Nearsightedness of Electronic Matter As Seen by a Physicist and a Chemist

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The theorem of Hohenberg and Kohn, that the electron density is a unique functional of the external potential, applies to a closed system with a fixed number of electrons. Transferability of the electron density of an atom between two systems, necessary to account for the fundamental role of a functional group with characteristic properties in chemistry, however, is a problem in the physics of an open system. Transferability in chemistry requires a new theorem stated in terms of the density: that the electron density of an atom in a molecule or crystal determines its additive contribution to all properties of the total system, its transferability being determined by a paralleling degree of transferability in the atom's virial field, the virial of the Ehrenfest force exerted on its electron density. Transferability of the virial field is found in spite of unavoidable changes in the external potential that occur on transfer. The properties of an atom in a molecule are determined by the Heisenberg equation of motion for a "proper open system" derived from the principle of stationary action. The theorem is grounded in the common sense observation that two atoms that "look the same", i.e., have the same charge distribution, must possess identical properties. Transferability is discussed in terms of the properties of the electron density, the one-density and the two-density matrix, the latter demonstrating that both the Coulombic and exchange contributions to the energy of a group are separately transferable. It is demonstrated that the exchange indices determined by the two-density matrix provide a readily determinable measure of the effective range of the exchange energy.

1. Near Sightedness As Seen by Physicists

A paper by Prodan and Kohn (PK)[1] was recently published in which they ascribe important chemical concepts such as transferability and the possibility of understanding the properties of large molecules "one neighborhood at a time" to the "near sightedness of electronic matter", a phrase they abbreviate to NEM. They propose that NEM can be attributed to "the fact that, for fixed chemical potential, local electronic properties, such as the density $n(\mathbf{r})$, depend significantly on the effective external potential only at nearby points. Changes of that potential, *no matter how large,* beyond a distance R have *limited* effects on local electronic properties, which rapidly tend to zero as a function of R." These predictions are held to hold only in the absence of long-range ionic interactions.

Although stated to deal with chemical concepts such as transferability and Pauling's concept of the chemical bond, their discussion specifically treats metals and insulators containing "many charged or uncharged electrons". Their discussions refer to one- and higher-dimension systems of noninteracting fermions using models such as jellium, concluding with a brief discussion of interacting fermions, where it is stated that replacement of an atom or ion by another atom or ion in a metal has short-ranged electronic consequences, whereas in an insulator, ions lead to classical long-range electronic effects. It is the purpose of the present work to point out that as physicists, they are addressing a problem that resides at the core of chemistry. NEM in chemistry has been described and its many facets illustrated with the conditions for transferability quantified in terms of the forces acting on the electron density of an open quantum system—on an atom in a molecule.[2]

2. Near Sightedness As Seen By Chemists

2.1. Role of Functional Groups in Chemistry. To a chemist, NEM is rooted in the concept of a functional group, a concept that forms the cornerstone of experimental chemistry. By the close of the 19th century, it was realized that atoms and functional groupings of atoms can exhibit characteristic sets of static, reactive, and spectroscopic properties which, in general, vary between relatively narrow limits. The knowledge of chemistry is ordered, classified, and understood by assigning properties to functional groupings of atoms, properties which are then used to identify the presence of a given group or to understand the behavior of some total system. Experimentally, it is an atom that is responsible for transmitting chemical information from one system to another, and transferability requires the definition of an atom in a molecule whose properties are characteristic, additive, and transferable.

2.2. Definition of an Atom As an Open Quantum System. Clearly, a discussion of NEM in chemistry requires the definition of an atom in a molecule or crystal together with its properties. This is accomplished by the extension of Schwinger's principle of stationary action to an open system.[3−5] Schwinger extended the concept of the stationarity of the action integral operator to include the variation of the time end points of some total system and of the state vector at these points, that is, to include a variation of the space-like surfaces and of the state vector on those surfaces.[6] His space-time formulation of the principle makes it possible to further extend the stationarity of the action to include a variation of the time-like surfaces, the evolving boundary of an open system. A concise description of the procedure is obtained by augmenting the Lagrange-function operator by the divergence of the gradient of the density operator. This step leaves the equations of motion unaltered, leading to a class of generators whose associated infinitesimal

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transformations yield variations of the action-integral operator for an open system, similar in form and content to those obtained for the total, isolated system.[7] Modifying the generators in this manner is shown to be equivalent to requiring that the open system Ω be bounded by a surface $S(\Omega,\mathbf{r})$ through which there is a local zero flux in the gradient vector field of the electron density $\rho(\mathbf{r})$

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

Only the observables of such "proper open systems" are described by the correct equations of motion, and as amply illustrated in the literature, only proper open systems recover the measured values of atoms and functional groups in chemistry.[8] The resulting theory is referred to as the quantum theory of atoms in molecules (QTAIM).

Schwinger's principle, by combining the action principle with Dirac's transformation theory, yields both the field equations and Heisenberg's equation of motion for an observable, the two fundamental and necessary equations for the prediction of the properties of a quantum system, open or closed. Thus, Schwinger's principle generalized to a proper open system Ω yields, in addition to Schrödinger's equation of motion $i\hbar\dot{\Psi} = \hat{H}\Psi$, an expression for the variation of the Lagrange function-operator expressed in terms of the Heisenberg commutator of $\hat{H}$ and the infinitesimal generator $\hat{F}$, eq (2)[2,5].

$$\delta\hat{\mathscr{L}}[\hat{\Psi},\Omega,t]=(1/2)\{(i/\hbar)<\hat{\Psi}[\hat{H},\hat{F}]\hat{\Psi}>_{\Omega}+cc\} \qquad (2)$$

The expectation value of a Hermitian operator is not necessarily real when evaluated over an open system; hence the addition of the complex conjugate, cc. The variation $\delta\hat{\mathscr{L}}[\hat{\Psi},\Omega,t]$, with the action of the infinitesimal generator expressed in terms of the observable $\hat{G}$ ($\hat{F} = \varepsilon\hat{G}$), yields the time rate of change of the generator $\hat{G}$, the flux in its associated current through the surface of Ω and the contribution from the time rate-of-change of the surface. When expressed in the Schrödinger representation, the generalized equation of motion is as follows:

$$d\int_{\Omega}\rho_{\mathrm{G}}(\mathbf{r})/dt=(N/2)\{(i/\hbar)\langle\Psi|[\hat{H},\hat{G}]|\Psi\rangle_{\Omega}+cc\}- \\ (1/2)\{\oint dS(\mathbf{r},\Omega)\mathbf{J}_{\mathrm{G}}\bullet\mathbf{n}+cc\} \\ +(1/2)\{\oint dS(\mathbf{r},\Omega)(\partial S/\partial t)\rho_{\mathrm{G}}(\mathbf{r})\} \qquad (3)$$

The property and current densities of a property G are given by the following:

$$\rho_{\mathrm{G}}(\mathbf{r})=1/2\{N\int d\tau'(\Psi^{*}\hat{G}(\mathbf{r})\Psi+(\hat{G}(\mathbf{r})\Psi)^{*}\Psi)\} \qquad (4)$$

$$\mathbf{J}_{\mathrm{G}}(\mathbf{r})=(N\hbar/2mi)\int d\tau'\{\Psi^{*}\nabla_{\mathbf{r}}(\hat{G}(\mathbf{r})\Psi)-\nabla_{\mathbf{r}}\Psi^{*}(\hat{G}(\mathbf{r})\Psi)\} \qquad (5)$$

The change in representation from field theory to the Schrödinger representation leads to the transformation of every property into an effective single-particle density and associated current defined in real space; the symbol $\int d\tau'$ implies a summation over spins and the integration over all coordinates save those denoted by **r**, the coordinates of the electron integrated over the open system. The symbol $<>_{\Omega}$ implies the same mode of integration, followed by integration of **r** over Ω. Aside from the summation over spins, this mode of integration is that introduced by Schrödinger in his fourth paper to define the "electric density", the same paper in which he introduced the current density and related ρ to **J** via the equation of continuity.[9] The resulting real space representation of density and current for every property is a most important result, for it yields, through the Heisenberg equation, a real-space "dressed" representation of *all* of a system's definable properties, including those such as the total energy and Ehrenfest force that involve two-particle interactions. The real-space representation of properties is obviously of great importance in discussions of transferability and in illustrating its occurrence. The basic single-particle nature of the expectation values follows from the generator acting only on the coordinates of a single electron in the field theoretic expressions, Schwinger pointing out that, "the essence of field theory is to provide a conceptually simpler and more fundamental description depending on the particle as the basic entity."[10]

The quantum mechanics of an open system may be derived heuristically[11] by deriving the equation of motion, eq (3), directly from Schrödinger's equation followed by appeal to experiment to determine the correct boundary condition. Delimiting the equations of motion derived for arbitrary fragments of some total system to the open systems whose predicted properties yield agreement with the experimentally measured additive atomic properties is accomplished by applying the "zero-flux" boundary condition stated in eq (1).

