Atomic Charges Are Measurable Quantum Expectation Values: A Rebuttal of Criticisms of QTAIM Charges

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The charge on an atom in a molecule is defined by the quantum theory of atoms in molecules (QTAIM) as the expectation value of the number operator, a Dirac observable. An atomic charge is measurable and it, together with its change, contributes to numerous measurable properties: to all molecular moments, to molecular polarizability, to intensities of electronic, infrared, and Raman absorption intensities, and to the polarization of a dielectric. The properties resulting from an applied magnetic field parallel those induced by an electric field, with the induced atomic charge being replaced by the atomic current. The phenomena of polarization and magnetization, permanent or induced, have a common physical basis when described in terms of the physics of an open system, all expressions exhibiting a single underlying structure in terms of their atomic contributions. The paper points out that this physics and the appeal the experiment it affords are lost when one employs other definitions of an atomic charge.

Atomic Properties as Quantum Expectation Values

Quantum mechanics defines the average value of a property as the expectation value of a Dirac observable, a linear Hermitian operator with a complete set of eigenstates.[1] Expectation values may or may not be measurable, the expectation value of the Hamiltonian operator, the energy, being an example of a property for which only differences can be obtained from experimental observation. The generalization of quantum mechanics to an open system provided by Schwinger's principle of stationary action[2] extends the definition of the expectation value of an observable to an atom in a molecule to yield QTAIM, the quantum theory of an atom in a molecule.[3] As with expectation values for the total system, only certain atomic properties are experimentally accessible, as delineated in this paper. Schwinger's work was characterized by a strict adherence to the phenomenological approach to physics through his insistence that one appeal to and compare with experimental observation whenever possible.[4] So this paper, since it follows his path to the physics of an open system, is offered with the caveat that it necessarily emphasizes the ties that link QTAIM with observation and measurement, an approach that will necessarily distance it from other definitions of an atomic charge.

A previous paper in this Journal uses the physics of an open system to counter arguments against the interpretation of a bond path, the principal structural element of QTAIM, as providing a universal indicator of bonding.[5] The present paper serves a similar role in countering published assertions that atomic properties, atomic populations in particular, are neither unique nor 'observable'. This view is typified by the statement "Because atomic charges do not correspond to any physical observable quantity, and thus are not uniquely defined quantum mechanically, many different definitions have been proposed.".[6] This statement is in disagreement with the known and experimentally demonstrated physics of an open system.[7] Such statements together with possible arguments against the extension of quantum mechanics to an atom in a molecule are forestalled through the demonstration that atomic properties when measurable are in full agreement with those predicted by the physics of an open system. QTAIM predicts what can be measured.

Despite the wide acceptance and use of the theory of atoms in molecules by both chemists and physicists, a well-catalogued example being the dominant role it plays in the analysis of experimental charge distributions,[8] one finds statements in the literature questioning its use. Typical examples regarding atomic populations are as follows: QTAIM charges are 'exaggerated',[9] are 'larger than "commonly accepted" values',[10] 'the Bader charges are not realistic, yielding too extreme values',[11] or "..tend to be of high magnitude".[6] These statements are in some cases coupled with the criticism that the QTAIM atomic charges will not on their own reproduce a molecule's dipole nor quadrupole moment, nor yield a particularly good representation of the electrostatic potential, compared to charges fitted to do so. For example, Brom et al. commenting on the QTAIM charge on B in BF_3 state 'these large positive charges would seriously overestimate the quadrupole moment of BF_3.',[12] a remark coupled with the opening statement in their Discussion "Because partial atomic charges are not unique...". Brom et al. use a parametrized mapping of charges obtained from a population analysis in a fitting of the point-charge model of a dipole moment to the calculated dipole. The fitting of point charges to a molecular dipole or higher moment, or to an electrostatic field, is a procedure proscribed by physics and results in charges that are not physically related to any measurable property. The point-charge model ignores the very atomic polarizations—dipolar and quadrupolar—that one is attempting to model, polarizations that must accompany any interatomic charge transfer. This elementary physics was implemented into discussions of ionic charge distributions over 50 years ago.[13] The

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atomic polarizations are necessarily opposed to the direction of charge transfer and thus reduce or, in some cases, overwhelm the contribution to the dipole from the atomic charges. Thus the magnitudes of QTAIM charges are necessarily larger than those obtained by ignoring counter polarizations of the density, since their use requires expressions that necessarily employ all moments up to and including the moment in question. An early argument that AIM charges exhibit a 'size dependency'[14] was countered by demonstrating that no charge transfer necessarily occurs between atoms of different size, such as He and Ar[15] and in the demonstration that 'atomic size' is a property determined by the nuclear-electron potential.[16] QTAIM atomic moments reproduce all measurable molecular moments to the accuracy of the density employed and reproduce the electrostatic field to any desired degree of accuracy.[17,18] The QTAIM electrostatic potential has recently been employed in the dynamical simulation of the properties of liquid HF, obtaining agreement with five important bulk properties from one and the same model.[19]

The advent of the physics of an open system brings to the fore the interdependence of atomic contributions in the understanding of measured properties, the point of departure for the discussion of atomic charge presented in this paper. Not only is an atomic charge a measurable quantum expectation value, it appears in the expressions determining a wide range of experimentally measurable properties: atomic charges contribute to the dipolar, quadrupolar, and all higher molecular moments; their field induced changes appear in the measurable contributions to the atomic polarizability and in the cell contributions to the polarization of a dielectric; their vibrationally induced changes appear in the expressions for infrared and Raman intensities; the displacement of the atomic charges caused by a molecule's interaction with light as described by the relevant transition density appears in the expression for the atomic contribution to the intensity of an electronic transition. The atomic charge or its change is not the sole contributor to any of these properties, all being dependent upon the requisite dipolar or quadrupolar atomic polarizations as well.

The property corresponding to the electric polarization in the presence of a magnetic field is the field induced atomic magnetization, and this property plays a similar role in determining the atomic contributions to the magnetic susceptibility and chemical shielding.[20] The atomic charge is paralleled in the magnetic case by the atomic current, the basin average of the field induced electronic velocity. Thus atomic charges and atomic currents that to some may appear to be 'too big' are not properties to be viewed in isolation but rather as essential contributions to the values and understanding of measurable properties, all recovered in their entirety by the physics of an open system.

