the directed accumulation of the density between neighboring ions of similar charges to form bond paths, thereby further lowering the energy of the crystal. There is no physical distinction that can be made between the bond paths linking cations to anions and those linking anions or cations to one another. All are characterized by vanishing Feynman forces on the nuclei and attractive Ehrenfest forces acting on the atoms, forces that, via the virial

theorem, lead to a lowering of the atom's energy. It is well to remember that the density distribution for any system in any geometry is the one that minimizes its energy.

Pauling was not the only one to consider the important role played by the close approach of anions in a crystal lattice.<sup>65</sup> Slater devotes a section entitled “Interaction of Negative Ions in Crystals” in the second volume of his treatise on *Quantum Theory of Molecules and Solids*.<sup>67</sup> The spinel structure is particularly rich in oxygen, and Slater points out that the oxygen atoms are in contact with one another if one uses Pauling's ionic radii. His Figure 4-2 displaying the ions as spheres in  $\text{Al}_2\text{MgO}_4$  shows that, using these radii, the spheres for the oxygen atoms, represented as  $\text{O}^{2-}$  ions, are in contact with one another and share a common surface. To the extent that such spheres represent atomic sizes as determined by their density distributions, the oxygen atoms share an interatomic surface and are connected by a bond path. Such contacts between anions are not restricted to oxide ions of course, and Slater points out in particular, the case of  $\text{LiI}$  in considering the contacts between halide ions, where, as pointed out by Pauling, the distance between the  $\text{I}^-$  ions is less than the sum of their ionic radii. Interestingly enough, Slater also draws attention to the similar “touching” of  $\text{Cs}$  ions in  $\text{CsF}$ . In other words, one now understands that, for the cases wherein one is faced with the close contacts of ions of similar charges, their supposedly repulsive interactions are in effect stabilizing: atoms that touch one another in an equilibrium geometry share an interatomic surface and are thus linked by a bond path.

The classical view of the energetics of an ionic crystal structure and the model employed by Pauling and Slater and in the criticism proffered by Abramov,<sup>64</sup> is based on the calculation of the Madlung electrostatic energy of a lattice composed of spherical ions, with the addition of a term representing the non-Coulombic, closed-shell repulsions between them. Unlike Pauling who postulated possible bonding between the iodide anions in  $\text{LiI}$ , Slater, in his discussion of the repulsion between the anions in contact required by the classical model, argues that “the crystal as a whole is held together by Coulomb attractions and the anions are pushed together by these attractive forces until they balance the repulsion between their inert gas shells.” While the classical model has obvious pedagogical appeal, it should not be used as a basis for criticizing the quantum mechanical description of the forces acting on an ion in a crystal. The energy so calculated is not the quantum mechanical energy of the crystal and it does not satisfy the virial theorem, a theorem stating that the virial of the Ehrenfest force acting on an anion in a crystal determines its contribution  $V(\Omega)$  to the potential energy and thus its contribution to the energy of the lattice with  $E(\Omega) = (1/2)V(\Omega)$ , and this energy is stabilizing since the force is attractive.

Thus it is important to distinguish between the force on an atom and the force on its nucleus. The only electronic contribution to the Feynman force that determines a crystal's equilibrium geometry is the attractive force exerted by the electron density. This is the beauty of the electrostatic theorem: the electron–electron repulsions are subsumed in the determination of the electron density, and the only forces acting on a nucleus are its attraction by the density and its repulsion by the other nuclei.

**V.3. Nonbonded or van der Waals Interactions.** The Lewis electron pair model was understandably never extended to account for the attractive interactions that exist between closed-shell molecules that lead to the condensed states of matter. Instead, text books and the literature refer to “nonbonded” interactions between molecules in crystals and the existence of

condensed states of matter is attributed to the operation of isotropic van der Waals forces that have traditionally been distinguished from those responsible for chemical bonding. Invoking “nonbonded interactions” between atoms whose contacts are less than the sum of their van der Waals radii, is a model frequently invoked in discussions of both intramolecular and intermolecular interactions and their correct physical description in a given situation is essential to understanding the structures of molecules and crystals. Close contacts are frequently relegated to a repulsive role and described as “Pauli or exchange repulsions” between atoms. The term “nonbonded” sums up the notion that van der Waals interactions are to be distinguished from chemical bonding. This is a frequently expressed view, as exemplified by the recent statement: “... but most chemists will have no difficulty in distinguishing between a molecule held together by chemical bonds and a weakly bound aggregate such as a noble gas dimer which is held together by weak van der Waals forces.”<sup>68</sup>

