

A Quantum Theory of Molecular Structure and Its Applications

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I. Introduction

A. An Atom in a Molecule as an Open Quantum System

The role of physics in chemistry is to predict what can be observed and to provide an understanding of these observations. The dominant operational concept of chemistry is that of an atom in a molecule with a determinable and characteristic set of properties. Thus the physics of chemistry is necessarily the physics of an atom in a molecule, that is of an open system, one



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which is free to exchange charge and momentum with neighboring atoms. To extend the predictions of physics to the domain of chemistry it is therefore, necessary to generalize quantum mechanics to a subsystem of a total system. Such a generalization is indeed possible, but only if the open system satisfies a particular boundary condition. When this condition is met, one obtains a definition of an atom in a molecule and a prediction of its properties. Inseparable from the quantum definition of an atom in a molecule is the definition of the bonds which link the atoms to yield a molecular structure. In essence, the quantum description of an open system recovers the molecular structure hypothesis—that a molecule is a collection of atoms each with a characteristic set of properties, that are linked by a network of bonds. The emergence of this hypothesis from 19th century experimental chemistry is thus seen as having been an inevitable consequence of physics.

B. Outline of the Theory and Its Applications

It is the purpose of this article to review the derivation of the quantum mechanics of an open system and to illustrate its use in the development and application of a theory of atoms in molecules.¹ The article begins with a review of the generalization of quantum mechanics that leads to the definition of an open system and to a prediction of its properties.¹⁻³ This generalization is accomplished through an extension of Schwinger's principle of stationary action,⁴ an extension

which is possible only if a certain boundary condition is satisfied. The boundary condition demands that the flux in the gradient vector field of the charge density $\rho(\mathbf{r})$ vanish at every point of the surface $S(\Omega, \mathbf{r})$ which bounds an open system Ω . That is, the surface is one of zero flux in $\nabla\rho$.⁵ As a consequence of the boundary

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

being stated in terms of a property of the electronic charge density, quantum subsystems are defined in real space. Because of the dominant topological property of a molecular charge distribution—that it exhibits maxima at the positions of the nuclei—the boundary condition leads to the partitioning of a molecular system into a set of disjoint spatial regions, each region containing in general, a single nucleus. These regions are identified with the chemical atoms. The properties of the gradient vector field also contain the information needed for a definition of molecular structure and its stability,⁶ by using the mathematics of qualitative dynamics. The result is a theory of atoms, bonds, structure, and structural stability.

It is a primary purpose of this paper to demonstrate that quantum mechanics predicts the properties of atoms in molecules just as it predicts the properties of the total system. Following the review of the generalization of quantum mechanics to an open system which yields a definition of an atom and its properties, examples of the application of the resulting theory of atoms in molecules to chemical problems are presented. These examples are chosen to illustrate the principal features of the theory:

(a) The demonstration that each atom makes an additive contribution to the average value of every property of a molecular system. This is the principle underlying the cornerstone of chemistry—that atoms and functional groupings of atoms make recognizable contributions to the total properties of a system. One predicts the properties of some total system in terms of the properties of the functional groups it contains and conversely, one confirms the presence of a given group in a molecule through the observation of its characteristic properties. In those limiting situations wherein a group is essentially the same in two different systems, one obtains a so-called additivity scheme for the total properties, for in this case the atomic contributions as well as being additive are transferable between molecules. It will be shown that the methyl and methylene groups as defined by the theory of atoms in molecules predict the additivity of the energy which is experimentally observed in normal hydrocarbons. The deviations in this additivity which are found for small cyclic molecules and which serve as the experimental definition of strain energy are also predicted by theory. The recovery of these experimentally measurable properties of atoms in molecules by the atoms of theory confirms that they are the atoms of chemistry.

(b) The definition of bonds, molecular structure, and structural stability as determined by the gradient vector field of the charge density is exemplified in a number of systems, including those whose charge distributions are accessible to experimental measurement. The importance of distinguishing between molecular geometry and the generic concept of molecular structure is illustrated and discussed, and it is shown that a theory of molecular structure is obtained without recourse to

the Born–Oppenheimer approximation.

Second only to the molecular structure hypothesis in the ordering, understanding, and predicting of chemical events is the Lewis model of the electron pair.⁷ This model and its associated models of molecular geometry and chemical reactivity find physical expression in the topological properties of the Laplacian of the electronic charge density.^{8,9} This scalar field, defined by the second derivatives of the electronic charge density, determines where electronic charge is locally concentrated and depleted, and it plays a dominant role throughout the theory of atoms in molecules. Thus the review also illustrates the following:

(c) The recovery of the Lewis model of the electron pair in terms of the topological properties of the Laplacian of the charge density and the use of the Laplacian to predict molecular geometries and chemical reactivity.

(d) The ability of the Laplacian of the charge density, when used in conjunction with the definition of a chemical bond and the local mechanics governing the charge density as afforded by theory, to yield a classification of atomic interactions. This classification scheme is directly applicable to experimentally measured charge distributions.

II. The Quantum Mechanics of an Open System

A. The Need for a Quantum Description of an Open System

It is a postulate of quantum mechanics that everything that can be known about a system is contained in the state function Ψ . The value of a physical quantity is obtained through the action of a corresponding operator on Ψ . Thus quantum mechanics is concerned with observables, the linear Hermitian operators associated with the physical properties of a system, and their equations of motion. The theorems of quantum mechanics that yield relationships between various observables, such as the virial and Ehrenfest theorems, are derived from the Heisenberg equation of motion. Questions we have about a quantum system are therefore, answered in terms of the values and equations of motion for the relevant physical observables. These values and relationships refer to the total system. The use of the atomic concept in our attempts to understand and predict the properties of molecules and solids, however, requires answers of a more regional nature and it would appear that to find chemistry within the framework of quantum mechanics one must find a way of determining the observables and their properties for pieces of a system. How is one to choose the pieces? Is there one or are there many ways of partitioning a system into pieces in such a way that quantum mechanics predicts their properties? If there is an answer to this problem then the necessary information must be contained in the state function Ψ , for Ψ tells us everything we can know about a system.

Therefore, the question, “Are there atoms in molecules?” requires the asking of two equally important questions: (a) Does the state function predict a unique partitioning into subsystems? (b) Does quantum mechanics provide a complete description of the subsystems so defined? To answer questions a and b one must turn to a development of physics that introduces the

quantum observables and their equations of motion in a nonarbitrary way, as opposed to one based on what would be an arbitrary extension of the correspondence principle. Such is Schwinger's principle of stationary action.⁴ It replaces the conventional array of assumptions based on classical Hamiltonian dynamics and the correspondence principle with a single quantum dynamical principle. The approach is also a very general one, one that enables the asking of questions a and b.

B. The Action Principle in Quantum Mechanics and Schwinger's Principle of Stationary Action

In 1933 Dirac published a paper entitled "The Lagrangian in quantum Mechanics". After presenting a discussion as to why the Lagrangian formulation of classical mechanics could be considered to be more fundamental than the approach based on the Hamiltonian theory, Dirac went on to say, "For these reasons it would seem desirable to take up the question of what corresponds in the quantum theory to the Lagrangian method of classical mechanics."