An Open System and Its Properties

The theory underlying QTAIM has been presented on a number of occasions.[3,21,22] The presentation here singles out the steps essential to the demonstration of the wide-ranging role of atomic charges and currents in determining molecular properties. Among the most important of the measurable quantum expectation values is the density $\rho(\mathbf{r})$. The density is the expectation value of the density operator $\hat{\rho}(\mathbf{r})$, a Dirac observable whose eigenstates are the complete set of coordinate states $|\mathbf{r}\rangle$.[7] In his fourth paper in 1926, Schrödinger[23] defined the electron density and the vector current density along with the equation of continuity relating them, stating that these are the properties that should be used to understand the electrical and magnetic properties of matter, cautioning against the use of the wave function (orbitals) for such a purpose. In following Schrödingers's advice and using the electron density to define an atom in a molecule, we have the bonus of using a measurable property of the system, one that describes the distribution of negative charge in the presence of the pointlike nuclei in real space.

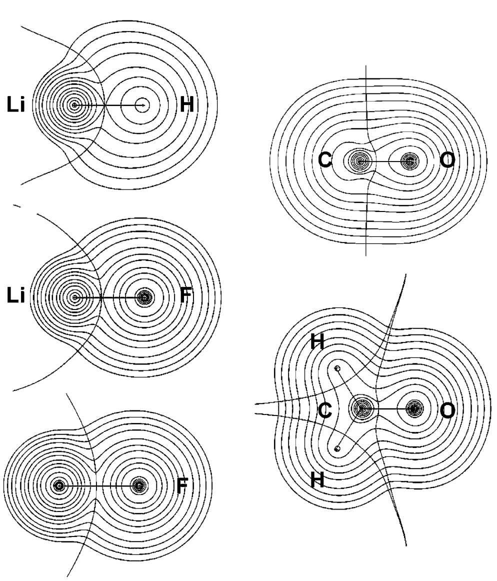

Figure 1. Contour diagrams of the electron density in LiH, LiF, NaF, CO, and H_2CO overlaid with bond paths and with the intersections of the interatomic surfaces. These maps, obtained using the 6-311++G(3d,f;2p,d) basis set, are essentially superimposable with the corresponding near Hartree−Fock STO densities displayed in "Atoms in Molecules".[3] Note the similarity in the charge distributions of the Li atom in LiH and LiF, with populations of ±0.91 and ±0.94e, and of the oxygen atom in CO and H_2CO, with respective populations of 1.33 and 1.24e. The outermost contour has the value 0.001 au and the remaining ones 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 to a maximum value of 20.

An atom in a molecule is defined as a region of space bounded by a surface $S(\mathbf{r})$ that exhibits the property of 'zero-flux', meaning that $S(\mathbf{r})$ is not crossed by any gradient vectors of $\rho(\mathbf{r})$, Figure 1.[3] This condition is expressed in eq 1 where $\mathbf{n}(\mathbf{r})$ is a unit vector perpendicular to the surface at the point $\mathbf{r}$

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0 \text{ for every point } \mathbf{r} \text{ on the surface } S(\mathbf{r}) \quad (1)$$

This zero-flux condition, one that is both defined and measurable in real space, serves a dual purpose: it defines the boundary condition for the application of quantum mechanics to an open system—to an atom in a molecule, *a proper open system*[21]—thus uniting the topological and quantum definitions of an atom. The application of eq 1 to a molecular charge distribution yields an exhaustive partitioning of a molecule into nonoverlapping atoms or of a solid into discrete cells, the latter generalizing the definition of a Wigner-Seitz cell.[24]

The atomic property most directly related to the density is a population, the expectation value of the number operator. This operator counts the average number of particles in a given spatial region. It is defined in terms of a corresponding integral of the density operator and, as previously detailed, is necessarily a Dirac observable.[7] Thus the expectation value of the number operator for atom A, denoted by N(A), obtained by integration of the density over an atomic basin whose boundaries are themselves defined for a proper open system is, like the density itself, a measurable quantity. An atomic charge, the net of the nuclear and electronic charges, is defined as $q(A) = Z_A - \mathrm{N}(\mathrm{A})$. *An atomic population or charge, as defined within QTAIM, is the measurable expectation value of a Dirac observable and is now routinely determined in accurate X-ray diffraction experiments on crystals.* A recent example is the determination of the charges and their transferability between chemically equivalent atoms comprising the backbones of a number of polypeptides.[25] Many examples from both experiment[25−30] and theory[31−34] have demonstrated the remarkable transferability of the charge distributions and properties of chemical groups defined as open systems, particularly of main chain and functional groups common to the amino acids and polypeptides. The advent of the availability of synchrotron radiation sources and CCD detectors has greatly enhanced the accuracy of the experimentally determined density and enabled charge-density studies on molecules of ever increasing size. The agreement between experiment and theory is similar to the agreement between different theoretical calculations.[35]

The difficulty some have in accepting QTAIM is illustrated by a recent statement in the *Journal of Chemical Education* viz. “Most chemists would probably describe a molecule as consisting of approximately spherical, overlapping atoms or ions.”,[9] a model whose origins lie in early MO and VB theory, certainly not with Dalton. Any modeling of atomic properties in terms of overlapping atoms, through the use atomic centered basis functions or by the introduction of a promolecule density, as employed in the Hirshfeld[36] and Voroni deformation density (VDD)[11] atomic charges, fails in two respects. First, it is readily demonstrated in a few lines beginning with Schrödinger’s equation, that to apply physics to an atom in a molecule, the atom must be a bounded space-filling object.[3,37] Second, and most important with respect to experimental chemistry, such models are incapable of recovering the observation essential to all of chemistry, that atoms and functional groups can exhibit characteristic properties *despite changes in their immediate environments*. This chemistry is lost when physics is replaced by models of overlapping atoms. Consider the simple example of the marked similarity in the QTAIM charge distributions of a Li atom bonded to H in LiH and to F in LiF, Figure 1. The Li atoms, because of this similarity in form, possess like properties, as reflected in the charges, q(Li) = +0.94 (F) and +0.91e (H) and in their energies that differ by only 8 kcal/mol.[3] This is in contrast to the use of overlapping atomic densities or basis functions that unavoidably assigns different populations q(Li) in each of the two cases [LiF followed by LiH]: Mulliken, 0.66, 0.19; VDD, 0.54, 0.46; Hirshfeld, 0.59, 0.41.[11] One further notes that models of overlapping atoms are incapable of yielding atomic charges that approach the limiting ionic values, as found experimentally for the halides and oxides of alkali and alkaline earth metals. QTAIM is the only definition of an atom to recover atomic charges at the ionic limit.

