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The Quantum Mechanical Basis of Conceptual Chemistry

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Summary. An experimentalist approaching theory for an understanding of conceptual chemistry that can be related to measurable properties, focuses on the electron density distribution. One finds in the topology of the electron density the definition of an atom, of the bonding between atoms, and of the boundary condition for the extension of quantum mechanics to an open system – to an atom in a molecule. This paper describes this approach, as it evolved from the failure of existing models to a study of molecular charge distributions and of how these studies resulted in the extension of quantum mechanics to an open system using the action principle.

Keywords. Electron density; Atoms; Molecular structure.

Introduction

Conceptual Chemistry

Science is observation, experiment, and theory. This is the path that led to the development of the molecular structure hypothesis – that a molecule is a collection of atoms with characteristic properties linked by a network of bonds that impart a structure – a concept forged in the crucible of nineteenth century experimental chemistry. One hundred and fifty years of *experimental* chemistry underlie the realization that the properties of some total system are the sum of its atomic contributions. The concept of a functional group, consisting of a single atom or a linked set of atoms, with characteristic additive properties forms the cornerstone of chemical thinking of both molecules and crystals and *Dalton*'s atomic hypothesis has emerged as the operational theory of chemistry. We recognize the presence of a functional group in a given system and predict its effect upon the static, reactive, and spectroscopic properties of the system in terms of the characteristic

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properties assigned to that group. When one enters the laboratory to make a measurement on a system, this is the conceptual model underlying the planning and the design of the experiment. It certainly was paramount in my mind when, as a student, I was presented with an 'unknown' upon entering the qualitative organic laboratory (in the days before infrared and NMR spectroscopy). We shall refer to this approach as 'conceptual chemistry' and the purpose of this account is to demonstrate that it has a basis in physics.

One might have hoped that with the advent of quantum mechanics in the 1920s, the linking of experimental chemistry to theory would have been both extended and strengthened. This certainly occurred in the field of spectroscopy where molecular orbital (MO) theory, as developed in the early papers of *Mulliken* [1–3] and *Hund* [4], provided a prediction, ordering and classification of many-electron states in terms of the component one-electron states. This theory provided the link with experimental spectroscopy, as admirably illustrated by the work of *Herzberg* [5]. It is *the* theory that one employs to predict the electronic structure of molecular systems. Thanks in large to *Roothaan* [6], MO theory, both *Hartree-Fock* and beyond, and the derivative *Kohn-Sham* [7] self-consistent orbital approach with *HF* exchange, are the procedures that are presently used to obtain approximate wave functions for the prediction of expectation values for an atom, molecule, or crystal. The eminently useful and predictive models that come from MO theory, the crystal field/ligand field descriptions of electronic structures of metal complexes and *Hückel*'s $4n+2$ rule of aromaticity, for example, exemplify the proper use of MO theory – the prediction of a molecule's electronic structure by the successive occupation of the orbitals. Orbital ordering forms the basis for the application of the 'second-order *Jahn-Teller*' symmetry rule [8] that underlies *Fukui*'s frontier orbital theory [9].

Impact of Quantum Mechanics on Conceptual Chemistry

Unfortunately this linking of quantum mechanics with experiment did not extend to the basic concepts essential to the molecular structure hypothesis – of atoms with characteristic and additive properties and of the bonding underlying molecular structure. Indeed one can find numerous literature statements to the contrary: 'that while the concepts of atoms and structure are undeniably useful if not essential to chemistry, they are not recoverable from quantum mechanics' and the link between experiment and conceptual theory was not established. Such statements come at the end of arbitrary or failed attempts to define the elements of conceptual chemistry using either valence bond or molecular orbital theory and are frequently expressed in terms of the 'atomic orbital' basis functions used in their expansion. This is an acknowledged failure of the orbital approach. *Libit* and *Hoffmann* [10], for example, after stressing the logic of substituent effects that made possible the great strides in synthetic and mechanistic organic and inorganic chemistry state: "Nothing like this logic comes out of molecular orbital calculations. Every molecule is treated as a whole and no set of transferable properties associated with a functional group emerges." Not only are the properties of functional groups known experimentally to be characteristic, the properties can in some instances appear to exhibit perfect transferability [11], giving rise to the existence of experimental additivity schemes. These schemes were early on documented for molar volumes, heats of formation, magnetic and electric susceptibilities, as well as for thermodynamic properties. An experimental chemist knows that the conceptual framework of chemistry is so deeply rooted in experiment that it must be encompassed and predicted by physics. One must only decide where to look.

The solution to the problem requires first that one abandons orbital and *Hilbert* space in the search for conceptual chemistry. Atoms and structure exist in real space – the space of observation and measurement. Wave functions and orbitals on the other hand, are mathematical functions expressed in terms of a linear superposition of elements in the abstract *Hilbert* space, a dual vector space of infinite dimension. From the time of the classic paper on the hydrogen molecule by *Heitler* and *London* [12], interpretive chemistry has been steeped in the language of wave functions and orbitals, an approach that necessarily precludes establishing any connection to atoms and structure that occur in real space. Much of present day interpretive chemistry employs individual orbitals and/or the atomic centred basis functions used in their expansion, as the basis for subjective and arbitrary definitions of atoms and their properties, as exemplified by the many definitions of an atomic charge to be found in the chemical literature. An atomic charge is in fact, a uniquely defined expectation value of a quantum mechanical observable [13]. The knowledge that measurable properties are invariant to a unitary transformation of the orbitals has not impeded the use of particular sets of orbitals, such as localized orbitals, to model bonded and nonbonded pairs of electrons, concepts that *Lennard-Jones* demonstrated are determined by the quantum mechanical pair density [14]. When the orbital approach is used in an attempt to answer a chemical question, there can be as many different answers as there are attempts, in line with the philosophy espoused by *Hoffmann* in the statement "accept that a bond will be a bond by some criteria, maybe not by others" that appears in the abstract to his talk presented at the 2004 ACS meeting in New York. An experimentalist does not choose the result he favours from a set of observations, nor should he be asked to choose between alternative often competing explanations concerning conceptual chemistry. If a question can be couched in the language of physics, it will have a unique answer if one uses quantum mechanics, rather than orbitals. We neither anticipate nor accept different answers for expectation values that are predicted by quantum mechanics for the total system. Energy is the expectation value of the Hamiltonian operator and, for a given level of theory, this value is unique. What is required is a quantum mechanics of an atom in a molecule [15, 16]. Such a theory would enable one to obtain correspondingly unique answers to chemical questions by translating them into the language of physics.

Schrödinger's Advice on How to Apply Quantum Mechanics

In 1926 *Schrödinger* published a series of four papers on 'Quantisation as an Eigenvalue Problem', paper I presenting his derivation of the 'wave equation' [17], paper IV providing the definition of the electron density, the current density, and the equation of continuity that relates them [18]. It is in this paper that he comes to grips (in Section 7) with the significance of the 'field scalar' Ψ and it makes for fascinating reading as he grapples with the knowledge that Ψ can be imaginary. He concludes that earlier musings of 'Ψ-vibrations' as something real are false and that the quantity of physical interest is instead $\Psi^*\Psi$, or the corresponding quantity for a many-particle system that he obtains by an integration over the coordinates of all the N electrons but one, the manner in which one presently defines the *electron density* $\rho(\mathbf{r})$, Eq. (1).

$$\rho(\mathbf{r}) = N \int d\mathbf{r}' \Psi^* \Psi \tag{1}$$

The symbol $\int d\mathbf{r}'$ denotes a summation over all spins and an integration over all electronic coordinates save those denoting the position $\mathbf{r}$, a mode of integrations that appears throughout the theory to be presented here. *Schrödinger* goes to considerable lengths to distance himself from any attempts to use Ψ in a way other than to obtain $\Psi^*\Psi$. He concludes by emphasizing the non-physical nature of the Ψ-function and with the hope and belief that the electronic charge and current densities, $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$ respectively, will prove useful in the understanding of the magnetic and electrical properties of matter, a belief that foreshadowed the development of the quantum mechanics of an atom in a molecule [19]. Indeed, the very first derivation of the physics of an open system for a stationary state was obtained by generalizing *Schrödinger*'s derivation of his wave equation as given in paper I to a system with a finite spatial boundary, a generalization shown to be possible only if the boundary satisfied a particular topological condition stated in terms of the density [20].

The densities, $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$, are real measurable fields, the former describing the distribution of negative charge throughout space, the latter describing its temporal evolution or its flow in the presence of a magnetic field. *Schrödinger* also introduced the quantum stress tensor $\boldsymbol{\sigma}(\mathbf{r})$ and it along with $\rho(\mathbf{r})$ and $\mathbf{j}(\mathbf{r})$, are the three quantities that determine the definition and the mechanics of an atom in a molecule. These three fields form the basis for the theory that will link the atomic concept to quantum mechanics. The reader is asked to anticipate and watch for their appearance as the physics of an atom in a molecule unfolds.

An Interlude on the Principle of Least Action

In line with the philosophy espoused in the opening sentence of this treatise, the search for a theory of an atom in a molecule necessarily begins with observation in answer to the question: 'What physical property of a system reflects the elements of conceptual chemistry?' One's search for the answer to this question leads to a most fundamental principle of physics – *the principle of least action* – first enunciated somewhat imperfectly by *Maupertuis* in 1744, stated in its present form by *Hamilton* in 1834, and most recently used by *Feynman* and *Schwinger* in 1948 and 1951, respectively, as the starting point of their fundamental reformulation of physics. *Feynman*'s *path integral* [21] and *Schwinger*'s *principle of stationary action* [22], the latter being a differential statement of the former, provide formulations of quantum mechanics that are more fundamental than the familiar Hamiltonian presentation and most importantly, extend its scope of application.

As a physical organic chemist interested in reaction mechanisms, my knowledge of physics did not include any familiarity with the principle of least action, a lack that applies to some theoreticians as well. *Feynman*'s use of the principle in his path integral approach to quantum mechanics is familiar to some in the field of dynamics, but *Schwinger*'s statement of the principle of stationary action appears to be known to a rather select audience of theoretical physicists – those whose area of interest requires the use of field theory in the search for answers to questions ranging from the structure of the nucleus internal to the atom, to the quarks and gluons internal to the nucleons, and ultimately, for very short separations, to models of the origin of the universe. This lack of familiarity is unfortunate, because the same principle defines the top of the chain as well; the atom containing the nucleus. *Schwinger*'s principle enables one to ask and answer questions that cannot be formulated within Hamiltonian mechanics, an example being 'what is at atom in a molecule?' The development underlying this statement is given here, together with an introductory account of *Schwinger*'s principle that may wet the intellectual curiosity of the reader. One can surely strive to have some familiarity with the principles that 'may provide the real foundation of quantum mechanics and thus of physical theory', *Gell-Mann*'s description [23] of the work of *Feynman* and *Schwinger.*

We begin with a quotation from *Richard Feynman* [24]. "When I was in high school, my physics teacher – whose name was Mr. *Bader* – called me down one day after physics class and said. 'You look bored; I want to tell you something interesting.' Then he told me something which I found absolutely fascinating. Every time the subject comes up, I work on it. . . .The subject is this – the principle of least action." Mr. *Bader* threw a piece of chalk in the air and upon catching it, told *Feynman* that the trajectory traced out by the chalk in space and time was such that it corresponded to the unique path, consistent with initial and final conditions, that minimized a quantity called the action. A simple, profound idea, one that appears to by-pass the classical equations of motion.

Formally, the principle of least action states that a quantity called the action is minimized as a system moves from one configuration to another or mathematically, the action is stationary with respect to variations in the space-time path connecting the two configurations. Such a path is depicted in Fig. 1 for a classical trajectory

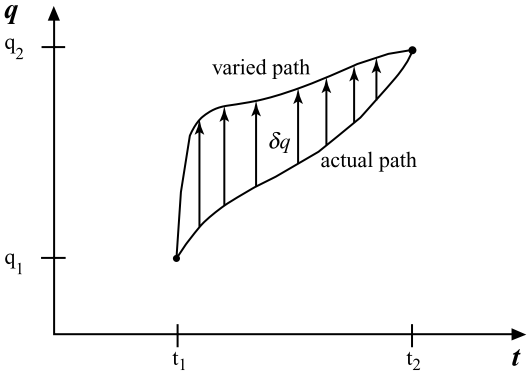


Fig. 1. Schematic representation of the actual path and of a possible varied path obtained by a variation of the position coordinate q, linking the initial and final space-time points for a classical system

connecting initial and final points in space; q_1 and q_2, at the corresponding times t_1 and t_2. The action, denoted by W_{12}, with the dimensions of h (energy×time) is the time integral between the limits t_1 and t_2, of the Lagrangian $L(q, \dot{q}, t)$, a function of the coordinates q, their velocities $\dot{q}$ and the time t, Eq. (2).

$$W_{12} = \int_{t_1}^{t_2} L(q, \dot{q}, t)\, \mathrm{d}t \tag{2}$$

The classical Langrangian equals the difference between the kinetic and potential energies, $L = T - V$. It has a value at each point on the trajectory and the 'sum' of these values between the two time limits is to be a minimum. This problem is distinct from finding an extremum in some function at a single point in space using differential calculus. Determining an extremum of a function over an entire path is accomplished using the 'calculus of variations'. Assuming the existence of the 'actual path' that is to be found, one generates a 'varied path' co-terminus in space and time, by displacing q on the actual path by an amount δq at each time t as depicted in Fig. 1, thereby causing a variation or first-order change in the action integral, δW_{12}. Since W_{12} is to be a minimum for the true path, the variation δW_{12} must vanish, and the action is said to be 'stationary'. One of *Feynman*'s lectures presents a clear and very readable presentation of the elementary mathematics underlying the derivation of the expression for $\delta W_{12} = 0$ [24].