A knowledge of the transformation function or transition amplitude $\langle q_{r_2, t_2} | q_{r_1, t_1} \rangle$ suffices to determine the dynamical behavior of a system with time, since it relates that state function $\Psi(q_{r_2, t_2})$ at time t_2 to that at time t_1 according to¹⁰

$$\langle q_{r_2, t_2} | \Psi \rangle = \Psi(q_{r_2, t_2}) = \int \langle q_{r_2, t_2} | q_{r_1, t_1} \rangle dq_{r_1} \Psi(q_{r_1, t_1}) \quad (2)$$

The symbol \hat{q}_{r_1} is used to denote the complete set of commuting position operators for the particles at time t_1 and q_{r_1} , their eigenvalues. Dirac was the inventor of transformation theory and through repeated use of the multiplicative law of transformation functions he was able to express the function connecting states at times t_1 and t_2 by a sequence of transformation functions for times intermediate between the initial and final times. Taken to the limit of the successive intermediate times differing only infinitesimally one from the next, the multiplicative law yields a product of all the transformation functions associated with the successive infinitesimal increments of time. Dirac then stated that the transformation function associated with the time displacement from t to $t + dt$ corresponds to $\exp[(i/\hbar)L dt]$, where the Lagrangian L was to be considered as a function of the coordinates at time t and the coordinates at time $t + dt$, rather than of the coordinates and velocities. The transformation function then becomes $\exp[(i/\hbar)W]$ where W , the action integral equal to $\int L dt$ between the limits t_1 and t_2 , is interpreted as the sum over all the individual coordinate-dependent terms in the succession of values of t . With this construct Dirac was able to answer the question of what in quantum mechanics corresponds to the classical principle of stationary action.

Feynman built on this work and in 1948¹⁰ it culminated in his path integral formulation of quantum mechanics. In the classical limit considered by Dirac, only one trajectory connects the system at time t_1 to that at time t_2 and he limited his discussion to this case. What Feynman did was to consider all the trajectories or paths that connect the states at the initial and final times, since he wished to obtain the corresponding quantum limit. Each path has its own value for the

action W and all the values of $\exp[(i/\hbar)W]$ must be added together to obtain the total transition amplitude. Thus the expression for the transition amplitude between the states $|q_{r_1}\rangle$ and $|q_{r_2}\rangle$ is the sum of the elementary contributions, one from each trajectory passing between \hat{q}_{r_1} at time t_1 and \hat{q}_{r_2} at time t_2 . Each of these contributions has the same modulus, but its phase is the classical action integral $(1/\hbar) \int L dt$ for the path. This is expressed as

$$\langle q_{r_2, t_2} | q_{r_1, t_1} \rangle = (1/N) \int \exp\left\{(i/\hbar) \int_{t_1}^{t_2} L dt\right\} \delta q_r(t)$$

The differential $\delta q_r(t)$ indicates that one must integrate over all paths connecting q_{r_1} at t_1 and q_{r_2} at t_2 and $1/N$ is a normalizing factor.¹¹

Schwinger's quantum action principle put forth in 1951⁴ is also concerned with the determination of the transformation function. A statement of this principle is

$$\delta \langle q_{r_2, t_2} | q_{r_1, t_1} \rangle = (i/\hbar) \langle q_{r_2, t_2} | \delta \hat{\mathcal{W}}_{12} | q_{r_1, t_1} \rangle = (i/\hbar) \langle q_{r_2, t_2} | \delta \int_{t_1}^{t_2} \hat{\mathcal{L}}[t] dt | q_{r_1, t_1} \rangle \quad (3)$$

where $\hat{\mathcal{W}}_{12}$ is the action integral operator and $\hat{\mathcal{L}}$ is the Lagrange function operator. Equation 3 is a differential statement of Feynman's path integral formulation, and while Schwinger developed it independently, it can be obtained as a consequence of Feynman's principle (see for example, Yourgrau and Mandelstam¹¹). The action principles afford conceptual advantages in formulating the laws of quantum mechanics and represent more than alternative formulations of the laws of quantum mechanics. In fact, they may provide the real foundation of quantum mechanics and thus of physical theory.¹²

The quantum action principle (eq 3) embodies Schwinger's postulate that if variations are effected in a quantum mechanical system, the corresponding change in the transformation function between the eigenstates $|q_{r_1, t_1}\rangle$ and $|q_{r_2, t_2}\rangle$ is (i/\hbar) times the matrix element of the variation of the action integral $\hat{\mathcal{W}}_{12}$ connecting the two states. The action integral operator $\hat{\mathcal{W}}_{12}$ is defined as

$$\hat{\mathcal{W}}_{12} = \int_{t_1}^{t_2} \hat{\mathcal{L}}[t] dt \quad (4)$$

where $\hat{\mathcal{L}}[t]$ is an invariant Hermitian function of the field Ψ and its first derivatives. The principle of stationary action is obtained from eq 3 by noting that an infinitesimal unitary transformation can also be used to obtain a differential characterization of a transformation function. The operator \hat{U}

$$\hat{U} = \hat{1} - (i\epsilon/\hbar)\hat{G} \quad (5)$$

and its inverse

$$\hat{U}^{-1} = \hat{1} + (i\epsilon/\hbar)\hat{G} \quad (6)$$

where ϵ denotes an infinitesimal real quantity and \hat{G} is a linear Hermitian operator, induce infinitesimal unitary transformations. In what follows, $\epsilon\hat{G}$ will be represented by the infinitesimal unitary operator \hat{F} , where \hat{F} is referred to as the generator of the transformation. The infinitesimal transformation induced on an observable $\hat{\alpha}$ is defined to be⁴

$$\delta\hat{\alpha} = \hat{\alpha} - \hat{\alpha}' = (i\epsilon/\hbar)[\hat{G}, \hat{\alpha}] = (i/\hbar)[\hat{F}, \hat{\alpha}] \quad (7)$$

and the same transformation when applied to the associated state vector yields

$$\delta|\alpha\rangle = |\alpha'\rangle - |\alpha\rangle = -(i/\hbar)\hat{F}|\alpha\rangle \quad (8)$$

The effect of altering the two commuting sets of position operators at times t_1 and t_2 in the transformation function $\langle q_{r2}, t_2 | q_{r1}, t_1 \rangle$ into $\hat{q}_{r1} - \delta\hat{q}_{r1}$ and $\hat{q}_{r2} - \delta\hat{q}_{r2}$ by the action of the two infinitesimal generating operators $\hat{F}(t_1)$ and $\hat{F}(t_2)$ is given by

$$\delta\langle q_{r2}, t_2 | q_{r1}, t_1 \rangle = \langle \delta q_{r2}, t_2 | q_{r1}, t_1 \rangle + \langle q_{r2}, t_2 | \delta q_{r1}, t_1 \rangle = (i/\hbar)\langle q_{r2}, t_2 | \hat{F}(t_2) - \hat{F}(t_1) | q_{r1}, t_1 \rangle \quad (9)$$

If the parameters of a system are not altered, then the variations of the action integral in eq 3 arises only from infinitesimal changes of the sets of commuting observables at the two times t_1 and t_2 . However, by eq 9, such a transformation is characterized in terms of the generators of infinitesimal unitary transformations $\hat{F}(t_1)$ and $\hat{F}(t_2)$ acting on the two eigenvectors. Thus by comparing eqs 3 and 9 one obtains for such variations the result

$$\delta\hat{\mathcal{W}}_{12} = \hat{F}(t_2) - \hat{F}(t_1) \quad (10)$$

which is the *operator principle of stationary action*. It states that the action integral operator is unaltered by infinitesimal variations in state functions between the times t_1 and t_2 , being affected only by the action of generators at the two time endpoints.