There is 150 years of experimental chemistry underlying the realization that the properties of some total system are the sum of its atomic contributions. Group contributions to the electric polarization and volume were determined as early as the late 1800s, followed by demonstrations of group additivity for heats of formation[38] and magnetic susceptibility[39] in the early 1900s. The concept of a functional group, consisting of a single atom or a linked set of atoms, with characteristic properties now forms the cornerstone of chemical thinking of both molecules and crystals and additivity is well documented for thermodynamic,[40] as well as molecular properties. The measured, additive group contributions to these properties are recovered by QTAIM.[41]

Atomic Charges, Molecular Moments, Static and Induced

Essential points of QTAIM are introduced in the development of the equations relating the atomic charge to measurable static and field induced molecular moments. All of these involve expectation values of a dipolar polarization density, the quantity $-e\mathbf{r}\rho(\mathbf{r})$. The total density of charge resulting from the nuclei, each of charge $+eZ_A$ with position vector $\mathbf{X}_\mathrm{A}$, and from the electrons, with the electronic charge density given by $-e\rho(\mathbf{r})$, is denoted by $\rho_t(\mathbf{r})$, expressed in eq 2

$$\rho_t(\mathbf{r}) = -e\rho(\mathbf{r}) + \sum\nolimits_A eZ_A\delta(\mathbf{r} - \mathbf{X}_\mathrm{A}) \tag{2}$$

The dipole moment is given by

$$\boldsymbol{\mu} = \int \mathbf{r}\rho_t(\mathbf{r})d\mathbf{r} = -e\int \mathbf{r}\rho(\mathbf{r})d\mathbf{r} + e\sum\nolimits_A Z_A\mathbf{X}_\mathrm{A} \tag{3}$$

with the electronic and nuclear position vectors referenced to an arbitrary origin. The polarization of a dielectric **P**, defined as the dipole moment per unit volume, is also described by eq 3. In addition to the permanent dipole moment, a number of measurable properties are determined by dipolar polarization densities induced by electric and magnetic fields:[20,42] (a) The polarization density $\alpha(\mathbf{r})$ induced by an external electric field, whose integral over all space yields the molecular polarization α, is determined by the polarization density $-e\mathbf{r}\rho^{(1)}(\mathbf{r})$, where $\rho^{(1)}(\mathbf{r})$ is the first-order electron density. The field-induced change in density is expressed in terms of a sum over states of contributions proportional to a product of the transition density $\rho_\mathrm{nk}(\mathbf{r})$ and a transition dipole matrix element $\mathbf{M}_\mathrm{kn} = -e\int\mathbf{r}\rho_\mathrm{nk}(\mathbf{r})\,\mathrm{d}\mathbf{r}$, linking state k and the perturbed state n. (b) The transition probability n → k induced by a molecule’s interaction with light is determined by $-e\mathbf{r}\rho_\mathrm{nk}(\mathbf{r})\cdot M_\mathrm{nk}$, the product of the transition dipole density and the transition moment. (c) The magnetic susceptibility is determined by the magnetization density $\chi(\mathbf{r})$ induced by an applied magnetic field **B**. It is also a polarization density dependent upon the position operator and is expressible as $\chi(\mathbf{r})\cdot\mathbf{B} = (1/2c)\mathbf{r} \times \mathbf{j}^{(1)}(\mathbf{r})$, the cross product of **r** with the first-order induced current. The field-dependent properties are derived using second-order perturbation theory for an open system.[20]

Because of the presence of the electronic position vector, each of these properties will necessarily generate origin dependent atomic or cell contributions. *The origin dependence of atomic contributions to these properties must, however, be only apparent, since it is well established that one can experimentally assign additive atomic and group contributions to measured dipole moments and electric and magnetic susceptibilities.* The physics of an open system yields a single origin independent expression for the additive atomic contributions that is applicable to all properties dependent upon the electronic position operator.[43]

To express $\boldsymbol{\mu}$, the dipole moment of a molecule or the polarization of an extended system in terms of atomic or cell contributions, it is necessary to introduce a local coordinate system for each atom into eq 3; $\mathbf{r} = \mathbf{r}_\mathrm{A} + \mathbf{X}_\mathrm{A}$ where $\mathbf{r}_\mathrm{A}$ is referenced to the nucleus of atom A with position coordinate $\mathbf{X}_\mathrm{A}$. As previously described, this substitution equates an atomic contribution $\boldsymbol{\mu}(\mathrm{A})$ to a contribution from the polarization of the density within the atomic basin, $\mathbf{M}(\mathrm{A}) = -e\int\mathbf{r}_\mathrm{A}\rho(\mathbf{r})$, and an origin dependent term, $q(A)\mathbf{X}_\mathrm{A}$. The definition of an atomic charge $q(A)$ necessarily introduces a contribution from the polarization of the atom’s density $\mathbf{M}(\mathrm{A})$. The important step—the one unique to an open system—is the removal of the dependence of $\boldsymbol{\mu}(\mathrm{A})$ on the external origin defining $\mathbf{X}_\mathrm{A}$

through the introduction of surface terms that describe the contribution to the dipole resulting from the transfer of charge across each of the individual interatomic surfaces bounding atom A. The presence of surface terms is a distinguishing feature of the physics of an open system.

Poisson's equation relates the divergence of the molecular electrostatic field $\mathbf{E}_t(\mathbf{r})$ to the total charge density $\rho_t(\mathbf{r})$ by the expression $\nabla\cdot\mathbf{E}_t(\mathbf{r}) = 4\pi\rho_t(\mathbf{r})$, and integration of $\rho_t(\mathbf{r})$ over atom A to obtain $q(A)$, the charge on atom A will, by Gauss' theorem, be given by the flux in $\mathbf{E}_t(\mathbf{r})$ through its atomic surface $S(A)$. The surface $S(A)$ is, in general, composed of a set of interatomic surfaces $S(A|B)$, there being one such surface for each group B linked to atom A by a bond path and thus $q(A)$, for a neutral system, may be expressed as

$$q(A) = -\sum_{B\neq A} q(B) = (1/4\pi)\sum_{B\neq A}\oint dS(A|B;\mathbf{r}_s)\mathbf{E}_t(\mathbf{r}_s)\cdot\mathbf{n}_A(\mathbf{r}) = \sum_{B\neq A} Q(A|B) \quad (4)$$

The charge transferred from A to a neighboring group B, across the surface $S(A|B)$, is denoted by $Q(A|B)$. The dipolar contributions arising from the charge transferred across the surfaces of A must, like the contribution from the density within the atomic basin, $\mathbf{M}$(A), be measured relative to $\mathbf{X}_\mathrm{A}$. Thus $Q(A|B) = -Q(B|A)$, the charge transferred across the surface $S(A|B)$, is weighted by the bonded radius of the atom enabling the dipole moment to be expressed as a sum of atomic (or cell) contributions *that is independent of the choice of external origin*, as shown in eq 5[42,44]

$$\boldsymbol{\mu} = \sum_A \boldsymbol{\mu}(A) = \sum_A [\mathbf{M}(A) + \sum_{B\neq A}[\mathbf{X}_c(A|B) - \mathbf{X}_\mathbf{A}]Q(B|A)] \quad (5)$$

where $\mathbf{X}_c(A|B)$ is the coordinate of the bond critical point. The contribution of an atom or cell to the dipole moment, the quantity $\boldsymbol{\mu}(A)$ in eq 5, is given by two terms: $\mathbf{M}(A)$ describing the polarization of the density of A relative to its nucleus and the sum of the dipoles resulting from the flux in the electric field through each of its interatomic surfaces. $Q(B|A)$ is equal to $q(B)$, the charge transferred from A across the surface $S(A|B)$ to group B. Thus $Q(B|A)$ in eq 5 describes the manner in which the electronic charge lost or gained by A is shared with each of its bonded neighbors.