The question boils down to determining whether atoms that “touch” are bonded to one another or repelling one another. This question has an immediate answer in terms of the topology of the density. Atoms that “touch” necessarily share an interatomic surface and in an equilibrium geometry are linked by a bond path. They are thus bonded to one another. An example of atoms “touching” is provided by the contacts found between anions in ionic crystals discussed above, a feature addressed by Pauling and Slater.

Because they lie outside the range encompassed by the Lewis model, nonbonded interactions fall in the category of phenomena that require an extension of the model. This requirement differs in no way from earlier extensions to the model described in section II that were occasioned by our ability to determine increasingly complex structures. This extension is readily accomplished because both the model and its extension to the realm of nonbonded interactions are encompassed by one and the same measurable physical attribute: the presence of a bond path linking atoms that touch. A molecular graph recovers all known classical structures. The same physics should apply to cases that arise when two classical structures approach one another or when any two “nonbonded” atoms approach to within their van der Waals radii. Acceptance of this broadening of the concept of chemical bonding requires only the acceptance of the physics underlying the statement that van der Waals interactions are bonded interactions in the chemical sense of the phrase.

**V.3.1. van der Waals Interactions Are Bonded Interactions.** One can do no better in introducing this topic than to quote Slater’s view: “The writer believes that there is no very fundamental distinction between van der Waals binding and covalent binding. If we refer them back to the electronic charge distribution, which, as we have seen, is solely responsible for the interatomic forces, we have the same type of behaviour in both cases.”<sup>69</sup> Slater’s view is borne out by the homeomorphic displays of the variation in  $E$ ,  $T$ , and  $V$  with  $R$  presented in Figure 4 and elsewhere,<sup>58,59</sup> which demonstrate that all bonded interactions, including those responsible for “van der Waals bonding” in  $\text{Ar}_2$ , are governed by the same underlying physics.

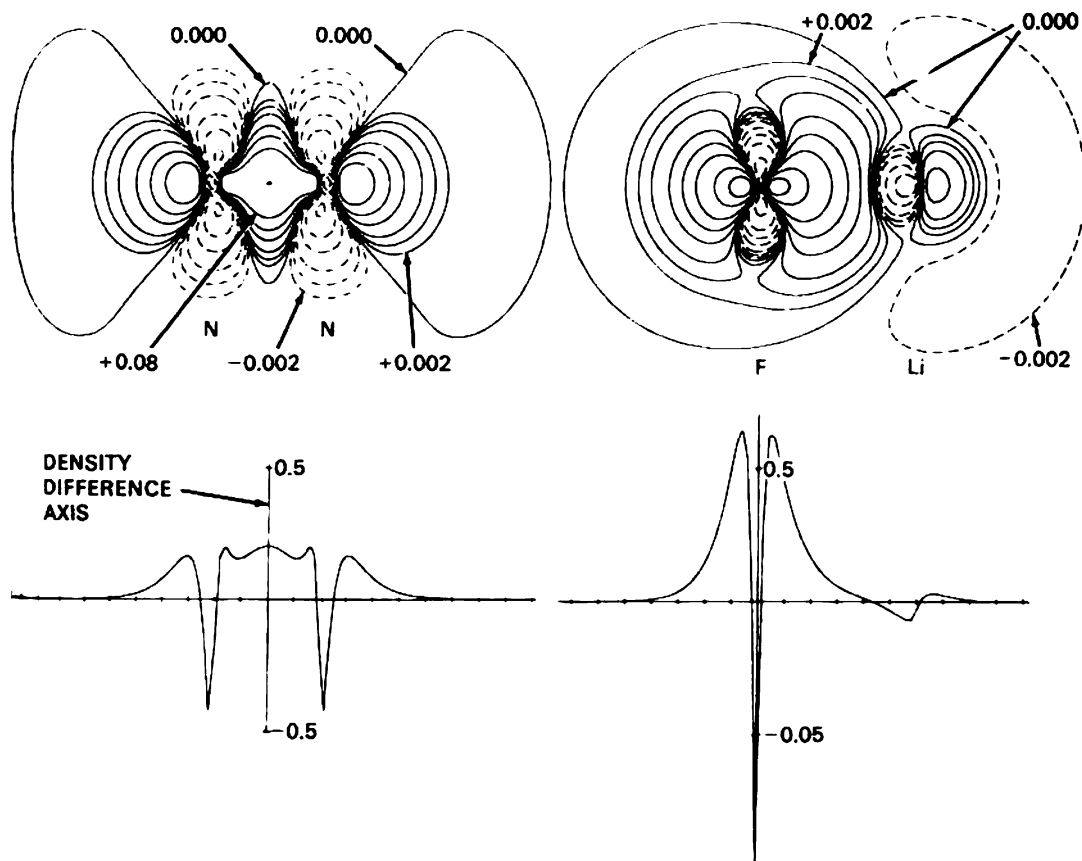
Interactions classically labeled as ionic, polar, covalent, hydrogen bonded, or van der Waals are equally the result of the accumulation of electron density between the nuclei with the above-described consequences. Elementary considerations demonstrate that chemical bonding is dominated by the electrostatic interaction of each nucleus with the density of the atom or atoms to which it is bonded.<sup>70</sup> What distinguishes the bonding