In the principle of stationary action, the variation of the action integral does not vanish as it does in Hamilton's principle, but instead equals the difference in the effects of infinitesimal generators acting at the two time endpoints. This result requires that the variation of the action integral appearing in eqs 3 and 10 be generalized to include the variations of the state functions and of the time at the time endpoints. The principle of stationary action then implies the equation of motion of the systems as obtained in Hamilton's principle, and the endpoint variations define the generators of the infinitesimal canonical transformations which induce changes in the dynamical properties of the system. In this way a single dynamical principle recovers not only the equation of motion, but also defines the observables, their equations of motion, and the Heisenberg commutation relations.

This generalized variation of the action integral may be illustrated and its analogy with the corresponding classical principle made clear by expressing the Lagrangian operator in terms of the commuting set of position operators \hat{q}_{rt} and their time derivatives. A summary of the more complete discussion given in ref 1 is presented here. The action integral operator is

$$\hat{\mathcal{W}}_{12} = \int_{t_1}^{t_2} \hat{\mathcal{L}}(\hat{q}_{rt}, \dot{\hat{q}}_{rt}, t) dt \quad (11)$$

To first order in the infinitesimals, the required generalization of the action integral reduces to the change in $\hat{\mathcal{L}}$ along the varied path between the unvaried time endpoints and the unvaried integrand times the variation in the time at the two time endpoints.¹³ That is

$$\delta\hat{\mathcal{W}}_{12} = \int_{t_1}^{t_2} \delta\hat{\mathcal{L}}(\hat{q}_{rt}, \dot{\hat{q}}_{rt}, t) dt + \hat{\mathcal{L}}(\hat{q}_{rt}, \dot{\hat{q}}_{rt}, t) \delta t|_{t_1}^{t_2} \quad (12)$$

After using an integration by parts to rid the resulting variation in $\hat{\mathcal{L}}$ of the variations $\delta\dot{\hat{q}}_{rt}$, one obtains the result

$$\delta\hat{\mathcal{W}}_{12} = \int_{t_1}^{t_2} \{(\partial\hat{\mathcal{L}}/\partial\hat{q}_{rt}) - d(\partial\hat{\mathcal{L}}/\partial\dot{\hat{q}}_{rt})/dt\} \delta\hat{q}_{rt} dt + \hat{F}(t_2) - \hat{F}(t_1) \quad (13)$$

where the generators are defined in terms of the variations in \hat{q}_r and the time at the time endpoints, and following a Legendre transform of $\hat{\mathcal{L}}$ they may be expressed as

$$\hat{F}(t) = \{(\partial\hat{\mathcal{L}}/\partial\dot{\hat{q}}_{rt})\Delta\hat{q}_{rt} - \hat{H}(\hat{q}_{rt}, \partial\hat{\mathcal{L}}/\partial\dot{\hat{q}}_{rt})\delta t\} \quad (14)$$

The symbol $\Delta\hat{q}_{rt}$ denotes the complete change in the coordinate operator

$$\Delta\hat{q}_{rt} = \delta\hat{q}_{rt} + \dot{\hat{q}}_{rt}\delta t \quad (15)$$

A comparison of eq 13 with the principle of stationary action, eq 10, yields the equation of motion:

$$\delta\hat{\mathcal{L}}/\partial\hat{q}_{rt} = d(\partial\hat{\mathcal{L}}/\partial\dot{\hat{q}}_{rt})/dt \quad (16)$$

since satisfaction of this principle requires that the quantity under the time integral multiplied by the arbitrary variations $\delta\hat{q}_{rt}$ must vanish, as it does in the restricted variation of the action integral where one sets $\delta\hat{\mathcal{W}}_{12} = 0$.

The generator defined in eq 14 is composed of two parts: the temporal generator $-\hat{H}\delta t$ yields the Heisenberg equation of motion for an observable \hat{a} when used in eq 7, while the generator $(\partial\hat{\mathcal{L}}/\partial\dot{\hat{q}}_{rt})\delta\hat{q}_{rt}$ is the generator of purely spatial changes.^{1,13} The use of this latter generator in eq 7 to induce infinitesimal changes in the operators $\delta\hat{q}_{rt}$ and $\hat{p}_{rt} = \partial\hat{\mathcal{L}}/\partial\dot{\hat{q}}_{rt}$ yields the Heisenberg commutation relations.^{1,13} Thus the principle of stationary action provides a complete description of a quantum dynamical system. The demonstration that this principle applies to a properly bounded subsystem of some total system is sufficient to establish the quantum mechanics of a subsystem.

A number of alternative expressions of the principle of stationary action will prove useful in its application to a subsystem. The first is a restatement of eq 10 to give

$$\delta\hat{\mathcal{W}}_{12} = \int_{t_1}^{t_2} (d\hat{F}/dt) dt \quad (17)$$

By dividing both sides of this equation by $t_2 - t_1$ and subjecting the result to the limit $\Delta t \rightarrow 0$, one obtains an expression for the principle of stationary action in terms of a variation of the Lagrange function

$$\delta\hat{\mathcal{L}}[t] = d\hat{F}/dt \quad (18)$$

This result can be equivalently expressed, by using Heisenberg's equation for $d\hat{F}/dt$, as

$$\delta\hat{\mathcal{L}}[t] = (i/\hbar)[\hat{H}, \hat{F}] \quad (19)$$

where it is understood that the variation in $\hat{\mathcal{L}}$ is effected by the action of the infinitesimal generator \hat{F} . Equation 19 is the operational statement of the principle of stationary action.¹ It determines the equations of motion for the observables and the related theorems, such as the Ehrenfest and virial theorems, which determine the mechanics of a given system.

C. Atomic Principle of Stationary Action

The generalization of the principle of stationary action to a subsystem is necessarily stated in the coordinate basis, as the boundary condition is defined in real

space and the Schrödinger representation of the state vector is employed in what follows.

The action integral $\mathcal{W}_{12}[\Psi]$ for the total system is

$$\mathcal{W}_{12}[\Psi] = \int_{t_1}^{t_2} \mathcal{L}[\Psi, t] dt = \int_{t_1}^{t_2} dt \int d\tau L[\Psi, \nabla\Psi, \dot{\Psi}, t] \quad (20)$$

where the Lagrangian integral $\mathcal{L}[\Psi, t]$ is obtained by the integration of the Lagrangian density over the coordinates of all the particles in the system. In the absence of external fields, the Lagrangian density for the system of many particles interacting via a many-particle potential energy operator \hat{V} is

$$L[\Psi, \nabla\Psi, \dot{\Psi}, t] = (i\hbar/2)(\Psi^*\dot{\Psi} - \dot{\Psi}^*\Psi) - (\hbar^2/2m) \sum_i \nabla_i \Psi^* \cdot \nabla_i \Psi - \hat{V}\Psi^*\Psi \quad (21)$$

The variation to first-order of this action integral with respect to the independent variables Ψ and Ψ^* and with $\delta\Psi$ and $\delta\Psi^* = 0$ at the time endpoints, yields for the extremum condition that $\delta\mathcal{W}_{12} = 0$, Schrödinger's equations

$$i\hbar\dot{\Psi} = \hat{H}\Psi \quad \text{and} \quad -i\hbar\dot{\Psi}^* = \hat{H}\Psi^* \quad (22)$$

where the Hamiltonian \hat{H} is given by

$$\hat{H} = -(\hbar^2/2m) \sum_i \nabla_i^2 - \sum_i \sum_\alpha Z_\alpha e^2 (|r_i - X_\alpha|)^{-1} + \sum_{i < j} e^2 (|r_i - r_j|)^{-1} + \sum_{\alpha < \beta} e^2 Z_\alpha Z_\beta (|X_\alpha - X_\beta|)^{-1} \quad (23)$$

Terms of the form $\nabla\Psi^* \cdot \mathbf{n} \delta\Psi$ appear in an integral over the surface of the system when an integration by parts is used to rid the variation in \mathcal{W}_{12} of terms of the form $\delta\nabla\Psi$. Thus to obtain eqs 22 as the Euler equations in the variation of the action integral requires that one either demand that $\delta\Psi$ vanish on the boundaries of the system at infinity or, that the state function satisfies the so-called natural boundary conditions, that $\nabla\Psi \cdot \mathbf{n} = 0$ and $\nabla\Psi^* \cdot \mathbf{n} = 0$ on the same infinite boundaries.