The contribution to the polarization from the surface transfer charge terms are present even if the group or cell is electrically neutral. A unit cell in a centrosymmetric solid exhibits no polarization. If compressed along a given axis it can undergo a change in structure and become polarized, an example of a piezoelectric crystal. The compressed cell is still neutral, but the compression results in a flow of electronic charge into the cell through one surface and to an equal flow out across its mirror image surface.[45] All systems are open to study, including a recent use of QTAIM in the study of the curvature-induced surface polarization in nanotubes revealing a linear correlation between the QTAIM dipoles and the curvature.[46]

It is important to note that the charge flows described by the surface polarization terms $Q(A|B)$ however induced are determined by the relevant physics. Guerra et al.[11] claim that an advantage of their approach is that their subtraction of the density of a promolecule from the density previously partitioned into Voronoi cells focuses on the density change in each cell in going from the superposition of atomic densities to the final molecular density. But these changes, unlike the charge transfers described by $Q(A|B)$, are not the result of real physical fields or changes in the system but are rather changes with respect to an imagined arbitrary and unrealizable promolecule density. The dipole moment of a molecule or the polarization of a crystal do indeed involve the transfer of charge from one atom or cell to another, flows that are precisely described by the physics of an open system.

The atomic contributions to the second-order properties are also given by eq 5 with the substitution of the appropriate first-order contributions. Thus the atomic polarization $\mathbf{M}^{(1)}$(A) and surface transfer charges $Q^{(1)}(B|A)$ in the atomic expression for the field induced electric polarization $\boldsymbol{\alpha}$ are expressed in terms of the first-order induced density $\rho^{(1)}(\mathbf{r})$. In this case, the sum of the surface transfer charges equals $-q^{(1)}(A)$, the charge induced on atom A. In the expression for the atomic contributions to the probability of a transition from state n → k the same terms are determined by the transition density $\rho_{nk}(\mathbf{r})$.

The substitution $\mathbf{r} = \mathbf{r}_\mathrm{A} + \mathbf{X}_\mathrm{A}$ in the expression for the magnetization density and its integration over the basins of the atoms yields a result for the sum of atomic contributions to the magnetic susceptibility, eq 6, which consists of a basin and a surface contribution, in complete analogy with the corresponding expression for the dipolar polarization, eq 5. In the magnetic case, the basin average of the induced current, $\mathbf{J}$(A), replaces $q(A)$, and the origin dependent term corresponding to $\mathbf{X}_\mathrm{A}q(A)$ becomes $\mathbf{X}_\mathbf{A}\times\mathbf{J}(\mathrm{A})$. This term, as in eq 5, is replaceable by a sum of surface terms, each term $\mathbf{C}$(B|A) denoting the flux in the position weighted flow of current through the surface $S(A|B)$.[44]

$$\chi\cdot\mathbf{B} = \sum_A \chi(A)\cdot\mathbf{B} = \sum_A [\int_A \mathbf{r}_A \times \mathbf{j}^{(1)}(\mathbf{r})d\mathbf{r} + \sum_{B\neq A}[\mathbf{X}_c(A|B) - \mathbf{X}_\mathbf{A}]C(B|A)] \quad (6)$$

The atomic integral of the cross product $\mathbf{r} \times \mathbf{j}^{(1)}$ is the contribution to χ arising from the magnetization of the density within the basin of atom A, the term replacing $\mathbf{M}$(A) in eq 5, while $C(A|B)$ describes the position weighted flow of current through the surface $S(A|B)$, the term replacing $Q(A|B)$. Thus the form of the atomic contributions to the magnetic susceptibility is in complete analogy with the expressions for the atomic contributions to the dipole moment, the polarizability and the transition probability.

The phenomena of polarization and magnetization, permanent or induced, have a common physical basis when described in terms of the physics of an open system, the expressions for all four cases exhibiting a single underlying structure in terms of their basin and surface contributions. All involve contributions from the atomic charges or currents or their change. There are no restrictions as to the applicability of these expressions.

Atomic Properties and Experiment

The atomic properties determined by QTAIM necessarily recover all molecular properties, since QTAIM is an extension of the statement of the principle of stationary action to an open system.[21] The single necessary and sufficient criterion for determining their relevance to chemistry is provided by the agreement of the predicted atomic and group contributions with their measured values.[41] This has been demonstrated and documented for many properties in numerous systems: among them, the experimental additive contributions to the heats of formation,[33,47] electric polarizability,[48]and magnetic susceptibility[44] of the homologous series of saturated hydrocarbons. The two latter properties depend on the induced atomic charges and induced atomic currents, respectively, in addition to the associated dipolar polarizations.

The energies of a number of substituted homologous series of hydrocarbon molecules have been determined by Neugebauer and Häfelinger who demonstrated linear fittings of the energies with the number of electrons at various levels of theory.[49] While the intercept in the linear expressions was found to be dependent upon the nature of the substituent, all were found to possess the *same* slope, the proportionality with respect to the number of electrons. QTAIM partitioning of the molecular energies requires that the slope equals one-eighth of the energy $E°(|CH_2|)$, the energy of the transferable methylene. Since the population of the methylene group is equal to 8.000 ± 0.001e at all levels of theory,[50] one finds that eight times the slope is precisely $E°(|CH_2|)$.[51] The identification of eight times the slope in the regression analyses linear in N, with the energy of a region of space bounded by two C|C zero-flux surfaces, obtained from the expectation value of its electronic kinetic energy using the open system virial theorem, is striking proof of the physical relevance of the charges and energies defined by QTAIM.