The mathematical result of varying the action integral is shown in Eq. (3) for a single coordinate q.

$$\delta W_{12} = \int_{t_1}^{t_2} \{(\partial L/\partial q) - \mathrm{d}(\partial L/\partial \dot{q})/\mathrm{d}t\}\delta q\, \mathrm{d}t = 0 \tag{3}$$

The variations in $\dot{q}$ are re-expressed in terms of δq using an integration by parts (refer to *Feynman*'s lecture) and the resulting terms at the time end points are discarded. Thus, the result of the variation is given by the group of terms enclosed in the curly brackets in Eq. (3), all multiplied only by δq, the variations in q. Since δq is arbitrary, the only way in which the variation δW_{12} can vanish is for the group of terms in the curly brackets to equal zero, yielding a differential equation. This is a general result; minimizing the action generates a differential equation, called the *Euler-Lagrange* equation that, for the classical action, are *Lagrange*'s equations of motion which apply to any generalized set of coordinates. For a single particle $L = m\dot{q}^2/2 - V(q)$ and the equations reduce to *Newton*'s equation of motion, that the force given by $-\partial V/\partial q$, equals mass times acceleration, $m\ddot{q}$.

If one employs the quantum mechanical Lagrangian, a functional of the state function, its gradient, and time derivative, $L(\Psi, \nabla\Psi, \dot{\Psi}, t)$, and causes the action to be stationary with respect to first-order variations in Ψ, one obtains *Schrödinger*'s time dependent equation, $\mathrm{i}\hbar\partial\Psi/\partial t = \hat{\mathrm{H}}\Psi$, as the *Euler-Lagrange* equation. $\Psi(q, t)$ is a function of the coordinates and time, and one must carry out the variations over the whole of configuration space – all values of q – between the two time limits, a procedure that again clearly requires the methods of the calculus of variations. *Schrödinger* in his revolutionary paper I [17] constructed an expression for the energy of a quantum system in a stationary state expressed as a functional of a 'wave function $\psi(q)$', $\mathrm{J}(\psi, \nabla\psi)$, whose constrained variation yielded $\hat{\mathrm{H}}\psi = E\psi$. He based the form of $\mathrm{J}(\psi, \nabla\psi)$ on the classical *Hamilton-Jacobi* equation which expresses mechanics in terms of a function of space and time (as does Ψ) that equals the classical action. Thus, unsurprisingly, the quantum Lagrangian reduces to $\mathrm{J}(\psi, \nabla\psi)$ in the case of stationary state. One must ensure that the wave function remains normalized for variations of ψ in a stationary state. This is accomplished by including an undetermined multiplier in $\mathrm{J}(\psi, \nabla\psi)$, equal to $-E$, to give the new functional $G(\psi, \nabla\psi)$. Thus *Schrödinger*'s variation of $G(\psi, \nabla\psi)$ to obtain $\hat{\mathrm{H}}\psi = E\psi$ as the *Euler-Lagrange* equation is another example of the principle of least action, being equivalent to the variation of a constrained action integral for an infinitesimal time interval.

Since the functional $\mathrm{J}(\psi, \nabla\psi)$ equals the total energy E when minimized, the use of the calculus of variations to obtain *Schrödinger*'s equation is equivalent to minimizing the energy in the case of a stationary state. One should distinguish use of the calculus of variations to obtain *Schrödinger's equation* from that of the more familiar 'variational principle', for obtaining *approximate solutions to Schrödinger's equation*. The variational principle states that the energy obtained by averaging the Hamiltonian operator over a 'trial function' φ, which usually includes the variation of parameters in the minimization of the 'variational integral', is an upper bound to the true energy E.

$G(\psi, \nabla\psi)$ and $L(\Psi, \nabla\Psi, \dot{\Psi}, t)$ are functionals of $\nabla\psi$ or $\nabla\Psi$ because they both express the kinetic energy in the form $+(\hbar^2/2m)\langle\nabla\Psi \cdot \nabla\Psi\rangle$ rather than as $-(\hbar^2/2m)\langle\Psi\nabla^2\Psi\rangle$, the form of the kinetic energy appearing in the *Schrödinger* equation. This has important consequences on the extension of the variation of the action to an open system. One readily establishes that the difference between the two forms of the kinetic energy is locally proportional to the *Laplac*ian of the electron density, as given without loss of generality in Eq. (4) for a one-electron system [25], a result alternatively expressed as $K(\mathbf{r}) - G(\mathbf{r}) = L(\mathbf{r})$.

$$-(\hbar^2/2m)\Psi^*\nabla^2\Psi - (\hbar^2/2m)\nabla\Psi^* \cdot \nabla\Psi = -(\hbar^2/4m)\nabla^2\rho \tag{4}$$

Integration over a region of space Ω bounded by a surface $\mathrm{S}(\Omega, \mathbf{r}_\mathrm{s})$, yields Eq. (5) identifying the average kinetic energies as $K(\Omega)$ and $G(\Omega)$, respectively.

$$K(\Omega) - G(\Omega) = -(\hbar^2/4m)\int_\Omega \nabla^2\rho(\mathbf{r})\mathrm{d}\tau = -(\hbar^2/4m)\oint \mathrm{dS}(\Omega, \mathbf{r}_\mathrm{s})\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \tag{5}$$

The volume integral of $\nabla^2\rho = \nabla \cdot \nabla\rho$, the divergence of a vector in Eq. (5), is replaced by the surface integral of the flux in $\nabla\rho$ through the surface of the region Ω using *Gauss*' theorem. When the region Ω refers to all space then $K(\Omega) = G(\Omega)$ because of the vanishing of ρ and its gradients at infinity, but for a region with finite boundaries the two quantities differ by the flux in $\nabla\rho$ through the surface of Ω and the kinetic energy is ill-defined. If however, the surface $\mathrm{S}(\Omega)$ is one of zero-flux in $\nabla\rho$ as defined in Eq. (6), where $\mathbf{n}(\mathbf{r})$ is a unit vector normal to the surface, then $K(\Omega) = G(\Omega)$ and the kinetic energy is a well-defined quantity.

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad \text{for all points } \mathbf{r}_\mathrm{s} \text{ on the surface } \mathrm{S}(\Omega, \mathbf{r}_\mathrm{s}) \tag{6}$$

Equation (6) defines a surface that is not crossed by any trajectories traced out by the vector $\nabla\rho(\mathbf{r})$ and is consequently referred to as a 'zero-flux surface'. This condition is exemplified in the maps of the gradient vector field of the density illustrated in the next section.

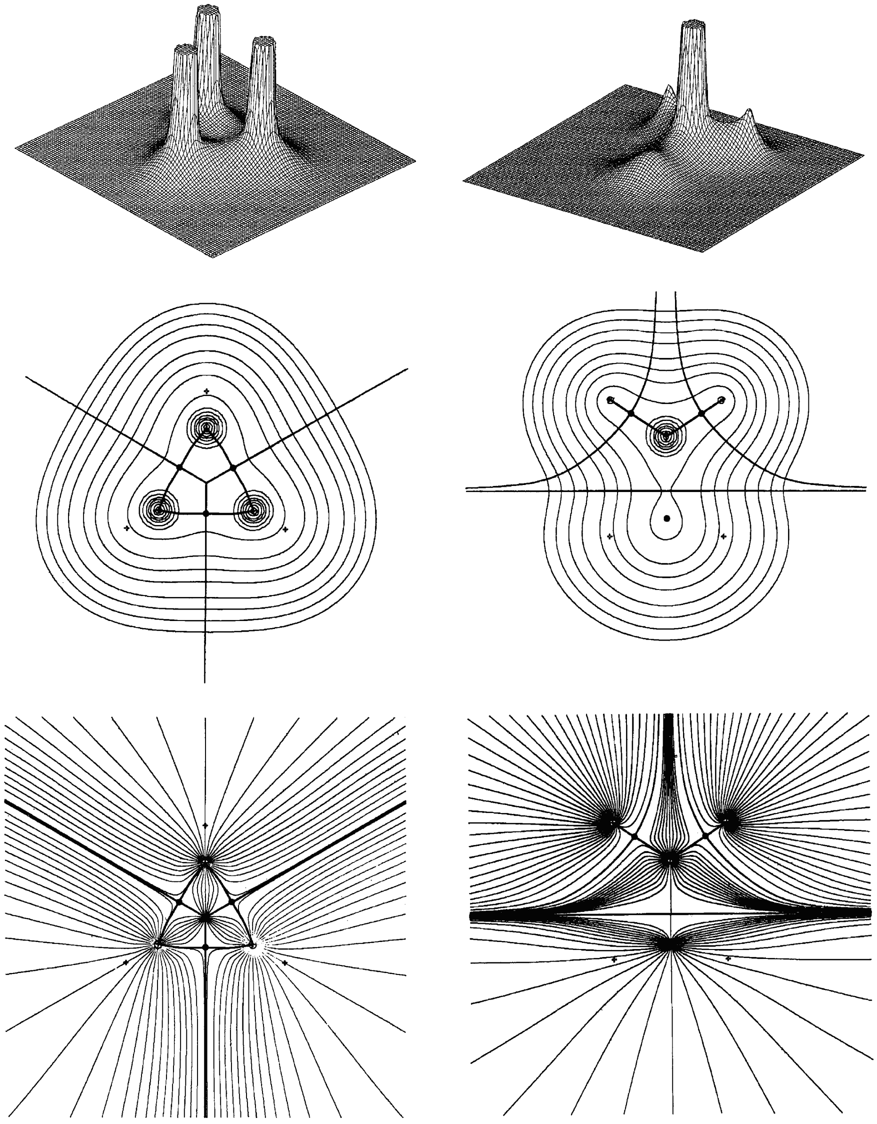
The variation of $G(\psi, \nabla\psi)$ and of $L(\Psi, \nabla\Psi, \dot{\Psi}, t)$ requires that one rid the resulting expressions for $\delta G(\psi, \nabla\psi)$ and $\delta L(\Psi, \nabla\Psi, \dot{\Psi}, t)$ of variations in $\nabla\Psi$ and $\dot{\Psi}$, just as the variation δW_{12} was cleared of variations of $\dot{q}$. This is again accomplished through an integration by parts that leaves the term $i\hbar\Psi^*\delta\Psi$ at each time end-point in the case of $\delta\dot{\Psi}$ and the surface integral of the flux of the quantity $\nabla\Psi^*\delta\Psi\mathbf{n}(\mathbf{r})$ in the case of $\delta\nabla\Psi$. These terms are easily disposed of in the principle of least action, the first by requiring the variations to vanish at the time end-points and the latter by defining the *Lagrang*ian for a closed, isolated system that is, the entire molecule, whose boundaries are at infinity where variations in Ψ and $\nabla\Psi$ vanish. This digression prepares one for the generalization of the action principle by *Schwinger* [22] who retains the variations at the time end-points and provides the possibility of applying the variation of the action to a system with finite boundaries.

