A Bond Path: A Universal Indicator of Bonded Interactions

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The quantum mechanics of proper open systems yields the physics that governs the local behavior of the electron density, $\rho(\mathbf{r})$. The Ehrenfest force $\mathbf{F}(\mathbf{r})$ acting on an element of $\rho(\mathbf{r})$ and the virial field $\nu(\mathbf{r})$ that determine its potential energy are obtained from equations of motion for the electronic momentum and virial operators, respectively. Each is represented by a "dressed" density, a distribution in real space that results from replacing the property in question for a single electron with a corresponding density that describes its average interaction with all of the remaining particles in the system. All bond paths, lines of maximum density linking neighboring nuclei in a system in stable electrostatic equilibrium, have a common physical origin in terms of $\mathbf{F}(\mathbf{r})$ and $\nu(\mathbf{r})$, regardless of the nature of the interaction. Each is homeomorphically mirrored by a virial path, a line of maximally negative potential energy density linking the same nuclei. The presence of a bond path and its associated virial path provide a universal indicator of bonding between the atoms so linked. There is no net force acting on an element of $\rho(\mathbf{r})$ or on an atom in a molecule in a stationary state, and $\nu(\mathbf{r})$ is attractive everywhere. Thus, contrary to what has appeared in the literature, no repulsive forces act on atoms linked by a bond path, nor on their nuclei. All atomic interactions, including those described as nonbonded and responsible for binding in condensed states of matter, result from a local pairing of the densities of opposite spin electrons. This local pairing, which varies throughout space and with the strength of the interaction, should be distinguished from the notion of an electron pair, as embodied in the Lewis model.

Definition of an Atomic Interaction Line and a Bond Path

The response of the electron density to the interaction between a pair of atoms is ubiquitous. It results in the formation of a line of maximum density linking the nuclei of the two atoms and in the formation of a surface defining their mutual boundary which intersects this line at the point where the density attains it minimum value.[1−5] These topological features are the result of the creation of a (3,−1) critical point (CP), a point where the gradient vector field of the density vanishes, $\nabla\rho(\mathbf{r}) = \mathbf{0}$, and the Hessian matrix of which, composed of the nine second derivatives of the density at the CP, yields upon diagonalization, three eigenvalues (two negative and one positive). The eigenvectors associated with the two negative eigenvalues define a two-dimensional manifold spanned by an infinite set of trajectories of $\nabla\rho$ that terminate at the CP, thereby defining a surface, the interatomic surface $S(\mathbf{r}_s)$, that separates the basins of the two interacting atoms. The third eigenvalue is positive and its associated eigenvector defines a unique pair of trajectories of $\nabla\rho$ that originate at the CP, each of which terminates at a nucleus of one of the neighboring atoms. This pair of trajectories defines a line through space along which the electron density is a maximum with respect to any neighboring line,[1] designated an atomic interaction line.[5,6] These general properties of the gradient vector field are illustrated in Figure 1 for the cubic-like cluster $Li_{14}F_{13}^{-}$, a model for the central F in the *fcc* lattice of LiF.

An interatomic surface $S(\mathbf{r}_s)$ is one of zero-flux in the gradient vector field of the electron density, the boundary condition for the definition of a proper open system[5,7]

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0 \qquad \forall\mathbf{r} \in S(\mathbf{r}_s) \qquad (1)$$

The name derives from the derivation, unique to such systems, of the Heisenberg equation of motion for an observable from Schwinger's principle of stationary action.[8] Proper open systems are thus subject to the same quantum mechanical description as is the total system of which they are a part and they satisfy the necessary theoretical requirements for the definition of an open system: they are bounded in real space and the expectation values of the observables and their equations of motion are uniquely defined.[7]

Proper open systems have been identified with the atoms of chemistry, because they have been shown to recover the essential notions associated with the atomic concept: (i) the atomic properties are characteristic and additive, summing to yield the corresponding values for the total system; (ii) they are as transferable from one system to another as are the forms of the atoms in real space; that is, as transferable as are the atomic charge distributions. In particular, atomic and group properties predicted in this manner have been shown to recover the experimentally determined contributions to the volume, energy, polarizability, and magnetic susceptibility in those cases in which the group contributions are essentially transferable, as well as additive.[5,9]

For a system in a stationary state, the wave function and the electron density it determines are such as to minimize the total energy. Thus, the appearance of an atomic interaction line is associated with the minimization of the energy of interaction between a pair of atoms. Its presence is a necessary condition for two atoms to be bonded to one another, the situation obtained when the initially attractive Hellmann−Feynman forces acting on the approaching nuclei, and resulting from the accumulation of electron density associated with the formation of the atomic interaction line, vanish and attractive restoring forces act on

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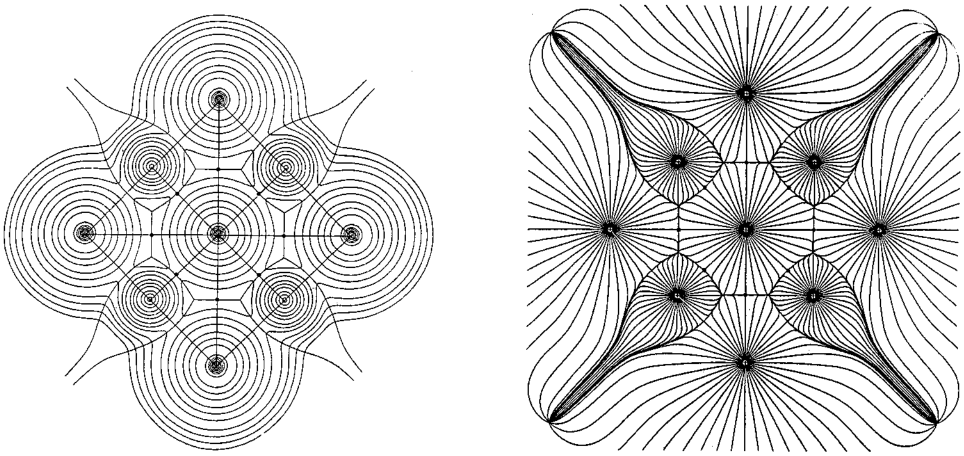

Figure 1. Contour map and gradient vector field map of the electron density in the middle plane of the cubic-like cluster $Li_{14}F_{13}^{-}$ containing a central F ion, $q(F) = -0.94e$, Li being the central ion in the two outer planes. The contour map is overlaid with the intersections of the interatomic surfaces with this plane and with the atomic interaction lines, which are bond paths in this equilibrium geometry. In the map displaying the trajectories of $\nabla\rho$, each nucleus acts an attractor and the region of space spanned by the trajectories that terminate at a given nucleus define its atomic basin, the basin for the central F being bounded by 18 interatomic surfaces. The (3,−1) CPs for the bond paths linking the central F are indicated by dots. Each (3,−1) CP serves as the origin for the unique pair of trajectories that define the bond path and as the terminus for the trajectories of the two-dimensional manifold defining the surface of zero-flux. By symmetry, the diagrams illustrate that the central F is linked by bond paths to the 6 nearest neighboring Li ions and to the 12 next nearest F ions. The central F is in contact with 18 other ions. A (3,+1) CP is found at the intersection of the interatomic surfaces of the central F, an outer F and a Li which form bonded three-membered rings. The outer contour has the value 0.001 au and the remaining contours increase in value in the order 2×10^n, 4×10^n, and 8×10^n, with n beginning at -3 and increasing in steps of unity.

the nuclei for any displacement from their final equilibrium positions. The presence of a (3,−1) CP and its associated atomic interaction line in such a stable state of electrostatic equilibrium is thus both necessary and sufficient for the two atoms to be bonded to one another in the usual chemical sense of the word. The atomic interaction line is in this case called a bond path and the associated (3,−1) CP is called a bond CP[5,6] (Figure 1).