The Lagrangian density and the integrals it defines exhibit an important property at the point of variation where Schrödinger's equations hold, i.e., where $\delta\mathcal{W}_{12} = 0$. Denoting by L° the Lagrangian density obtained at the point of variation, one has, using eqs 22,

$$L^\circ = -(\hbar^2/4m) \sum_i \{ \Psi^* \nabla_i^2 \Psi^* + \Psi \nabla_i^2 \Psi + 2 \nabla_i \Psi^* \cdot \nabla_i \Psi \} \quad (24)$$

This can be further simplified by using the following identity which relates the kinetic energy as it appears in Schrödinger's equation with that appearing in the Lagrangian

$$-(\hbar^2/4m) \sum_i \{ \Psi^* \nabla_i^2 \Psi + \Psi \nabla_i^2 \Psi^* \} = (\hbar/2m) \sum_i \nabla_i \Psi^* \cdot \nabla_i \Psi - (\hbar^2/4m) \sum_i \nabla_i^2 (\Psi^* \Psi) \quad (25)$$

Thus at the point of variation, the Lagrangian density reduces to a sum of single-particle Laplacian operators acting on $\Psi^* \Psi$. Integration of this quantity over the

$$L^\circ = -(\hbar^2/4m) \sum_i \nabla_i^2 (\Psi^* \Psi) \quad (26)$$

coordinates of the particles causes it to vanish since the integration reduces to surface integrals of $\nabla\Psi^* \cdot \mathbf{n}$ and $\nabla\Psi \cdot \mathbf{n}$. Thus the Lagrangian integral at any time t and its associated action integral for any time interval Δt , for a quantum mechanical system described by Schrödinger's equation, must vanish. Because of the

single-particle nature of the operator in eq 26, one can define a related single-particle density $\mathcal{L}^\circ(\mathbf{r}, t)$. This is accomplished by a summation over the spins of all the electrons, followed by an integration over all coordinates but those of one electron, a process denoted by the symbol $\int d\tau'$. When this result is multiplied by N , the number of electrons in the system, this is the same procedure used to obtain the charge density $\rho(\mathbf{r}, t)$ from $\Psi^* \Psi$. The density obtained in this manner is

$$\mathcal{L}^\circ(\mathbf{r}, t) = \int d\tau' L^\circ = -(\hbar^2/4mN) \nabla^2 \rho(\mathbf{r}, t) \quad (27)$$

Because of the natural boundary condition that $\Psi^* \nabla \cdot \Psi \cdot \mathbf{n}$ and $\Psi \nabla \cdot \Psi^* \cdot \mathbf{n}$ vanish on the boundaries of the system at infinity, the vanishing of the Lagrangian integral $\mathcal{L}^\circ[\Psi, t]$ can be taken to be a consequence of the vanishing of the flux in the gradient vector field of the charge density at the infinite boundary of the system, since

$$\mathcal{L}^\circ[\Psi, t] = -(\hbar^2/4mN) \int d\mathbf{r} \nabla^2 \rho(\mathbf{r}, t) = -(\hbar^2/4mN) \oint d\mathbf{S}(\mathbf{r}, t) \nabla \rho(\mathbf{r}, t) \cdot \mathbf{n}(\mathbf{r}, t) = 0 \quad (28)$$

In anticipation of the identification of a quantum subsystem with an atom, the subsystem Lagrangian and action integrals are referred to as atomic integrals. The atomic Lagrangian integral is obtained from the Lagrangian density in eq 21 by the summing of all spins and integration over the coordinates of all electrons but one, followed by the integration of the final electronic coordinate, denoted by \mathbf{r} , over the basin of the atom Ω , as indicated in eq 29. Correspondingly, the atomic

$$\mathcal{L}[\Psi, \Omega, t] = \int_\Omega d\mathbf{r} \int d\tau' L(\Psi, \nabla\Psi, \dot{\Psi}, t) \quad (29)$$

action integral is

$$\mathcal{W}_{12}[\Psi, \Omega] = \int_{t_1}^{t_2} dt \mathcal{L}[\Psi, \Omega, t] \quad (30)$$

It is clear from eq 28 that at the point of variation where eq 26 is obtained, the atomic Lagrangian and action integrals will also vanish, as a consequence of the zero flux surface condition (eq 1). It is a consequence of this equivalence in properties of $\mathcal{L}^\circ[\Psi, t]$ and $\mathcal{L}^\circ[\Psi, \Omega, t]$ that the action integrals for the total system and each of the atoms which comprise it have similar variational properties.

The generalized variation of the atomic action integral in the manner outlined in eq 12, and including a variation of the surface bounding the atom, yields the atomic statements of the quantum action principle and principle of stationary action, if one imposes a particular variational constraint. This constraint amounts to delimiting the class of possible subsystems to those which satisfy the zero flux surface condition given in eq 1. As detailed in ref 1 and 2 this constraint is imposed by demanding the fulfillment of the condition given in eq 31.

$$\delta \left\{ \int_\Omega \nabla^2 \rho(\mathbf{r}, t) d\mathbf{r} \right\} = 0 \quad (31)$$

To impose the variational constraint given in eq 31 and thereby define a particular class of open system, one must vary the surface of the subsystem. This requirement necessarily leads to the relaxation of the usual variational constraint that $\delta\Psi$ vanish at all

boundaries of the system and at the time endpoints, the constraint imposed on the variation of the action integral in Hamilton's principle to obtain the equations of motion. Thus the variation of Ψ in the atomic action integral with the necessary retention of $\delta\Psi$ on the boundaries and hence at the time endpoints necessarily leads to the generalization of the variation of the action integral that yields Schwinger's principle of stationary action.

Such a generalized variation of the atomic action integral given in eq 30 is detailed elsewhere^{1,2} and the result is

$$\delta\mathcal{W}_{12}[\Psi, \Omega] = \int_{t_1}^{t_2} dt \oint dS(\Omega, \mathbf{r}) (i\hbar/2) \left\{ \delta_{\Psi} \mathbf{j}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + cc - \int d\tau' (\delta S/\delta t) \Psi^* \delta\Psi + cc \right\} + \left\{ (i\hbar/2) \int_{\Omega} d\mathbf{r} \int d\tau' \Psi^* \delta\Psi + cc \right\} \Big|_{t_1}^{t_2} \quad (32)$$

The quantity \mathbf{j} is the vector current and it is defined as

$$\mathbf{j}(\mathbf{r}) = (\hbar/2mi) \int d\tau' (\Psi^* \nabla \Psi - \nabla \Psi^* \Psi) \quad (33)$$

Its variation $\delta_{\Psi} \mathbf{j}(\mathbf{r})$ as it appears in eq 32 is

$$\delta_{\Psi} \mathbf{j}(\mathbf{r}) = (\hbar/2mi) \int d\tau' (\Psi^* \delta \nabla \Psi - \nabla \Psi^* \delta \Psi) \quad (34)$$