Observational Basis for an Atom in a Molecule

My laboratory was fortunate in the 1960s in establishing a collaboration, through Dr. *P. E. Cade* presently at the University of Massachusetts, with the *Mulliken-Roothaan* group at the University of Chicago. As a result, we were given access to the near *Hartree-Fock* quality wave functions then being obtained by this group

Fig. 2. The electron density for the cyclopropane molecule in the form of a relief map and a contour map together with a display of the gradient vector field in two planes: LHS in plane of the carbon nuclei; RHS in symmetry plane containing one carbon nucleus and two bonded protons; the density is a local maximum at each nucleus with the result that space is partitioned into atomic basins, each basin being defined by its own set of trajectories traced out by $\nabla\rho$, the gradient vectors of the density, that terminate at a given nucleus. Shown in bold are the pairs of trajectories in both planes that terminate at the (3, -1) or bond critical points (CPs); these CPs, whose positions are denoted by dots, are found only between certain pairs of nuclei; each such pair of trajectories is part of a set defining a two-dimensional manifold embedded in three-dimensional space, which terminate at each bond CP and define an interatomic surface; the non-nuclear maximum appearing in the display of ρ on the RHS is in the plane of the interatomic C|C surface for the out-of-plane C nuclei, that is, ρ is a maximum at the bond CP in the interatomic surface; the associated set of set of trajectories defining the C|C interatomic surface is represented by the trajectories that terminate at the bond CP in the lower portion of the associated gradient vector map; these are zero-flux surfaces – they are not crossed by any trajectories of $\nabla\rho$; unique pairs of trajectories, also shown in bold, originate at each bond CP, and define a bond path – a line of maximum density linking nuclei sharing an interatomic surface and the nuclei are bonded to one another; trajectories originate at the ring or (3, $+1$) CP at the centre of the ring and define a ring surface in LHS diagram and a single pair of trajectories terminate at this point to define the ring axis in the RHS diagram; thus the behaviour of the trajectories for a ring CP is just the opposite to that found for a (3, -1) CP; 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 contours are used in all density maps

using large STO basis sets (s, p, d, and f functions) with optimized orbital exponents for about 300 neutral and charged states of A_2, AB, and AH diatomic molecules. Our interests centred on the use of *Feynman*'s electrostatic theorem [26] in the interpretation of chemical binding and therefore, on the electron density distributions obtained from these wave functions. *The electron density is the measurable expectation value of a quantum observable and is now routinely measured in accurate x-ray diffraction experiments* [27]. This was not the case in the 60s however, and we based our 'observations' on the properties of the density distributions obtained from the Chicago wave functions. Our initial work involved the use of density difference maps to determine the changes in the atomic densities encountered in molecule formation – 'bond density maps' – together with an orbital analysis of the forces exerted on the nuclei [28–31]. The force analysis



provided a classification of the canonical orbital densities as binding, antibinding, and nonbinding, the counterparts of the bonding, antibonding, and nonbonding classification introduced by *Mulliken* based on energy considerations. To someone coming to theory from experiment these studies were unsettling. The density difference maps depended upon the 'states' one chose for the separated atoms and the orbital analysis was similarly dependent upon the choice of orbitals. All of the results were removed from experiment.

If one is interested in the density, then why introduce subjective elements into the analysis? The electron density is a measurable scalar field whose form is subject to topological analysis. The atomic form of matter stares 'out' at one from the total density, see Fig. 2. This form is a consequence of the principal topological feature of the density – that in general, it exhibits maxima at the positions of the nuclei. This is a manifestation of the single, most dominant force operative in an atom, molecule, or crystal – the attraction of the point-like nuclei for the diffuse distribution of electron density. It is well to bear in mind that this is the only attractive force operative in an atomic system and is the sole force responsible for chemical bonding, the mechanics of which are determined by the *Ehrenfest* force acting on the electron density and the *Feynman* force acting on the nuclei, forces that are combined in the virial theorem to inter-relate the potential, kinetic, and total energies of a molecule [32, 33, 19].

The dominant topological feature of the density leads to an exhaustive partitioning of real space into a set of non-overlapping mono-nuclear domains Ω, as illustrated in Fig. 2, each of which is bounded by a surface $S(\Omega, \mathbf{r}_s)$ that exhibits a zero-flux in the gradient vector field of the electron density, a condition expressed above in Eq. (6) [34]. It is now well-documented that the topology of the density, as revealed in the associated gradient vector field, yields a definition not only of atom-like regions, but also delineates lines of maximum electron density that link the nuclei of neighbouring atoms – the 'bond paths' [19, 35]. The network of bond paths generate a molecular graph that defines a system's structure. The topological structures have been shown to recover the 'chemical structures' in a multitude of systems, in terms of densities obtained from both theory and experiment, structures that were previously inferred from classical models of bonding in conjunction with observed physical and chemical properties. The dynamics of the gradient vector field as caused by displacements of the nuclei, defines all possible structures and, through the theory of structural stability, the mechanisms of structural change [36, 37]. Clearly if the nuclear dominated domains could be identified with the atoms of chemistry and the lines of maximum density with 'bond paths' linking bonded atoms [38], then 'conceptual chemistry' is both revealed in and is a consequence of the form of the distribution of electronic charge throughout real space.

It soon became apparent from the study of the 'Chicago densities' that the Ω regions were transferable to varying extents between molecules [34]. Indeed, if one insisted that the partitioning exhausts a system, they had the property of maximizing any transferability that was present. Most importantly, this transferability was observed not only for the density but for other properties as well, in particular for the kinetic energy. Consider, as a simple example, observations that focused on the topological regions Ω identified with the Li atoms in the charge distributions

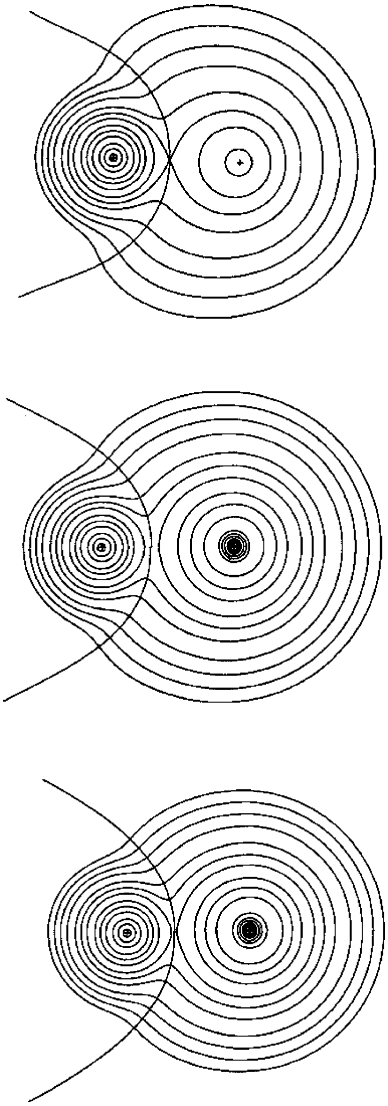


Fig. 3. Contour maps of the ground state electron density distributions in the plane of the nuclei for LiH ($^1\Sigma^+$), LiO ($^2\Pi$), and LiF ($^1\Sigma^+$) in descending order; the intersection of the zero-flux surface with the plane is indicated; the reader is asked to note the high degree of similarity in the distribution of the density over the basins of the Li atoms defined in this manner and to contrast this with the very different distributions found within the basins of its neighbours, differences that extend up to the interatomic surface; any other choice of surface would either include a portion of the neighbouring density, which changes radically in each case, or assign to the neighbour a portion of the Li density that is similar in all three molecules; the densities are obtained from the 'Chicago' near *Hartree-Fock* wave functions

of three molecules being shown in Fig. 3. One must regard the observed similarity in the forms of the Li atoms so defined, as no less than remarkable when one considers the very different natures of its bonded neighbours, hydrogen, oxygen, and fluorine. The electron populations are obtained by integration of $\rho(\mathbf{r})$ over the atomic basin and they yield similar net charges for the Li atoms of +0.91, +0.93, and +0.94 in LiH, LiO, and LiF, 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 changes in their immediate neighbours. This observation is not recoverable from any model employing 'overlapping atoms'.

The kinetic energy densities $K(\mathbf{r})$ and $G(\mathbf{r})$ are also scalar fields and their forms and properties were studied in parallel with the density [25] resulting in a most important observation: both $K(\mathbf{r})$ *and* $G(\mathbf{r})$ *exhibit the same degree of transferability as does* $\rho(\mathbf{r})$ *for a topological atom* [34]. Thus the conservation in the form of $\rho(\mathbf{r})$ and in its integrated electronic population on transfer between molecules is paralleled by a conservation in the form of the electronic kinetic energy density and its integrated value, the averages of the kinetic energy densities for the Li atom in three molecules falling within 8 kcal/mol of one another. (Since each region is bounded by a zero-flux surface, the average kinetic, energy $T(\Omega)$ is well-defined for a topological atom, with $K(\Omega) = G(\Omega) = T(\Omega)$, Eqs. (4) and (5).) This paralleling behaviour 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 *Coulomb* 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 one could show that there is a virial theorem 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, in terms of its electronic kinetic energy $T(\Omega)$, using the expression $E(\Omega) = -T(\Omega)$. Since $T(\Omega)$ is additive, the same additivity would apply to $E(\Omega)$ and the energy of a molecule would be the sum of its atomic contributions, $E = \Sigma_{\Omega} E(\Omega)$. The atomic virial theorem, if it indeed exists, accomplishes what was said to be impossible – a unique physical partitioning into atomic contributions of all of the electrostatic interactions, both repulsive and attractive, between the nuclei and the electrons.[a]

The identification of $E(\Omega)$ with $-T(\Omega)$ has a number of important consequences. A statement of the virial theorem for a topological atom would predict that when the form of an atom in real space remains unchanged on transfer, so would 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

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[a] The spatial partitioning of the energy is a consequence of the virial theorem. The electronic potential energy is determined by virial of the *Ehrenfest* force exerted on an electron at some position $\mathbf{r}$. This quantum mechanical force determines a force density at a point in space and its multiplication by $\mathbf{r}$ to yield the 'virial of the force' transforms the force density into a potential energy density which upon integration over all space yields the total potential energy of the molecule, including the repulsions between the nuclei. Thus physics, coupled with observation, accomplishes what was deemed impossible. As detailed below, all open system properties are defined in terms of *real-space density distributions*, in the same manner as is the electron density, Eq. (1). This is direct a consequence of the field-theoretic generator acting on the coordinates of a single electron

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. Thus the form of a topological atom, since it is defined by its charge distribution as a bounded region of real space, necessarily reflects its properties and one understands why the atoms and functional groups defined by the topology of the density maximize the transferability of properties from one molecule to another.

What is remarkable, is the exceptional degree of transferability that the charge distribution of an atom or a functional grouping of atoms can exhibit. 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 [39–43] and theory [11, 19, 44–46]. Transferability of form and properties is found to be particularly evident for the groupings of atoms that correspond to the building blocks of biological macromolecules. Recent work, both experimental [47, 48] and theoretical [49–51], has demonstrated 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 for example, it requires a theory of atoms in molecules to implement and make quantitative use of this knowledge.

From *Schrödinger* to an Atom in a Molecule

The observations made on the properties of molecular electron density distributions enable one to reformulate the question of 'how does one define at atom in a molecule?' into 'can one show that the virial theorem applies to a region of space bounded by a zero-flux surface?' It is clear that if the virial theorem applies to such a region, then all theorems should apply and one is therefore, asking whether a region bounded by a zero-flux surface and its properties are derivable from quantum mechanics. In essence, can one define the quantum mechanics of an open system?

It is always best to begin at the beginning and we therefore started our search by asking whether or not *Schrödinger*'s derivation of the 'wave equation' given in paper I from 1926 could be generalized to an open system [20]. He obtained his equation $\hat{\mathrm{H}}\psi = E\psi$ by making the functional $G(\psi, \nabla\psi)$ stationary with respect to first-order variations in ψ in the manner outlined in the section on the principle of least action. The limits of integration on the electronic coordinates in $G(\psi, \nabla\psi)$ coincided with a surface infinitely removed from all of the nuclei, that is, the functional described a closed system with infinite boundaries. What would one obtain from the variation of *Schrödinger*'s functional defined for a region of real space Ω with finite boundaries, a functional denoted by $G(\psi, \nabla\psi; \Omega)$?

The result of *Schrödinger*'s variation of $G(\psi, \nabla\psi)$ is summarized in Eq. (7). It consists of a contribution from the integral over the entire system and another from an integration over its surface,[b] the surface terms arising from the removal of the terms involving $\delta\nabla\psi$ by an integration by parts.

$$\delta G(\psi, \nabla\psi) = \int d\mathbf{r}\{\hat{\mathrm{H}}\psi^* - E\psi^*\}\delta\psi + \oint dS(\mathbf{r}_s)\{(\hbar^2/2m)\nabla\psi^* \cdot \mathbf{n}(\mathbf{r})\delta\psi\} = 0 \quad (7)$$

Since the surface in this case resides at infinity where $\delta\psi = 0$, the surface term does not contribute to the variation. Thus $\delta G(\psi, \nabla\psi)$ will vanish for arbitrary $\delta\psi$ only if $\hat{\mathrm{H}}\psi^* = E\psi^*$ or equivalently for variations in ψ^*, only if $\hat{\mathrm{H}}\psi = E\psi$ and making $G(\psi, \nabla\psi)$ stationary yields *Schrödinger*'s equations for a stationary state. In the introduction to paper I, Schrödinger states that the 'customary quantum conditions' previously introduced in an *ad hoc* manner, are recovered by the 'whole numbers' (quantum numbers) generated in the solutions to his eigenvalue equation.