The derivation points to an important property of an open system: operators representing observables are no longer necessarily Hermitian when the domain of integration is restricted to a system with finite boundaries. Thus, the proof that the expectation value of the commutator $\langle[\hat{H},\hat{G}]\rangle$ vanishes for a stationary state through the use of the Hermitian property of $\hat{H}$ to obtain the so-called hypervirial theorem $\langle[\hat{H},\hat{G}]\rangle = 0$ is not obtained for an open system, with the commutator average being instead given by the flux in the current of the observable $\hat{\mathrm{G}}$ through the surface of the open system. Thus, in a stationary state, eq (3) reduces to eq 6[2]

$$(1/2)\{N(i/\hbar)\langle\Psi|[\hat{H},\hat{G}]|\Psi\rangle_{\Omega}+cc\}= \\ (1/2)\{\oint dS(\Omega)\mathbf{J}_{\mathrm{G}}\bullet\mathbf{n}+cc\} \qquad (6)$$

While there is no flow of current in a stationary state, eq 6 equates the effect of the surroundings on the open system expectation value of the commutator to the instantaneous flux in the current through its surface.

An important point to be made concerning the zero-flux boundary condition is that the kinetic energy of a proper open system is a well-defined quantity. The Schrödinger expression $K(\mathbf{r}) = -(1/2)\Psi^{*}\nabla^{2}\Psi$ and the positive definite expression he employed in his energy functional $G(\mathbf{r}) = (1/2)\nabla\Psi^{*}\cdot\nabla\Psi$, differ locally by $-(1/4)\nabla^{2}\rho(\mathbf{r})$, whose integral over an atomic basin vanishes as a consequence of the zero-flux boundary condition.[12]

QTAIM, by providing the quantum basis for an atom in a molecule, necessarily recovers all of the related concepts of experimental chemistry yielding definitions of molecular structure in terms of bond paths—lines of maximum density linking neighboring atoms—and of structural stability in terms of the dynamics of the gradient vector field of $\rho(\mathbf{r})$.[13] The Lewis model and the associated ideas of electron localization/delocalization are determined by the atomic expectation value of the exchange density[14] and given physical expression in the topology of the Laplacian of the electron density, the quantity $\nabla^{2}\rho(\mathbf{r})$.[15]

3. Transferability of Atoms in Molecules

3.1. Observational Basis of an Atom in a Molecule. Extensive studies of molecular charge distributions[16−20] using near Hartree−Fock wave functions obtained from the Mulliken−Roothaan laboratory of molecular structure and spectra (LMSS) at the university of Chicago in the 1960s led in 1971 to the observation that *the extent to which properties are additive (i.e., transferable) between different systems is determined by the extent to which the charge distributions of atomic fragments are unchanged during transfer between systems.*[21] This observation was placed on firm theoretical footings with the observation in 1972 that the atomic form imposed on the structure of matter by the dominance of the nuclear-electron force defines an atom in a molecule as a region of space bounded by a surface of local zero-flux in the gradient vector field of the electron density, eq 1.[12] The atoms so defined were found to have the property of maximizing the transferability of their charge distributions in an exhaustive partitioning of space. The observations made in this 1972 paper bring to the fore some of the difficulties a chemist has with the conditions for NEM given by PK.

Consider the charge distributions shown in Figure 1 for the ground states of LiH, LiO and LiF, the examples used in 1972 to illustrate the all important observation that the transferability of atom's density was accompanied by a paralleling transferability in its kinetic energy density.[12] One must concede that the similarity in the Li atomic densities defined by the intersections of their zero-flux surfaces with the plane of the diagram is no less than remarkable considering the change in its bonded neighbor from H to F resulting in a 9-fold increase in the contribution of the bonded atom to the external potential. Integration of the density over the atom and its subtraction from the nuclear charge of Li yields net charges of +0.91, +0.93, and +0.94, respectively. This is a simple example of the most important observation underlying the concept of a functional group: *that atoms or linked groupings of atoms can exhibit characteristic forms and properties in spite of gross changes in their immediate neighbors.* Thus chemistry requires that transferability must apply to the atom's properties as well as to its density, which brings one to the second important observation made in the 1972 paper:[12] contour displays of the kinetic energy densities $K(\mathbf{r})$ or $G(\mathbf{r})$ and their integrated values for the Li atom, T(Li), were found to exhibit a paralleling transferability with $\rho(\mathbf{r})$. The average values of T(Li) for the three molecules exhibits a spread of only 9 kcal/mol, a change of 0.2% in the total energy of ~7.37 au. Thus, by observation, both $K(\mathbf{r})$ and $G(\mathbf{r})$ exhibit the same degree of transferability as that of $\rho(\mathbf{r})$ for a topological atom.

This paralleling behavior of $\rho(\mathbf{r})$ and $G(\mathbf{r})$ was the crucial *observation* that led to the theory of atoms in molecules, as deduced from the following chain of reasoning. The virial theorem for a system governed by Coulombic forces states that the total energy of a molecule in electrostatic equilibrium (no Feynman forces acting on the nuclei) equals the negative of the average kinetic energy of the electrons, $E = -T$. If the virial theorem exists for an atom in a molecule—that is, for a region of space bounded by a zero-flux surface—then one could use this theorem to define $E(\Omega)$, the energy of an atom in a molecule, as $E(\Omega) = -T(\Omega)$. Since $T(\Omega)$ is additive, the same additivity applies to $E(\Omega)$, and the energy of a molecule would be given by the sum of its atomic contributions, $E = \sum_{\Omega} E(\Omega)$. The existence of the atomic virial theorem, proven a few years later in 1975,[22] accomplishes a unique physical partitioning into atomic contributions of all of the electrostatic interactions, both repulsive and attractive, between the nuclei and the electrons.

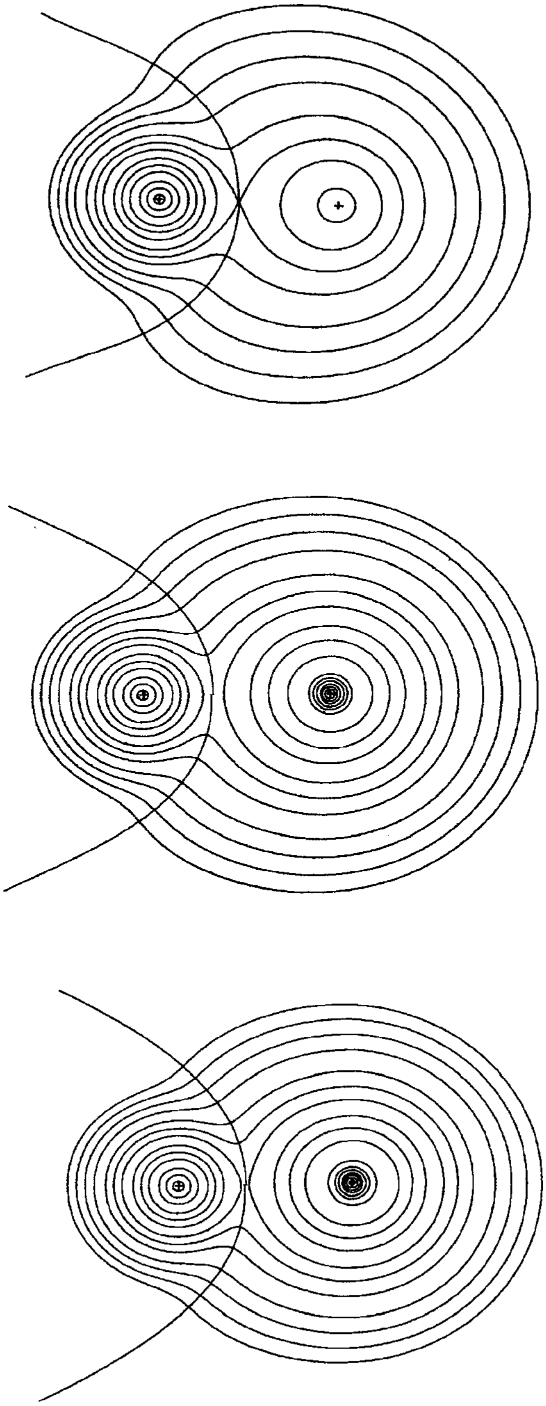

Figure 1. Contour maps of the ground-state electron density distributions, in descending order, of the molecules LiH, LiO, and LiF, showing the intersection of the zero-flux interatomic surface, eq (1), with the plane of each diagram. One is to note the similarity in the density distribution of the Li atom that is obtained in spite of the very different nature of its bonded neighbor, the populations of the Li atom equalling 2.09, 2.07, and 2.06 e, respectively. The diagram illustrates one of the paramount concepts of chemistry: that an atom of a given element can be recognized in any environment. The outer contour value is 0.001 au and the remaining contours increase in value in the order 2×10^n, 4×10^n, 8×10^n au with n beginning at -3 and increasing in steps of unity. The same contour values are used in all density maps. The densities are calculated from near Hartree−Fock wave functions obtained from LMSS employing large STO basis sets.[12]

The identification of $E(\Omega)$ with $-T(\Omega)$ has a number of important consequences. A statement of the virial theorem for the topological atom—a proper open system—predicts that when the form of an atom in real space remains unchanged on transfer, so does its contribution to the total energy. That is, based on these *observations*, the energy of an atom and thus surely its other properties, would be transferable to the same extent as is its charge distribution. The identification $E(\Omega) = -T(\Omega)$

satisfies in a single stroke the two essential requirements of the atoms of "conceptual chemistry"—*additivity and transferability of properties*. It is common sense that two identical pieces of matter must possess identical properties and consequently, two atoms possessing identical charge distributions, that is, atoms indistinguishable in real space, must exhibit identical properties.