This term is obtained by combining the surface term arising from the variations with respect to $\nabla \Psi$, with the surface term arising from the imposition of the variational constraint (eq 31). Thus the variation of the surface of the subsystem together with the restriction that the subsystem be bounded by a zero flux surface causes the quantum mechanical current density \mathbf{j} to appear in the variation of the action integral, a term whose presence is a necessary requirement for the description of the properties of an open system.¹

By proceeding as before, the variations in the state function are replaced by operators which act as generators of infinitesimal unitary transformations. That is, $\delta\Psi = (-i/\hbar) \hat{F} \Psi$ where \hat{F} is an infinitesimal Hermitian operator ($\hat{F} = \epsilon \hat{G}$). Introducing the notion of generators into the result for the variation of the atomic action integral yields

$$\Delta\mathcal{W}_{12}[\Psi, \Omega] = F(\Omega, t_2) - F(\Omega, t_1) - \int_{t_1}^{t_2} dt \oint dS(\Omega, \mathbf{r}) \{ (\delta S/\delta t) \rho_{\mathbf{F}} - [(1/2)(\mathbf{J}_{\mathbf{F}}(\mathbf{r}) + cc)] \cdot \mathbf{n}(\mathbf{r}) \} \quad (35)$$

The result is expressed in terms of property averages for N electrons, so $\Delta\mathcal{W} = N\delta\mathcal{W}$. The atomic averages of the generator at the time endpoints $F(\Omega, t)$ and the corresponding property density $\rho_{\mathbf{F}}$ are defined as

$$F(\Omega, t) = \int_{\Omega} d\mathbf{r} \rho_{\mathbf{F}}(\mathbf{r}, t) = (N/2) \int_{\Omega} d\mathbf{r} \int d\tau' \{ \Psi^* \hat{F} \Psi + (\hat{F} \Psi)^* \Psi \} \equiv \langle \hat{F} \rangle_{\Omega} \quad (36)$$

and

$$\rho_{\mathbf{F}}(\mathbf{r}, t) = (N/2) \int d\tau' \{ \Psi^* \hat{F} \Psi + (\hat{F} \Psi)^* \Psi \} \quad (37)$$

The contribution to the current density for the observable \hat{F} is

$$\mathbf{J}_{\mathbf{F}}(\mathbf{r}, t) = (N\hbar/2mi) \int d\tau' \{ \Psi^* \nabla (\hat{F} \Psi) - (\nabla \Psi^*) \hat{F} \Psi \} \quad (38)$$

In the case that \hat{F} is a vector, $\mathbf{J}_{\mathbf{F}}$ is a second-rank tensor.

To reexpress the result given for $\Delta\mathcal{W}$ in eq 35 in the form analogous to eq 17, we need the Heisenberg equation of motion for $F(\Omega, t)$. This is obtained by using eq 22 for Schrödinger's equation of motion to give

$$dF(\Omega, t)/dt = (1/2) \{ (i/\hbar) \langle [\hat{H}, \hat{F}] \rangle_{\Omega} + cc \} + \oint dS(\Omega, \mathbf{r}) \{ (\delta S/\delta t) \rho_{\mathbf{F}}(\mathbf{r}) - [(1/2)(\mathbf{J}_{\mathbf{F}}(\mathbf{r}) + cc)] \cdot \mathbf{n}(\mathbf{r}) \} \quad (39)$$

Comparison of this expression with that for the change in action in eq 35 shows that the terms subtracted from the endpoint averages of the generator are just those which account for the surface contributions to this difference, integrated over the time-like surface connecting the two time endpoints. Thus what remains is the difference in the values of the generator at the two time endpoints averaged over the interior of the subsystem, the essence of the principle of stationary action. The change in the atomic action integral can be expressed entirely in terms of the interior averages of the generator as

$$\Delta\mathcal{W}_{12}[\Psi, \Omega] = \int_{t_1}^{t_2} dt \{ (i/\hbar) \langle [\hat{H}, \hat{F}] \rangle_{\Omega} + cc \} / 2 \quad (40)$$

a result equivalent to the statements of stationary action obtained for the total system, eq 17. The principle of stationary action for a subsystem can be expressed for an infinitesimal time interval in terms of a variation of the Lagrangian integral, as given in eq 19 for the total system. For the atomic Lagrangian this statement is

$$\delta\mathcal{L}[\Psi, \Omega, t] = (1/2) \{ (i/\hbar) \langle [\hat{H}, \hat{F}] \rangle_{\Omega} + cc \} \quad (41)$$

For stationary state, the Lagrangian integral, apart from the presence of a Lagrange multiplier to insure normalization of ψ , reduces to the energy functional used by Schrödinger¹⁴ in the derivation of the stationary-state wave equation. For an atom in a molecule in a stationary state this energy functional is

$$\mathcal{G}[\psi, \Omega] = \int_{\Omega} d\mathbf{r} \int d\tau' \{ (\hbar^2/2m) \sum_i \nabla_i \psi^* \cdot \nabla_i \psi + (\hat{V} + \lambda) \psi^* \psi \} \quad (42)$$

where \hat{V} denotes the full many-electron potential energy operator, and λ , the variational constraint on the normalization of ψ , is identified with $-E$, the negative of the total energy. The atomic statement of the stationary action in terms of this functional is^{1,3}

$$\delta\mathcal{G}[\psi, \Omega] = -(1/2) \{ (i/\hbar) \langle [\hat{H}, \hat{F}] \rangle_{\Omega} + cc \} \quad (43)$$

The derivation of the principle of stationary action for an atom in a molecule in the time-dependent case or in a stationary state, or in the presence of an electromagnetic field,¹⁵ yields the corresponding Schrödinger equation of motion for the total system, identifies the observables with the variations of the state function, defines their average values, and gives their equations of motion. The statements of the atomic principle of stationary action as expressed in terms of variations in $\mathcal{L}[\Psi, \Omega]$ and $\mathcal{G}[\psi, \Omega]$ are variational statements of Heisenberg's equation of motion and of the hypervirial theorem for a generator \hat{F} , respectively. They yield the theorems and relations governing the mechanics of an atom in a molecule. Because of the variational derivation of these atomic statements of the principle of stationary action, they are satisfied by the

same class of approximate wave functions, RHF and UHF, as satisfy the derived theorems, such as the generalized Hellmann–Feynman and hypervirial theorems, for a total system. The reader is referred to Epstein's book on the variational method in quantum chemistry for a discussion of the validity of these theorems for a total system.^{16a}

Equations 40–42 represent a generalization of quantum mechanics. They enable one to obtain a quantum mechanical description of the properties of any region of space bounded by a surface of zero flux in the gradient vector field of the charge density. In this sense, the mechanics of a total system is obtained as a special case of these more general equations.

D. Open Systems and Fluxes in Vector Currents

Corresponding to eq 35 for the variation in $\mathcal{W}_{12}[\Psi, \Omega]$, the subsystem projection of the variation of the energy functional for a stationary state is equal to the infinitesimal flux in the current density through the surface of the subsystem, eq 44.

$$\delta\mathcal{G}[\psi, \Omega] = -(1/2) \left\{ \oint dS(\Omega, \mathbf{r}) \mathbf{j}_F(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + cc \right\} \quad (44)$$

The same surface integral appears in the subsystem statement of the hypervirial theorem^{16b} (the stationary state analogue of eq 39)

$$\{(i/\hbar) \langle \psi, [\hat{H}, \hat{F}] \psi \rangle_{\Omega} + cc\} = \left\{ \oint dS(\Omega, \mathbf{r}) \mathbf{j}_F(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + cc \right\} \quad (45)$$

and because of the dependence of the both quantities on the current flux one obtains the atomic statement of the principle of stationary action for a stationary state as given in eq 43. This principle forms the basis for the discussion of the mechanics of an atom in a molecule.