A molecular graph is defined as the network of bond paths that link neighboring nuclei. For stable structures, its form is invariant to displacements of the nuclei from their equilibrium positions and a molecular structure is defined as an equivalence class of molecular graphs.[4] This equivalence relation leads to a definition of structural stability and to the demonstration that a change in structure can occur by only one of two mechanisms: through the bifurcation or conflict mechanism.[4] Both the static and dynamic aspects of the structural theory have been demonstrated to be of universal applicability, to any and all types of atomic interactions, from weak to strong, and as applied to densities obtained from both experiment and theory. The literature of these applications is too extensive to review here, but papers illustrative of application of the theory to the following types of interactions are included: hydrocarbons,[10] electron deficient molecules,[11] metals and alloys,[12,13] ionically[14,15] and covalently[16,17] bonded crystals, van der Waals molecules,[18] hydrogen bonded systems,[19−21] and so-called "nonbonded interactions",[22] as found in molecular and atomic crystals. The use of a bond path to denote a bonded interaction frees the definition of bonding from the constraints of the Lewis electron pair model, a model that is unable to describe the bonding in metals and in condensed phases composed of closed-shell atoms or neutral or charged molecules.

The purpose of this paper is to propose that the presence of a bond path provides a universal indicator of bonding between the atoms so connected. The argument is based on the physics that governs the local behavior of the electron density, as provided by the quantum mechanics of an open system. Its justification requires clarification of discussions that have appeared in the literature suggesting that the presence of a bond path in certain systems is actually indicative of a "repulsive interaction" rather than a bonded interaction. These statements have appeared with reference to bond paths between neighboring "sterically interacting" atoms,[23] between atoms experiencing nonbonding interactions[24] or involving charged atoms in nonclassical structures,[25,26] and between anions in a crystal, the arguments in the latter case being based upon an electrostatic model of the lattice energy.[27] The present paper affirms the definition of a bond path as signifying that the atoms so linked are indeed bonded to one another, by demonstrating that the qualitative arguments and classical models presented to argue otherwise, are not in accordance with the quantum mechanical description of the bond path that is obtained from the theorems for an open system expressed in their local form.

Two forces are involved in the discussion of bonding, the Hellmann−Feynman force exerted on the nuclei and the Ehrenfest force exerted on the electron density. It is the virial of the latter force that determines the virial field, a local description of a system's potential energy, including that of a crystal. The virial field and the electron density yield a structural homeomorphism.[28] *This implies that every bond path is mirrored by a virial path, a line linking the same neighboring nuclei, along which the potential energy density is maximally negative, i.e., maximally stabilizing, with respect to any neighboring line.* It is this homeomorphism that underlies the energy lowering that accompanies the appearance of an atomic interaction line in general, and a bond path in particular. The discussion of the mechanics of a bond path is prefaced with a review of the underlying theorems: the Ehrenfest force theorem, the virial theorem, and the Hellmann−Feynman electrostatic theorem, as derived from the Heisenberg equation of motion for the appropriate operator.

Atomic and Local Theorems Governing Atomic Interactions

The theory of atoms in molecules complements the quantum mechanical theorems that govern the properties of a total system by providing both atomic and local statements of each theorem obtained from the Heisenberg equation of motion for a given observable.[5,7] For example, the equation of motion obtained for the electronic momentum operator $\hat{\mathbf{p}}$ yields the Ehrenfest force theorem, whereas the action operator, the dot product of the momentum and position operators for an electron, $\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}$, yields the virial theorem. One of the important consequences of this application of the principle of stationary action to an open system is that both the atomic and local forms of the theorem for any observable are expressed in terms of a "dressed" density. This is a density distribution in real space for the property in question, force or energy for example, that results from replacing the property for a single particle at some point in space with a corresponding density that describes its average interaction with all of the remaining particles in the system.

The manner in which this averaging is done is identical to that used to define the electron density which is itself N times the probability of finding a particle at some point as determined by the average motions of all the remaining electrons. That is, $\psi^*\psi$ is integrated over the coordinates of the remaining electrons and summed over all spins, an operation denoted by the symbol $\int \mathrm{d}\tau'$ as in eq 2:

$$\rho(\mathbf{r}) = N\int \mathrm{d}\tau' \psi^*\psi \tag{2}$$

That all property densities are defined in a like manner follows directly from the field theoretic derivation of the principle of stationary action wherein a generator, the observable causing the change in the system, acts on a single field point. To quote Schwinger, "The essence of field theory is to provide a conceptually simpler and more fundamental description by depending on the particle as the basic entity."[29]

The Ehrenfest Force. A theorem for an open system and its local form necessarily involves fluxes of a corresponding current density through the surface bounding the system, whether this be a surface of zero-flux for an atom in a molecule, or the surface bounding an infinitesimal volume element, the properties of which are described in the local form of the theorem. This is illustrated for the primal force theorem, the Heisenberg equation of motion for the momentum operator, or the Ehrenfest force theorem.[30]

The atomic statement of the Ehrenfest force is given in eq 3:

$$m\int_\Omega \mathrm{d}\mathbf{r}\,\partial \mathbf{j}(\mathbf{r})/\partial t = \int_\Omega \mathrm{d}\mathbf{r}\int \mathrm{d}\tau' \Psi^*(-\nabla\hat{\mathbf{V}})\Psi + \oint \mathrm{d}\mathbf{S}(\mathbf{r}_\mathrm{s})\cdot\sigma(\mathbf{r}) \tag{3}$$

The current $\mathbf{j}(\mathbf{r})$ is the electronic velocity density and when multiplied by the electronic mass, gives the momentum density at the point $\mathbf{r}$. The integral on the left hand side (LHS) of eq 3 gives the time rate of change of the total momentum of the electron density in the basin of the atom Ω, that is, the force acting on the atom. The first term on the right hand side (RHS) of eq 3 comes from the averaging of the commutator $(\mathrm{i}/\hbar)[\hat{H},\hat{\mathbf{p}}]$. It is the atomic integral of the Ehrenfest force $\mathbf{F}(\mathbf{r},t)$ acting on the electron density at the point $\mathbf{r}$:

$$\mathbf{F}(\mathbf{r},t) = N\int \mathrm{d}\tau' \Psi^*(-\nabla\hat{V})\Psi \tag{4}$$

The operator $\nabla\hat{V}$ represents the gradient taken with respect to the coordinates of the electron located at the point $\mathbf{r}$, of the total potential energy operator $\hat{V}$ that describes all of the interactions within the system. Thus, $-\nabla\hat{V}$ is the operator describing the force exerted on the electron at position $\mathbf{r}$ by all of the remaining electrons and the nuclei in the system, each of the particles being held fixed in some arbitrary configuration. The averaging of this operator implied by $\int \mathrm{d}\tau'$ in eq 4 yields the force density $\mathbf{F}(\mathbf{r},t)$, the force exerted on the electron density at $\mathbf{r}$ by the nuclei and by the average distribution of the remaining electrons in the total system. Note that the definition of the force density in eq 4 differs from the definition of the electron density in eq 2 only by the inclusion of the force operator between the state functions. The Ehrenfest force[30] is likened to a classical force because the operator $-\nabla\hat{V}$, defined in terms of the gradient of a potential, is identical to the expression for the classical force exerted on an electron at $\mathbf{r}$.