In the variation of $G(\psi, \nabla\psi; \Omega)$ for a bounded region of space Ω, the integration has finite limits and one must include a term corresponding to a variation of the boundary, since its form must be determined in the variational procedure. The result of varying $G(\psi, \nabla\psi; \Omega)$ is given in Eq. (8). A term corresponding to the first terms on the RHS of Eq. (7) is again obtained and again vanishes since the *Euler-Lagrange* equation $\hat{\mathrm{H}}\psi = E\psi$ still applies to the total system of which Ω is a part, and only the surface terms remain in the variation.

$$\delta G(\psi, \nabla\psi; \Omega) = \oint dS(\Omega, \mathbf{r}_s)\{(\hbar^2/2m)\nabla\psi^* \cdot \mathbf{n}(\mathbf{r}) + \delta S(\Omega, \mathbf{r}_s) f(\psi, \nabla\psi)\} + \mathrm{cc} \quad (8)$$

The first surface term, as explained above, arises by ridding the expression of variations in $\nabla\psi$. The function $f(\psi,\nabla\psi)$ in the second term denotes the integrand in *Schrödinger*'s functional and when evaluated in the surface and multiplied by the infinitesimal shift in the surface $\delta S(\Omega)$, gives the contribution to the variation resulting from the variation in the surface of the region Ω. Since functions are not necessarily Hermitian over an open system Ω, the variation must include contributions from the complex conjugate (cc) terms. Equation (8), which does not define any particular surface, does not appear promising. Clearly the requirement of the principle of least action that the variation of the appropriate functional vanishes must be discarded and the concept of stationarity broadened. We were initially unprepared for this result, little realizing that it forms the basis for the generalization of the principle of least action introduced by *Schwinger.*

Equation (8) is transformed into a statement of physics by two rather remarkable consequences of the properties of the Laplacian of the electron density, $\nabla^2\rho(\mathbf{r})$. The first is that when *Schrödinger*'s equation is satisfied, the integrand $f(\psi,\nabla\psi)$ of *Schrödinger*'s functional reduces to $-L(\mathbf{r})$, the term proportional to

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[b] This and the following expressions are written for a single electron to keep the mathematical formalism as simple as possible. However, the integration in Eq. (7) is readily extended to the many-electron case by the simple insertion of the symbol $N\int d\mathbf{r}'$ which denotes a summation over all spins and an integration over all electronic coordinates other than $\mathbf{r}$, the coordinate that is averaged over the open system, the same integration that is used to define the electrons density, Eq. (1). The symbol $\langle\ \rangle_\Omega$ that is employed at a later stage, denotes the same mode of integration followed by an integration of the coordinate $\mathbf{r}$ over the region Ω

$\nabla^2\rho(\mathbf{r})$ defined in Eq. (4). This same property obtains when the integrand is the full Lagrangian density of the action integral in the general time-dependent case and persists even in the presence of an electromagnetic field. So the term involving the variation of the surface may be re-expressed as a term proportional to $\delta\mathrm{S}(\Omega,\mathbf{r}_s)\nabla^2\rho(\mathbf{r})$. The second of the remarkable consequences of the Laplacian is its appearance in the constraint that determines the surface of the open system. This constraint is presented in detail in a number of places, being only briefly outlined here. Imposing the zero-flux surface condition expressed in Eq. (6) at every stage of the variation is equivalent to requiring that the variation of the integral of $\nabla^2\rho(\mathbf{r})$ over the region Ω vanishes. This condition in turn enables one to replace the term $\delta\mathrm{S}(\Omega,\mathbf{r}_s)\nabla^2\rho(\mathbf{r})$ appearing in the surface integral with the expression that, when combined with the remaining surface term, transforms the contribution from one without any discernable physical content for a surface of unspecified form, into an integral describing the flux in the variation of the quantum mechanical current density, the quantity $\delta\mathbf{j}(\mathbf{r})$, through a surface of zero-flux in $\nabla\rho$, as shown in Eq. (9).

$$\delta G(\psi, \nabla\psi; \Omega) = -(\mathrm{i}\hbar/2)\oint \mathrm{dS}(\Omega, \mathbf{r}_s)\delta\mathbf{j}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) + \mathrm{cc} \tag{9}$$

Thus the imposition of the *zero-flux boundary condition* on the variation of *Schrödinger*'s functional causes it to be ‘stationary’ by requiring its variation to equal the surface flux in the current generated by the variations in ψ. While unknown to us at the time, Eq. (9) is a result of *Schwinger*'s principle of stationary action for a time-independent system.

The variational result given in Eq. (9) is put in an operational form by replacing the variations in ψ with the action of quantum mechanical operators on ψ. That is, one makes the substitution $\delta\psi = -\varepsilon(\mathrm{i}/\hbar)\hat{\mathrm{G}}\psi$ where ε denotes an infinitesimal change resulting from the action of the operator $\hat{\mathrm{G}}$ on ψ. $\hat{\mathrm{G}}(\mathbf{r})$ may be any linear Hermitian operator constructed from the electronic position and/or momentum coordinates of a single electron and as such, it can describe any and all possible changes in ψ and in the properties of the system. $\hat{\mathrm{G}}$ is referred to as the generator of the change in the system. With this substitution, Eq. (9) becomes Eq. (10) where $\mathbf{j}_\mathrm{G}(\mathbf{r})$ is the current density for the property determined by the generator $\hat{\mathrm{G}}$.

$$\delta G(\psi, \nabla\psi; \Omega) = -(\varepsilon/2)\left\{\oint \mathrm{dS}(\Omega, \mathbf{r}_s)\mathbf{j}_\mathrm{G}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) + \mathrm{cc}\right\} \tag{10}$$

Thus the variation in *Schrödinger*'s energy functional for an open system bounded by a zero-flux surface – an atom in a molecule – is proportional to the surface flux in the current density of the infinitesimal generator causing the change in the system. Fluxes in currents through the bounding surface is the feature that distinguishes the physics of an open system from that of a total system, for which all surface terms vanish.

The final, encompassing statement of the principle of stationary action for an open system in a stationary state is obtained through the use of the equation of motion for the generator $\hat{\mathrm{G}}$. In the general time-dependent case, the time derivative of the average value of $\hat{\mathrm{G}}$, $\mathrm{d}\langle\hat{\mathrm{G}}\rangle/\mathrm{d}t$ is determined by the average of the commutator

$(i/\hbar)\ [\hat{H}, \hat{G}]$. This average vanishes for a molecule in a stationary state yielding the result shown in Eq. (11).

$$\langle \psi, [\hat{H}, \hat{G}]\psi \rangle = 0 \tag{11}$$

The same commutator average does not however, vanish for an atom in a molecule, the contribution from the commutator being balanced by the flux in the current of $\hat{G}$ through the bounding surface, a result readily obtained from *Schrödinger*'s equation [19] and given in Eq. (12).

$$(i/\hbar)\langle \psi, [\hat{H}, \hat{G}]\psi \rangle_{\Omega} + \mathrm{cc} = \oint \mathrm{d}S(\Omega, \mathbf{r}_s)\mathbf{j}_G(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + \mathrm{cc} \tag{12}$$

Equation (12) yields the same surface term obtained in the variation of $G(\psi, \nabla\psi; \Omega)$ and substitution of this result into Eq. (10) yields the atomic statement of the principle of stationary action for a stationary state (Eq. (13)) [19].

$$\delta G(\psi, \nabla\psi; \Omega) = -(\varepsilon/2)\{(i/\hbar)\langle \psi, [\hat{H}, \hat{G}]\psi \rangle_{\Omega} + \mathrm{cc}\} \tag{13}$$

This statement determines the physics of an atom in a molecule. All of the theorems of quantum mechanics are obtained by the appropriate choice of the generator, $\hat{G} = \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}$, the product of the electronic position and momentum coordinates, yielding the virial theorem for example. *Equation (13) applies to any system bounded by a zero-flux surface and thus a single principle provides the quantum mechanical description of the total system and of its constituent atoms.* Indeed one may regard the physics of some total system – of the entire molecule – as a special limiting case of the more general expression pertaining to an open system given in Eq. (13). Thus when Ω refers to the total molecule, the commutator average equals zero, Eq. (11), and the variation in *Schrödinger*'s functional becomes stationary in the usual sense that $\delta G(\psi, \nabla\psi; \Omega) = \delta G(\psi, \nabla\psi) = 0$. It is important to note that the derivation of Eq. (13) yields *Schrödinger*'s equation, as well as all of the theorems of quantum mechanics. Thus a single principle serves to completely determine the physics of a stationary state. This statement is a consequence of *Schwinger*'s principle.

From *Dirac* to *Schwinger*

The above identification of the variations in ψ with the action of infinitesimal generators $\varepsilon\hat{G}$ has deep implications, beyond yielding operational expressions for the mechanics of an open system. In classical mechanics one can perform a transformation – termed a canonical transformation – from one set of position and momentum coordinates to another which again satisfy *Hamilton*'s equations of motion with respect to a Hamiltonian expressed in the new coordinates. The transformation leaves all of the numerical values of a system's properties unchanged. The same freedom of choice is afforded by quantum mechanics in the form of a 'unitary transformation', one that when applied to both the state function and observables of a system, leaves the description of the system unchanged and one is free to choose the representation most convenient to the problem at hand.

Of particular importance to both classical and quantum mechanics are the infinitesimal forms of the canonical and unitary transformations. Unlike the latter transformations that leave all system properties unchanged, their infinitesimal forms are defined such that their use causes real infinitesimal changes in a system and its properties. These transformations are driven by so-called generators that are defined in terms of functions of the position and/or momentum coordinates. For example, the generator of a classical temporal change is given by H(q,p)d*t*, H(q,p) being the Hamiltonian, and when applied to q(*t*) and p(*t*), both are transformed into the values they have at the time $t + \mathrm{d}t$, as predicted by *Hamilton*'s equations of motion. Similarly in quantum mechanics, the temporal generator is given by$-\hat{\mathrm{H}}\delta t$, and its action causes a displacement in time of the state vector and of a system's observables as predicted by *Schrödinger*'s equation and the *Heisenberg* equations of motion, respectively.[c]

The present account only serves to summarize in words the important consequences of infinitesimal transformations. The underlying mathematics is not difficult and is given in my book [19] and admirably presented in *Goldstein*'s book on classical mechanics [53]. What is important is that infinitesimal unitary transformations, whose definition and operation lie at the heart of *Dirac*'s transformation theory, enable one to describe any and all possible changes that can occur in a quantum system and its properties.

Our generalization of the variation of *Schrödinger*'s functional necessarily led to the generation of surface terms, terms that are discarded in the principle of least action when applied to a total system, but which play a crucial role in the physics of an open system. Corresponding terms arise in the variation of the time derivative of the state vector Ψ in the general time-dependent case, leading to contributions at the time end-points, contributions that are again discarded in the usual statement of the principle of least action. *Schwinger* took the bold step of not only retaining the variations of the state vector at the time end-points but of varying the end-points themselves and followed these steps with the identification of these variations with the generators of infinitesimal unitary transformations [22]. By doing so he combined the action principle, which yields the equation of motion, with *Dirac*'s transformation theory, the latter though infinitesimal transformations, enabling him to obtain from a single dynamical statement 'all of physics'.

Dirac set the stage for the work of *Feynman* and *Schwinger*. First and foremost it was he who introduced transformation theory into quantum mechanics. This is the underlying mathematical formulation of the new physics which consists of the general mathematical scheme of linear operators and state vectors with its associated probability interpretation. In doing so, he stressed how the theory of infinitesimal unitary transformations in quantum mechanics parallels the infinitesimal canonical transformations of classical theory, a parallelism the importance of which has been commented on above.

In particular, in 1933 these ideas led *Dirac* to write what was to be a paper of singular importance [54]. In it he posed the question of what would correspond to

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[c] One feels compelled to quote *Dirac* at this point [52]: "In classical mechanics the dynamical variables at time $t + \delta t$ are connected with their values at time *t* by an infinitesimal contact [canonical] transformation and the whole motion may be looked upon as the continuous unfolding of a contact transformation. We have here the mathematical foundation of the analogy between classical and quantum equations of motion..."

the limiting classical expression for the quantum probability amplitude for the passage of a system with a set of coordinates denoted collectively by q_1 at a time t_1 to another set denoted by q_2 and t_2, a quantity denoted by the transformation amplitude $\langle q_1, t_1|q_2, t_2\rangle$. The transformation amplitude suffices to determine the dynamical behaviour of the system with time, since it relates the state function at time t_2 to that at time t_1. In effect, *Dirac* was asking for the correspondence of quantum mechanics with the Lagrangian method of classical mechanics, a formulation he considered to be more fundamental than the one based on Hamiltonian theory.

We have discussed above how *Lagrange*'s equations of motion, that determine the motion of a system from one classical state (q_1, t_1) to another (q_2, t_2), are obtained from the principle of least action by the minimization of the action integral W_{12}. *Dirac* was led to propose that the transition amplitude $\langle q_1, t_1|q_2, t_2\rangle$ be given by exp (i $W_{12}/\hbar$) where W_{12} is the classical action evaluated along the unique path that causes it to be stationary. This proposal set the stage for the reformulations of quantum mechanics put forth by *Feynman* and *Schwinger*.

The classical concept of a system following a uniquely defined trajectory must be abandoned in the quantum description. Thus *Feynman*, in 1948, replaced the expression given by *Dirac* for the single classically allowed path, by a corresponding sum over all possible paths connecting the two space-time points to obtain his 'path integral expression' for the probability amplitude [21]. *Feynman* went on to show that the path integral expression yields *Schrödinger*'s equation and the quantum commutation relations. The introductory remarks that lay the foundation for this approach that he makes in his 1948 paper are as readable as are the books "The *Feynman* Lectures on Physics" [24].