Near perfect transferability is both anticipated and found in the 'building blocks' of biological molecules, and one may take advantage of this to construct a polypeptide by the simple conjoining of the density distributions of amino acid residues |Aa| previously determined in the model tripeptide Gly′|Aa|Gly″. Here again, the atomic charge plays an essential role. The two surfaces defining |Aa| form a pair of *complementary surfaces*, since ideally they are different sides of identical amidic surfaces, the concavity of the C-surface complementing the convexity of the N-surface. Complementarity requires that the flux in the electric field through the N-surface should be equal and opposite to the flux through the C-surface and thus the net charge on each |Aa| residue must be zero, as a consequence of Gauss' divergence theorem.[52] The magnitude of the average net charge for the |Aa| residues equals 0.002e, a value that lies within the integration error in the determination of the atomic populations. For a charged residue, such as $His^{(+)}$ or $Tyr^{(-)}$ the net charge is found to equal $+1.00$ or -1.00e, respectively. Recovery of the proper net charge, 0 or ± 1 e are among the properties of the |Aa| residues that demonstrate the complementarity of the two amidic surfaces and the consequent near perfect transferability of the amino acid residues enabling their use in the construction of a polypeptide.[32]

QTAIM atomic properties, because of their transferable nature, find wide use in biological studies.[53] The charge separation index for an amino acid side chain, defined by Collantes and Dunn[54] as the sum of the absolute charges of the atoms, provides an excellent descriptor of their experimental properties when the QTAIM charges are employed. These include the electrorestriction contribution to partial molar volumes, energies of hydration, partition coefficient between polar and nonpolar solvents, changes in protein stability upon single-point mutations and for correlating the second letter of the triplet genetic code with the degree of polarization of the electron density of the encoded amino acid.[31]

QTAIM has been employed in the determination of the dipole moments of the individual molecular constituents in crystals of water, urea, and *p*-nitroaniline to demonstrate the enhancement of the moments caused by the intermolecular interactions within the crystal.[55−57] QTAIM moments have been used to determine the change in dipole moment responsible for the infrared absorption intensities in CH_4, ethylene, and SiH_4.[58] The relaxation of the density of the carbon atom in the antisymmetric stretch of CH_4 makes the largest single contribution to the induced dipole moment, while the changes in the atomic charges dominate in the more polar SiH_4. The intensities in CH_4, when fitted to an atomic charge-bond dipole model with rigid following of the density, lead to the charge assignment C^-H^+,[59] a consequence of the model ignoring the dipolar relaxations of the charge density that are an essential characteristic of a vibrational displacement. Similarly, the changes in the atomic polarizabilities, involving both the induced atomic charge and polarizations, have been shown to recover the intensities of Raman active modes.[60,61] QTAIM has also been applied to the electronic charge flows and Raman trace scattering intensities in alkanes.[62,63] The atomic contributions to the electronic transition moments, when applied to the study of the 'σ-conjugation' believed to underlie the bathochromic shift with an increasing chain length in the oligosilanes, demonstrate that each additional SiH_2 makes a constant additive contribution to the intensity of the transition, in agreement with experiment.[64] The origin of the contribution is understood in terms of the induced charge and transition moment for each atom in the group.

The quantum theory of atoms in molecules leads to a method of calculating the induced current in a divergence-free manner[65] (the continuous set of gauge transformations or CSGT) enabling for the first time the calculation and displays the field induced currents, including the 'ring' currents induced in aromatic molecules by a field applied perpendicular to the molecular plane.[66] The magnetic properties calculated from the CSGT divergence-free fields are in excellent agreement with experiment and when used in the expression for the atomic contributions to the magnetic susceptibility, eq 6, yield atomic contributions that recover the experimental additive group contributions to the magnetic susceptibility assigned by Pascal.[44] The ring currents, whose presence in an aromatic system are clearly displayed in the CSGT calculated currents, lead to an enhancement in the measured susceptibilities being termed 'aromatic exaltations' by Pascal. The exaltation assigned to the benzene ring in Pascal's experimental additivity scheme is -15×10^{-6} emu, and this value is precisely six times the amount by which the calculated atomic susceptibility for a carbon atom in benzene exceeds that for a correspondingly conjugated atom in nonaromatic butadiene, the hydrogen atom contributions being identical. To complete the picture, one notes that the QTAIM energy of the aromatic CH group is more stable than that of the butadiene analogue by one-sixth the resonance energy of benzene.[67]

These examples demonstrate that the atomic expectation values obtained from the physics of an open system recover experimentally measurable group contributions. They also demonstrate that the atomic expectation values are applicable to any and all measurable properties, as required by physics. The very existence of experimental additivity schemes demonstrates that an atomic partitioning is both physically possible and necessary.

Rebuttal of Criticisms of QTAIM Charges

Criticims Based on Point-Charge Model. The criticism voiced by Brom et al.[12] to the effect that QTAIM atomic charges seriously overestimate the quadrupole moment of BF_3 does not apply when the charges are employed in the quantum mechanical expression for the quadrupole moment. The molecular quadrupole moment $\mathbf{\Theta}$ is origin dependent and referenced to the center of mass. Substitution of the operator $1/2(3z^2 - r^2)$ into the expression for the total charge density, eq 2, followed by the substitution $\mathbf{r} = \mathbf{r}_A + \mathbf{X}_A$ yields $\Theta_{ZZ}(A)$, the atomic contribution to the diagonalized z component of $\mathbf{\Theta}$, expressed as a traceless tensor, eq 7

$$\Theta_{ZZ}(A) = (3Z_A^{\ 2} - R_A^{\ 2})q(A)/2 + 3Z_AM(A) - \mathbf{R}_A\cdot\mathbf{M}(A) + Q_{zz}(A)/2 \quad (7)$$

where $Q_{zz}(A) = -e\int_A(3z_A^2 - r_A^2)\rho(\mathbf{r})d\mathbf{r}$ and $\mathbf{R}_A = \mathbf{i}X_A + \mathbf{j}Y_A + \mathbf{k}Z_A$ is a nuclear position vector. The atomic contribution to $\mathbf{\Theta}$ is seen to depend on the monopole, dipole, and quadrupole polarizations. Laidig applied the atomic expression to the moments of benzene and its hexafluoro derivative that are of similar magnitude but of opposite sign, to account for their role in the formation of the 1:1 complex.[68] All theoretical results reported here are for restricted self-consistent calculations coupled with scaling of the electronic coordinates, to satisfy the virial theorem (RHF SCVS) using the 6-311++G(3d,f;2p,d) basis set. The calculated value of Θ_{ZZ} for BF_3 is 3.36 au, compared to the best theoretical estimate reported to be 2.98 au.[12]

The atomic contributions to eq 7 in au, which necessarily recover the molecular value for Θ_{ZZ}, are 2.578 for the monopole term and -1.284 and -0.146, respectively, from the dipolar and quadrupolar polarizations for F, while the quadrupolar polarization for B, its sole contribution, equals to -0.075. The charge on F, $q(F) = -0.86$, dominates Θ_{ZZ} in this polar molecule. The largest polarization contributions are from the negatively charged F atoms that are dipole polarized toward the positively charged B atom. For very polar or closed-shell type interactions (low value of ρ_b and $\nabla^2\rho_b > 0$), the atoms are quadrupole polarized so as to remove density from along the axis of approach, each B−F axis, and place it in a torus encircling the axis causing the perpendicular contributions, $Q_{zz}(B)$ and $Q_{zz}(F)$ in the present case, to be less than zero. This polarization facilitates the approach of the charged atoms by reducing the closed-shell repulsions, a similar polarization occurring in hydrogen bonding.[69] Thus the QTAIM atomic moments provide a physical understanding that is directly interpretable in terms of the charge distribution.