within each set is not its physical origin, which in each case is a result of the increase in the stabilizing interaction of the nuclei with the electron density, primarily in the new attraction of each nucleus for the density of its bonded neighbor, but rather the manner in which the density is distributed over the atomic basins, covalency being characterized by an equal sharing of the density, the ionic extreme by its localization within a single basin.<sup>57</sup> This contrasting behavior is illustrated by the density difference maps for  $\text{LiF}$  and  $\text{N}_2$  shown in Figure 7. The variations in  $E$ ,  $T$ , and  $V$  with  $R$  pictured in Figure 4 are universal,<sup>58,59</sup> though they may differ in the theoretical methods employed in their determination. The method of calculating the wave function, however, should play no role in the interpretation of the results so obtained. Instead, following Schrödinger’s advice,<sup>71</sup> the use of the wave function should be restricted to the determination of the expectation values of observables, which includes the electron density.

This discussion is to be contrasted with the interpretation of van der Waals bonding resulting from the pioneering calculations of London<sup>72</sup> and Eisenschitz and London,<sup>73,74</sup> who employed second-order perturbation theory to calculate the long-range dispersion energy between neutral molecules. The leading dipole–dipole interaction determining the wave function may be interpreted as resulting from the interaction of the “fluctuating dipoles” on the atoms induced by the correlated motions of their electrons, a term that, as shown by London, can be related to the polarizabilities of the atoms.<sup>72</sup> The oscillating dipole picture is, however, misleading as it is an attempt to portray an interaction requiring six-dimensional electron-pair space in the three-dimensional space of the electron density. Dispersion forces are not caused by “oscillating dipoles” but rather, as pointed out by Feynman in 1939, are a result of the density of each atom being polarized in the direction of the other and the van der Waals force is the result of “the attraction of each nucleus for the distorted charge distribution of its own electrons that give the attractive  $1/R^7$  force.”<sup>54</sup> The forces exerted by a density derived from opposing atomic dipoles would lead to Feynman forces of repulsion acting on the nuclei. Feynman’s inwardly directed polarization of the atomic densities is that portrayed in the density change illustrated in Figure 6 for  $R = 8$  or  $6$  au and, as discussed above, is responsible for the attractive Feynman forces on the nuclei. As in all bonding, the accumulation of density in the internuclear region increases to the point where it is eventually balanced by the growing force of nuclear repulsion at the equilibrium separation resulting in  $\Delta T = -\Delta E$ .