Schwinger, in 1951, demonstrated how one could combine the action principle with *Dirac*'s transformation theory by basing it on the differential form of *Dirac*'s proposal [22]. *Schwinger* realized that infinitesimal unitary transformations can be used to provide a differential characterization of the transformation function as done in Eq. (14) where the infinitesimal generators $\varepsilon\hat{G}(t) = \hat{F}(t)$ act separately on the state vectors $\langle q_1, t_1|$ and $|q_2, t_2\rangle$ at the two time end-points.

$$\delta\langle q_1, t_1|q_2, t_2\rangle = (i/\hbar)\langle q_1, t_1|\hat{F}(t_1) - \hat{F}(t_2)|\, q_2, t_2\rangle \tag{14}$$

This led him to propose his new dynamical principle, the 'quantum dynamical principle' given in Eq. (15).

$$\delta\langle q_1, t_1|q_2, t_2\rangle = (i/\hbar)\langle q_1, t_1|\delta\hat{W}_{12}|q_2, t_2\rangle \tag{15}$$

A comparison of the two expressions leads to *Schwinger*'s *principle of stationary action* (Eq. (16)).

$$\delta\hat{W}_{12} = \hat{F}(t_1) - \hat{F}(t_2) \tag{16}$$

This principle states that the 'action' is unaltered by changes between the times t_1 and t_2, being effected only by the action of generators at the two time end points. Equation (16) implies *Schrödinger*'s equation of motion (just as it is implied in Eq. (10) in the variation for a stationary state) and it also yields the quantum commutation relations.

The time evolution of an open system will sweep out a space-time volume and, in the detailed formulation of his principle, *Schwinger* allows for generators to act not only at the time end points, but also on the spatial boundaries of the open system by retaining the variations both on and of its surface at each time *t*. The retention of the variations of and on the zero-flux surface at a single time *t* followed by their identification with the action of infinitesimal generators, is precisely the step made in our generalization of *Schrödinger*'s variation of his energy functional leading to Eqs. (10) and (13). These variations give rise to the same surface terms that are found in *Schwinger*'s formulation and are dealt with in precisely the same manner. While we proceeded out of necessity, *Schwinger* realized that by making such an identification at both the space-like and time-like surfaces bounding the space-time volume, he could incorporate all of physics into a single dynamical principle.

By 1978 it was realized that our generalization of the variation of *Schrödinger*'s functional was but a special case of the general statement of physics provided by *Schwinger*'s principle of stationary action and the theory of an atom in a molecule was readily extended to the general time-dependent case and shown to be derivable from *Schwinger*'s principle of stationary action [15, 55]. The derivation of the principle for an atom in a molecule was presented from a new perspective in an article in Physical Review in 1994 where the term '*proper open system*' was introduced along with the designation 'quantum theory of atoms in molecules' (QTAIM) [16].

We note in closing this section, that *Schwinger*'s work was characterized by a strict adherence to the phenomenological approach to physics through his insistence that one appeals to and compares with experiment whenever possible. So QTAIM, since it follows his path to the physics of an open system, necessarily emphasizes the ties that link it with observation and measurement, an approach that will necessarily distance it from other attempts to define an atom in a molecule and its properties.

Chemistry Using QTAIM

Experimental Confirmation and Chemical Relevance of QTAIM

Since QTAIM is the statement of the principle of stationary action applied to an open system, it necessarily recovers all molecular properties in terms of additive atomic or group contributions. The single necessary and sufficient criterion for determining the relevance of QTAIM atoms to chemistry is agreement of the predicted atomic and group contributions with their experimental values. This has been demonstrated and documented for many properties in numerous systems: among them, the experimental additive contributions to volumes, heats of formation, electric polarizabilities, and magnetic susceptibilities of the homologous series of saturated hydrocarbons as previously summarized [44], along with more recent examples [11, 45, 46]. Agreement with observation is the only test of theory. That some experimental group contributions predicted by QTAIM were previously known, the magnetic contributions measured by *Pascal* in 1910 [56] and the heats of formation by *Rossini* and co-workers in 1946 [57] is irrelevant. Recovery of established observations as a test of theory is as old as *Newton* and exemplified in quantum mechanics by *Schrödinger*'s first paper [17] wherein he recovered quantization of the angular momentum and energy in the hydrogen atom and predicted its spectrum, in agreement with the measured values of *Balmer* and *Lyman*, and by *Schwinger*'s calculation of the 'anomalous magnetic moment of the electron' following its measurement by *Rabi* and co-workers [58], showing that the value was not 2 as predicted by *Dirac*'s theory but rather $g/2 = 1 + \alpha/2\pi$, an important step in the development of QED [59]. The demonstration that measured values of group properties are predicted by quantum mechanics, while perhaps less momentous for physics, is of vital importance to an experimental chemist. The reader is asked to realize that there are no 'adjustable parameters' in applying QTAIM, the appropriate Hamiltonian being the sole input to its predictions.

The physics of an open system brings to the fore the interdependence of atomic contributions in the understanding of measured properties, as exemplified by an atomic charge defined by QTAIM. Not only is an atomic charge a measurable quantum expectation value [13], it appears in the expressions determining a wide range of experimentally measurable properties [60]: 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 [61] and in the cell contributions to the polarization of a dielectric [62, 63]; their vibrationally induced changes appear in the expressions for infrared and *Raman* intensities [64, 65]; 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 [68]. The atomic charge or its change is not the sole contributor to any of these properties, all being dependent upon the requisite atomic polarizations as well.

In the presence of a magnetic field, the property corresponding to an atomic polarization is the atomic magnetization, and this property plays a similar role in determining the atomic contributions to the magnetic susceptibility and chemical shielding [66, 67]. The atomic charge is paralleled in the magnetic case by the atomic current, the basin average of the field induced electronic velocity. The phenomena of polarisation and magnetisation, permanent or induced, have a common physical basis when described in terms of the physics of an open system; all exhibit a single underlying structure that is expressed in terms of a contribution from the polarization within the atom's basin and from the surface flux of the electric field caused by the inter-atomic charge transfer in the electric case and from the surface flux of the induced current in the magnetic case [60, 63]. There are no restrictions as to the applicability of the expressions. This physics and the appeal to experiment it affords are lost when one employs other definitions of an atomic charge.

Examples of Atoms as Open Systems

Figure 4 displays the Cr, Fe, and Ni atoms in their hexa-, penta-, and tetra-carbonyl complexes respectively, as regions of space bounded by the inter-atomic surfaces that are shared by the metal atom *M* with the carbons of the CO groups. The bonding in these molecules using QTAIM in a study to demonstrate its complementarity with molecular orbital *theory* has appeared recently [69a]. A companion paper, using the vehicle of an oxidative addition reaction, demonstrates how

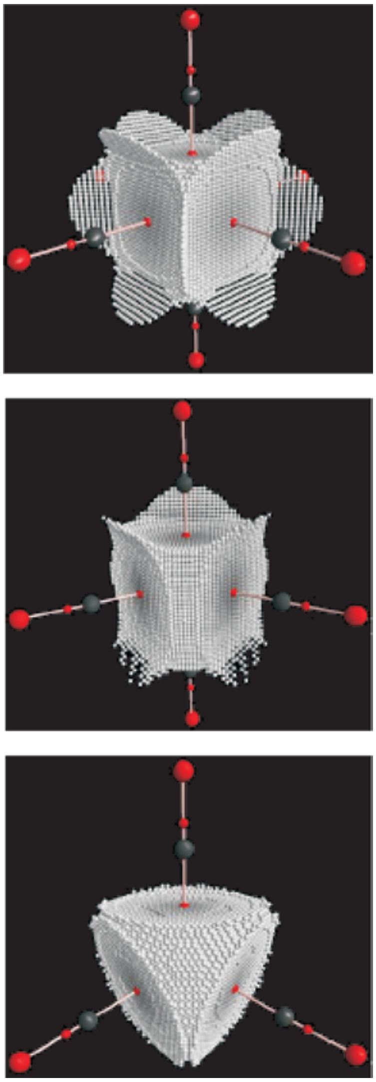

Fig. 4. The Cr, Fe, and Ni atoms in their carbonyl complexes defined by the metal|carbon (M|C) interatomic surfaces; there is a bond path emanating from the bond critical point (bcp) denoted by a red dot in each M|C surface; the bond path links a carbon nucleus, denoted by a black sphere, that is in turn linked to an oxygen denoted by a red sphere, the associated bcp being denoted by a second red dot; all of the properties of each enclosed region of space are defined and make additive contributions to the properties of the complex; note the planarity of the M|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

QTAIM recovers the rationalizations of frontier orbital theory and illustrates its use in predicting possible structural instabilities in the addition product [69b]. Every property defined by a quantum observable is determinable for these bounded regions of real space. The change in the energy of *M* in forming the complex – the contribution of *M* to the energy of formation – stated in terms of its separate attractive and repulsive contributions is determined. The energy of interaction of *M* with every other atom in the complex is also defined; the attractive interaction of the nucleus of M with the charge density of another atom; the repulsion of the charge distribution on M with the charge distribution of another atom and the reduction in this contribution resulting from the exchange of electrons on M with those on the second atom, quantifying the notion of 'α, β-spin exchange resonance'. One finds that the binding in the metal carbonyls is a result of two contributions: (1) the dominant and exceptional decrease in the energy of interaction of the atomic density on M, bounded by the surfaces shown in Fig. 4, with the nuclei of the surrounding cage of ligand atoms; (2) the stabilization of the carbon atoms resulting from the transfer of density primarily from the metal atom. As discussed below, the electronic charge transferred to carbon from M is demonstrated to be distributed in the form of a π-like torus of density encircling the C–O axis, in the manner envisaged in the *Dewar-Chatt-Duncanson* model of $d\pi$–$p\pi^*$ back bonding [70, 71]. This approach to the bonding in the carbonyl complexes wherein every quantity is related to the expectation value of a quantum operator, is contrasted with those based on arbitrary and physically unrealizable partitionings of the energy of formation [72–74] using energy decomposition schemes [75, 76].

Electron Localization and Delocalization

The concepts of localization and delocalization of electrons play essential roles in chemistry [77]. These concepts transcend orbital models, being instead consequences of the exclusion principle as embodied in the pair density. The spatial localization/delocalization of electrons is determined by the corresponding properties of the density of the *Fermi* hole [78], a negative quantity that describes the extent to which the density of a second electron is excluded from the neighbourhood of another electron possessing the same spin. If the density of the *Fermi* hole is *localized* about some point, then all other α-spin electrons will be excluded from the space corresponding to the exclusion of one electronic charge. In a closed-shell system, the *Fermi* hole of an electron of β-spin will be similarly localized, resulting in a pair of electrons being localized about that point. If on the other hand, the density of the *Fermi* hole is diffuse, then the exclusion of same spin electrons occurs over an extended region of space and the electron is *delocalized*. The extent of the localization of the density of the *Fermi* hole to one atom is obtained by the double integration of the exchange density, over its basin yielding $\lambda(A)$, the localization index for atom A. Its delocalization over two atoms, A and B, is obtained by a corresponding integration of the exchange density over both atomic basins to yield $\delta(A, B)$, the delocalization index [79]. One has the simple understanding that if the exchange of electrons is largely confined to a given atomic basin, then the electrons are correspondingly localized on that atom, while if the electrons exchange between atomic basins, then the electrons are delocalized over both atoms or, equivalently, are shared by both atoms. Electrons that exchange are indistinguishable and consequently, *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.*

In the examples of the metal atoms in their carbonyl complexes, the most important observation is the significant degree of delocalization between the metal and the carbon atoms, with $\delta(M,\mathrm{C})$ values clustered around unity, indicating a close to equal sharing of one *Lewis* pair between M and each of the C atoms [69]. The number of electrons of M that are *delocalized* onto the carbonyl groups amounts to 2.9, 3.0, and 2.3 respectively for Cr, Fe, and Ni, ~86% of which are delocalized onto the carbon atoms in each case. The relatively small charge *transfer of electronic charge* from M to each carbon atom, of 0.19e for Cr, 0.15e for Fe, and 0.13e for Ni, is consistent with the nearly equal sharing of the density delocalized between M and each C. These properties of charge transfer and equal sharing are reflected in the planar form of the $M|\mathrm{C}$ inter-atomic surfaces, Fig. 4, a property associated with homonuclear interactions, but found to be characteristic of a transition metal|carbonyl carbon interaction.