The second term on the RHS of eq 3 is a measure of the force exerted on the atom arising from the flux in the momentum current density through its surface. In eq 3, this "momentum flux" density[31] is expressed in terms of the quantum stress tensor $\sigma(\mathbf{r})$:

$$-\{\mathbf{j}_\mathrm{p}(\mathbf{r}) + \mathrm{cc}\} = \sigma(\mathbf{r}) = (\hbar^2/4m)\int \mathrm{d}\tau'\{(\nabla\nabla\Psi^*)\Psi - \nabla\Psi^*\nabla\Psi - \nabla\Psi\nabla\Psi^* + \Psi^*\nabla\nabla\Psi\} \tag{5}$$

It has the dimensions of an energy density, that is, force per unit area, and $\mathrm{d}\mathbf{S}\cdot\sigma(\mathbf{r})$ is thus the force exerted on the element of surface $\mathrm{d}\mathbf{S}$. The quantum stress tensor, first introduced by Schrödinger,[32] plays a dominant role in determining the mechanics of the electron density and a proper open system. The surface force vanishes for the total system with boundaries at infinity. The local form of the force theorem that governs the motion of an infinitesimal volume element $\mathrm{d}\mathbf{r}$ and obtained directly from Schrödinger's equation is

$$m\partial\mathbf{j}(\mathbf{r})/\partial t = \mathbf{F}(\mathbf{r},t) + \nabla\cdot\sigma(\mathbf{r}) \tag{6}$$

an expression that is term for term, a local form of the atomic theorem, eq 3.

The use of the Ehrenfest force theorem in the interpretation of the mechanics of the electron density is facilitated by noting that it is analogous in both its local and atomic forms to a basic postulate of classical continuum mechanics called the momentum principle.[33] This principle states that the time rate of change of the total momentum of a given set of particles, forming a part Ω of some total system, equals the vector sum of all the external forces acting on the particles of the set, provided Newton's third law of action and reaction governs the internal forces. This statement of momentum balance leads to the equation

$$\int_\Omega \mathrm{d}\mathbf{r}\,\partial\rho\mathbf{v}/\partial t = \int_\Omega \mathrm{d}\mathbf{r}\mathbf{f} + \oint \mathrm{d}\mathbf{S}(\mathbf{r}_\mathrm{s})\cdot\mathbf{t} \tag{7}$$

which equates the temporal change in the momentum density $\rho\mathbf{v}$ (ρ the mass density and $\mathbf{v}$ the velocity density) over the region Ω to the action of the body forces per unit volume $\mathbf{f}$ acting within Ω and the surface forces $\mathbf{t}$ acting per unit area of the surface bounding Ω. Because the volume Ω is arbitrary, the momentum balance applies to an infinitesimal volume to yield Cauchy's first equation of motion[33]

$$\rho\mathrm{d}\mathbf{v}/\mathrm{d}t = \mathbf{f} + \nabla\cdot\mathbf{T} \tag{8}$$

where $\mathbf{T}$ is the classical stress tensor. The classical expressions for the force acting on a continuous system, of finite or infinitesimal extent, eqs 7 and 8, are equivalent in form and physical content to the corresponding quantum mechanical expressions, eqs 3 and 6.

The present use of the equation of motion for $\hat{\mathbf{p}}$ applies to a stationary state where the acceleration $\partial\mathbf{J}(\mathbf{r})/\partial t$, or $\mathrm{d}\mathbf{v}/\mathrm{d}t$ in the classical case, is zero and the system is in a state of static equilibrium. In this case, the Ehrenfest force $\mathbf{F}(\mathbf{r})$, or the body force $\mathbf{f}$, is balanced by the divergence of the corresponding stress tensor,

$$\mathbf{F}(\mathbf{r}) = N\int d\tau' \psi^*(-\nabla\hat{V})\psi = -\nabla\cdot\sigma(\mathbf{r}) \qquad (9)$$

and one has the important result that the Ehrenfest force acting on the electron density over the basin of the atom, the quantity $\mathbf{F}(\Omega)$, is balanced by the flux in the momentum current density through its surface,

$$\mathbf{F}(\Omega) = \int_\Omega d\mathbf{r}\, \mathbf{F}(\mathbf{r}) = -\oint d\mathbf{S}(\mathbf{r}_s)\cdot\sigma(\mathbf{r}) \qquad (10)$$

Thus, for a system in static equilibrium, classical or quantum, the force determined by the gradient of the potential that acts on the density locally or over a region of space, is balanced by a momentum flux density, as described in terms of the stress tensor. Because this result is obtained for a classical as well as for a quantum system, one cannot argue that the classical-like force $\mathbf{F}(\mathbf{r})$ is balanced by a quantum counterpart $\nabla\cdot\sigma(\mathbf{r})$. It is instead the mechanical description of a state of static equilibrium in a continuous medium. *There are no net forces acting on an element of the electron density for a system in a stationary state.*

The Virial Field and the Potential Energy Density. It is the virial of the Ehrenfest force that determines the electronic potential energy of a molecule or crystal, a result obtained from the virial theorem is the equation of motion for the generator $\mathbf{r}\cdot\mathbf{p}$. For a stationary state, a local form of the virial theorem is[5,34]

$$2G(\mathbf{r}) + \mathbf{r}\cdot\mathbf{F}(\mathbf{r}) = \nabla\cdot\{\mathbf{r}\cdot\sigma(\mathbf{r})\} + (\hbar^2/4m)\nabla^2\rho(\mathbf{r}) \qquad (11)$$

where the terms on the RHS originate with the commutator and those on the LHS are derived from the current density for the generator $\mathbf{r}\cdot\mathbf{p}$. The kinetic energy density $G(\mathbf{r})$ is the positive definite form $(\hbar^2/2m)\hat{\mathbf{p}}^+\cdot\hat{\mathbf{p}}$ and $\mathbf{r}\cdot\mathbf{F}(\mathbf{r})$, the virial of the Ehrenfest force density can alternatively be expressed as $-\mathbf{r}\cdot\nabla\cdot\sigma(\mathbf{r})$ using eq 9. The virial field $\nu(\mathbf{r})$ is defined in terms of the stress tensor in two equivalent ways:

$$\nu(\mathbf{r}) = -\,\mathbf{r}\cdot\nabla\cdot\sigma(\mathbf{r}) + \nabla\cdot\{\mathbf{r}\cdot\sigma(\mathbf{r})\} = \mathrm{Tr}\,\sigma(\mathbf{r}) \qquad (12)$$