Explicit proof of Feynman’s explanation has been provided by Hirschfelder and Eliason<sup>75</sup> using Feynman’s electrostatic theorem in the calculation of the second-order correction to the  $R^{-7}$  force on a proton in  $\text{H}_2$  from which they conclude: “The force on the nucleus is then due to its attraction to the centroid of its “own” electron cloud as originally suggested by Feynman.” Hunt<sup>76</sup> has extended this work by providing an explicit general proof of Feynman’s statements that are applicable to molecules of any symmetry, stating that the “attraction of a given nucleus is the result of the dispersion-induced change in the density of the same molecule.”

A distinguishing feature of the bonding resulting from dispersion forces is that it occurs for separations where there is no appreciable overlap of the interacting densities. It is for this reason that perturbation theory is successful in its description. However, any correlated variational calculation such as that of Das and Wahl employing “optimized valence configurations”,<sup>77</sup> whose results are illustrated in Figure 6 for  $\text{H}_2$ , as well as the QCISD wave functions used in the calculation of the energy



**Figure 7.** Density difference maps for ground states LiF and  $N_2$  calculated from separated atoms in proper valence states. The contours are as given in the caption for Figure 6. 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  $q(X) \pm 0.94e$ . 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  $q(X) \pm 0.94e$ ) debyes to 7.1 debyes.<sup>108</sup>

curves shown in Figure 4, predict the same changes in the electron density as that found by Hirschfelder and Eliason. Whether or not bonding is the result of “atomic overlap” as invoked in covalent bonding, its physical origin is the same: an accumulation of density between the nuclei. The bond paths characterizing the intermolecular interactions in dimers and trimers of “van der Waals” complexes were studied in detail by Bone and Bader<sup>78</sup> and found to exhibit the hallmarks of closed-shell interactions.<sup>50</sup>

**V.3.2. Contentious Bond Paths.** That a bond path must be created on the approach of two He atoms is a lingering source of contention with those who question its physical significance. First, it is important to point out that the He dimer does exist in a bound state and liquid helium does exist as a condensed state of matter. The existence of the He dimer was first demonstrated in 1993 with the mass spectroscopic observation of bound  $^4\text{He}_2$  in an extreme pulsed supersonic beam of He at temperatures of less than 1 mK, as reported in a paper entitled “The weakest bond: Experimental observation of helium dimer”.<sup>79</sup> This work was independently confirmed in 1994 in a diffraction experiment employing a nanoscale transmission grating.<sup>80</sup> The original work was extended by the measurement of the “size” of the helium dimer by passage through a set of nanoscale sieves that determined the mean internuclear distance to be  $62 \pm 10 \text{ \AA}$ , making the “bond” in  $\text{He}_2$  not only the weakest but also the longest.<sup>81</sup> The molecule exists in only a single state,  $j = 0$ ,  $v = 0$ , and is 4 orders of magnitude weaker than a typical van der Waals bond. Thus, to the workers who detected the helium dimer and confirmed the existence of a bound state, there was no hesitation in associating this observation with the presence of a “bond” in the dimer, or equivalently stated,

that the atoms are bonded to one another as denoted by the presence of a  $(3,-1)$  cp in its equilibrium density and the associated bond path.<sup>49</sup>

It is not that long ago that the elements in column VIII of the periodic table were labeled the “inert gases”, a connotation that had to be discarded with the observation of a bound complex of Xe with  $\text{PtF}_6^-$ .<sup>82</sup> This discovery was followed by the synthesis of many molecules containing noble gas atoms, laying to rest another “rule of valency”.<sup>83</sup> Krapp and Frenking have considered the interactions between noble gas dimers ( $\text{Ng}_2$ ) bound within a fullerene cage,  $\text{Ng}_2@C_{60}$ .<sup>68</sup> In each case the encapsulated Ng atoms are linked to one another by a bond path, and the dimers are linked to six C atoms in the Ar, Kr, and Xe complexes and to three C atoms in the He and Ne molecules. They conclude, primarily on the basis of the strength of the interaction of the dimer with the cage, that only in the case of the Xe complex should the bond paths be considered as representing “genuine chemical bonds”.