The exceptional degree of transferability that the charge distribution of an atom or a functional grouping of atoms can exhibit is remarkable. While the initial observations regarding properties paralleling form were for atoms in diatomic molecules, they have since been extended to encompass many types of functional groups, obtained from experiment[23−27]and theory.[2,28,29] Transferability of form and properties is found to be particularly evident for atomic groupings corresponding to the building blocks of biological macromolecules. Recent work, both experimental[30,31] and theoretical,[32−34] demonstrates the remarkable transferability of the charge distributions and properties of the main-chain and other functional groups common to the amino acids. While such a finding must come as no surprise to a chemist used to understanding the properties of a protein in terms of its amino acid residues, it requires a theory of atoms in molecules to implement and make quantitative use of this knowledge. The transferability of proper open systems in biology is so complete that one may construct a polypeptide for example, by linking the mirror image amidic interatomic surfaces of amino acid residues determined as the central members in accurate calculations of tripeptides.[33] The amino acid residues defined by their amidic surfaces exhibit a zero net charge (or a charge of ± 1 for the residues bearing a net side-chain charge), a necessary requirement for the use of the residues as repeating units in the construction of a polypeptide.

The conditions put forth by PK for NEM and transferability do not appear to anticipate chemical transferability. PK state that the density $\rho(\mathbf{r})$ depends significantly on the external potential only at nearby points, a condition that fails to account for the principal observation of chemistry: that the electron density of an atom can exhibit a characteristic form and properties in spite of gross changes in its immediate neighbors. It is not clear how one can apply their condition of constant chemical potential to finite molecular systems, the Li examples ranging from four to twelve electrons. The next section presents the mechanics of an open system—of an atom in a molecule—and demonstrates that transferability in chemistry is not directly related to the external potential but to the virial field, the virial of the Ehrenfest force acting on the electron density, of which the external potential is but one component.

3.2. Mechanics of Atomic Transferability. The virial theorem, postulated in 1972 for a topological atom, was derived in 1975[22] by a scaling of the energy functional $\mathscr{G}(\psi,\nabla\psi)$ used by Schrödinger[35] to obtain his stationary state equation $\hat{H}\psi = E\psi$. This derivation yields, in addition to Schrödinger's equation, the stationary state analogue of Schwinger's principle of stationary action for an open system, eq 2.

$$\delta\mathscr{G}(\psi,\nabla\psi;\Omega) = -(N\varepsilon/2)\{(i/\hbar)\langle\psi,[\hat{H},\hat{G}]\psi\rangle_\Omega + cc\} \tag{7}$$

With the realization that one was following the path traced out by Schwinger—the variation of a boundary and of the state vector on that boundary—the stationary state result was quickly extended to yield Schwinger's statement of the principle of stationary action for an open system.[4,5]

3.3. Atomic Statements of the Ehrenfest Force and Virial Theorems. The Ehrenfest and virial theorems are obtained from the Heisenberg equation of motion for an open system, eq 3, with $\hat{G}$ given by the electronic operators—$i\hbar\nabla$ and $\mathbf{r}\cdot\mathbf{p}$, respectively.[5] The commutator term for the momentum operator yields $-\nabla_\mathbf{r}\hat{V}$ which determines the force exerted on the electron at $\mathbf{r}$ by the remaining electrons and by the nuclei, all in fixed positions. By taking the expectation value of this force in the manner denoted by $N\int d\tau'$ one obtains an expression for $\vec{\mathscr{F}}(\mathbf{r})$, the force exerted on an electron at position $\mathbf{r}$ by the *average distribution* of the remaining electrons and by the rigid nuclear framework—a "dressed density"—giving the force exerted on the electron density. The physics of an open system defines a corresponding "dressed" density distribution for every measurable property, one whose integration over an atomic basin yields the atom's additive contribution to that property. A dressed density distribution for some particular property accounts for the corresponding interaction of the density at some point in space with the remainder of the molecule. The force density is an example of a physical quantity that clearly involves two-electron operators, and yet is expressible terms of a real-space density. In a stationary state, the force exerted on an atom is given by the surface integral of the momentum flux density expressed in terms of the stress tensor, eq 8.

$$\begin{aligned}\vec{\mathscr{F}}(\Omega) &= \int_\Omega d\mathbf{r}\int d\tau'\{\psi^*(-\nabla_r\hat{V})\psi\} = \int_\Omega d\mathbf{r}\vec{\mathscr{F}}(\mathbf{r})\\ &= -\oint dS(\Omega;\mathbf{r}_\mathbf{s})\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})\end{aligned} \tag{8}$$

where the stress tensor is given by

$$\begin{aligned}\overleftrightarrow{\sigma}(\mathbf{r}) = (\hbar^2/4m)\{(\nabla\nabla + \nabla'\nabla') - (\nabla\nabla' +\\ \nabla'\nabla)\}\Gamma^{(1)}(\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'}\end{aligned} \tag{9}$$

The Ehrenfest force is the one measured in an atomic force microscope.[36]

The expectation value of the commutator for the virial operator $\hat{G}(\mathbf{r}) = \hat{\mathbf{r}}\cdot\hat{\mathbf{p}}$ yields $2T(\Omega) + \mathscr{V}_\mathrm{b}(\Omega)$, twice the atom's electronic kinetic energy plus $\mathscr{V}_\mathrm{b}(\Omega)$, the virial of the Ehrenfest force exerted over the basin of the atom. In a stationary state, these contributions are balanced by $\mathscr{V}_\mathrm{s}(\Omega)$, the virial of the Ehrenfest force acting over the surface of the atom. Expressing by $\mathscr{V}(\Omega)$ the total virial for atom Ω, the virial theorem for a stationary state may be stated as follows:[2,5]

$$-2\mathrm{T}(\Omega) = \mathscr{V}(\Omega) = \mathscr{V}_\mathrm{b}(\Omega) + \mathscr{V}_\mathrm{s}(\Omega) \tag{10}$$

The virials of the Ehrenfest force exerted over the basin and the surface of the atom with the origin for the coordinate $\mathbf{r}$ placed at the nucleus of atom Ω are given in eqs 11

$$\begin{aligned}\mathscr{V}_\mathrm{b}(\Omega) &= -\int_\Omega \mathrm{d}\mathbf{r}\mathbf{r}_\Omega\cdot\nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r}) = \int_\Omega \mathrm{d}\mathbf{r}\mathbf{r}_\Omega\cdot\overleftrightarrow{\mathscr{F}}(\mathbf{r})\\ \mathscr{V}_s(\Omega) &= \oint \mathrm{dS}(\Omega,\mathbf{r}_\mathrm{s})\mathbf{r}_\Omega\cdot\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})\end{aligned} \tag{11}$$

The definition of pressure requires the mechanics of an open system, since the pressure is exerted on the system's surface.[37,38] It has been shown that the pressure−volume product pv is proportional to the viral of the forces exerted on the open system, that is the virial of the force resulting from the momentum flux through the system's surface.[39]