Integration of eq 11 over an atom Ω yields the atomic virial theorem $-2T(\Omega) = \nu(\Omega)$, as obtained from the statement of stationary action.[5,7] The divergence term in eq 12 vanishes upon integration over the space of the total system (it yields the virial of the surface forces) to obtain the total virial ν,

$$\nu = \int \nu(\mathbf{r})\, d\mathbf{r} = N\int d\mathbf{r}\int d\tau'\{\psi^*(-\mathbf{r}\cdot\nabla\hat{\mathbf{V}})\psi\} \qquad (13)$$

which satisfies the virial theorem for the total system $-2T = \nu$. The total virial ν equals V, the total potential energy of the system that appears in the expression for the total energy $E = T + V$, and the virial of the Hellmann−Feynman forces exerted on the nuclei,[35,36] $\mathcal{F}_\alpha = -\nabla_\alpha E$, as given in eq 14:

$$\nu = \langle\hat{V}_{ne}\rangle + \langle\hat{V}_{ee}\rangle + \langle\hat{V}_{nn}\rangle + \sum\nolimits_\alpha \mathbf{X}_\alpha\cdot\nabla_\alpha E = V - \sum\nolimits_\alpha \mathbf{X}_\alpha\cdot\mathcal{F}_\alpha \qquad (14)$$

The term in eq 13 corresponding to the virial of the nuclear−electron force yields $\langle\hat{V}_{ne}\rangle$ and the virial of the forces that the nuclei exert on the electrons. Summing this latter virial over the nuclei yields the negative of the force the electron density exerts on all the nuclei, a term that reduces further to yield the terms $\langle\hat{V}_{nn}\rangle - \sum\mathbf{X}_\alpha\cdot\mathcal{F}_\alpha$ in eq 14.[5]

It is the negative of the virial field $\nu(\mathbf{r})$, defined in eq 12, that is structurally homeomorphic with the electron density.[28] The field $-\nabla\nu(\mathbf{r})$ exhibits local attractors at the positions of the nuclei that are linked by unique pairs of trajectories associated with its (3,−1) CPs to yield a molecular graph identical to the one defined by the $\nabla\rho(\mathbf{r})$ field. *The virial field is negative everywhere and there are no locations or regions where the electronic potential energy is repulsive.*

The Hellmann−Feynman Force and Electrostatic Equilibrium. For the total system in a stationary state, the Heisenberg equation for an operator that contains a derivative with respect to a parameter s contained in $\hat{H}$ yields the Hellmann−Feynman theorem[35,36]

$$-\langle\psi|[\hat{H},\partial/\partial s]|\psi\rangle = \langle\psi,(\partial\hat{H}/\partial s)\psi\rangle = \partial E/\partial s \qquad (15)$$

When s is a nuclear coordinate $\mathbf{X}_\alpha$, eq 15 gives the Hellmann−Feynman electrostatic theorem

$$\langle\psi,(-\nabla_\alpha\hat{V})\psi\rangle = -\nabla_\alpha E = \mathcal{F}_\alpha \qquad (16)$$

where $\mathcal{F}_\alpha$ is the force exerted on nucleus α by the electron density and the remaining nuclei. The integration of the forces acting on the nuclei over a range of nuclear coordinates determines the Born−Oppenheimer potential energy surface and the points in nuclear configuration space where $\mathcal{F}_\alpha = 0$ for all the nuclei determine the extrema in this surface.

A local minimum in the energy surface denotes a stable state of electrostatic equilibrium with respect to the forces acting on the nuclei. The minimum serves as an attractor in the negative of its associated gradient vector field, the Hellmann−Feynman force field. That is, all trajectories representing the forces acting on the displaced nuclei terminate at the attractor. Thus, the forces acting on the nuclei for any displacement from equilibrium restore the system to its equilibrium geometry—the forces are attractive. If the energy minimum is of a depth greater than the zero point energy with respect to any and all of the nuclear displacements, then the corresponding geometry is referred to as an equilibrium geometry and in general, all nuclear configurations associated with motions within the potential well yield the same molecular graph.

The Mechanics of Atomic Interactions

The formation of an interatomic surface and a bond path is a result of a competition between the perpendicular compressions of the density toward the bond path and its expansion in a direction parallel to the path away from the interatomic surface. These stresses in the density are determined by the corresponding perpendicular and parallel curvatures that sum to equal $\nabla^2\rho_b$, the trace of the Hessian of the density at $\mathbf{r}_c$, which deviates the position of the bond CP.[6] The compressions are given by the duo of negative eigenvalues of the Hessian at $\mathbf{r}_c$ which lead to a concentration of electronic charge along the bond path, whereas the expansion is given by the positive eigenvalue which leads to a depletion of charge in the surface and to its separate concentration in the basins of the neighboring atoms. The sign of $\nabla^2\rho_b$ determines which of these two competing effects is dominant.

Because of the appearance of $\nabla^2\rho(\mathbf{r})$ in the local expression of the virial theorem, which can be written as in eq 17,

$$(\hbar^2/4m)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + \nu(\mathbf{r}) \qquad (17)$$

the competing behavior of the curvatures can be related to the mechanics of the interaction. Interactions for which $\nabla^2\rho(\mathbf{r}_c) <$

TABLE 1: Bond Critical Point Data in Atomic Units ($-x = 10^{-x}$)

system	R	D_e	ρ_b	$\nabla^2\rho_b$	G_b	G_b/ρ_b	ν_b	E_b^e
$C_2(^1\Sigma_{1g}^+)^a$	2.354	2.03 (−1)	3.20 (−1)	−6.55 (−1)	2.89 (−1)	0.90	−7.42 (−1)	−4.53 (−1)
$LiF(^1\Sigma^+)^a$	2.964	2.14 (−1)	7.60 (−2)	+7.24 (−1)	1.61 (−1)	2.12	−1.42 (−1)	+1.98 (−2)
$Ar_2(^1\Sigma_{1g}^+)^b$	7.133	6.10 (−4)	2.89 (−3)	+1.22 (−2)	3.88 (−3)	1.34	−3.05 (−3)	+8.29 (−4)
$F_c{-}F_e{}^c$	5.201		1.32 (−2)	+5.91 (−2)	1.41 (−2)	1.08	−1.35 (−2)	+6.40 (−4)
$Ar\text{-}CO_2{}^d$	6.513	1.08 (−3)	3.78 (−3)	+1.65 (−2)	1.75 (−2)	4.64	−1.65 (−2)	+1.02 (−3)

[a] QCISD(SCVS)/6-311++G2df. [b] MP2/MC+sp3d2f.[18] [c] Between center F and F in edge of cubic cluster $Li_{14}F_{13}^-$, HF/6-31G*.[42] [d] MP2/TZ2P+df for CO_2.[18]

0, shared interactions, are dominated by the lowering of the potential energy resulting from the charge concentrated between the nuclei along the bond path. Closed-shell interactions for which $\nabla^2\rho(\mathbf{r}_c) > 0$ are dominated by the kinetic energy in the region of the interatomic surface, a result of the tightening of the curvature of the density along the bond path. They achieve their stability as a result of the electronic charge being separately concentrated within the atomic basins, rather than shared. The electronic energy density $E^e(\mathbf{r})$, which integrates to the total electronic energy, is given by[5]

$$E^e(\mathbf{r}) = G(\mathbf{r}) + \nu(\mathbf{r}) = -K(\mathbf{r}) \qquad (18)$$

where the final equality shows that the energy density obeys a local virial theorem in terms of the kinetic energy density $K(\mathbf{r})$ expressed in terms of the operator $-(\hbar^2/2m)\nabla^2$, the form appearing in Schrödinger's equation and related to $G(\mathbf{r})$ by the expression

$$K(\mathbf{r}) = G(\mathbf{r}) - (\hbar^2/4m)\nabla^2\rho(\mathbf{r}) = -E^e(\mathbf{r}) \qquad (19)$$

Unlike $G(\mathbf{r}) > 0$, $K(\mathbf{r})$, as does $E^e(\mathbf{r})$, exhibits both negative and positive values and because of the relation of $K(\mathbf{r})$ and $E^e(\mathbf{r})$ to the Laplacian of $\rho(\mathbf{r})$, as shown in eq 19, they exhibit atomic shell structure. $E^e(\mathbf{r})$ is the energy density H_b defined by Cremer and Kraka.[37,38] The atomic interactions are thus characterized by ρ_b, $\nabla^2\rho_b$, ν_b, and G_b, the values of the parameters at the bond critical point. Their contrasting values for shared and closed-shell interactions are illustrated in Table 1 for the isoelectronic molecules C_2 and LiF, respectively.