The nonvanishing of the flux of a quantum mechanical current is what distinguishes the mechanics of a subsystem from that of the total system in a stationary state. The flux in the current density will vanish through any surface on which ψ satisfies the natural boundary condition, $\nabla\psi \cdot \mathbf{n} = 0$, a condition which is satisfied by a system with boundaries at infinity. Thus for a total system the energy is stationary in the usual sense, $\delta\mathcal{G}[\psi] = 0$, and the usual form of the hypervirial theorem is obtained with the vanishing of the commutator average

$$\langle \psi, [\hat{H}, \hat{F}] \psi \rangle = 0 \quad (46)$$

Equation 46 is a consequence of the Hermitian property of \hat{H} , a property not enjoyed by a subsystem. The difference between the average of the Hamiltonian and its Hermitian conjugate equals the flux in the current density through the surface bounding the system.²

When an observable \hat{G} does not possess a sharp value in a stationary state, i.e., its commutator with H does not vanish, there is a nonvanishing current whose net outflow from any infinitesimal region is determined by the corresponding commutator

$$\nabla \cdot \mathbf{j}_G = (i/\hbar) \psi^* [\hat{H}, \hat{G}] \psi \quad (47)$$

The energy is not stationary over a volume Ω in such a situation, its change being determined by the flux of the current of \hat{G} through the surface, eq 44, or equiva-

lently, by the average of the commutator, eq 43. From this discussion it is clear that \hat{H} retains the property of a Hermiticity over a subsystem in the case

$$\int_{\Omega} \psi^* \hat{H} (\hat{G}\psi) d\tau = \int_{\Omega} \hat{H} \psi^* (\hat{G}\psi) d\tau$$

only when \hat{H} and \hat{G} commute.

In summary, a subsystem is an open system, free to exchange charge and momentum with its environment. Thus the current density \mathbf{j}_G for any observable \hat{G} is of particular importance in the mechanics of a subsystem, since a nonvanishing flux in this current implies a fluctuation in the subsystem average value of the property G . Because of the presence of the surface term in eq 45, the hypervirial theorem for a subsystem leads to important physical results which have no counterpart for the total system.

E. Consequences of the Zero Flux Boundary Condition

The fundamental result of the theory, as contained in eq 40 for a time-dependent system and in eq 43 for a stationary state, is that the properties of a region of space bounded by a surface of zero flux in the gradient vector field of the charge density are predicted by quantum mechanics. These are the only physically realizable quantum subsystems defined by the action principle.^{1,2} The question still to be answered is whether such regions exist and whether they correspond to the atoms of chemistry. Affirmative answers to these questions are obtained as a consequence of the principal topological property exhibited by the electronic charge distribution—that in general, it exhibits local maxima only at the positions of the nuclei. This is illustrated in Figure 1 by the charge density for the molecule SF_6 which exhibits behavior that is typical of the vast majority of systems. Shown is a plot of the trajectories traced out by the gradient vectors of the charge density, each vector originating at infinity. Every trajectory or gradient path terminates at a nucleus and this behavior is found in all three dimensions. The nuclei are the attractors of the gradient vector field of the charge density and the result is a partitioning of the total space of a system into a set of disjointed mononuclear regions or basins, a basin being the open region of space traversed by all of the trajectories of $\nabla\rho$ terminating at a given attractor. This is a partitioning into atoms where an atom is defined as the union of an attractor and its basin.^{1,6} It is clear from the figure that each such region is bounded by a zero flux surface in $\nabla\rho$ and that its properties are therefore, predicted by quantum mechanics.

Every trajectory of $\nabla\rho$ originates and terminates at a critical point in this field, a point where $\nabla\rho = 0$. A critical point, with coordinate \mathbf{r}_c , is characterized by the number of zero eigenvalues of the associated Hessian matrix, the matrix of second derivatives of $\rho(\mathbf{r}_c)$ which determines its rank σ , and the algebraic sum of their signs which determine its signature λ . The local maxima, as found at the positions of the nuclei, behave topologically as do $(\sigma, \lambda) = (3, -3)$ critical points.⁶ There is a $(3, -1)$ critical point between sulfur and each fluorine nucleus, but not between the fluorines themselves. The eigenvectors associated with the two negative eigenvalues of such a critical point generate a set of gradient

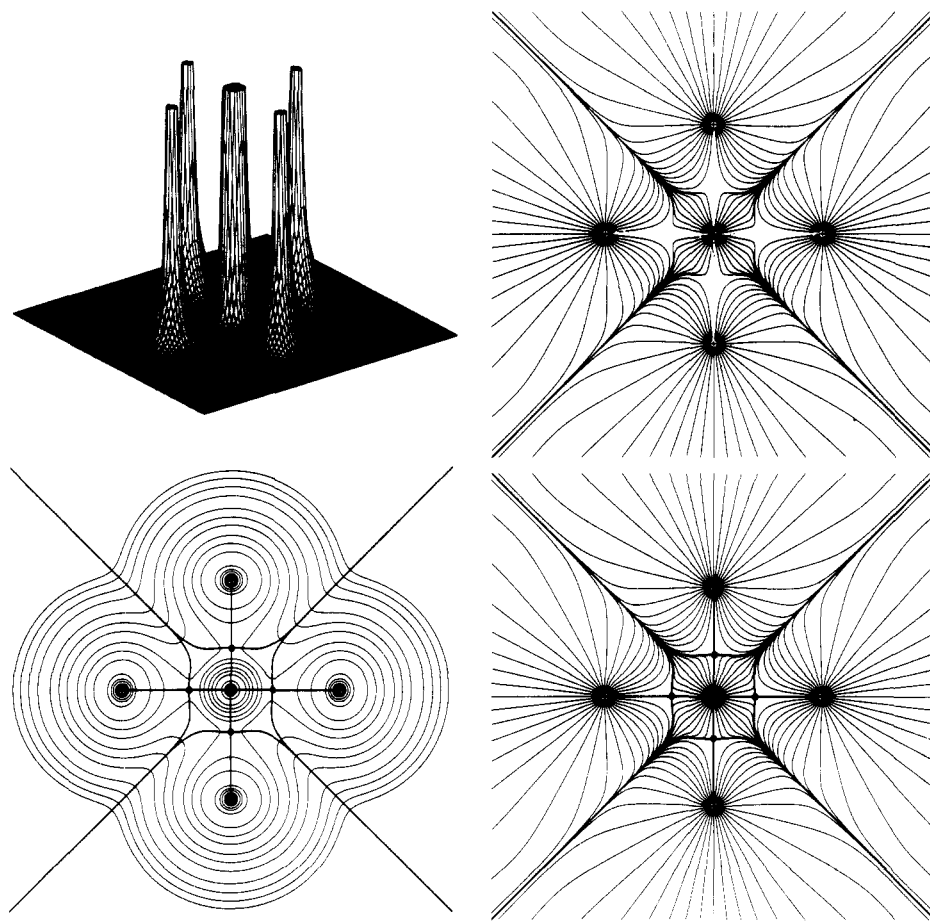


Figure 1. Displays of the charge density in the form of a relief (upper) and contour maps (left-hand side) and of the gradient vector field of the charge density (right-hand side) for a symmetry plane containing the sulfur and four of the fluorine nuclei in SF_6 . The (3,-1) critical points (dots) are indicated on the lower diagrams. The upper gradient vector field map shows only those trajectories which originate at infinity and terminate at the nuclei whose positions are denoted by crosses. The property of a nucleus to act as an attractor in this field leads to a disjoint partitioning of space into a set of atomic basins each of which is bounded by a zero flux surface (eq 1). The lower diagram also shows (in bold) the pair of gradient paths which originate at each (3,-1) critical point and define the atomic interaction lines, and the pair of gradient paths of the set of paths which terminate at each critical point and define the intersection of the interatomic surface with this plane. The molecular graph consists of S octahedrally linked by bond paths to six F nuclei. The outer contour of the charge density equals 0.001 au. The succeeding contours increase in value in the order 2×10^n , 4×10^n , 8×10^n with n beginning at -3 and increasing by unity. The same set of contours is used throughout the paper.

paths all of which terminate at the critical point and define a two-dimensional manifold in three-dimensional space—an interatomic surface, Figure 1. Each atom is bounded by one or more such surfaces, which are clearly zero flux surfaces, since $\nabla\rho$ is tangent to a trajectory at any point on the surface.