In addition to equating dipole moments to atomic charges with the exclusion of the atomic polarizations, one finds the opposite approach in descriptions of the polarization of a dielectric. Textbooks on the solid state[70,71] employ the classical treatment of dielectric polarization,[72] one that relates it solely to the polarization of the density within each cell, an approach shown to be inadequate in terms of the ‘modern theory of dielectric polarization’.[73] Martin, in 1974,[74] demonstrated that one must include, in addition to the cell polarization, the contribution to the dipole resulting from the transport of charge across each of the surface elements bounding the cell, a result in agreement with the expressions obtained using the physics of an open system, eq 5.

Voronoi Cell Model. The Voronoi polyhedron when employed to define an atomic domain is defined as ‘the region of space closer to that nucleus than to any other nucleus’.[75] However, the resulting atomic domains are not used to define an atomic population in terms of the corresponding integral of the density. Instead another model, the promolecule density, is introduced to achieve that end, an atomic charge being defined as the difference between the molecular and promolecule densities integrated over the Voronoi cell, a result termed the Voronoi Deformation Density (VDD).[11] The Voronoi cell is the result of the partitioning of a geometrical space defined by the nuclear position coordinates. This is the sole physical input to the model, one that is devoid of even the charges residing at the nuclear positions, the total charge density $\rho_t(\mathbf{r})$, eq 2, being mapped onto the cells after the partitioning is complete. One cannot extract more physics from a model than one puts into it, and this model lacks any and all information pertinent to a molecular charge distribution. Because of different possible definitions of the promolecule density, its use yields a corresponding number of possible results. For example, in line with the concept of maximal conservation of information proposed by Parr and Nalewajski,[76] should Li in LiF be considered maximally similar to the free ion or to the neutral atom? This question has no answer in physics, only in the mind of the questioner. The authors of VDD report the use of ground state and “valence state” atoms in the promolecule density for the Ni atom in $Ni(CO)_4$ yielding $q(Ni) = 0.18e$ for the d^8s^2 ground state and 0.54e for its d^{10} valence state. There is only one ground-state charge distribution of $Ni(CO)_4$. The tetrahedral Ni atom, bounded by its four Ni|C interatomic surfaces, is displayed in Figure 2. Its contributions to *all* of the properties of $Ni(CO)_4$ are defined, with $q(Ni) = +0.51e$. One may bridge aspects of molecular orbital and QTAIM theory using the atomic overlap matrix.[77] This matrix shows that the Ni atom in the complex has a d orbital population of 9.09e.

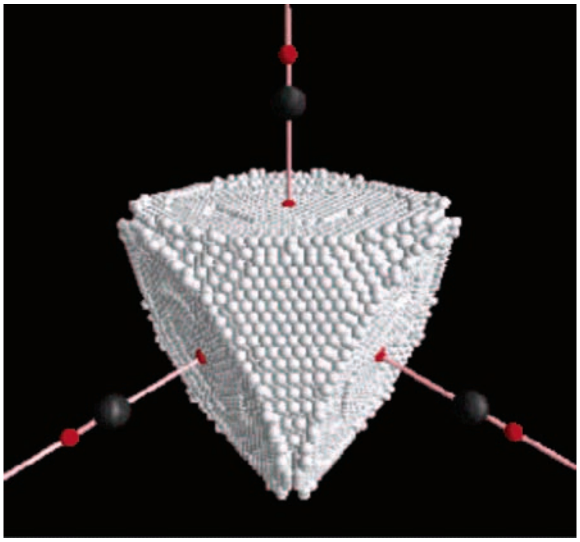

Figure 2. The four Ni|C interatomic surfaces defining the Ni atom in $Ni(CO)_4$. There is a bond path emanating from the bond critical point (bcp), denoted by a red dot, in each Ni|C surface. The bond path links a carbon nucleus, denoted by a black sphere, that is in turn linked to oxygen, the associated bcp being denoted by the second red dot. All of the properties of this enclosed region of space are defined and make additive contributions to the properties of the complex. Note the planarity of the Ni|C surfaces, an apparent characteristic of metal carbonyl complexes, a result in line with the nearly equal sharing of the density between the two atoms, as determined by the exchange index. The principal source of bonding is from the electrostatic interaction of the electron density of the Ni atom with the nuclei of the ligands, with a smaller contribution from the charge transferred from Ni to the ‘π’ density on each carbon.

The criticism of QTAIM charges contained in the VDD paper[11] exhibits a lack of knowledge of the forms and properties of molecular charge distributions, the *sole* source of physical input for any discussion of its properties. It is characteristic of papers critical of QTAIM, that molecular charge distributions—the objects of the inquiries—are never displayed, discussed, nor analyzed. Concerning the QTAIM charges in CO, the VDD authors state: “...the magnitude of the Bader charge (for instance, for carbon +1.110 au in CO) is too large for the nature of the bond in these molecules. They falsely suggest an ionic bond in CO and the other isoelectronic diatomics.” One should

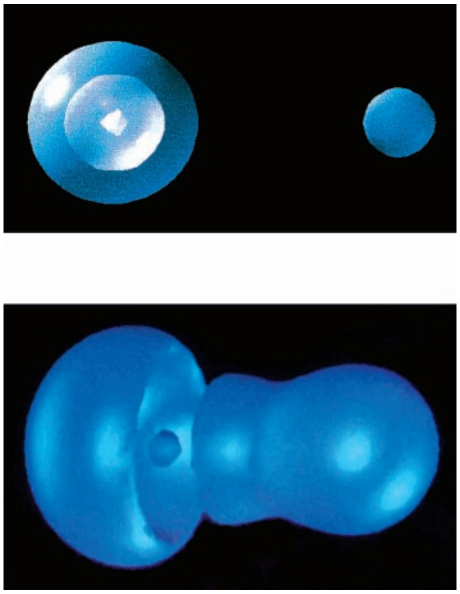

Figure 3. The zero envelopes of the Laplacian distributions for LiF (F on the left) and CO. The zero envelopes separate the regions of charge concentration ($\nabla^2\rho < 0$) from regions of charge depletion ($\nabla^2\rho > 0$). The three surfaces encompassing each F nucleus indicate the presence of two quantum shells: an inner shell and a valence shell, the two outermost envelopes defining the valence shell charge concentration (VSCC). The Li atom exhibits only an inner-shell charge concentration as found for a Li^+ ion. This distribution is to be contrasted with that for CO where both atoms exhibit VSCCs, the nonbonded charge concentration on C being particularly pronounced.