One must ask why, with the discarding of the notion that the noble gases are chemically inert, coupled with the observation of the bound states of all the Ng dimers,<sup>84</sup> that an Ng dimer with the possible exception of  $\text{Xe}_2$ , is not considered a molecule, “but a weakly bound aggregate ... held together by weak van der Waals forces”?<sup>768</sup> Bound is the operational word, and there is no physical distinction between strong bonding and weak bonding, the weak bonding in  $\text{He}_2$  being similarly offered as a reason for it not possessing a “chemical bond”. Who is to decide at what point a given bonded interaction denoted by a bond path in the density ceases to be a “chemical bond”? There are no “experts in science” to whom one can appeal. Instead, one arrives at his or her own



decision by appeal to observation and physics, the sole arbiters of the natural world. Classification without an observational or theoretical basis serves no useful purpose.

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. Gatti<sup>51</sup> has given an extensive review of intermolecular interactions in crystals covering the literature up to 2005 that reviews the properties of bond paths covering interactions from moderate, as exemplified by hydrogen bonded systems, to those of weak strength, as between bonded halogen atoms or guest–host interactions in metal frameworks and metal–guest encapsulation. New applications are constantly appearing, particularly applications to the study of the structure of naturally occurring minerals from the group of Gibbs.<sup>85</sup> Recent contributions include a paper on the role of directed van der Waals bonded interactions in the determination of the structures of arsenate solids<sup>86</sup> and another on the bonded interactions in silica polymorphs and silicates.<sup>87</sup> One should be prepared to find bond paths between atoms in situations where classical notions would suggest repulsion, the approach of head to head “lone pairs” for example. While such an interaction will be weak, one should recall that all neutral molecules attract one another at large separations and will, therefore, generate a bond path, one that on closer approach will become a repulsive atomic interaction line. All such interactions can play a stabilizing role in determining crystal geometries, in solid ammonia for example.

A particularly important bonded interaction in understanding the structure of condensed organic materials is the finding of bond paths between essentially neutral hydrogen atoms on neighboring molecules, as demonstrated by their experimental detection in many materials.<sup>88,89</sup> So-called H–H interactions occur intramolecularly as well.<sup>90</sup> Among these is the finding of bond paths between the ortho H atoms in planar biphenyl, an interaction considered classically to result in Pauli repulsions. The criticisms of the finding of H–H bonding in this and other examples have been commented on,<sup>32,53,91</sup> but criticisms that contravene simple physics continue.

This is well illustrated by a recent e-mail from a critic who asks how one can explain the barrier to internal rotation in biphenyl to first year students, other than to state “pi-delocalization favors the planar  $D_{2h}$  but it is pushed up and becomes a transition state due to H–H Pauli repulsion”, an explanation we were all taught as undergraduates, but some questioned. Physics is common sense and in studying a reaction, one should first consider its important geometrical changes, since these determine where changes are induced in the electron density and hence in the energy, a point ignored in the critic’s explanation. Even if one does not accept the quantum basis of QATAIM, one may use its atomic boundaries to determine which “atoms” undergo changes in density as a result of geometrical changes, thus spatially localizing the energy changes.