The positive eigenvalue of a (3,-1) critical point defines a unique pair of eigenvectors each of which originates at the critical point and terminates at a neighboring nucleus. They define a line linking the nuclei whose basins share an interatomic surface and along which the charge density is a maximum with respect to any neighboring line. Such a line is called an atomic interaction line,⁸ Figure 1. The presence of such a line linking two nuclei in a molecule which exists in a minimum energy geometry implies that the two atoms are bonded to one another and in this instance the line is called a bond path.^{8,17} This topic is expanded upon in section V, which presents the development of the theory of molecular structure.

The discussion of the general topological properties of the charge distribution has served to demonstrate that the application of the boundary condition for the

definition of a quantum subsystem yields a partitioning of a molecule or solid into a set of basins each with a single nuclear attractor, a partitioning into atoms. In the great majority of cases, the nuclei are the sole attractors of a charge density. Quantum mechanics states that the properties of a total system are determined by the properties of these individual forms and the success of the atomic concept in the classification and prediction of chemical knowledge is accounted for by this congruence in a dominant physical form and its predicted quantum mechanical consequences. It is possible in some systems however, to observe local maxima in the charge density without the presence of a nuclear attractor.^{18,19} In such cases the zero flux boundary condition is still satisfied and quantum mechanics identifies such nonnuclear attractors or pseudoatoms as having a definable set of properties which contribute to the properties of the total system. Examples of such pseudoatoms are found in clusters of group I atoms. The quantum theory of structure describes these systems as consisting of positively charged atomic cores with very localized charge distributions bound by an intermeshed network of negatively charged pseudoa-

toms. The pseudoatoms are regions of very diffuse and loosely bound electronic charge density. The atomic cores are not linked to one another directly, but only through intervening pseudoatoms which form a connected network throughout the cluster. The absolute value of ρ at a maximum in a pseudoatom and the extent by which it exceeds the values of ρ at neighboring critical points is extraordinarily small and, in accordance with the uncertainty principle, the electron density of the pseudoatoms is loosely bound and unconfined with a very low kinetic energy per electron. It is the pseudoatoms which are responsible for the binding and for the conducting properties of these systems.¹⁹

These examples illustrate the ability of the quantum theory of structure to always identify those components of a system that are responsible for determining its properties at the atomic level, and we now pursue the development of the mechanics of an atom in a molecule.

III. Definition of Atomic Properties

A. Variational Derivation of Atomic Force and Virial Theorems

The present discussion will be limited to systems in stationary states. The derivations of the same theorems for the general time dependent case can be found in ref 1 and 2. The atomic statement of the principle of stationary action, eq 43, yields a variational derivation of the hypervirial theorem for any observable \hat{F} , a derivation which applies only to a region of space Ω bounded by a surface satisfying the condition of zero flux in the gradient vector field of the charge density (eq 1). This principle will be used to obtain a variational definition of the force acting on an atom in a molecule and of the atomic virial theorem. The derivations will illustrate the important point that the definition of an atomic property follows directly from the atomic statement of stationary action. A full discussion appears in ref 1.

The Hamiltonian is taken to be the many-electron, fixed-nucleus Hamiltonian given in eq 23. The symbol \hat{V} will be used to denote the complete potential energy operator, the sum of the electron-nuclear \hat{V}_{en} , electron-electron \hat{V}_{ee} , and nuclear-nuclear \hat{V}_{nn} potential energy operators

$$\hat{V} = \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn} \quad (48)$$

The commutator of this Hamiltonian and the momentum operator of a single electron is equal to $i\hbar\nabla\hat{V}$.

The method of obtaining the subsystem average of the commutator and hence of the force acting on the atom Ω is determined by the definition of the functional $\mathcal{G}[\psi, \Omega]$ via eq 43. It has been demonstrated that the mode of integration used in the definition of the subsystem functional $\mathcal{G}[\psi, \Omega]$ (eq 42) is the only one which leads to a physically realizable boundary condition.¹ Because of eq 43, this same mode of integration (see eq 36) defines the atomic average of the commutator and thus of the atomic force, $F(\Omega)$

$$(N/2)\{(i/\hbar)\langle\psi, [\hat{H}, \hat{p}_1]\psi\rangle_{\Omega} + cc\} = N \int_{\Omega} dr_1 \int d\tau' \{\psi^*(-\nabla_1 \hat{V})\psi\} = F(\Omega) \quad (49)$$

The result is multiplied by N , the total number of electrons, in the definition of an atomic property. The

mode of integration indicated by $N \int d\tau' \psi^* \psi$ as used in this definition of an atomic average is the same as that employed in the definition of the electronic charge density, $\rho(\mathbf{r})$. It implies a summation over all spins and an integration of the spatial coordinations of all electron but one. From this point on the subscript "1" will be dropped from the coordinates of the electron whose coordinates are integrated only over Ω and all single-particle, unlabeled coordinates and operators will refer to this electron.

The corresponding variation of $\mathcal{G}[\psi, \Omega]$, subject to the constraint which gives rise to the zero flux boundary condition (eq 1) is given by the surface integral in eq 50

$$(N/2) \left\{ \oint dS(\Omega, \mathbf{r}) j_p(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) + cc \right\} = - \oint dS(\Omega, \mathbf{r}) \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \quad (50)$$

where $\vec{\sigma}(\mathbf{r})$ is the quantum mechanical stress tensor. It is defined as

$$\vec{\sigma}(\mathbf{r}) = (N\hbar^2/4m) \int d\tau \{ \nabla(\nabla\psi^*)\psi + \psi^*\nabla\nabla\psi - \nabla\psi^*\nabla\psi - \nabla\psi\nabla\psi^* \} \quad (51)$$

a result which may be expressed in terms of the one-electron density matrix $\Gamma^{(1)}$ as

$$\vec{\sigma}(\mathbf{r}) = (\hbar^2/4m) \{ (\nabla\nabla + \nabla'\nabla') - (\nabla\nabla' + \nabla'\nabla) \} \Gamma^{(1)}(\mathbf{r}, \mathbf{r}')|_{\mathbf{r}=\mathbf{r}'} \quad (52)$$

The stress tensor is a symmetric dyadic. It has the dimensions of pressure, force/unit area, or equivalently of an energy density. The quantum stress tensor plays a dominant role in the description of the mechanical properties of an atom in a molecule and in the local mechanics of the charge density.