Closed-Shell Interactions. In general, conceptual difficulties arise in the association of a bond path with closed-shell rather than shared interactions, as exemplified by nonbonded[23−25] and anion−anion interactions[27] being described as repulsive. In closed-shell interactions the requirement of the Pauli exclusion principle leads to the removal of density from the region of contact of the interacting atoms, the interatomic surface. The positive curvature of $\rho(\mathbf{r})$ along the bond path is dominant, $\nabla^2\rho_b > 0$, and because the density contracts away from the surface, the interaction is characterized by a relatively low value of ρ_b. These interactions are thus dominated by the kinetic energy in the region of the bond CP, with $G_b > |\nu_b|$ and the energy density $E_b^e > 0$. The dominance of the kinetic energy is placed on an absolute footing by the quantity G_b/ρ_b, the kinetic energy per electron which in general is in excess of unity for closed-shell interactions (compare LiF and C_2 in Table 1). It is important to note that a positive value for E_b^e can result only from the kinetic energy density exceeding the magnitude of the potential energy density. Thus, because $\nu(\mathbf{r}) < 0$, a positive value for E_b^e does not indicate a repulsive potential energy of interaction but instead one wherein the potential energy, while stabillizing, is locally dominated by a larger kinetic energy. Closed-shell interactions are found in van der Waals molecules,[18] hydrogen bonds,[19−21] ionic bonds,[14] and in molecular crystals.[22]

van der Waals and Nonbonded Interactions. The relatively weak interactions between closed-shell neutral, nonpolar molecules that account for the existence of condensed phases of such substances are sometimes referred to as nonbonded interactions to distinguish them from the stronger valence interactions associated with the pairing of electrons as per the Lewis model. The term nonbonded is also used to describe supposed "repulsive" interactions in molecules, the term used, for example, by Cioslowski and Mixon to describe the interactions between pairs of hydrogen atoms bonded to carbon atoms in 1,4-positions in planar benzenoid hydrocarbons[24] and the steric crowding effects in perhalogenated cyclohexanes.[23]

The weak interactions responsible for the binding present in van der Waals molecules give rise to atomic interaction lines (bond paths in the equilibrium structures) with the characteristics of closed-shell interactions as described above.[5,18] Because such interactions are primarily the result of a correlation of the motions of the electrons on the two interacting species, their description requires the use of densities obtained from correlated wave functions. MP2 calculations using large basis sets including *f* functions provide good agreement with the experimental geometries and binding energies of van der Waals molecules formed between the following species: Ar, C_2H_2, CO_2, OCS, and SO_2. The bond critical point data for the weak interactions in these molecules have been determined and are found to exhibit all of the hallmarks of closed-shell interactions,[18] as typified by the data for the bond path in the Ar_2 molecule given in Table 1.

The interaction present in Ar_2 can be considered prototypical of a nonbonded interaction, its potential energy curve being among the first to be approximated by fixing the parameters empirically from crystal and second virial coefficient data.[39] The most recent theoretical and experimental data describe the Ar_2 interaction in terms of a Morse potential with a well depth of 4.49 ($-4 \equiv 10^{-4}$) au, an equilibrium separation of 7.13 au, and a frequency of 30.5 cm^{-1} which yields a zero-point energy of 7.0 (−5) au.[40] The depth of the well is sufficient to support at least three vibrational quanta over the zero-point energy level and attractive restoring forces act on the nuclei during these displacements. A collision resulting in an energy transfer sufficient to reduce the internuclear separation to less than 6.3 au would result in dissociation, because the system is no longer bound within the potential well and forces of repulsion act on the nuclei which are now linked by an atomic interaction line. The use of a Morse curve to describe the interaction in Ar_2 and its attendant nuclear motions shows that aside from a difference in the well depth, the potential energy of interaction exhibits the same fundamental form as does that for a bound diatomic state resulting from the "pairing of valence electrons". Both interactions result in the formation of bond and virial paths that lead to the balancing of the forces of repulsion on the nuclei and to the lowering of the molecule's total energy, respectively.

Solid argon forms an *fcc* close-packed structure, which by the Poincarè−Hopf relation for solids,[16] requires each argon atom to form bond paths with its 12 nearest neighbors. The interactions in the crystal are of the closed-shell type as described for the argon dimer, although somewhat weaker. The experimental cohesive energy for solid argon, with a nearest neighbor distance of 7.11 au compared to 7.13 in the dimer, expressed as the energy per atom and extrapolated to 0 K and zero pressure, is 2.9 (−3) au yielding an interaction energy per bond path that is 56% of that found in the dimer. The cohesive energy of solid argon results from the interaction of each atom with its 12 nearest neighbors, as indicated by the 12 bond paths. In this situation one must abandon the Lewis electron pair model and replace it with a universal indicator of bonding, as provided by the presence of a bond path and its associated virial path. Each bond path is a result of the correlative accumulation of electron density between the nuclei sufficient to balance the forces of repulsion on the argon nuclei and result in attractive restoring forces for all displacements from their equilibrium positions.

Note that an interaction resulting from the action of dispersion forces results in the accumulation of electron density between the nuclei and hence to the formation of a bond path. As first emphasized by Feynman in his 1939 paper,[35] dispersion forces, with their R^{-7} dependence for the approach of two neutral spherical atoms, result from a polarization of the density on each of the approaching atoms toward the other (this inward polarization of both atomic densities is a static effect for a fixed R, as are all properties for a stationary state), thereby leading to an increasing accumulation of density between the nuclei upon their approach and to the formation of a bond path. This correct description of what happens to the electron density in real space differs from the often-quoted description of relating the dispersion energy to the interaction of induced oscillating dipoles on each atom. This latter description is an attempt to obtain a real space picture of the second-order perturbative description of the dispersion energy resulting from the electron−electron correlation, an effect determined by the pair density defined in the six-dimensional configurational space of two electrons. The net effect of this correlation in real space is as described by Feynman[35] and as previously illustrated in terms of a density difference map for the approach of two hydrogen atoms separated by 8 au.[5]