3.4. The Virial Field. The virial $\mathscr{V}$ for a total system is given in eq 12;[40]

$$\mathscr{V} = V_{en} + V_{ee} - \sum_\alpha \mathbf{X}_\alpha\cdot\mathbf{F}_{\alpha e} \tag{12}$$

the sum of the electron−nuclear (e-n) and electron−electron (e-e) potential energies and the virial of the electronic contribution to the Feynman forces exerted on the nuclei, where $\mathbf{X}_\alpha$ is the coordinate of nucleus α. This latter term can be equated to the sum of the virials of the Feynman forces exerted on the nuclei, $\sum_\alpha \mathbf{X}_\alpha \cdot \mathbf{F}_\alpha$, and the nuclear–nuclear repulsion energy $V_{nn} = \sum_\alpha \mathbf{X}_\alpha \cdot \mathbf{F}_{\alpha n}$. It is in this manner that V_{nn} enters into the molecular virial to yield the result that *$\mathscr{V}$, the virial of the Ehrenfest force acting on the electron density, equals the total potential energy V and the virial of the Feynman forces on the nuclei,* eq 13,

$$\mathscr{V} = V_{en} + V_{ee} + V_{nn} - \sum\nolimits_\alpha \mathbf{X}_\alpha \cdot \mathbf{F}_\alpha = V - \sum\nolimits_\alpha \mathbf{X}_\alpha \cdot \mathbf{F}_\alpha \tag{13}$$

The same expressions are obtained for an open system and, thus, one obtains the usual statements of the virial theorem when applied to an atom in a molecule:

$$T(\Omega) = -E(\Omega) + W(\Omega) \text{ and } \mathscr{V}(\Omega) = 2E(\Omega) - W(\Omega) \tag{14}$$

where $W(\Omega)$ is the atomic contribution of the virial of the external (Feynman) forces acting on the nuclei.[41] Each theorem obtained from eq 3 can be stated in a local form, the local form of the viral theorem being

$$(\hbar^2/4m)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + \mathscr{V}(\mathbf{r}) \tag{15}$$

where the virial field $\nu(\mathbf{r})$ may be expressed as follows:[2]

$$\mathscr{V}(\mathbf{r}) = -\mathbf{r}\cdot\nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r}) + \nabla\cdot(\mathbf{r}\cdot\overleftrightarrow{\sigma}(\mathbf{r})) = Tr\overleftrightarrow{\sigma}(\mathbf{r}) \tag{16}$$

Integration of eq 16 over an atom yields the atomic virial theorem, eq 10. The virial field $\mathscr{V}(\mathbf{r})$ is a dressed density distribution of particular importance. It describes the energy of interaction of an electron at some position $\mathbf{r}$ with all of the other particles in the system, averaged over the motions of the remaining electrons. When integrated over all space, it yields the total potential energy of the molecule, including the nuclear energy of repulsion and for a system in electrostatic equilibrium, with $\mathscr{V} = V$, it equals twice the molecule's total energy. The virial field condenses all of the electron–electron, electron–nuclear and nuclear–nuclear interactions described by the many-particle wave function into an energy density that is distributed in real space. The electronic energy density is defined as[2]

$$E_e(\mathbf{r}) = G(\mathbf{r}) + \mathscr{V}(\mathbf{r}) = -K(\mathbf{r}) \tag{17}$$

The electronic energy E_e equals the total energy E in eq 14 in the absence of external forces with $W = 0$.

An atomic self-consistent potential contains the long-range *e-n* and *e-e* Coulombic interactions. In describing the interactions that arise when atoms approach one another to form a molecule, a new interaction is introduced, the repulsion between the nuclei. The interatomic repulsions, V_{ee} and V_{nn} are both approximately one-half the magnitude of the interatomic *e-n* attractive interaction V_{en}, the resulting difference between the repulsive and attractive interactions yielding the relatively small change in energy accompanying the approach of the atoms. Thus, because of the nuclear–nuclear contribution, the energy changes resulting from the formation of a molecule or from the relative vibrational displacements of its nuclei, are governed by a field that is short-ranged compared to that determined by just the *e-n* and *e-e* interactions. *The virial field $\mathscr{V}(\mathbf{r})$, because it includes all contributions to the potential exerted at a point in space, is the most short-range possible description of the potential interactions in a many-electron system.* It is the near balance in these attractive and repulsive contributions making up the virial field that lead to the transferability of an atom's charge distribution and its properties and to the concept of a functional group as the carrier of chemical information. The statement of PK that "NEM is not screening of charges, which renders long-range Coulomb potentials short-range" is to be compared with the finding that the transferability of an atomic charge distribution is determined by the documented paralleling transferability of the virial field.

3.5. Transferability and the Virial Field. An experimentally based "additivity scheme" requires not only that the atomic properties be additive to yield the molecular expectation value, as is always the case for proper open systems, but that the atoms be transferable between molecules.[2] Groups are said to exhibit "perfect transferablity" (PT) when the changes in their charge densities exhibit such small spatial perturbations that the values in their properties fall within the limits of the experimental or theoretical accuracy, generally accepted to be ± 1 kcal/mol for the energy and 1×10^{-3} e for an atomic population. More common is "compensatory transferability" (CT) observed in the face of unavoidable perturbations induced in the groups by their transfer between molecules.[28] In these instances, the charge density of the groups exhibit measurable changes but the molecular properties are found to be conserved. In CT, for which many examples may be found in the extensive tables of experimental thermodynamic properties by Benson et al.,[42] the intergroup transfer of electron density that accompanies the formation of a product molecule results not only in the conservation of charge but also in the conservation or near conservation of other properties. Thus, energy is conserved if the energy lost by one group equals the energy gained by another.

The classic case of group additivity is that of the heats of formation of the linear hydrocarbons $CH_3(CH_2)_nCH_3$ beginning with ethane $n = 0$, measured by Rossini in 1931.[43−46] The heats of formation or energies corrected for group enthalpies from 298 to 0 K and for zero-point energies may be fitted to the linear energy relationship

$$E(CH_3(CH_2)_nCH_3) = 2E^\circ(CH_3) + nE^\circ(CH_2) \tag{18}$$

where the intercept is given by twice the energy of the standard methyl group, $2E^o(CH_3) = E(C_2H_6)$ and the slope, by the energy of the standard repeating methylene group $E^o(CH_2)$.

The hydrocarbons exhibit both PT and CT.[28,47] A methyl group bonded to another methyl in ethane clearly must differ from one bonded to a methylene group, that is for $n \geq 1$, from which it withdraws a small amount of electronic charge, 0.017e and undergoes a decrease of 9 kcal/mol in its energy. A methylene bonded to methyl, however, exhibits compensatory changes in its charge and energy such that the sum of the changes for the methyl and its bonded methylene group is zero. From $n = 2$ onward the methyl and the neighboring methylene groups exhibit PT, the methylene in propane, $n = 1$, necessarily exhibiting twice the changes in energy and charge as in the molecules with $n > 1$. The methylene groups bound only to other methylenes as found for $n \geq 3$ exhibit perfect transferability with energies equal to $E^o(CH_2)$, the standard repeating energy of the group in eq 18, and a zero net charge. For example, the energies of the four interior CH_2 groups in dodecane differ from the standard value, the slope $E^o(CH_2)$ in eq 18, by 0.2 kcal/mol and possess net charges of 0.001 e, both values lying within the integration errors.[48] Energies calculated at all levels of theory, including those that employ self-consistent scaling of the electronic coordinates to ensure satisfaction of the virial theorem, satisfy the linear relationship eq 18 with $R^2 = 1.00000$. The slope $E^o(CH_2)$ in eq 18 is given by the energy of the methylene group defined by the integration of its kinetic energy density up to the two C|C surfaces of zero-flux that separate it from the remainder of the molecule, a direct demonstration of the physical significance of the boundary condition, eq 1. The central methylene group in pentane has the energy $E^o(CH_2)$ and it density distribution, along with that of one of the two central methylene groups in hexane, are displayed in Figure 2. The densities are obtained from RHF calculations with self-consistent scaling (SCVS) to satisfy the virial theorem, employing a large basis set. The electronic density plots are indistinguishable and are examples of the transferable methylene group of the linear hydrocarbons. This being the case, their electronic kinetic energy densities and their virial fields are equally transferable, as further illustrated in Figure 2. The integrated densities yield group populations that differ by 0.001 e, average kinetic energies (and hence total energies) that differ by 0.4 kcal/mol and virials (total potential energies) that differ by 0.8 kcal/mol.