contrast this statement with the displays of the charge distributions in Figure 1. In LiF and NaF, the zero-flux surfaces clearly define near spherical charge distributions anticipated for atoms approaching the ionic, closed-shell limit. Only contours with values less than 0.08 and 0.05 au, the bond critical point (BCP) values for LiF and NaF, respectively, encompass both nuclei. These distributions are anticipated for the respective QTAIM charges of ±0.937 and ±0.944e, leaving all four atoms only 0.06e short of a closed-shell structure. There is no suggestion of such ionic-like behavior in the CO density, despite the zero-flux surfaces yielding QTAIM charges of ±1.35e in CO. Density contours up to 0.51 au encompass both nuclei, and the charge distributions are dominated by the valence density, in the amount of 2.65e on C, enclosing the inner cores on C and O. Neither the C nor the O distributions display any of the closed-shell characteristics associated with ionic bonding.

The Laplacian of the electron density, $\nabla^2\rho$, also a measurable quantity,[8,78] is known to recover the shell structure of an atom, in agreement with that determined by the quantum conditional pair density for all atoms, including transition metals.[79] Figure 3 displays the surfaces on which $\nabla^2\rho = 0$, the surfaces that separate the regions of charge concentration from those of charge depletion. The fluorine atom in LiF exhibits three such surfaces denoting the presence of two quantum shells. The first defines the boundary of the inner shell charge concentration centered on the nucleus, the second, the boundary of the inner shell charge depletion, and the third, the boundary of the outer or valence shell charge concentration (VSCC) separating it from the outer shell of charge depletion which extends to infinity. The surfaces appear spherical as anticipated for a fluoride ion. The Li atom exhibits only a single spherical surface that separates the inner shell charge concentration from the neighboring shell of depletion, the pattern characteristic of a single quantum shell. Because of the extensive transfer of electronic charge from Li to F, the Li atom does not possess a VSCC, and the structure of its Laplacian is isomorphic with that for a Li^+ ion. In the corresponding map for CO, the inner core of the carbon atom is seen to be enveloped by the pronounced valence shell charge concentration extending into its nonbonded region, the same shell totally encompassing the oxygen inner shell. The Laplacian distribution, as well as ρ, reflects the presence of the surface of zero-flux that determines the atomic populations, the surface in CO coinciding with the bonded edge of the shell of charge concentration on oxygen. Thus even though both the charge and Laplacian distributions clearly delineate the atomic boundary yielding atomic charges of ±1.3e, one cannot infer ‘ionic’ character for CO. Appeal to the physical distribution of charge yields a clear and simple lesson; *charge transfer is indicative of ionic bonding only when sufficient to yield atomic distributions that approach the ionic limit, as occurs in LiF and NaF, but not in CO.* Why should one have difficulty in accepting that C transfers 1.3 of its four valence electrons to O when the more electronegative oxygen has two vacancies in its valence shell?

Consequences of Counter Polarization. A significant degree of interatomic charge transfer is accompanied by a polarization of the atomic densities in the counter direction.[3] This effect is particularly pronounced for C in CO, where the remaining valence density is strongly polarized into the nonbonded region to yield a diffuse distribution, its nonbonded radius exceeding its free atom value by 0.15 au. Thus the near vanishing dipole moment of CO is a result of the polarization of the nonbonded density on C essentially nullifying the charge-transfer contribution to the molecular dipole, eq 5. A QCISD correlated density[77] recovers the correct sign C^-O^+. The atomic charges are reduced to ±1.22e from the RHF values of 1.35e to give a charge-transfer contribution q(C)R equal to 2.603 au, while the countering dipolar polarizations contribute −1.675 and −0.966 au for **M**(C) and **M**(O), respectively. These values yield $|\mu| = 0.037$ au compared to the experimental value of 0.048 au, (C^- O^+).[80]

Figure 1 also displays the charge distribution for CH_2CO, which has $|\boldsymbol{\mu}| = 1.11$ au with the dipole directed as anticipated, C^+O^-. The C|O interatomic surface is similar to that in CO, and the properties of the oxygen atom are correspondingly similar, q(O) = −1.24 e and **M**(O) = −0.597 au. The charge on C is approximately equal and opposite to that on O and hence q(H) = 0.00. The only significant change in the CO and CH_2O distributions is the absence of the nonbonded charge density on C, a consequence of C bonding with hydrogen, reducing its atomic polarization to −0.912 au. Thus the presence of a charge-transfer dipole in formaldehyde is seen *not* to be due to a significant change in the degree of charge-transfer C→O, one that actually decreases somewhat in formaldehye, but rather to be a consequence of the reduction of 1.1 au in the atomic polarizations, particularly that of C. De Proft et al.[6] state that the small dipole for CO suggests ‘a small charge separation, that is only encountered in CHELPG and Hirshfeld’. Such ‘small’ charge assignments are incompatible with the similarities exhibited by charge distribution of the oxygen atom up to the C|O surface in CO, with a zero moment and in CH_2O with the anticipated charge-transfer moment.

Because of the atomic polarization of C in CO, its VSCC exhibits a pronounced nonbonded charge concentration (CC) imparting to it the characteristics of a Lewis base. The topology exhibited by the Laplacian of the electron density in real space is a consequence of the electron pairing determined by the conditional pair density in six-dimensional space, a

Figure 4. The Laplacian envelope map for the $Cr(CO)_6$ donor-addition complex. The nonbonded charge concentration on each ligand carbon is directed at a 'hole', a region of charge depletion, in the VSCC of the Cr atom.

result of the topology of the Laplacian of the density being homeomorphic with the Laplacian of the conditional pair density.[79] Thus the CCs displayed in $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$ signify the presence of *regions of partial pair condensation, that is, of regions with greater than average probabilities of occupation by a single pair of electrons, as determined by the quantum pair density, thereby imparting properties attributed to a Lewis base*.