The bond paths associated with the nonbonded repulsive interactions between the hydrogen atoms in the planar benzenoids[24] and between the chlorine and bromine atoms in perhalogenated cyclohexanes[23] exhibit the same characteristics as those found for Ar_2: low values for ρ_b and $\nabla^2\rho_b > 0$. These bond paths are found for equilibrium geometries, a finding that requires all nuclear displacements be governed by attractive restoring forces, including the relative motions of the protons or halogen nuclei. Cioslowski and Mixon correctly indicated the advantage of using atomic interaction lines to determine the presence of links between atoms that classically would be considered nonbonded.[23] Only atoms linked by an atomic interaction line share an interatomic surface and are in contact. Thus, the linking of the three axial chlorines or bromines by a cyclic structure of bond paths on each side of the perhalogenated cyclohexane ring is not found for the case of smaller fluorines. That standard geometrical parameters are changed to accommodate the larger halogen atoms does not imply the presence of repulsive forces in the final equilibrium geometry. Contributing to the lowering of the energy in attaining this geometry is the formation of the bond and associated virial paths between the axial Cl or Br atoms, as made possible by their larger and more diffuse charge distributions compared to that of a bound F atom, the interactions of which are identical to those that provide the cohesive energy of solid argon. The question is not how the final geometry is attained in some mental process involving passage over a repulsive barrier, a situation that is in fact common to most chemical changes, but rather how the mechanics determines the final distribution of charge.

Bond paths between chlorine atoms with similar characteristics to those found in the substituted cyclohexanes are found to link the atoms of neighboring molecules in solid molecular chlorine.[22] The Cl−Cl separation in the crystal exceeds that in the perchlorinated molecule by 0.05 Å, resulting in small reductions in the values of ρ_b and $\nabla^2\rho_b$ between the two systems. Because of the presence of this dominant directed intermolecular bond path in the solid, molecular chlorine forms a layered structure, as opposed to the simpler structure anticipated on the basis of a nondirectional van der Waals-type potential.[41] This principal interaction in the crystal is present in and accounts for the formation of the gas-phase dimer of Cl_2.[22] In fact, the Laplacian of the electron density dictates the angle of approach of the two monomers in the formation of the dimer through an alignment of the charge concentration on one atom with a center of charge depletion on another, which produces an angle that is preserved in the solid, giving rise to its layered structure. Thus, a bond path, responsible for the formation of the Cl_2 dimer and for the cohesive energy of solid chlorine, is described by Cioslowski et al.[23] as indicative of a repulsive interaction when present in perchlorocyclohexane.

The phrase "attractor interaction lines between nonbonded atoms" used by Cioslowski et al.[23] is an oxymoron and makes clear that they restrict their definition of bonding to the Lewis model of the electron pair bond. Any bond paths found between atoms not formally linked using the classical model are termed nonbonding and repulsive, an interpretation that would preclude the existence of condensed states of matter composed of closed-shell neutral molecules. Cioslowski and Mixon[24] would replace the universal definition of bonding based on the topologies of the electron density and virial field with the statement "The term bond path should be reserved for the interaction lines describing ordinary strong bonds." The classification of atomic interaction lines is determined by physics, not by subjective judgements of relative bond strengths.

Bond Paths between Ions in Crystals. An ionic interaction is classified as one in which the atomic species exhibit charges approaching the values anticipated for the corresponding closed-shell ions, a condition that ensures that the values of ρ_b and $\nabla^2\rho_b$ at the associated bond critical points are typical of closed-shell interactions. The data given for LiF in Table 1 are illustrative of this type of interaction, the charges on the ions being ±0.93e. The electron density in an ionic system is very localized within each atomic basin, a result of the corresponding localization of the Fermi correlation. Thus, the central fluorine in the cubic-like cluster $Li_{14}F_{13}^-$ provides an excellent model of fluorine in an *fcc* lattice, the optimized cluster exhibiting only a slight compression compared to the unit cell in the crystal.[42] The central F has a charge of −0.94e and, as seen from Figure 1, is linked by bond paths to not only the 6 nearest neighboring lithiums, but also to the 12 neighboring fluorines, with CP values given in Table 1. The linking of neighboring anions in an ionic crystal by bond paths, while not a topological necessity,[15] is a feature frequently encountered; in the experimental densities of LiF[27] and in theoretical densities of LiF,[22] MgO,[43] and LiI.[15] Luaña, Costales, and Pendás[15] performed a topological analysis of 120 ionic perovskites of the form AMX_3. In addition to the bond CPs for the M−X and A−X interactions, they find bond CPs linking neighboring anions for X = F, Cl, and I. Bond paths are also predicted to link neighboring cations in the A position, but in only two cases, $CsSrF_3$ and $CsBaF_3$, and with the smallest of all the ρ_b values in the set of 120 crystals. The presence of the A−A bond paths is a consequence of two distinctive features: a very large A to X size ratio and a large cell side length a due to the large size of M, thus leading to a contact of the Cs^+ ions. In general, the more diffuse distribution of density and hence greater ionic radius of anions compared to cations results in anion−anion contacts in the crystal and the formation of associated bond paths, as exemplified in Figure 1. The values of ρ_b for the CPs between ions of like charge are found to be smaller than the values for the primary anion−cation interactions with the exception of that for Li−I compared to I−I, a result of the very tight density of Li^+ compared to its very diffuse nature in I^-.

Abramov[27]argues that the presence of bond paths for these secondary interactions should not be taken to imply that the ions so connected are bonded to one another. He based his argument on the result that the calculation of the lattice energy of LiF in terms of the electrostatic Madelung energy coupled with a short range noncoulombic repulsive contribution yields a result in reasonable agreement with the experiment. He uses an experimental pseudoatom charge density to calculate the Madelung energy and the experimental value of the lattice parameter a. The valence density population parameters are treated as variables to improve the agreement of the calculated result with the experiment. Because this model does not include any term representing an attractive potential between the neighboring fluorines, he concludes that the F−F interaction must be repulsive. "... an unknown specific bonding interaction between neighboring ions, cannot counterbalance the strong pair-wise F−F electrostatic repulsive interaction and thus lead to the formation of a chemical bond between these ions."[27] This conclusion is incorrect for two principal reasons: the inadequacy of the model and the use of its associated classical notions of force and energy in the discussion of the electron density, the properties of which are determined by quantum mechanics.

The model assumes a crystal to be composed of spherical ions in contact, thereby limiting the electrostatic potential energy to point charge terms of the form q_iq_j/R_{ij}. The model is thus incapable of describing or accounting for any electrostatic contributions to the potential arising from distortions of the spherical ion densities. This failure of the model remains unaltered by the author's use of atomic charges obtained from a fit of an experimental prodensity which predicts the presence of bond paths, a failure that can be directly demonstrated using the cubic cluster. If a spherical density distribution for the central F is assumed and the optimized geometry is used, the attraction of its 9.940 electrons by the 14 Li and 12 F nuclei is found to be less stable than the actual interaction by −0.3688 au, which is the energy determined by averaging the appropriate operators over the density within the basin of the central F atom, a quantity determined by the theory of atoms in molecules. Thus, the distortion of the central ion's charge distribution from spherical symmetry caused by the formation of the bonds paths, contributes to the lowering of the electrostatic energy of interaction. In any event, the simple classical model is known to give a reasonable account of the lattice energy of ionic crystals and the answer obtained by Abramov for the experimental lattice constant is a foregone conclusion using any reasonable set of charges, which were in any event, treated as parameters.