The strain energy of a cyclic molecule with less than six carbon atoms is determined by comparing the energy of one of its methylene groups with that of the standard $E^o(CH_2)$, and the theoretically determined energies of the methylene groups recover the experimental stain energies to 0.2 kcal/mol or less.[47] Linear group additivity relationships exist for magnetic susceptibility[49] and electric polarizability[50] of hydrocarbons and the corresponding group additivities are recovered by the methyl and methylene group contributions determined in the presence of external magnetic and electric fields. These examples, of many that include transition probabilities[51] along with atomic charges and dipolar polarizations determined by the atomic polar tensors obtained from infrared intensity sums,[52−54] are given to demonstrate that QTAIM recovers the *experimentally measured properties of atoms and functional grouping of atoms in molecules.* The recovery of second-order field induced properties such as magnetic susceptibilities, electric polarizabilities and transition probabilities demonstrates that the truism that atoms that look the same exhibit the same properties is maintained in the presence of external magnetic and electric fields. Thus, the map of the current induced in a methyl group is as transferable as is the map of its electron density,[49] a comparison made possible by the development of the method of the continuous set of gauge transformations (CSGT) that enabled the first calculations of divergence-free representations of the induced current.[55]

4. External Contributions to the Energy of a Functional Group

In cases of perfect transferability such as that pictured in Figure 2 for the methylene group, wherein the virial field necessarily exhibits the same degree of transferability as does the density in order to ensure transferability of the atom's energy, the separate changes in the contributions to the atomic virial—in the external potential energy and in the repulsive contributions—differ in general, by many thousands of kcal/mol between members of a homologous series, only the total potential energy density—the virial field—remains unchanged on transfer.[12] The contribution of the "external potential" to the energy of a system is given by the internal contribution $V_{en}{}^o(\Omega)$, the energy of interaction of the density in Ω with the nuclei internal to it, together with the external contribution $V_{en}{}^e(\Omega)$, the interaction of the density of Ω with all of the external nuclei.

Table 1 lists the changes in the values of the following quantities for the indicated groups in pentane and hexane: a methyl group, a methylene group bonded to methyl and an interior transferable methylene group labeled $CH_2{}^o$; $N(\Omega)$, the number of electrons, $E(\Omega)$, the energy of the group, and the internal contributions to the electron−nuclear attractive and electron−electron repulsive potential energies, $V_{en}{}^o(\Omega)$ and $V_{ee}{}^o(\Omega)$, respectively, the latter just for the standard methylene group. Also given are the changes in the external contributions to the same two quantities, $V_{en}{}^e(\Omega)$ and $V_{ee}{}^e(\Omega)$, respectively. In keeping with the perfect transferability of the methyl and methylene groups, the changes in $N(\Omega)$ are 0.001 e or less and those in $E(\Omega)$ and the internal contributions to the potential energy are all less than one kcal/mol. These near-zero changes are found in spite of very large changes in the external contributions to the potential energy of interaction of each group with the remainder of the molecule, values in excess of 3500 kcal/mol for V_{en} and 2500 kcal/mol for V_{ee}.

4.1. Separate Transferability of Coulomb and Exchange Contributions. The Coulomb and exchange contributions to V_{ee} are separately conserved on transfer, as illustrated by data for the standard methylene group in Table 2[56] which gives the relevant data for the $CH_2{}^o$ group in pentane and hexane. There is of course, a large change in the total electron−electron repulsion energy for a methylene group in pentane compared to hexane, the values of $V_{ee}(CH_2{}^o)$, but the internal contributions $V_{ee}{}^o(CH_2{}^o)$ remain unchanged on transfer to within 0.001 au. The same is true of the separate internal Coulomb and exchange contributions and the total change in the repulsion arises from the increase in the external contribution, but only in the Coulombic term. Not only is the internal exchange contribution to the energy of a standard methylene group conserved on transfer, so is its external contribution. While this may seem surprising at first, it is a required result. As discussed in a later section, the integration of the exchange density over an atomic basin or over a pair of basins determines respectively, the extent to which the electrons are localized within the atom or delocalized into the basin of another. Since the localization of the electron density within an atomic basin and its degree of delocalization over the remaining atoms of a system are necessarily separately conserved, the exchange density, weighed by $-1/r_{12}$ to give the exchange energy, must be separately conserved in the case of PT.

4.2. Separate Conservation of the Basin and Surface Virials. Since the molecules are in equilibrium geometries, the atomic virial equals twice the atom's energy and the virial is conserved to the same extent as is the energy in these examples. An interesting property of the atomic virial is that it may be equated to the virial of the forces acting over the basin of the atom $\mathcal{V}_b(\Omega)$, and the virial of the forces exerted on its surface, $\mathcal{V}_s(\Omega)$, isolating the internal from the external contributions, eqs 11. The important point is that basin and surface contributions are separately conserved. For example, the changes in the two quantities for a methyl carbon atom in pentane and hexane being $\Delta\mathcal{V}_b(\Omega) = 0.00$ kcal/mol ($\mathcal{V}_b(\Omega) = 75.12$ au) and $\Delta\mathcal{V}_s(\Omega) = 0.13$ kcal/mol ($\mathcal{V}_{\mathcal{V}s}(\Omega) = 0.237$ au), the bracketed values being the totals for a single carbon atom. *The constancy in the surface virial is a result of the virial of the total force exerted on an atom remaining constant on transfer, in spite of the very large changes in the individual contributions to the external potential acting on the atom.*

Perfect transferability of a group requires that the geometry of the group be equally transferable, since the equilibrium geometry is determined by the vanishing of the Feynman forces on the nuclei. This is documented for the hydrocarbons where equivalent bond lengths differ by less than 0.0001 au and bond

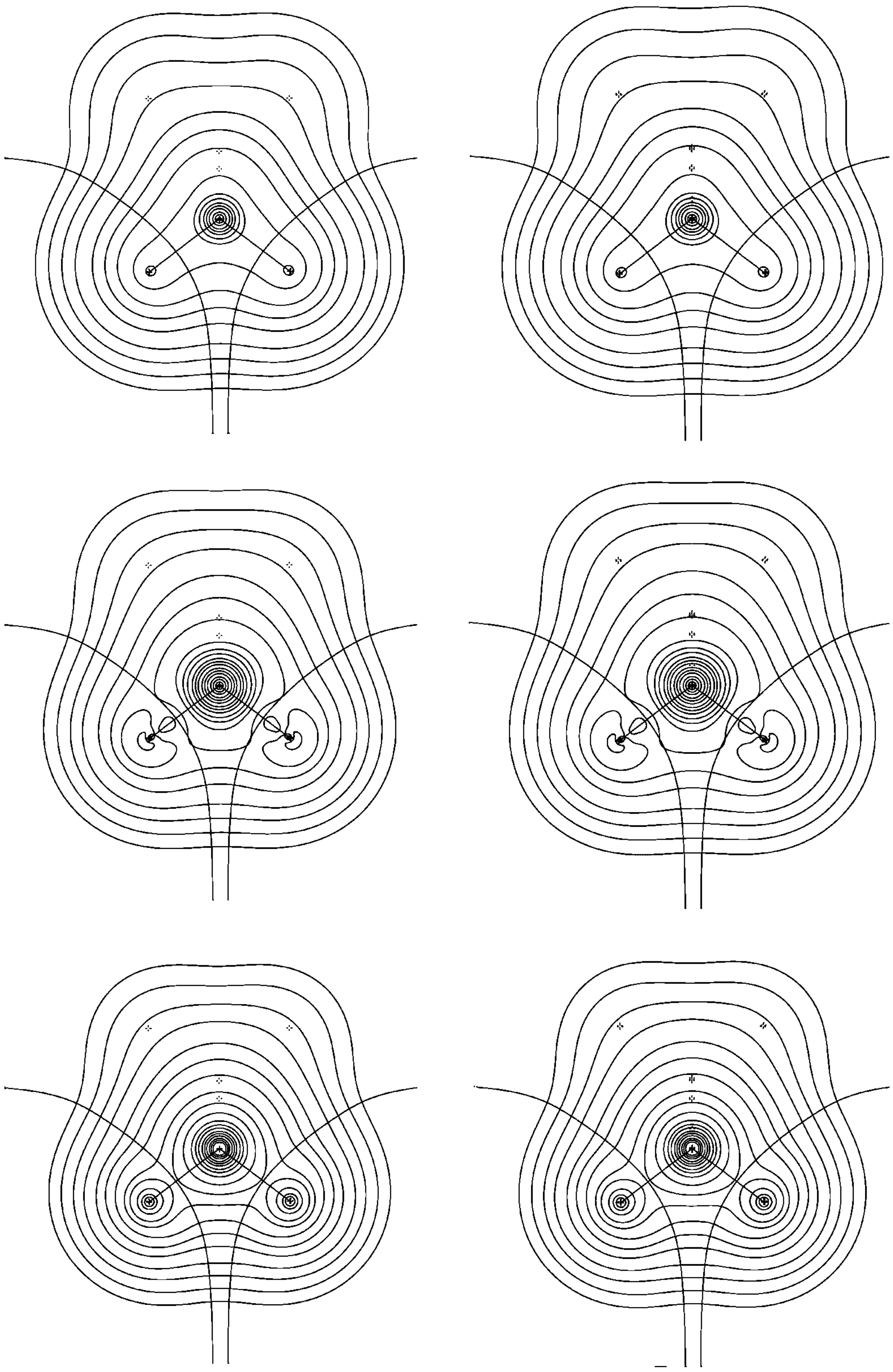

Figure 2. Contour maps, in descending order, of the electron density $\rho(\mathbf{r})$, the positive definite kinetic energy density $G(\mathbf{r})$ and the virial field $\mathcal{V}(\mathbf{r})$, eq 16, for the transferable methylene groups in pentane (RHS) and hexane. The plots are in the plane of the C and H nuclei and show the intersections of the C|H interatomic surfaces with this plane and the bond paths— lines of maximum electron density—that link the C nucleus with each of the protons. Projected positions of out-of-plane nuclei are indicated by open crosses. Each plot is superimposable with that of its neighbor. This pictorial representation of the paralleling transferability of the electron density and energy densities is made quantitative by the vanishingly small differences in their integrated values as quoted in the text. The field $|\mathcal{V}(\mathbf{r})|$ is topologically homeomorphic with the electron density, while $G(\mathbf{r})$, as is clear from the diagram, is not. The bond path defined by $\rho(\mathbf{r})$ is superimposed on the virial path in the field $|\mathcal{V}(\mathbf{r})|$, the line of maximally negative potential energy density linking neighboring nuclei. The bond critical point, found at the intersection of the bond path and an interatomic surface, is clearly in close proximity to the corresponding critical point in $|\mathcal{V}(\mathbf{r})|$. The plots and numerical results are obtained from RHF SCVS calculations using the 6−311++G(2d,2p) basis.