The nonbonded CC on C that counters the charge transfer dipole moment is demonstrably responsible for the remarkable facility of CO to act as a ligand in metal carbonyl complexes. Figure 4 presents a display of the Laplacian distribution for $Cr(CO)_6$, showing how the nonbonded CC on each C is directed at a region of charge depletion in the VSCC of the Cr atom, a clear physical picture of the donor−acceptor interaction responsible for the bonding in metal carbonyl complexes.[77] The effect of complex formation on the atomic charge distribution of C is made clear by the change in its quadrupole polarization. In free CO, this moment is dominated by the presence of the nonbonded CC and the axial contribution is negative. Upon complexation, density is transferred from the metal to C causing a reversal in the signs of its axial and equatorial moments, a result of the transferred density being distributed in the form of a π-like torus of density encircling the axis, in the manner envisaged in the Chatt-Duncanson model of $d\pi-p\pi^*$ backbonding. The transfer of density to C from the metal reduces q(C) and leads to a stabilization of 60 kcal/mol in the formation of $Cr(CO)_6$. Physics links the static and reactive properties of the carbon atom in CO by appealing to three fields; the density, the Laplacian of the density, and the conditional pair density. The chemistry of CO is fully accounted for, including its contribution to the bonding energy. The VDD authors suggest that one employs the promolecule density in conjunction with the zero-flux surfaces to reduce the atomic charges, leading to a value of ±0.13e for CO. It is not clear what if any chemical properties of CO are accounted for by such a charge assignment.

The Ionic Limit and Electron Exchange. As a final critique of the VDD charges we comment on their rather extraordinary finding that the alkali fluorides are not ionic but are rather moderately polarized molecules, the VDD charges on Li, Na, K, and Rb atoms in their fluorides ranging from a minimum value of 0.544e in LiF to a maximum of 0.620 in NaF. They dismiss the QTAIM atomic charges for the halides with the remark "...the Bader charges are again quite high". They make no comment as to how their charges are to be reconciled with the properties exhibited by the charge and Laplacian distributions of the halides illustrated in Figures 2 and 4 nor with the success of the ionic model in accounting for the cohesive energies and other physical properties of alkali halide crystals, as documented in texts on solid-state physics[70,71] or freshman chemistry texts, for that matter. Some examples of 'ionic' properties are the exceedingly narrow electronic bandwidths, as anticipated for the small overlap of ionic charge distributions together with the ready explanation of point defects in the ionic lattice that account for the conductivity and properties of color centers. Ashcroft and Mermin[70] present a display of the charge distribution of the NaCl lattice obtained from X-ray diffraction data, as confirming the picture of an alkali halide as a set of slightly distorted spherical ions, forms, and properties recovered in the charge distributions of LiF and NaF, Figure 1. Applications of QTAIM in defining atomic constituents of ionic crystals have been published and correlated with their physical properties.[81,82] The properties of the MgO lattice, with atomic charges of ±1.82e, and its surface defects were determined by QTAIM, in a study of the activation of surface oxygen atoms in the chemisorption of CO.[83]

There is a particular atomic expectation value that brings to the fore the physics underlying the differences between shared (i.e., 'covalent'), polar and closed-shell, or in this case, ionic distributions. This is the expectation value of the exchange operator, termed the delocalization index. The spatial localization/delocalization of electrons is a consequence of electron exchange and is determined by the pair density.[84,85] *The physical picture underlying electron delocalization is exceedingly simple—it is determined by the extent to which the electrons on one atom exchange with those on another.* The delocalization index for a pair of atoms, $\delta(A,B)$, the integral of the exchange density over two atomic basins, provides a determination of the number of electrons that are exchanged or shared between them. It thus provides a physical measure of a property that classical models of bonding associate with covalency by determining the number of α,β pairs participating in the exchange between the atoms. The role of exchange in determining the energy is to reduce the electron−electron Coulomb repulsion between a pair of bonded atoms, and $\delta(A,B)$ counts the number of pairs contributing to this reduction, the 'spin exchange resonance' of valence bond theory. Similarly, the integration of the exchange density over a single atomic basin A, determines the localization index $\lambda(A)$, the extent to which the electrons are localized within the basin of the atom. The limiting value of $\lambda(A)$ is N(A), the population of A, signifying the limiting case of complete localization of the electrons on A and the percent localization is defined as $l(A) = |\lambda(A)|/N(A) \times 100\%$. The exchange indices sum to N and thus account for all of the electrons, determining the number localized on each atom and the number delocalized or exchanged, between every pair of atoms.

The increasing interatomic charge transfer in the progression of bonding from shared to 'polar' to 'ionic' is paralleled by an increasing localization of the electrons within the atomic basins, causing a reduction in $\delta(A,B)$. Thus three electrons are exchanged between the atoms in homopolar N_2 (giving a Lewis bond order of 3) compared to only 1.6 in the isoelectronic, but polar molecule CO, a consequence of the interatomic charge transfer of 1.3e. In contrast, the close approach to ionic core distributions in LiF and NaF reduces the exchange between the atoms to just 0.18e and the atomic localizations $l(A)$ approach the idealized limit of localized core distributions: 95.5% and 99.1% in LiF and 99.5% and 98.7% in NaF.[3] *Thus the ionic limit is characterized by an almost total localization of the electrons within the basins of the individual atoms with a* *minimal exchange between them.* This finding is in accord with the exceedingly narrow bandwidths calculated for alkali halide crystals.[70] The ionic forms of the charge distributions of the fluorides are so pronounced that one can in these instances determine an interatomic surface by requiring a partitioning that maximizes the localization of the electrons within each atom and minimizes the exchange between them, the characteristics of ionic bonding. Such a procedure recovers the surface of zero flux, as first demonstrated for the case of LiH,[86] a molecule with QTAIM charges of ±0.911e and VDD charges of only ±0.414e. Thus the atomic localization of the electrons, as determined by the quantum mechanical exchange, is a property intrinsic to ionic charge distributions, one incompatible with VDD or other model charges for the fluorides.

Discussion and Conclusions

This paper has demonstrated how the concept of an atomic charge, when defined as a quantum expectation value for an open system, plays a central role in the determination of all related static and field induced properties, from permanent molecular moments to polarizations induced by external fields, by the absorption or emission of light or by pressure in the piezoelectric effect. The parallel role of the expectation value of the magnetically induced current follows from the corresponding expressions for the magnetic properties of an open system. The paper also demonstrates that atomic charges defined outside of the physics of an open system cannot be used in the quantum mechanical expressions for expectation values and are not related to measurable properties, thus curtailing their usefulness. None of the empirical atomic charges for CO for example can account for its exceptional role as a ligand in transition metal chemistry, since charges of less than ±1.0e preclude the presence of a ‘lone pair’ on C. QTAIM charges and moments, because of their grounding in physics, enable one to bring all related fields and all of the necessary physics to bear on any and all chemical problems.

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