The force that determines whether a system is in electrostatic equilibrium is the Hellmann−Feynman force acting on the nuclei. This force is zero for all of the nuclei in a crystal in an equilibrium geometry. This is not a trivial result of symmetry for an *fcc* lattice as suggested by Abramov,[27] because the displacement of any ion results in a restoring force returning it to its equilibrium position. Thus, attractive restoring forces are the only ones operative in a bound state and these are present only when the nuclei are displaced from equilibrium. If repulsive forces were present, the crystal would be unstable and would either atomize or distort to an equilibrium geometry of lower energy. To take a definite example, there is sufficient accumulation of density between the central F nucleus and each of its 12 neighboring fluoride nuclei in the cubic cluster to not only balance the attendant forces of repulsion between them, but to also create an attractive restoring force when the central ion is displaced relative to them, a result verified by the absence of any imaginary vibrational frequencies for the minimum energy geometry. There is no property of the crystal to suggest the existence of "the strong pair-wise F−F electrostatic repulsive interaction" as suggested by Abramov.[27]

Abramov refers not to forces acting on the nuclei but to the electrostatic repulsive force acting between neighboring fluoride ions in the crystal treated as point charges, the term q_Fq_F/a^2, or to the corresponding repulsive contribution to the potential energy, q_Fq_F/a. Such terms do not arise in the quantum mechanical expression for the energy of the crystal which determines the energy of the electrons moving in the field of the fixed nuclear lattice and thus consists of both kinetic and potential energy contributions. The individual contributions to the potential energy are as outlined in eq 14.

It is the Ehrenfest force and not just the electrostatic force that governs the motion of the electrons and the distribution of electron density, $\mathbf{F}(\mathbf{r})$, eq 9. As discussed above, this force is represented by a dressed density that describes the average interaction of an element of electronic charge with all of the remaining particles in the system, including the forces derived from the electrostatic potential. In a stationary state this force is balanced by the divergence of the stress tensor and no net force acts on an element of the density nor on an atom or ion in a crystal: the electron density distribution is at equilibrium for any configuration of the nuclei. The value of the balancing force $-\nabla\cdot\sigma(\mathbf{r})$, eq 9, can however, be used to provide a measure of $\mathbf{F}(\mathbf{r})$, whose balancing governs the formation of a bond path and whose virial determines the potential energy of the crystal. A large attractive contribution to $\mathbf{F}(\mathbf{r})$ yields a correspondingly large stabilizing contribution to $\nu(\mathbf{r})$.

Because $\nu(\mathbf{r})$, the potential energy density, eq 12, is negative everywhere, the total virial ν, eq 13, is also negative, a result required for a system governed by Coulombic forces: the virial theorem states that $-2T = \nu$, and because $T > 0$, ν must be negative. There are no repulsive contributions to the total potential energy locally or from atoms or ions within a system, as determined by $\nu(\mathbf{r})$ or its atomic averages. Only an excess electronic kinetic energy can lead to repulsions within the system, but these appear as Hellmann−Feynman forces of repulsion acting on the nuclei; the electronic potential energy is always stabilizing. It is of course, the virial theorem that ties these effects together:

$$-2T = \nu = V - \sum_\alpha \mathbf{X}_\alpha \cdot F_\alpha \tag{20}$$

where the final term is the contribution to the virial from the Hellmann−Feynman forces acting on the nuclei. For a system in equilibrium these forces vanish, ν equals the total potential

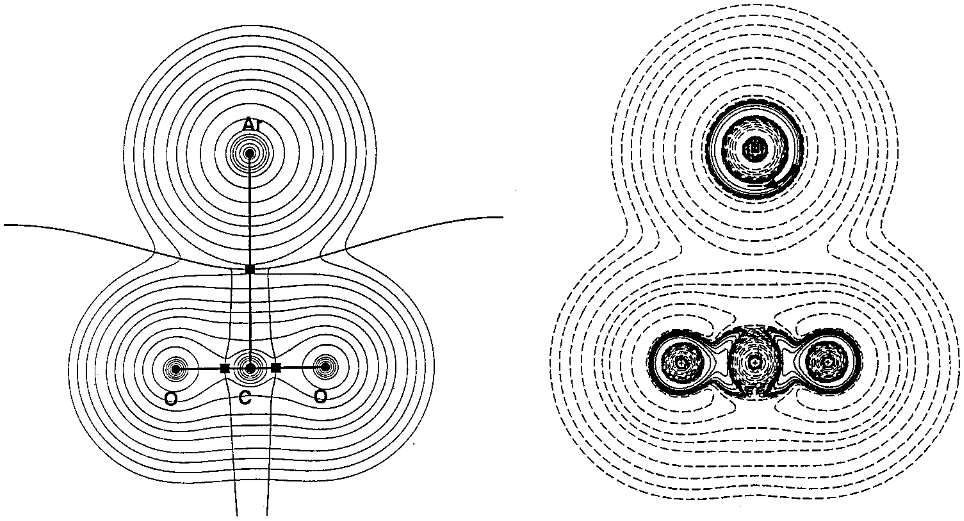

Figure 2. Contour maps of the electron density $\rho(\mathbf{r})$ and of its Laplacian, $\nabla^2\rho(\mathbf{r})$, for the minimum energy geometry of the $ArCO_2$ van der Waals complex. Contour values are the same as in Figure 1 with solid contours denoting regions of charge concentration ($\nabla^2\rho < 0$), and dashed contours denoting regions of charge depletion ($\nabla^2\rho > 0$) in the Laplacian map. The map for $\rho(\mathbf{r})$ is overlaid with bond paths and the intersections of the interatomic surfaces, the bond CPs being denoted by squares. The Ar is linked to the molecule by a bond path and by a virial path. The Laplacian map shows that the CC, a (3,−3) CP in $-\nabla^2\rho$, induced in the valence shell charge concentration (VSCC) of the Ar atom and indicated by an arrow, is directed at the very marked region of charge depletion on the carbon atom, the interaction causing the appearance of a (3,+1) CP in the torus of charge depletion encircling the carbon. All of the minimum energy geometries of the van der Waals complexes studied[18] can be rationalized on the basis of a CC on one molecule being aligned with a region of charge depletion on the other, the same behavior encountered in the formation of hydrogen bonds or a Lewis acid−base pair.

energy V and $2T = |V|$. However, if forces of repulsion act on the nuclei, $2T$ exceeds $|V|$ and the increase in the kinetic energy is balanced by the virial of the repulsive forces. Coppens points out that the use of the point charge model to determine the cohesive energy of a crystal assumes the kinetic energy of the electrons to be the same for the crystal as for the isolated ions.[44] Thus, the model does not satisfy the virial theorem, because T is required to increase by an amount equal to the magnitude of the decrease in E on forming the crystal, and the model should not be used to discuss the mechanics of bonding. One thus returns to the quantum mechanical result that the only forces acting within a molecule or crystal are the forces exerted on the nuclei, and their appearance as forces of repulsion is a result of twice the electronic kinetic energy exceeding the magnitude of the potential energy, not as a result of the presence of a repulsive potential energy.

In summary, the virial of the Ehrenfest force acting on the density along the line of neighboring fluorine nuclei in the cluster or in a crystal is sufficiently stabilizing to link the nuclei with a line of maximally negative potential energy density, a virial path. Because the electron density is homeomorphically determined by the virial field, the presence of the virial path yields a line of maximum electron density, a bond path, the charge accumulation of which leads to the balancing of the Hellmann−Feynman forces and results in a state of electrostatic equilibrium between the two nuclei. The two atoms are bonded to one another.