angles by less than 0.05°.[28] On the contrary, the finding that the geometrical parameters of a group—bond lengths and bond angles—are transferable, ensures that the electron density of the group is also transferable.

TABLE 1: Changes in Properties for Transferable Methyl and Methylene Groups[a,b,c]

Ω	$\Delta N(\Omega)$	$\Delta E\ (\Omega)$	$\Delta V_{en}^{o}(\Omega)$	$\Delta V_{en}^{e}(\Omega)$	$\Delta V_{ee}^{o}(\Omega)$	$\Delta V_{ee}^{e}(\Omega)$
CH_3	0.000	−0.1	+0.6	3543		
CH_2	0.000	−0.3	−0.5	4006		
CH_2^{o}	0.001	−0.4	−0.5	5037	0.6	−2523

[a] N in number of electrons; E in kcal/mol. [b] Group energies in au 1 au = 627.5 kcal/mol = 27.212 ev. [c] $E^{o}(CH_3) = -39.629$; $E^{o}(CH_2) = -39.046$; $V_{en}^{o}(CH_2^{o}) = -93.031$; $V_{ee}^{o}(CH_2^{o}) = +19.781$.

TABLE 2: Coulombic and Exchange Contributions to $V_{ee}(CH_2^{o})$ in Pentane and Hexane in au

	$V_{ee}(CH_2^{o})$	$V_{ee}^{o}(CH_2^{o})$	$V_{ee}^{e}(CH_2^{o})$
	total		
pentane	52.036	14.767	37.269
hexane	56.057	14.768	41.289
	Coulomb		
pentane	57.963	19.781	38.182
hexane	61.985	19.782	42.201
	exchange		
pentane	−5.928	−5.0140	−0.9140
hexane	−5.928	−5.0140	−0.9140

5. Transferability in Solids Ionic and Otherwise

Unit cells in solids—ionic, covalent or molecular—present countless examples of perfect transferability, the properties of the total system equalling the sum of the corresponding contributions from each repeating unit cell. (As discussed below, surface effects die off rather rapidly and may be quantitatively accounted for). PK make repeated statements to the effect that their conditions for and discussion of transferability do not apply to systems containing ions, stating: "It is generally accepted that in the absence of long-range ionic interactions, large molecules or materials systems can be studied and understood one neighbourhood at a time," and further, "in a metal replacement of an atom or ion by another atom or ion has short-ranged electronic consequences, whereas in an insulator, ions lead to classical long-range electronic effects."[1] These arguments do not apply to the chemical transferability of atoms. The virial field exhibits the same short-range nature in an ionic crystal or in the presence of an ion as it does in any other system. The zero-flux boundary condition when applied to a solid is a generalization of the Wigner−Seitz cell, defining atoms with characteristic definable properties. [57−60] Even perturbations, gross in terms of the change in external potential, die off quickly in an ionic system, as exemplified in the following examples.

Macroscopic Polarization. The macroscopic polarization **P**(**r**) is the induced dipole moment per unit volume placing the determination of **P**(**r**) within the domain of the physics of an open system. The same applies to magnetization **M**(**r**) of extended systems and the physics of an open system enables one to express the electron densities or currents associated with the individual unit cells within a crystal whether they be ionic, covalent, or molecular.[61,62] It is however necessary to correct the usual textbook description of polarization in an infinite periodic crystal that equates **P** solely to the polarization of the density in a unit cell.[63,64] Martin, using general arguments, has shown that one must include a surface term that accounts for the charge transferred across the boundary of the cell in addition to the polarization within the cell, no matter how the cell is defined.[65] This is precisely the result obtained when the dipole moment of any system, finite or extended, is expressed in terms of contributions from the open systems of which it is comprised. The contribution of an atom to the dipole moment of a finite or extended system, is given by the average of $-\mathbf{r}\rho(\mathbf{r})$ over the atom's volume with **r** referenced to the nucleus together with a position weighted term that describes the contribution from the charge lost or gained by the atom through the interatomic surfaces it shares with its bonded neighbors. For an atom in a crystal, this term is replaced with the dipole resulting from the flux in the electric field through each of the atom's interatomic surfaces, measured relative to its nuclear position.[41]

Simple model systems consisting of repeating units of a polyether capped by hydrogen atoms, $H|CH_2O|_nH$ or the ionic couple $F|NaF|_nNa$ were used to illustrate the applicability of transferability obtained from the physics of an open system and demonstrate the rapid falloff in surface effects on the electron densities and properties of the unit cells.[61] Figure 3 illustrates the superimposable nature of the electron and kinetic energy densities and of the virial field for the groups in the central portion of $H|CH_2O|_8H$. Each interior cell has a zero net charge to within the integration error of 0.003e, as required for the termination of surface effects on the density. In the cases where $n \geq 6$, a single outer cell serves to ensure electric neutrality of the interior cells. Similarly, the interior cells have energies that agree to within 0.003 ev or less and the magnitudes of their polarizations differing by less than 0.002 au.

F-Center Defect. As a further example, consider the removal of the central F atom from the cubic cluster $Li_{14}F_{13}^{+}$ leaving an electron which becomes bound as a non-nuclear attractor in its place thus creating an F-center defect.[66] The individual contributions to the potential energies of the ions forming the faces of the cube change by large amounts when the fluoride ion is replaced by a single negative charge, the change in the external potential for example, corresponding to the removal of a F nucleus. The nuclear-electron attractive potential energy increases by 480 eV for F and by 135 eV for a Li following the removal of F. These changes are however, closely matched by decreases in the repulsive contributions. Thus, the virials of the total forces exerted on the ions change by relatively modest amounts of ∼0.2 eV, their densities and other atomic properties exhibiting correspondingly small changes; the charge on F changing by −0.017e and its energy by 0.1 eV. Thus, even a gross perturbation, removal of a fluorine atom, results in relatively small changes in the density distributions and properties of the surrounding ions. The charge on the F-center non-nuclear attractor is −0.64e compared to −0.94e for the central F atom it replaces and is a further example of a group responding only to the total change in the potential exerted on it as given by the virial field, rather than to changes in its individual contributions, such as the external potential.

Localized Perturbations. Creating charge within a neutral system in general has only local effects as illustrated by the transfer of a hydrogen from the carboxyl group to the amino group in an amino acid to form its zwitter-ion.[67] Only the properties of the atoms directly involved in the tautomerization are significantly affected, the carbon and remaining atoms of the residue bonded to Cα for example exhibiting a change in population less than 0.00e. The constancy in the atomic properties of the atoms forming the backbone of a polypeptide, found in spite of the very different attached residues including those bearing net charges, has led to the construction of aspherical scattering models to replace the independent atom model in the determination of the electron density from high resolution crystallographic work.[68,69] This important and emerging field of crystallography is a result of the experimental verification of the transferability of atoms and groupings of atoms defined as proper open systems. The creation of a vacancy in a solid does not lead to any difficulties in applying QTAIM, as to the crystal face of MoS_2 in a study of its catalytic properties.[70]

6. The Nearsightedness of the One-Electron Density Matrix

The density distribution of an atom in a molecule clearly does not obey the theorem of Hohenberg and Kohn, that the electron density be a unique functional of the external potential.[71] QTAIM provides a new theorem, one based on observation; the electron density of an atom—a proper open system—determines the atom's contribution to all measurable properties of the total system. Whether the atom's density distribution changes by a little or a lot, its properties change by corresponding amounts.