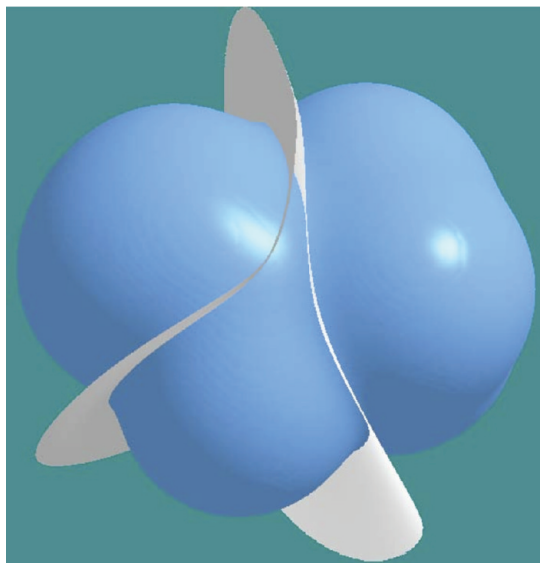
Examples of barriers ascribed to Pauli repulsions between hydrogen atoms, given without appeal to the changes in geometry, are the barriers to internal rotation in biphenyl and ethane. In both these examples, the principal geometrical change incurred in reaching the top of the barrier, but ignored in the models, is the stretching of the C–C bond in ethane and of the bridging C–C bond in biphenyl. These bond extensions clearly result in increases in energies, which in the case of ethane, is sole cause of the barrier.<sup>25,92</sup> In terms of overall energy contributions, the barrier in ethane is *not repulsive* but arises instead because of the decrease in the magnitude of the e–n attractions of one carbon nucleus for the density in neighboring

carbon basin that occurs on C–C lengthening. This decrease in the attractive interactions exceeds the accompanying decrease in e–e and n–n repulsions and the barrier is a result of the increased C–C separation. There are no repulsions between the hydrogen atoms in ethane whose energies and densities undergo only small perturbations. Even a rotation with the C–C separation fixed at the equilibrium value does not result in a repulsion between the H atoms.<sup>25</sup> The lack of any tie to experiment other than to the existence of the barrier led Bickelhaupt and Baerends to comment: “one can use neither physics nor observation to decide between the competing explanations of ‘Pauli repulsions’ or ‘hyperconjugative electron release’ as the cause of the barrier in ethane”.<sup>93</sup> This comment should be contrasted with the simple physical explanation provided here, based upon recognition of the central role played by the increase in C–C separation coupled with the ability to define the energy of an atom in a molecule.

In attaining the transition state in biphenyl, the C–C length increases by 0.016 au, causing the energy of the carbon atoms to increase by  $\sim 33$  kcal/mol, an increase that dominates the changes in energy and is the cause of the barrier. This energy increase is partly offset by the energy change arising from the other principal change in geometry: the decrease in the separation between the pairs of ortho hydrogen atoms. The approach of a pair of ortho hydrogen atoms causes density to be accumulated between them, *resulting in attractive forces* drawing them together and the eventual formation of H–H bond paths, thereby reducing the energy by  $\sim 21$  kcal/mol. All but 0.2 kcal/mol of the remaining reduction in energy of 9.4 kcal/mol comes from the ortho carbon atoms to give the resulting barrier of  $\sim 2$  kcal/mol. These are simple, physical explanations of barriers as the energy increases occasioned by bond extension, energy increases that can be mediated by the accompanying formation of stabilizing bonded interactions. One may write a resonance structure for planar biphenyl that permits the delocalization of electrons from one ring into the other, and there is indeed a small accompanying increase in the delocalization, as measured by the increase in the exchange of electrons between the rings, from 1.97% in the equilibrium geometry to 2.05% in the planar structure. Such a small increase in electron exchange and in the related exchange energy would hardly be sufficient to balance to within 2 kcal/mol the presumed “Pauli repulsions”, however defined or calculated between the ortho hydrogens. One can hope that knowledge of the dominant C–C bond lengthening in the rotation of biphenyl that must necessarily increase the energy will result in the questioning of the classical explanation.

**V.3.3. Role of the Laplacian in Predicting Intermolecular Bonding.** Nearly all of the investigations of intermolecular bond paths are complemented with a study of the topology of the Laplacian of the electron density,  $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ . The documented ability of  $L(\mathbf{r})$  to determine the regions of charge concentration (CC) and charge depletion (CD) in an electron density distribution,<sup>43,94</sup> as well as accounting for non-VSEPR geometries<sup>45,95</sup> and metal–ligand interactions,<sup>70</sup> is the basis for its use in predicting the alignment of molecules in a crystal by associating a CC on one molecule with a CD on its bonded neighbor, in a manner reminiscent of a Lewis acid–base interaction or Fischer’s lock and key analogy of substrate–enzyme interactions.<sup>96,97</sup>