QTAIM and Orbital Models

QTAIM provides the possibility of assessing the viability of orbital models. Orbital analyses for example, are equivocal regarding the operation of the *Dewar-Chatt-Duncanson* (*DCD*) model of $\mathrm{d}\pi$–$\mathrm{p}\pi^*$ backbonding in metal carbonyls [70, 71]. The atomic properties of carbon however, can be used to provide a quantitative demonstration that the charge transferred from M to a carbonyl carbon is localized primarily in a π-like distribution on C. The quadrupole moment of an axial molecule determines the extent of accumulation of σ-like electron density along the molecular axis, as opposed to its π-like accumulation in a torus about the axis. Because the component parallel to the axis $Q_{\|}(\mathrm{C})$, and its two perpendicular components $Q_{\perp}(\mathrm{C})$, sum to zero, the changes in the parallel or perpendicular components provide a direct determination of the extent of transfer of density between the σ and π systems of a linear molecule. In free CO at the DFT level of theory, there is a slight preponderance of the perpendicular (π) over the parallel (σ) components and the magnitude of the atomic moment is small, $|\mathbf{Q}(\mathrm{C})| = 0.18$ au. The change in the quadrupole polarization of CO upon complexation is restricted almost entirely to the increase in the π-like distribution within the basin of the carbon atom and the resulting changes are dramatic [69a]. $|Q_{\perp}(\mathrm{C})|$ increases by a factor of 8 for Cr and by 10 for Ni and $|\mathbf{Q}(\mathrm{C})|$ increases by factors ranging from 8 to 12, with the maximum occurring for the equatorial carbon in the iron complex and decreasing in the order $\mathrm{Ni} > \mathrm{Cr} \sim \mathrm{Fe}$ for axial C. The quadrupole polarisation of carbon in the complex is dominated by the toroidal accumulation of density, a consequence of the increase in its π density distribution. Thus $\mathbf{Q}(\mathrm{C})$ provides a quantifiable demonstration of the increase in π density, both absolutely and relative to the σ density of a carbon atom that accompanies its complexation. The effects are smaller by an order of magnitude for oxygen, with only a small increase in the magnitude of its perpendicular components. The increase in the magnitude of the perpendicular components of $\mathbf{Q}(\mathrm{C})$ and the associated large increase in $|\mathbf{Q}(\mathrm{C})|$ for a carbon atom in a CO ligand provide an unequivocal and quantifiable demonstration of the operation of the *DCD* $\mathrm{d}\pi$–$\mathrm{p}\pi^*$ back bonding model.

The atomic overlap matrix is particularly useful in bridging molecular orbital models and the atomic properties of QTAIM. A diagonal element of this matrix yields the number of electrons of a given orbital that reside within an atomic basin, enabling the assignment of contributions from individual orbitals to an atomic population. The orbital contributions clearly indicate the importance of dπ–pπ^* back-bonding from *M* to the carbons of the ligands, relative to σ donation from the ligands to the metal. Of the twelve electrons in the t_{1u}, e_g, and a_{1g} sigma bonding orbitals in $Cr(CO)_6$, only 0.95e reside on the metal atom, while of the 6 electrons in the t_{2g} set, 3.6e remain on Cr while the remaining 2.4e reside on the ligands, with 0.25e on each carbon. By symmetry, these electrons occupy the $2\pi^*$ antibonding orbital of CO. The association of the "a" and "e" orbitals of the axial ligands in $Fe(CO)_5$ with the respective σ and π orbitals of the ligands enables one to determine that the π population of an axial carbon atom increases by 0.32e on bonding to Fe, while its σ population undergoes a decrease of 0.22e.

The delocalization index $\delta(A, B)$ is of particular importance in bridging classical notions of bonding and quantum mechanics. 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. It thus provides a means to measure the contribution of the stabilizing exchange energy to bonding that classical models of bonding attribute to 'covalency'. The delocalization index provides a clear indication of the progression of bonding from 'covalent' to 'polar' to 'ionic', through the increasing localization of the electrons within the atomic basins that parallels the increasing inter-atomic charge transfer. The result is an accompanying reduction in $\delta(A, B)$ and a corresponding decrease in the stabilization resulting from the exchange of electrons between the two atomic basins. Thus the inter-atomic exchange energy $V_{ex}(A, B)$ amounts to 7% of the total exchange energy in the 'covalent' C_2 molecule where $\delta(C, C) = 2.7$, but for only 0.4% in the isoelectronic 'ionic' LiF molecule where $\delta(Li, F) = 0.18$, the ionic limit being characterized by a nearly complete localization of the electrons within each of the atomic basins. The terms 'covalency' and 'resonance' are used to account for bonding without specifying what forces are involved. These terms can now be quantified by determining the stabilizing contribution of $V_{ex}(A, B)$ to the energy of formation.

The Laplacian of the Density and the Lewis Model

The topology of the density, as revealed in its gradient vector field, provides the basis for the definition of the elements of molecular structure, but its relatively simple topology provides no evidence of the *Lewis* model of electron pairing. Instead, the *Lewis* model is recovered in the topology of the second derivative of the density, its Laplacian distribution $\nabla^2\rho(\mathbf{r})$ [80]. The Laplacian of the density determines where density is locally *concentrated*, where $\nabla^2\rho(\mathbf{r}) < 0$, and locally *depleted*, where $\nabla^2\rho(\mathbf{r}) > 0$. Since $\nabla^2\rho(\mathbf{r}) < 0$ denotes a concentration of density, one defines the function $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})/4$, Eq. (4), a maximum in $L(\mathbf{r})$ denoting a maximum in the concentration of the density, a local charge concentration or CC. It is well-documented that the topology of $L(\mathbf{r})$ provides a link between models of localized electrons and a measurable property of the electron density, a link originally surmised because of the faithful mapping of its local charge concentrations onto the number, relative size, and angular orientation of the bonded and non-bonded electron pair domains assumed in *Lewis* electron pair theory and the VSEPR model of molecular geometry [81]. This empirical link has since received theoretical justification. The conditional same spin density determines the extent to which the exclusion principle decreases the density of an α electron at some position $\mathbf{r}_2$ when another α electron is assigned the position $\mathbf{r}_1$ [It must be understood that neither electron is fixed at either of these points, the charge of each being spread out in space in the manner determined by the spin density $\rho^{\alpha}(\mathbf{r})$]. It is readily demonstrated that in the instance of the *Fermi* hole being strongly localized about some point $\mathbf{r}_1$, that the conditional same-spin density approaches the single-particle spin density in regions removed from the region of localization. In such regions, the sum of the α and β conditional pair densities will approach the total density $\rho(\mathbf{r}_2)$ for a closed-shell system and consequently, the Laplacian of the conditional pair density will approach the Laplacian of the total density, $L(\mathbf{r})$. Thus the topology of the Laplacian of the conditional pair density, which determines where electron pairing is concentrated relative to a given concentration, exhibits a homeomorphism with the topology of $L(\mathbf{r})$, one that approaches an isomorphic mapping of one field onto the other [82]. As a consequence of this mapping, the CCs displayed in $L(\mathbf{r})$, 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*. This determination of electron localization is thus model-independent.

Bonded interactions result in the formation of CCs on the surface of the outermost shell of charge concentration of an atom, termed its valence shell charge concentration (VSCC). Since the integral of $L(\mathbf{r})$ over an atom integrates to zero, the creation of local concentrations of charge within the VSCC of an atom must also result in the creation of regions of charge depletion. It is the complementary mapping of the maxima or 'lumps' with the minima or 'holes' between the reactant molecules that define *Lewis* acid-base reactions [83]. Such *Lewis* complementarity is the density embodiment of the ''lock and key'' analogy proposed by *Ehrlich* to account for the high degree of antibody specificity, an idea that resulted in his introduction of the term 'receptor' into the language of physiological chemistry [84]. *Lewis* complementarity is evidenced in the display of the Laplacian map given for $Cr(CO)_6$ in Fig. 5 which shows the alignment of the nonbonded charge

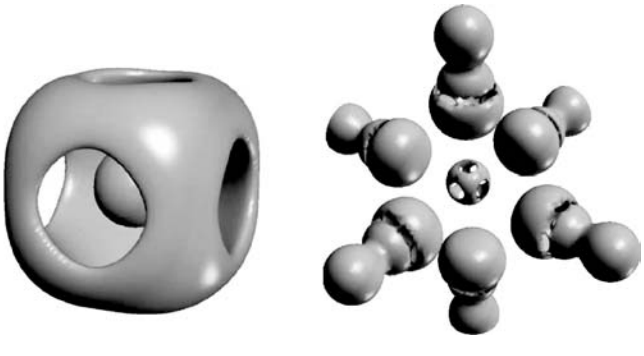

Fig. 5. Envelope maps of the Laplacian of the electron density for the Cr atom in $Cr(CO)_6$ and for the entire complex; the surface for the Cr atom is for $L(\mathbf{r}) = 5$ au while the surfaces for the CO molecules are for $L(\mathbf{r}) = 0$, the surface dividing the regions of charge concentration from those of charge depletion; note how the pronounced nonbonded charge concentration on each carbon atom is directed at a 'hole' in the Cr envelope in the manner denoting a 'donor–acceptor' interaction

concentrations on the carbons of the ligands with the regions of charge depletion – the holes – in the Laplacian envelope of the Cr atom, a physical realization of a donor–acceptor interaction.

The location of the maxima and minima in the Laplacian distribution for a transition metal atom coincides with the pattern predicted by crystal field theory [69]. In a d^6 complex the eight charge concentrations correspond to the occupied t_{2g} set and the six faces or regions of charge depletion, correspond to the empty e_g set, Fig. 5. Ligand field theory distinguishes between the t_{2g} and e_g orbitals through their differing overlaps with the ligand orbitals, the former with π, the latter with σ and it yields a modified interpretation of the atomic graph. The eight CCs in the Cr Laplacian distribution are associated with the t_{2g} orbitals that overlap with the π orbitals of the ligands, while the six faces or centres of charge depletion are associated with the e_g set that participate in σ bonding with the ligands. This association of the holes in the Laplacian envelope with the σ bonding to Cr is in accord with the small transfer of charge from the ligand σ orbitals to Cr, as determined in an analysis of the orbital contributions to the atomic population on the Cr atom. The analysis shows that only 0.5 of the four electrons in the e_g set reside on the Cr atom, an observation further strengthening the donor acceptor interpretation of the Cr–C interaction.

Atomic Contributions to Magnetic Properties

The extension of the theory to a molecule in the presence of a magnetic field requires the determination of the topology of the vector current density, the field that determines magnetic properties. The current is a vector field and its topology is more complex than that of the *gradient* vector field of the electron density. The existing procedures for calculating the induced first-order current $\mathbf{j}^{(1)}(\mathbf{r})$, the field that determines the second-order response properties such as magnetic susceptibility, were inadequate when its study was initiated. There is a problem in calculating $\mathbf{j}^{(1)}(\mathbf{r})$ in the choice of a 'gauge origin'. Magnetic properties are independent of the choice of gauge and so is the result obtained from an 'exact calculation'. The existing methods, all forms of coupled perturbed *HF* displayed a strong gauge dependence, so much so, that they were of no use in determining $\mathbf{j}^{(1)}(\mathbf{r})$ to the accuracy required for its topological analysis and marginally useful for calculating magnetic properties. A simple test of the 'goodness' of the calculated current is its satisfaction of the 'vanishing of its divergence', the condition that $\nabla \cdot \mathbf{j}^{(1)}(\mathbf{r}) = 0$ at all points in space. If this condition is not satisfied, it implies that electronic charge is either locally created or destroyed, in the manner described by *Schrödinger*'s equation of continuity.