Should one regard the virial field $\mathcal{V}(\mathbf{r})$ as playing the corresponding fundamental role in determining the electron density for a proper open system as does the external potential in the HK theorem for a total system? Not only does $\mathcal{V}(\mathbf{r})$ parallel the transferability of $\rho(\mathbf{r})$, the field $|\mathcal{V}(\mathbf{r})|$ is found to be structurally homeomorphic with the electron density and, thus, every structure and change in structure exhibited by the topology of $\rho(\mathbf{r})$ as revealed in its gradient vector field is recovered by the corresponding topology of $|\mathcal{V}(\mathbf{r})|$.[72] Thus, the electron density $\rho(\mathbf{r})$ appears as a locally scaled function of $|\mathcal{V}(\mathbf{r})|$, the magnitude of the electronic potential energy density.

Or does the relationship between the density and atomic properties lie deeper? The electron and kinetic energy densities together with the virial field are all determined by the one-electron density matrix $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$. Thus in a 1995 paper entitled "Chemistry and the Nearsighted Nature of the One-Electron Density matrix" it was argued that chemistry is a consequence of the near-sightedness of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$, since this matrix determines the electron density and all of the mechanical properties of an atom in a molecule.[73] There is an additional important observation bolstering this statement: all of the necessary physical information is contained in the expansion of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$ up to second-order with regard to both the diagonal and off-diagonal terms.[2] The expansion up to second-order about the diagonal elements $\Gamma^{(1)}(\mathbf{X}, \mathbf{x} = 0)$ with $\mathbf{X} = (\mathbf{r} + \mathbf{r})/2$ and $\mathbf{x} = (\mathbf{r} - \mathbf{r})/2$ yields

$$\begin{aligned}\Gamma^{(1)}(\mathbf{X}+\delta\mathbf{X},\delta\mathbf{x}) = \rho(\mathbf{X}) + \nabla\rho(\mathbf{X})\delta\mathbf{X} + \\ (1/2)\delta\mathbf{X}\cdot\nabla\nabla\rho(\mathbf{X})\cdot\delta\mathbf{X} + \\ (2m/i\hbar)\mathbf{J}(\mathbf{X})\cdot\delta\mathbf{x} + (2m/\hbar^2)\delta\mathbf{x}\cdot\overleftrightarrow{\sigma}(\mathbf{X})\cdot\delta\mathbf{x} + \\ (2m/i\hbar)\delta\mathbf{X}\cdot\nabla\mathbf{J}(\mathbf{X})\cdot\delta\mathbf{x} \quad (19)\end{aligned}$$

The diagonal terms yield the density, the gradient vector field of the density that determines structure and structural stability and the dyadic that determines the critical points in the density. The trace of the dyadic yields the Laplacian of the density, the bridge that provides a homeomorphic mapping of the information determining the spatial pairing of electrons contained in the second-order density matrix. The off-diagonal terms yield the current density $\mathbf{J}(\mathbf{r})$, the stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$ that determines the Ehrenfest force and energy densities and the divergence of the current $\nabla\mathbf{J}(\mathbf{r})$, the field that determines the critical points in $\mathbf{J}(\mathbf{r})$. The gauge origin problem in calculating a divergence-free representation of the induced current density and related second-order response properties determined by$\mathbf{r} \times \mathbf{J}(\mathbf{r})$, was first accomplished using the method of continuous set of gauge transformations derived from the theory of atoms in molecules.[55,74]

In a 1996 paper Kohn drew attention to the fact that his 'nearsightedness' principle applies to $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$.[75] The paper

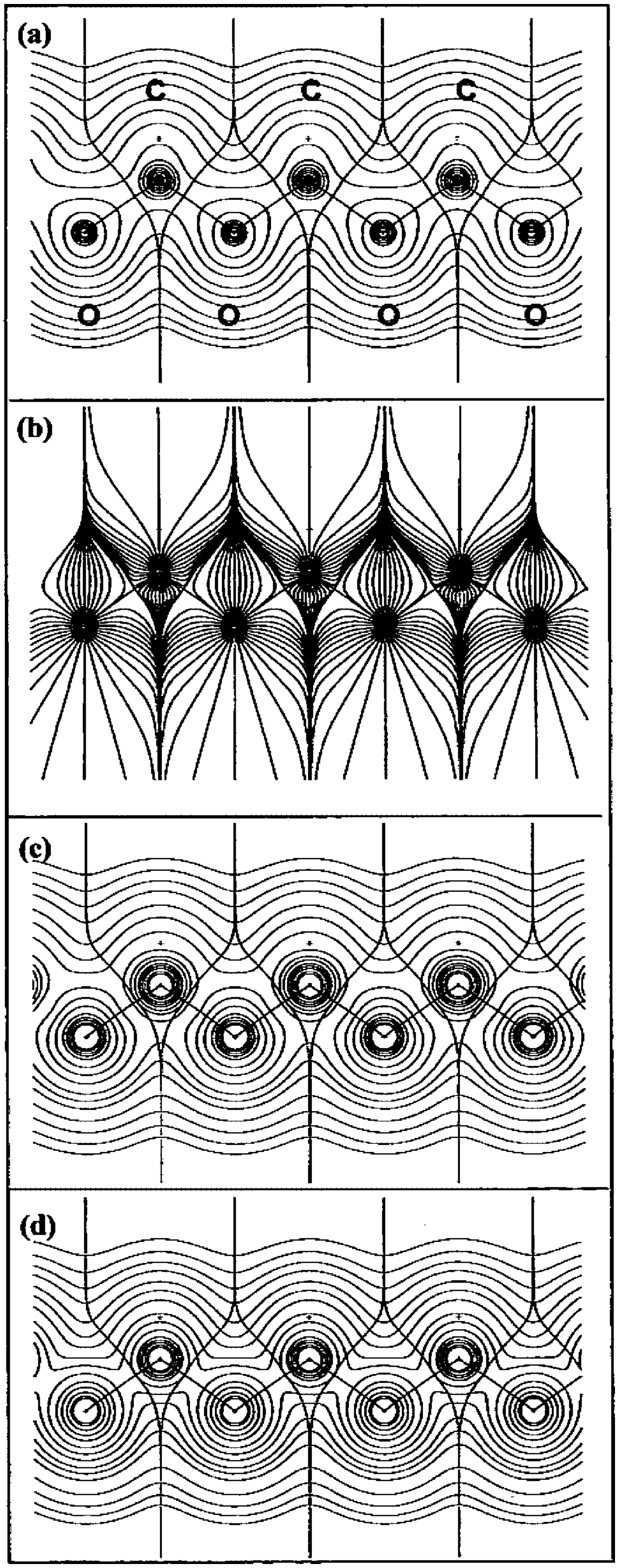

Figure 3. (a) Contour maps of the electron density for the central portion of $H|CH_2O|_8H$ in the plane of the C and O nuclei, overlaid with interatomic surfaces and bond paths. (a) the electron density $\rho(\mathbf{r})$. (b) The associated gradient vector field defining the atomic boundaries and bond paths. (c) Contour maps of $G(\mathbf{r})$, the positive definite kinetic energy density and (d), the virial field. The virial field for atom Ω integrates to twice the total energy $E(\Omega)$, the kinetic energy density to the negative of $E(\Omega)$. Both the kinetic energy density and virial field mirror the essentially perfect transferability of the electron density for each atom in the system. Atoms that look the same, i.e., that have the same electron density distribution, possess the same properties, whether free or bound.

proposed an approach to finding a computational method that scales linearly with the number of electrons based on a variational principle for $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$. Kohn proposed to replace the effective one-body potential $\upsilon(\mathbf{r})$ in the Kohn−Sham self-consistent equation for determining $\varphi_i(\mathbf{r})$ and ϵ_i by a scheme wherein $\upsilon(\mathbf{r})$ is determined directly in terms of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$ rather than by the set $\{\varphi_i(\mathbf{r}), \epsilon_i\}$ as in the K−S equations, to yield the density $\rho(\mathbf{r})$ and the total energy E. Another proposal for making use of the nearsightedness of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$ is to incorporate the virial field into the self-consistent equations to obtain a precise description of the short-range average field experienced by a single electron in a many-electron system wherein the potential energy is expressed in terms of the virial sharing operator for a single electron defined as $\mathbf{r}_1\cdot\hat{\mathbf{F}}_1 = -\mathbf{r}_1\cdot\nabla_1\hat{V}$.[76]

6.1. Transferability of the Pair Density. The question arises as to whether properties determined directly by the pair density $\Gamma^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$exhibit the same degree and pattern of transferable behavior as do group properties determined by the electron density and one-electron density matrix. The finding that properties such as the energy that involve two-electron interactions are transferable in terms of their expression in terms of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$ via the stress tensor, does not necessarily imply a separate transferability of properties expressed directly in terms of $\Gamma^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$.