The first application of a CC→CD interaction to a crystal structure was to the layered structure of solid chlorine<sup>98</sup> that could not be explained in terms of nondirectional van der Waals interactions.<sup>99</sup> The Laplacian distribution of a bound chlorine atom is characterized by a toroidal CC encircling its bonded axis with a pronounced nonbonded axial CD, a topology that



**Figure 8.** The 0.001 au density envelope for  $\text{CH}_3\text{CHO}$ . The intersections of the ClC and ClO interatomic surfaces with the envelope that define the  $\text{CH}_3$ , CH, and O groups are clearly defined.

emphasizes and gives operational roles to the principal features of its atomic density distribution. Thus the dimer of  $\text{Cl}_2$  has an intramolecular bond angle of  $\sim 90^\circ$  with the CC on the torus of one molecule aligning with the axial CD on another. This angular structure is carried over almost intact into the crystal with a “nonbonded” separation of 3.4 Å in the dimer compared to 3.3 Å in the crystals, and the structure of solid chlorine is both understood and predictable in terms of the Laplacian distribution of the Cl atom. That this is indeed a characterizing property of a Cl atom is its observed recurrence in the structure and Laplacian distribution of solid  $\text{FCl}^{100}$  and its role in determining the ring structure of the ubiquitous crystal synthon  $\text{Cl}_3$ ,<sup>101</sup> both systems exhibiting the identical  $\text{CC} \rightarrow \text{CD}$  interaction between chlorine atoms. The electron localization function (ELF)<sup>102</sup> has also proved very useful in the description and prediction of interactions in crystal structures.<sup>51</sup>

## VI. Real Atoms Do Not Overlap

Atoms are the primary constituents of matter, as Dalton proposed two hundred years ago, and they make their presence and properties known through their charge distributions.<sup>25</sup> This is illustrated in Figure 8 showing the 0.001 au density envelope of the  $\text{CH}_3\text{CHO}$  molecule. The charge distribution of an atom in a molecule completely determines its contribution to all molecular properties, including those induced by external fields or its interaction with light.<sup>103</sup> The intersections of the zero-flux interatomic surfaces with the envelope that define the boundaries of the individual atoms are clearly visible. The acceptance of this view of the atomic nature of matter requires a paradigm shift: that one foregoes the usual models of bonding couched in the language of overlapping atoms and replace it with one wherein bonded atoms share an interatomic surface. The model of overlapping atomic orbitals had its origin in 1928, with the Heitler–London wave function for the hydrogen molecule stated in terms of products of atomic orbitals, the famous “resonance” formulation,  $a(1)b(2) + a(2)b(1)$ . The use of orbital products is ubiquitous in models of chemical bonding. It has been of great pedagogical value and it will undoubtedly continue in this use. One need only refer to Coulson’s classic book *Valence*<sup>104</sup> to see the extensive use of the concept of orbital overlap, particularly in terms of the “criterion of maximum overlapping”, played in the

qualitative interpretation of bonding. Slater’s discussion of bond formation uses the overlap model to assess the accompanying changes in the electron density and relate these changes to the Feynman forces on the nuclei and to changes in  $E$ ,  $V$ , and  $T$  as demanded by the virial theorem and as reviewed in section V.1.3.<sup>55,67</sup> There is, however, no interjection of any step in his discussion that is not based upon the theorems of quantum mechanics, as can be seen in his summarizing statement “... both the virial theorem and Feynman’s theorem are exact consequences of wave mechanics. Both interpretations agree in pointing to the existence of the overlap charge density as an essential feature in the attraction between the atoms ...”.<sup>67</sup> It should be remembered that the use of atomic orbitals and orbital overlap provide but a model of the atomic changes that accompany chemical bonding. It is also worth noting that overlapping atoms cannot recover the cornerstone of conceptual chemistry—that of a functional group with characteristic and transferable properties, the central thesis of QTAIM.<sup>105,106</sup> An overlapped atom is unavoidably contaminated by its neighbors.

## VII. Epilogue

The purpose of this paper 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.

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