Existing methods based on orbital approaches to the problem using a single gauge origin or different gauges for each orbital did not satisfy the zero divergence condition. We decided to follow *Schrödinger*'s [18] advice and focus on the calculation of the current, since this is the physical field that determines magnetic properties. There is no gauge problem for an atom in a singlet S state – the nucleus serving as the 'natural gauge origin'. Only the diamagnetic contribution survives and the calculation of $\mathbf{j}^{(1)}(\mathbf{r})$ becomes trivial. But we were in possession of a theory of atoms in molecules! Why not calculate the current one atom at a time putting the gauge origin at the nucleus and then summing the current and its properties for each atomic basin, as determined by the physics of an open system? This resulted in the method of individual gauges for atoms in molecules (IGAIM) [85] an approach that yielded excellent results for diamagnetic susceptibilities, the diamagnetic susceptibility χ (with u = cgs ppm) for CO_2 was calculated to be −21.8 u compared to the experimental value of −21.0 u, while a single gauge origin at electronic centre of mass gave −31.7 u. However, IGAIM results in discontinuities in the current in the regions of the atomic boundaries. The co-author of these papers, Dr. *T. Keith*, had an idea: why not choose a new gauge origin for every point $\mathbf{r}$ in the calculation of $\mathbf{j}^{(1)}(\mathbf{r})$, in effect performing a continuous set of gauge transformations (CSGT) in a manner that maximized their dominance by a particular nucleus [86]. The result was the removal of the boundary problem and plots of $\mathbf{j}^{(1)}(\mathbf{r})$ that satisfy the vanishing divergence condition to high order. CSGT enabled the full topological analysis of the induced current [87] and provided its first accurate displays. The current maps illustrate the spatial interplay between the induced paramagnetic and diamagnetic currents that account for all of the subtleties of magnetic properties, making possible the accurate description of 'ring' currents in aromatic molecules for the first time. The induced current in the CO_2 molecule calculated by CSGT is displayed in Fig. 6, a map that gives physical

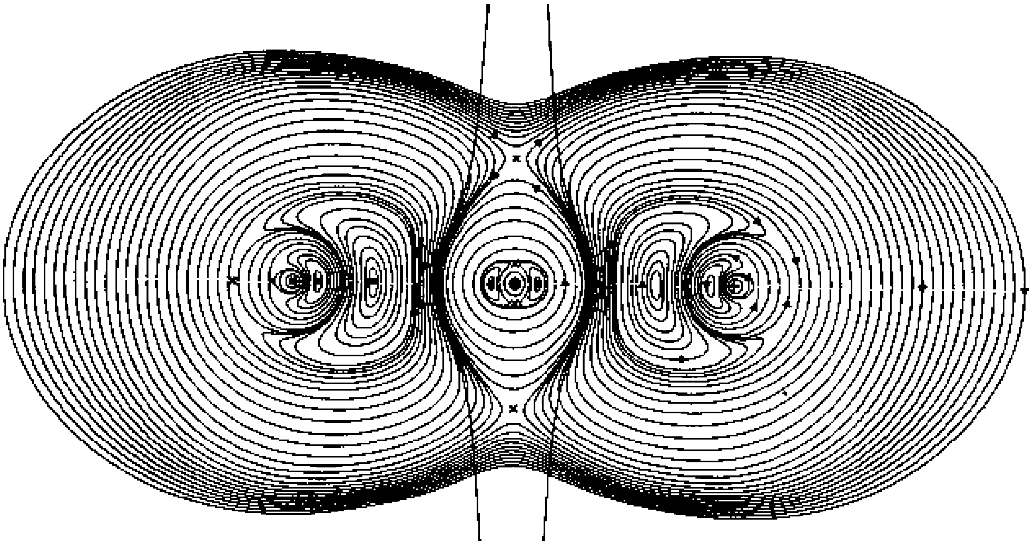

Fig. 6. A display of the current flow in the CO_2 molecule by a magnetic field applied perpendicular to and out of the plane of the figure obtained from a CSGT calculation; the plot is overlaid with the intersections of the C|O interatomic surfaces; note how the interatomic surfaces follow the demarcation of the paramagnetic flow-lines of the current (counter-clockwise) within the C basin from the neighbouring diamagnetic flow-lines in the O basins; the current within the basin of carbon is dominated by the paramagnetic flow, causing its contribution to χ to be positive and leading to a deshielding of the carbon nucleus; the dominant diamagnetic flows in the O basins result in negative contributions of large magnitude; the current flows, like the density, are very atomic-like in this polar molecule; thus the contribution to χ from the flux in current across the atomic boundaries, as opposed to the basin contributions, accounts for only 8% of the molecular value; in benzene, the presence of a substantial ring current for a perpendicular field results in a contribution from the flux in current across the C|C atomic boundaries that accounts for ~50% of the molecular value of χ

expression to the atomic contributions to its magnetic susceptibility and chemical shielding [66, 67].

CSGT made possible the application of QTAIM to the definition and calculation of the atomic and group contributions to magnetic susceptibilities [66], giving theoretical justification to *Pascal*'s demonstration of the assignment of additive group increments to the magnetic susceptibility [56]. Indeed the results are sufficiently accurate that his experimental values were recovered to within experimental error for a number of groups. To account for the 'aromatic exaltation' assigned by *Pascal*, a carbon atom in benzene should have a magnetic susceptibility of magnitude $|\chi(\mathrm{C})|$, greater than that of a correspondingly conjugated carbon in a non-aromatic molecule, carbon-2 in *cis*-butadiene, for example. The value of $|\chi(\mathrm{C})|$ in benzene is calculated by QTAIM to exceed that for C2 in butadiene by 2.5 u. Six times this value, or 15 u, equals precisely the exaltation assigned to the benzene ring by *Pascal* and *Pacault* [88]. The contributions from the H atoms in the two molecules are identical and do not contribute to the exaltation. Further analysis shows that the exaltation is a consequence of the flux in current through the C|C interatomic surfaces, that is, from the ring current [66]. Previous attempts to recover additive contributions to the magnetic susceptibility failed because they started from orbital models, see for example papers by *Pople* [89, 90], rather than from the physical field, the induced current.

The electron delocalization associated with the resonance model is also invoked to account for aromatic stabilization of the energy. Accordingly, the C atom in benzene should be more stable than the corresponding atom in butadiene, and QTAIM shows this to be the case with the difference in their energies equaling 41.9 kJ/mol. The H atom in butadiene possesses a slightly greater population and it is 14.6 kJ/mol more stable than H in benzene, making the C–H group in benzene more stable by 27.2 kJ/mol. Benzene is therefore, predicted to be more stable than six correspondingly conjugated acyclic C–H groups by 163 kJ/mol, compared with an experimental resonance energy of 151 kJ/mol. QTAIM recovers model quantities that can be related to experimental measurement.

How to Apply the Theory

The theory is readily applied using the programs AIMPAC [91] or AIM2000 [92] in the analysis of wave functions generated at all levels of theory. The topological components of the programs define the atomic boundaries, the bond paths and molecular structure, together with an analysis of the properties at the bond critical point used in the characterization of bonding. The integration packages yield most atomic properties of interest, from populations, to moments, to energies, their kinetic and potential components, to the localization/delocalization of the electrons. A separate program provides the average properties of operators integrated over an inter-atomic surface. All of this is possible without a detailed knowledge of the underlying quantum mechanics – just a belief in the presence of atoms in molecules. The following section is presented for those desirous of a fuller understanding of the quantum mechanics of an open system.

The Physics of an Open System

Quantum mechanics associates a linear Hermitian operator – a *Dirac* observable [52] – with every property of a system and the physics of the system is determined by the equations of motion for the observables – the theorems of quantum mechanics. Thus the implementation of *Schwinger*'s principle to a proper open system (one bounded by a zero-flux surface) is contained in the variational statement of the *Heisenberg* equation of motion obtained in terms of a variation in the Lagrangian for an infinitesimal time interval, Eq. (17) [19].

$$\delta L[\Psi, \Omega, t] = (\varepsilon/2)\big\{(\mathrm{i}/\hbar)\langle\Psi|[\hat{\mathrm{H}}, \hat{\mathrm{G}}]|\Psi\rangle_{\Omega} + \mathrm{cc}\big\} \tag{17}$$

This expression of the principle is to be compared with the corresponding expression for a stationary state obtained from the variation of *Schrödinger*'s functional, Eq. (13). The operational form of this statement is obtained by substitution of the expression for the variation of the Lagrangian that gives the explicit form for the time rate-of-change of the expectation value of the generator $\hat{\mathrm{G}}$, Eq. (18).

$$\begin{aligned}&(1/2)N\int_{\Omega}\mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\partial\{\Psi^{*}(\hat{\mathrm{G}}(\mathbf{r})\Psi) + \mathrm{cc}\}/\partial t\\ &\quad = (1/2)\{(\mathrm{i}/\hbar)\langle\Psi|[\hat{\mathrm{H}}, \hat{\mathrm{G}}(\mathbf{r})]|\Psi\rangle_{\Omega} + \mathrm{cc}\} - (1/2)\oint \mathrm{d}\mathbf{S}(\mathbf{r}_{\mathrm{s}}) \cdot \{\mathbf{J}_{\mathrm{G}}(\mathbf{r}_{\mathrm{s}}) + \mathrm{cc}\}\end{aligned} \tag{18}$$

The term $N\int \mathrm{d}\mathbf{r}'\{\Psi^{*}(\hat{\mathrm{G}}(\mathbf{r})\Psi) + \mathrm{cc}\}$ implies that the operator is averaged over the coordinates of all the electrons save those denoting the position **r**, the coordinate of the electron to be integrated over Ω. It thus defines the density of the property G associated with the operator $\hat{\mathrm{G}}(\mathbf{r})$. *All open system properties are thus defined in terms of a real-space density distribution, in the same manner as is the electron density, Eq. (1). This is direct a consequence of the field-theoretic generator* $\hat{\mathrm{G}}(\mathbf{r})$ *acting on the coordinates of a single electron.*[d] The physical understanding of the theory is greatly enhanced through the representation of all properties in terms of density distributions in real space, particularly those associated with force and energy. The term on the LHS of Eq. (18) gives the time rate-of-change of the property G and this is determined by the corresponding average of the commutator $(\mathrm{i}/\hbar)[\hat{\mathrm{H}}, \hat{\mathrm{G}}]$, as in the physics of a total system. The second term is unique to an open system, as it describes the flux in the vector current density $\mathbf{J}_{\mathrm{G}}(\mathbf{r})$ of the generator. If $\hat{\mathrm{G}} = \hat{\mathrm{N}}$ the number operator, then $\mathbf{J}_{\mathrm{G}}(\mathbf{r})$ is the usual quantum mechanical current that determines the flow of electron density across the surface of the open system corresponding to the loss or gain of electronic charge with time. The current $\mathbf{J}_{\mathrm{G}}(\mathbf{r})$ similarly determines the change in the property G as a result of its current flux. The physics of some total (closed) system may be viewed as a special limiting case of Eq. (18) for which the surface term vanishes.

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[d] In transforming from the field-theoretic expressions to the *Schrödinger* representation, the operator $\hat{\mathrm{G}}(\mathbf{r})$ is not replaced with a sum of corresponding operators for all N electrons but rather by N times the operator for a single electron, a crucial and physically essential step

The Atomic Force Theorem

We consider just two cases of generators to illustrate the use of Eq. (18). The time rate-of-change of momentum is force and setting $\hat{\mathrm{G}} = \hat{\mathbf{p}}$, an electronic momentum coordinate, yields the expression for the force acting on the electron density, the *Ehrenfest* force theorem [93], Eq. (19).

$$(1/2)\int_{\Omega} \mathrm{d}\mathbf{r}\{\partial(\mathbf{J}(\mathbf{r}) + \mathrm{cc})/\partial t\} = (N/2)\int_{\Omega} \mathrm{d}\mathbf{r}\int \mathrm{d}\mathbf{r}'\{\Psi^{*}(-\nabla_{\mathrm{r}}\hat{\mathrm{V}})\Psi\} + \oint \mathrm{dS}(\Omega, \mathbf{r}_{\mathrm{s}})\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) \qquad (19)$$

The term on the LHS of Eq. (19) is given by the time derivative of the electronic current which, being a velocity density, yields an acceleration that when multiplied by the mass m, yields the force resulting from the time derivative of the momentum density. The first term on the RHS, is determined by the commutator $(\mathrm{i}/\hbar)[\hat{\mathrm{H}}, \hat{\mathrm{p}}] = -\nabla_{\mathrm{r}}\hat{\mathrm{V}}$, where $\hat{\mathrm{V}}$ is the total potential energy operator. The operator $-\nabla_{\mathbf{r}}\hat{\mathrm{V}}$ determines the force exerted on the electron at **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 $N\int \mathrm{d}\mathbf{r}'$, that is, by summing over spins and integrating over the coordinates of all electrons save **r**, one obtains an expression for $\vec{F}(\mathbf{r})$, the force exerted on an electron at position **r** by the *average distribution* of the remaining electrons and by the rigid nuclear framework – the force exerted on the electron density. 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.

The final term on the RHS of Eq. (19) is the force exerted on the surface of the atom by the 'momentum flux density' that is expressed in terms of the quantum stress tensor $\overleftrightarrow{\sigma}(\mathbf{r})$, Eq. (20), introduced by *Schrödinger* and expressed in terms of the one-electron density matrix $\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')$,

$$\overleftrightarrow{\sigma}(\mathbf{r}) = (\hbar^2/4m)\{(\nabla\nabla + \nabla'\nabla') - (\nabla\nabla' + \nabla'\nabla)\}\Gamma^{(1)}(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \qquad (20)$$

The stress tensor, whose gradient and associated virial, determine the electronic force and potential energy densities, is a real-space function. It has the dimensions of pressure, force/unit area (F/L^2), or energy density (E/L^3). Equation (19) is the equation of motion for the electron density.