These statements are illustrated using the central fluorine in the cubic cluster. Any displacement of the ion from its central position results in a positive restoring force acting on its nucleus. It is bound. The only attractive contributions to the potential energy in a molecule or crystal arise from the interactions of the nuclei with the electron density. The interaction of the electron density of the central F with its own nucleus and with the remaining nuclei in the cluster yields a total attractive potential energy of −537.265 au. The sum of the electron−electron and nuclear−nuclear repulsive energies is +337.821 au to yield a total electronic potential energy of −199.444 au, a value equal to twice the total energy of the central fluorine. Its total energy is more stable than that of an isolated fluoride ion by 233 kcal/mol, a value that also determines the relative increase in its electronic kinetic energy. These results are obtained using a self-consistent scaling procedure that ensures satisfaction of the virial theorem (SCVS).[45] The possibility of using theory to determine the potential energy of interaction between a pair of linked fluorines is discussed in a footnote.[46]

Generalizing the Concept of Electron Pairing

The acceptance of the presence of a bond path as indicative of bonding between two atoms does not require that one abandon the idea of associating the pairing of electrons with bonding, but only that one distinguish between the action of the pairing of electrons and that of associating one pair of electrons per bond. The pairing of electrons is a local phenomenon that varies from point to point, a property determined by the conditional pair density for same-spin electrons.[47] This function so successfully recovers the geometrical models associated with differing numbers of valence electron pairs that form the basis of the valence shell electron pair repulsion (VSEPR) model, it has been termed the Lennard−Jones function or LJF.[48] The maxima in LJF show where the density of other same-spin electrons is most likely to be found relative to a fixed position of a reference electron e*. The resulting patterns of localization are maximized when e* is placed at the position of a charge concentration (CC) of $L(\mathbf{r})$, the negative of the Laplacian of the density. In this situation, in a closed-shell system, the maxima denote regions of local pairing of α and β spin densities. Thus, as previously demonstrated, the maxima in $L(\mathbf{r})$, its CCs, determine the spatial domains where electron pairing occurs.[47] Indeed, the electron density and LJF are found to yield identical Laplacian distributions in those regions of space where the density of the same spin electrons is most likely to be found when e* is positioned at a CC in $-\nabla^2\rho$.[48,49]

Because of the appearance of $L(\mathbf{r})$ in the local expression of the virial theorem eq 17, the formation of a local CC in $L(\mathbf{r})$ is indicative of a lowering of the potential energy, as well as of a pairing of electrons. Thus, the CCs in $L(\mathbf{r})$ formed as a result of atomic interactions provide a link between the associated pairing of electrons and energy stabilization. Because CCs corresponding to the presence of nonbonding electron pairs are also found, their formation also contributes to the lowering of the energy.

In general, the localization of the pair density is less than that required to localize individual pairs of electrons and then not to a single region, conditions realized only in simple hydrides such as LiH or BeH_2.[48] In closed-shell systems, the pairing occurs within each atomic basin. The extent to which electrons on one center are exchanged with those on another is measured by the extent to which the Fermi hole of a given reference electron is spread between the two atomic basins.[50] In a shared interaction, this can approach the exchange of one, two, and three pairs of electrons, respectively, for single, double, and triple bonds.[51,52] Thus, as originally pictured by Lewis, one has two extremes of bonding corresponding to the equal or unequal sharing of an electron pair between two "kernels".[53] This idea is generalized to include a less than complete pairing of the densities of two opposite spin electrons and for the pairing to occur in more than a single spatial region.

Consider for example, the pairing of electrons that occurs in the formation of weakly bound van der Waals molecules, as revealed by the CCs formed in the valence shell charge concentrations (VSCC) of the interacting atoms. In the equilibrium geometry of Ar_2, a torus of charge concentration, a torus of $(2,-2)$ CPS, encircling the axis is formed on the bonded side of each atom, along with an axial CC on the nonbonded side of slightly smaller magnitude. The formation of the van der Waals molecule $Ar-CO_2$, Table 1 and Figure 2,also results in the creation of similar bonding and nonbonding CCs in the VSCC of Ar. The resulting distortions of the VSCCs are, however, small. The magnitudes of the maxima induced in the VSCC of argon in the formation of these weakly bound molecules exceed those of the minima by only ~0.03 au, compared to the much larger differences encountered in the formation of stronger bonds, a difference amounting to 1.6 au in the VSCC of Cl in ClF_5, for example. Thus, the distortions of the sphere of maximum charge concentration and the extent of electron pairing are slight in the formation of van der Waals molecules, reflecting their small binding energies. However, the difference between a closed-shell interaction, weak or strong, and a shared interaction is one of degree and not a result of a differing mechanics of bond formation: both result from the pairing of the densities of opposite-spin electrons and in the formation of a bond and a virial path. The present practice of distinguishing between "valency" and "coordination number"[26] has relevance only with respect to the use of the Lewis model.

Conclusion

It has been shown that the only forces acting within a molecule or a crystal are the Hellmann−Feynman forces exerted on the nuclei and their appearance as forces of repulsion is a result of twice the electronic kinetic energy exceeding the magnitude of the potential energy, not as a result of the presence of a repulsive potential energy. By definition, there are no forces exerted on the nuclei of atoms linked by a bond path and all vibrational motions result in attractive forces restoring the system to its equilibrium geometry. All atomic interactions demarcated by a bond path have a common quantum mechanical origin in terms of the behavior of the force, potential energy, and electron densities.[54] Thus, the presence of a bond path and its associated virial path provide a universal indicator of bonding between atoms.

The adoption of the theory of atoms in molecules requires the replacement of the model of structure that imparts an existence to a *bond* separate from the atoms it links—the ball and stick model or its orbital equivalents of atomic and overlap contributions—with the concept of *bonding* between atoms; two atoms are bonded if they share an interatomic surface and are consequently linked by a bond path. In a sense, the interatomic surface replaces the bond in the theory of atoms in molecules, since it is through the exchange of electrons and the fluxes in properties across this surface described by the physics of a proper open system that atoms adjust to the presence of their bonded neighbors.

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(46) One could attempt to determine the potential energy of interaction between a pair of linked fluorines by calculating (a) the attraction of each nucleus for the other's density, (b) the repulsions of their electron distributions (requiring a six-dimensional integration over the neighboring atomic basins of the pair density weighted by e^2/r_{12}), and (c) their nuclear–nuclear repulsion energy. However, only the total virial for an atom and the electron–nuclear attractive energy (and hence the total repulsion energy) for an open system or atom are well defined, the separate repulsive contributions exhibiting an origin dependence, and the calculation is not rigorous.[5] It would in any event be irrelevant with regard to the presence or absence of a bond path, because the local values of $\mathbf{F}(\mathbf{r})$, $\nu(\mathbf{r})$, and the local expression for the virial theorem which together govern the mechanics of the electron density, are determined by dressed energy densities that include the interactions with the density and nuclei of all of the atoms in the system.

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(54) The same applies to a bond path linked to a non-nuclear attractor. Such local maxima in $\rho(\mathbf{r})$ are found in systems with losely bound electrons such as metals[12] and for an electron trapped at an F-center.[42]