One of the most important uses of the pair density in chemistry is its utilization in providing a precise determination of the extent to which electrons are *localized* to the basin of a given atom or *delocalized* over a pair of atoms.[77] Briefly, the localization of an electron is determined by the corresponding localization of the density of the Fermi hole, the physical manifestation of the exclusion principle. The Fermi hole describes how the density of an electron of given spin is spread out from a preassigned point into the space of another same-spin electron, thereby excluding the presence of an identical amount of same-spin density. It is a negative quantity and when integrated over the space of the second electron it yields −1, corresponding to the removal of one same-spin electron. If the density of the Fermi hole is maximally localized in the vicinity of the reference point, then all other same-spin electrons are excluded from its vicinity and the reference electron is localized and in a closed-shell system, the result is a localized pair of electrons. Contra-wise, the electron can go wherever its Fermi hole goes and if the Fermi hole of an electron referenced to a given atom is delocalized into the basin of a second atom, then the electron is shared between the atoms and is delocalized.

These ideas are made quantitative through the appropriate integration of the pair density.[14] The *localization* of the Fermi correlation contained within an atom is given by the double integration of the exchange density over the atomic basin, the quantity F(A,A), and its *delocalization* over a pair of atoms A and B is obtained by integrating the exchange density over the basins of both atoms, the quantity F(A,B). Delocalization is determined by the extent to which electrons on one atom are exchanged with those on another. For simplicity, from this point on we assume a closed-shell system and the total Fermi correlation integrates to −N, the total number of electrons.

The maximum possible value of $|F(A,A)| = \lambda(A)$, is N(A), meaning that the electrons in A are totally localized within its basin, something that is possible only for a closed, isolated system. Still, the degree of localization, given by $\lambda(A)/N(A)$, can be remarkably close to 100% in ionic systems, equalling 98.5 and 99.95% for centrally bonded F and Na atoms respectively, in an extended |FNa| chain.[61] The localization index $\lambda(A)$ together with the delocalization indices $|F(A,B)|$ sum to the average number of electrons on atom A, N(A) and one has

$$N(A) = \lambda(A) + \sum\nolimits_{B\neq A} |F(A,B)| \qquad (25)$$

and thus the exchange indices provide one with an atomic record of how the electrons not localized on atom A, are delocalized over the molecule. The exchange indices for the linear hydrocarbons exhibit the same pattern of transferability as found for the energy.[28] As in the case of the additivity schemes for the magnetic susceptibility and electronic polarizability, the exchange indices do not distinguish between the three different methylene groups as found for the additivity of the energy. The electrons of a methyl group are delocalized over other groups to the extent of 7.5% and those of a methylene group by approximately twice that mount. The delocalization decays monotonically with distance, decreasing to essentially zero with four intervening methylene groups.

There is added interest in the exchange indices, since the exchange density weighted by $-1/r_{12}$ determine the exchange energy and one may use the exchange indices to track the atomic behavior of the exchange energy. As noted in Table 2, not only is the internal contribution to the exchange energy conserved on transfer of a methylene group, but the external contribution is conserved as well. This result is made understandable in terms of the transferability of the exchange indices. Since N(A) and the localization index $\lambda(A)$ are conserved on PT of a group, the sum of the delocalization indices $|\Sigma_B(FA,B)|$ must be conserved as well, eq (25). However, the sum must not only be conserved, but in addition, it must be partitioned among the remaining groups in a manner required to maintain their transferable values. The result is a conserved value for the external contribution to the exchange energy for a transferable group. Consider the behavior of the exchange indices $\lambda(A)$ and $|(FA,B)|$ for the transferable methylene group $|CH_2^o|$ in pentane and hexane as outlined below:[28]

$CH_3\vert$	$\vert CH_2\vert$	$\vert CH_2^o\vert$	$\vert CH_2\vert$	$\vert CH_3$	
0.051	0.581	6.734	0.581	0.051	$\Sigma = 7.997 = N(CH_2^o)$

$CH_3\vert$	$\vert CH_2\vert$	$\vert CH_2^o\vert$	$\vert CH_2\vert$	$\vert CH_3$	$\vert CH_3$	
0.051	0.581	6.734	0.581	0.051	0.007	$\Sigma = 7.997)$

The value of λ $|CH_2^o|$, the number of electrons localized on $|CH_2^o|$, is 6.734 and the delocalization of the remaining 1.26 electrons onto neighboring groups decays evenly on each side, save for the final two groups in hexane which sum to the same value of 0.051 for a terminal group in pentane. The exchange density exhibits similar delocalized behavior with respect to the $|CH_2^o|$ group in the two molecules and the external contribution to the exchange energy is conserved.

Conservation of the external contribution to an atomic property is also observed in the external contributions to isotropic NMR nuclear shielding constants σ_N for nucleus N[78] and to the external contribution to the source function.[79] The source function $\mathcal{S}(\mathbf{r};\Omega)$, when integrated over the basin of atom Ω, determines the contribution of that atom to the density $\rho(\mathbf{r})$ at a point in space. The external contributions to σ_N and $\rho(\mathbf{r})$ are determined by integration of the shielding density[78] and the source function respectively, over atomic basins other than the atom in question. Thus one finds that the external contribution to σ_N for a carbon nucleus in a normal hydrocarbon is independent of chain length and position of the carbon nucleus within the chain, the methyl group in ethane contributing the same shielding to a methyl carbon as does the butyl group in pentane. The source function is of use in determining individual croup contributions to the density in the study of transferability.[79] Gatti et al.[80] for example, have shown that while the integrated properties of the Li atom in LiH and LiF, as discussed in the 1972 defining paper,[12] are very similar, the source function for the Li atom demonstrates that local variations do occur within the basin of Li upon replacement of H with F. That the integrated properties of the Li atom are little changed is another demonstration of the operation of the compensatory effect, the density changing so as to minimize the unavoidable changes accompanying the change in a bonded neighbor.

Clearly the delocalization indices referenced to a given atom or group, independent of any degree of transferability, provide an important measure of the fall-of in the exchange energy. The exchange indices are readily and simply calculated at all levels of theory by the suite of programs supplied for the implementation of QTAIM. The delocalization indices are a property characteristic of a given group and their prior knowledge enables one to make an informed guess of the distance required for the exchange density to be safely ignored. For example, a central carbon atom in a polyether $|CH_2O|_n$, has a percentage localization index, $\lambda(C)/N(C) \times 100\%$, equal to 64.3% compared to a value of 64.7% for the carbon of the $|CH_2{}^{o}|$ group and 99% of the carbon atom's exchange density is found within the $|CH_2O|$ group. The possibility of determining the atomic contributions to the exchange energy plays a role in helping to obviate the need for assigning separate 'ionic' and 'covalent' bonding mechanisms,[81] from the vanishingly small interatomic exchange found in ionic systems to the major role it plays in covalent interactions where its presence quantifies the role assigned to '$\alpha\beta \leftrightarrow \beta\alpha$ spin-exchange resonance'.[82]

8. Conclusions

The quantum theory of atoms in molecules provides an alternative approach to that of Prodan and Kohn, toward the understanding of transferability of the electron density and its properties. PK present their approach in terms of the concepts of density functional theory; the chemical potential and the dominant role of the external potential. The present approach focuses on the experimental basis of transferability, determined by the known chemistry of functional groups that when coupled with the observed properties of the electron density, results in the formulation of the physics of an open system - the quantum theory of atoms in molecules, QTAIM. The examples from experimental chemistry demonstrate that chemical transferability extends from the observation of properties characteristic of a given group up to and including perfect transferability. It is the latter limit that enables one to demonstrate the agreement of theory with experiment providing the basis for the new theorem regarding the density: *that the electron density of an atom in a molecule or crystal determines its additive contribution to all properties of the total system.* The agreement includes properties of groups perturbed by external electric, magnetic or electromagnetic fields.

The electron density is the principal carrier of information in both density functional theory and QTAIM; the HK theorem proves that the density determines the energy of a closed system, and observation demonstrates that the density determines the energy of an open system. The electron density should serve to bridge the two approaches. It is hoped that the present article, with its admittedly empirical grounding in experimental chemistry, will point the way to posing problems that should be addressed in obtaining a deeper and predictive understanding of NEM. Two examples are: a) To search for the functional relating the energy of a proper open system to its density, a problem that in the DFT formalism, requires its extension to a system with a noninteger number of electrons as treated by Perdew et al.[83] and adopted by Cohen et al. in the development of Partition Theory.[84,85] b) To formulate an extremization principle that minimizes the sum of the energy changes of two open systems when brought into contact, as exemplified by the many examples of compensatory transferability to be found in the tables of thermodynamic properties of Benson et al.[42] These are new questions whose formulation is made possible by QTAIM transcribing the chemistry of functional groups into the language of quantum mechanics.

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