For a molecule in a stationary state, Eq. (19) reduces to Eq. (21) and the force acting over the basin of the atom is equal and opposite to the force exerted on its surface.

$$\vec{F}(\Omega) = \int_{\Omega} \mathrm{d}\mathbf{r}\vec{F}(\mathbf{r}) = -\oint \mathrm{dS}(\Omega, \mathbf{r}_{\mathrm{s}})\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) \qquad (21)$$

The *Ehrenfest* force on the electron density plays a role that must be distinguished from the more familiar *Feynman* force acting on the nuclei. For example, in the initial approach of two neutral atoms, the *Ehrenfest* force is repulsive whereas the *Feynman* forces are attractive, the former correctly reflecting the initial increase in the potential energy [94]. The *Feynman* force eventually vanishes and becomes repulsive while the *Ehrenfest* force becomes increasingly attractive, reflecting the decrease in the potential energy required by the virial theorem on bonding. The *Feynman* force is invoked in situations where the *Ehrenfest* force is in fact the operative force, in situations that require the physics of an open system for their statement and solution. An example is the operation of the atomic force microscope (AFM) [95]. The AFM and the surface under study are two components of a total system separated by a zero-flux surface. It is the force transmitted from the tip of the probe to the attached cantilever arm of the AFM whose deflections are measured as the tip scans the surface of a sample. The *Feynman* force does not equal the force $\vec{F}$ exerted on the cantilever. Instead, it measures the force required to displace the nucleus α of the atom in the tip of the AFM. One is interested in the force not just on the nucleus of one atom in the tip of the probe, but rather in the force $\vec{F}$ that is exerted on all of the atoms that make up the open system "probe plus cantilever". This force is determined by the pressure exerted on every element of the surface separating the tip of the probe from the sample, as given in Eq. (21) in terms of the surface integral of the stress tensor. It is the *Ehrenfest* force $\vec{F}$ that the cantilever arm exerts on the attached spring, displacing it from its equilibrium position, the displacement measured in the AFM [95]. The force $\vec{F}$ is exerted on a surface determined by the zero-flux interatomic surfaces separating the atoms in the tip from those in the sample, and thus its response is a consequence of the atomic form of matter.

The definition of pressure requires the existence of a surface upon which the pressure is exerted, placing it within the realm of the physics of an open system. A scaling procedure demonstrates that the expectation value of the pressure-volume product of a proper open system is proportional to its surface virial, the virial of the *Ehrenfest* force exerted on its surface [96]. Thus the thermodynamic pressure is determined by the virial of the force resulting from the electronic momentum flux through its zero-flux surface, the force $\vec{F}$ acting on an open system. The pressure determined in this manner is a consequence of the mechanics of the interaction between the open system and its confining walls as opposed to previous treatments based on the analogy with the classical virial theorem for a contained gas wherein the pressure-volume product was incorrectly related to the virial of the "wall forces".

These examples demonstrate that the *Ehrenfest* force is the force acting on and between macroscopic systems, controlling in addition their relative motion. It is thus the one that determines the force required to separate two surfaces and the study of the adhesive properties of surfaces should be directed towards an understanding of the *Ehrenfest* force that is established when two surfaces are brought into contact. The physics of the *Ehrenfest* force and its use in the understanding of chemical bonding is only beginning to be studied in detail [94].

The Atomic Virial Theorem

Setting $\hat{\mathrm{G}}(\mathbf{r}) = \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}$ in Eq. (18) yields the virial theorem, a theorem that plays the central role in defining the energy of an open system [19]. Its statement for an open system is of the same form as that given in Eq. (19) for the *Ehrenfest* force with the time rate of change of $\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}$ equated to the expectation value of $(\mathrm{i}/\hbar)[\hat{\mathrm{H}}, \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}]$ plus a surface term denoted by $\mathcal{V}_{\mathrm{s}}(\Omega)$. The surface term determines the flux in the associated current density that is expressible as $\mathbf{r} \cdot \sigma(\mathbf{r})$, the virial of the surface forces.

The expectation value of the commutator yields $2T(\Omega)+\mathscr{V}_{\mathrm{b}}(\Omega)$, twice the electronic kinetic energy plus the virial of the *Ehrenfest* force exerted over the basin of the atom. Expressing by $\mathscr{V}(\Omega)$ the total virial for an open system Ω, the virial theorem for a stationary state may be stated as Eq. (22).

$$-2T(\Omega) = \mathscr{V}(\Omega) = \mathscr{V}_{\mathrm{b}}(\Omega) + \mathscr{V}_{\mathrm{s}}(\Omega) \tag{22}$$

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 Eq. (23).

$$\mathscr{V}_{\mathrm{b}}(\Omega) = -\int_{\Omega} \mathrm{d}\mathbf{r}\,\mathbf{r}_{\Omega}\cdot\nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r}) = \int_{\Omega} \mathrm{d}\mathbf{r}\,\mathbf{r}_{\Omega}\cdot\vec{F}(\mathbf{r}) \qquad \mathscr{V}_{\mathrm{s}}(\Omega) = \oint \mathrm{dS}(\Omega,\mathbf{r}_{\mathrm{s}})\mathbf{r}_{\Omega}\cdot\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) \tag{23}$$

It is most important to note that the virial, the electronic potential energy, is defined as the viral of the *Ehrenfest* force. The current in the surface virial has the dimensions of F/L or surface tension, and $\mathscr{V}_{\mathrm{s}}(\Omega)$ is a measure of the surface energy associated with the interactions of Ω with its bonded neighbours. An atomic surface $\mathrm{S}(\Omega)$ is in general composed of a number of interatomic surfaces, one for each atom bonded to Ω. Equation (22) yields the usual statements of the virial theorem for an atom in a molecule: $E_{\mathrm{e}}(\Omega) = -T(\Omega)$ and $-2T(\Omega) = \mathscr{V}(\Omega)$ where the electronic energy of open system Ω is defined as $E_{\mathrm{e}}(\Omega) = T(\Omega) + \mathscr{V}(\Omega)$. If the system is in electrostatic equilibrium with no external forces acting on the nuclei, then $E_{\mathrm{e}}(\Omega) = E(\Omega)$, the usual fixed nucleus energy such that the sum of $E(\Omega)$ over all the atoms in the molecule yields the total molecular energy E.

If one adds the surface virials for two atoms A and B sharing a common surface $\mathrm{S}(A|B)$, then the contribution to the energy of formation of the molecule arising from the formation of the surface is given by Eq. (24) where $\vec{\mathbf{R}}_{AB}$ is the vector distance from the nucleus of B to that of A [19].

$$\mathscr{V}_{\mathrm{s}}(A|B) = \vec{\mathbf{R}}_{AB}\cdot\oint \mathrm{dS}(A|B)\overleftrightarrow{\sigma}(\mathbf{r})\cdot\mathbf{n}_{A}(\mathbf{r}) \tag{24}$$

Thus the scalar product of $\vec{\mathbf{R}}_{AB}$ with the *Ehrenfest* force acting on the surface of A, equal and opposite to that acting on B, determines the energy of formation of the surface [19]. If the *Ehrenfest* force is attractive, drawing atom A towards atom B, then the energy contribution from surface formation is stabilizing. Like the *Ehrenfest* force, the understanding of bonding afforded by this energy change has yet to be fully explored.

Every theorem may be stated in its differential as well as its integrated form. The local statement of the virial theorem for example, for a system in a stationary state, is given by Eq. (25) where $\mathscr{V}(\mathbf{r})$ denotes the virial field, the electronic potential energy density. The sign of the Laplacian of the density determines whether the kinetic energy density $2G(\mathbf{r})>0$ or the potential energy density $\mathscr{V}(\mathbf{r})<0$ dominates their virial ratio at a particular point in space making it a useful quantity in the classification of chemical bonding. Since the integral of the Laplacian of the density over an open system Ω vanishes, integration of Eq. (25) clearly yields the virial theorem for an atom in a molecule, Eq. (22). The virial field, since it is expressible in terms of the stress tensor, is a representation of the electronic potential energy density in real space, determining the interactions, attractive and repulsive between all of the particles in a molecule. Its topology is homeomorphic with that of the density and thus every bond path is mirrored by a virial path, a line along which the potential energy density is maximally stabilizing [97]. All theorems hold in the presence of an electromagnetic field. In the presence of a magnetic field for example, the surface integral in the virial theorem includes a contribution from the magnetic pressures acting on the atomic surface [19].

$$(\hbar^2/4m)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) - \mathbf{r}\cdot\nabla\cdot\overleftrightarrow{\sigma}(\mathbf{r}) + \nabla\cdot(\mathbf{r}\cdot\overleftrightarrow{\sigma}(\mathbf{r})) = 2G(\mathbf{r}) + \mathscr{V}(\mathbf{r}) \tag{25}$$

Scheme 1 lists atomic theorems for a number of the most important generators $\hat{G}$ [98]. The use of these theorems extends beyond the asking of chemical questions

ATOMIC THEOREMS FOR MOLECULES AND CRYSTALS

Atomic force theorem $\hat{G} = \hat{p}$

$$m\int_{\Omega}\mathrm{d}\mathbf{r}\;\partial\mathbf{J}(\mathbf{r})/\partial t = \int_{\Omega}\mathrm{dr}\int\mathrm{d}\tau'\,\Psi^*(-\nabla\hat{V})\Psi + \oint\mathrm{dS}(\mathbf{r})\sigma(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$

Atomic virial theorem $\hat{G} = \hat{r}\cdot\hat{p}$

$$m\int_{\Omega}\mathrm{d}\mathbf{r}\;\mathbf{r}\cdot\partial\mathbf{J}(\mathbf{r})/\partial t = 2T(\Omega) + \int_{\Omega}\mathrm{d}\mathbf{r}\int\mathrm{d}\tau'\,\Psi^*(-\mathbf{r}\cdot\nabla\hat{V})\Psi + \oint\mathrm{dS}(\mathbf{r})\;\mathbf{r}\cdot\sigma(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$

Atomic torque theorem $\hat{G} = \hat{r}\times\hat{p}$

$$m\int_{\Omega}\mathrm{d}\mathbf{r}\;\mathbf{r}\times\partial\mathbf{J}(\mathbf{r})/\partial t = \int_{\Omega}\mathrm{d}\mathbf{r}\int\mathrm{d}\tau'\,\Psi^*(-\mathbf{r}\times\nabla\mathrm{V})\Psi - \oint\mathrm{dS}\;\sigma(\mathbf{r})\times\;\mathbf{r}\cdot\mathbf{n}$$

Atomic current theorem $\hat{G} = \hat{r}$

$$\int_{\Omega}\mathrm{d}\mathbf{r}\;\mathbf{r}\;\partial\rho(\mathbf{r})/\partial t = \int_{\Omega}\mathrm{d}\mathbf{r}\,\mathbf{J}(\mathbf{r}) - \oint\mathrm{dS}\;\mathbf{n}(\mathbf{r})\cdot\mathbf{J}(\mathbf{r})\mathbf{r}$$

Atomic continuity theorem $\hat{G} = \hat{N}$

$$\int_{\Omega}\mathrm{d}\mathbf{r}\;\partial\rho(\mathbf{r})/\partial t = -\oint\mathrm{dS}\;\mathbf{J}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$

Atomic power theorem $\hat{G} = \hat{p}^2/2m$, written without 1/2m

$$\int_{\Omega}\mathrm{d}\mathbf{r}\cdot\partial\rho_{\mathrm{p}}2(\mathbf{r})/\partial \mathrm{t} = \int_{\Omega}\mathrm{d}\mathbf{r}\int\mathrm{d}\tau'(\mathrm{h}/i)\{(\Psi\nabla\Psi^* - \Psi^*\nabla\Psi)\cdot\nabla\hat{V}\} + \oint\mathrm{dSRe}\{\mathbf{J}_{\mathrm{p}}2(\mathbf{r})\}$$

Quantum stress tensor density

$$\sigma(\mathbf{r}) = (\mathrm{h}^2/4m)\int\mathrm{d}\tau'\{(\nabla\nabla\Psi^*)\Psi - \nabla\Psi^*\nabla\Psi - \nabla\Psi\nabla\Psi^* + \Psi^*\nabla\nabla\Psi\}$$

Quantum vector current density

$$\mathbf{J}(\mathbf{r}) = (\mathrm{h}/2mi)\int\mathrm{d}\tau'\{\;\Psi^*\nabla\Psi - \Psi\nabla\Psi^*\;\}$$

Scheme 1

of bonding, structure, and reactivity. They apply to all questions regarding the properties of matter at the atomic level. The text has drawn attention to specific problems that require the use of the physics of an open system for their understanding and interpretation, such as the atomic force microscope [95] and the quantum definition of pressure [96]. The atomic current theorem that is obtained by setting $\hat{G} = \mathbf{r}$, an electronic position coordinate, plays an essential role in the atomic partitioning of the diamagnetic susceptibility by relating the atomic current induced within an atom to the flux in the current through its surface, an essential contribution to the atomic description of magnetic properties [66]. The atomic force is the equation of motion for an open system. It is capable of describing the motion of an adsorbed atom on the surface of a substrate or the forces required for the manipulation of individual atoms or molecules thereby providing a basis for nanotechnology. The physical understanding obtainable from the use of these theorems is only beginning to be explored.

Conclusion

The theory developed in this paper can be derived independently by any chemist familiar with the observable topology of the electron density and knowledgeable in physics. It is thus a scientific theory, its sole input being the information contained in the state vector and its predictions being verifiable by experiment.

Note Added in Proof

A paper entitled ‘‘Properties of atoms in molecules: Caged atoms and the *Ehrenfest* force’’ is to appear in J. Chem. Theory Compt., in May, 2005 by *R. F. W. Bader* and *De-Chai Fang*, that introduces the *Ehrenfest* force into the discussion of chemical bonding.

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