Combining eqs 49 and 50 yields eq 53, the atomic force law for a stationary state^{1,20}

$$F(\Omega) = - \oint dS(\Omega, \mathbf{r}) \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \quad (53)$$

The force may be equivalently expressed by using Gauss's theorem as an integration of the force density $-\nabla \cdot \vec{\sigma}(\mathbf{r})$ over the basin of the atom

$$F(\Omega) = N \int_{\Omega} d\tau \int d\tau' \psi^*(-\nabla\hat{V})\psi = - \int_{\Omega} d\tau \nabla \cdot \vec{\sigma}(\mathbf{r}) \quad (54)$$

Equation 53 has a classical analogue which states that the force exerted on the matter contained in a region Ω is equal to the negative of the pressure acting on each element of the surface bounding the region. A local form of the force law is readily obtained from the time derivative of the current density, and for a stationary state the result is

$$F(\mathbf{r}) = N \int d\tau' \psi^*(-\nabla\hat{V})\psi = -\nabla \cdot \vec{\sigma}(\mathbf{r}) \quad (55)$$

which is clearly the differential form of the integrated force law in eq 54. The integrated and differential force laws have a number of important consequences which are now explored.

The potential energy operator \hat{V} whose gradient is averaged in eq 49 and 55 is the many-particle operator defined in eq 48. The operator $-\nabla\hat{V}$, eq 56, is the force

exerted at the position \mathbf{r} of electron 1 by all of the other electrons and the nuclei in the system, each of the other particles being held fixed in some arbitrary configuration ($\nabla \equiv \nabla_1$ and $\mathbf{r} \equiv \mathbf{r}_1$)

$$\nabla_1 \hat{V} = \sum_{\alpha} Z_{\alpha} e^2 \nabla_1 (|\mathbf{r}_1 - X_{\alpha}|)^{-1} - \sum_{j>1} e^2 \nabla_1 (|\mathbf{r}_1 - \mathbf{r}_j|)^{-1} = -e^2 \sum_{\alpha} Z_{\alpha} \frac{(\mathbf{r}_1 - X_{\alpha})}{|\mathbf{r}_1 - X_{\alpha}|^3} + e^2 \sum_{j>1} \frac{(\mathbf{r}_1 - \mathbf{r}_j)}{|\mathbf{r}_1 - \mathbf{r}_j|^3} \quad (56)$$

The integration implied by $d\tau'$ in eq 55 averages this force on the electron at \mathbf{r} over the motions (i.e., positions) of all of the remaining particles in the system, and the result is *the force density* $F(\mathbf{r})$, *the force exerted on the electron at \mathbf{r} by the average distribution of the remaining particles in the total system*. Integration of this force density over the basin of the atom Ω then yields the average electronic or *Ehrenfest force* exerted on the atom in the system. Even though the force operator $-\nabla \hat{V}$ involves the coordinates of all the particles in the system, and includes their mutual interaction, the mode of integration employed in eq 55 yields a corresponding density in real space whose integration over an atom with a boundary defined in real space yields the force acting on the atom (eq 54).

The direct evaluation of the average value of this operator requires the information contained in the two-electron density matrix, yet according to eq 53 and 55, this force, in both its differential and integrated forms, is determined by the stress tensor which requires only the one-electron density matrix for its evaluation. One can view eq 55 as a statement that the forces acting on a particle arising from the electrostatic interactions between the particles and describable in terms of the gradient of a potential energy operator are balanced by a force $-\nabla \cdot \vec{\sigma}$, which is purely quantum in origin. The virial of the Ehrenfest force, which determines the potential energy of the electrons, is also describable in terms of the stress tensor $\vec{\sigma}$, and thus *the mechanics of a quantum system is determined by the information contained in the one-electron density matrix*.

An atomic surface for an atom Ω is the union of some number of interatomic surfaces denoted by $S(\Omega|\Omega', \mathbf{r})$, there being one such surface for each bonded neighbor Ω' . Thus the force acting on an atom is given in eq 54 can be expressed as a sum of surface terms

$$F(\Omega) = -\sum_{\Omega' \neq \Omega} \oint dS(\Omega|\Omega', \mathbf{r}) \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \quad (57)$$

The sum in this equation runs over the surfaces shared with atoms bonded to Ω , the atoms linked to Ω by atomic interaction lines. This expression for the force acting on an atom provides the physical basis for the model in which a molecule is viewed as a set of interacting atoms. It isolates, through the definition of structure, the set of atomic interactions which determines the force acting on each atom in a molecule for any configuration of the nuclei.

We now consider the use of the virial operator $\mathbf{r} \cdot \mathbf{p}$ in the atomic statement of the principle of stationary action eq 43, to obtain the atomic statement of the virial theorem. The virial theorem may be obtained by a scaling of the electronic coordinates,²¹ and the use of the virial operator as the generator of an infinitesimal unitary transformation is indeed equivalent to a scaling of the electronic coordinate \mathbf{r} .^{1,2}

Multiplication of the commutator average appearing in eq 45 by $N/2$ for $\hat{F} = \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}$ yields the result

$$(N/2) \{ (i/\hbar) \langle \psi, [\hat{H}, \hat{\mathbf{r}} \cdot \hat{\mathbf{p}}] \psi \rangle_{\Omega} + \text{cc} \} = 2N \int_{\Omega} d\mathbf{r} \int d\tau' (-\hbar^2/4m) \{ \psi^* \nabla^2 \psi + (\nabla^2 \psi^*) \psi \} + N \int_{\Omega} d\mathbf{r} \int d\tau' \psi^* (-\mathbf{r} \cdot \nabla \hat{V}) \psi = 2T(\Omega) + \mathcal{V}_b(\Omega) \quad (58)$$

The first term is twice the average electronic kinetic energy of the atom $T(\Omega)$ expressed in terms of the usual Laplacian operator. The second term, arising from the commutator and labeled $\mathcal{V}_b(\Omega)$, is the integrated average of the virial of the Ehrenfest force acting on an electron in the basin of the atom

$$\mathcal{V}_b(\Omega) = N \int_{\Omega} d\mathbf{r} \int d\tau' \psi^* (-\mathbf{r} \cdot \nabla \hat{V}) \psi \quad (59)$$

Starting from the identity given in eq 25 one may define two kinetic energy densities both of which integrate to the average kinetic energy when integrated over all space. Thus

$$-(\hbar^2/4m) N \int d\tau' \{ \psi^* \nabla^2 \psi + \psi \nabla^2 \psi^* \} = (\hbar^2/2m) N \int d\tau' \nabla \psi^* \cdot \nabla \psi - (\hbar^2/4m) N \int d\tau' \nabla^2 (\psi^* \psi) \quad (60)$$

Equation 60 may be expressed in symbols as

$$K(\mathbf{r}) = G(\mathbf{r}) + L(\mathbf{r}) \quad (61)$$

Integration of the final coordinate \mathbf{r} in eq 61 over a region of space Ω yields

$$\int_{\Omega} K(\mathbf{r}) d\mathbf{r} = \int_{\Omega} G(\mathbf{r}) d\mathbf{r} - (\hbar^2/4m) \int_{\Omega} \nabla \cdot \nabla \rho(\mathbf{r}) d\mathbf{r} \quad (62)$$

or

$$K(\Omega) = G(\Omega) - (\hbar^2/4m) \oint dS(\Omega) \nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = G(\Omega) + L(\Omega) \quad (63)$$

Because of the zero flux surface condition (eq 1) the term $L(\Omega)$ vanishes when the integration in eq 63 is carried out over an atomic basin. Thus for a quantum subsystem

$$K(\Omega) = G(\Omega) = T(\Omega) \quad (64)$$

as found for the total system and $T(\Omega)$ is a well-defined quantity.

The variation in $\mathcal{G}[\psi, \Omega]$ caused by the generator $\hat{\mathbf{r}} \cdot \hat{\mathbf{p}}$ is given by the surface integral in eq 65

$$(N/2) \left\{ \oint dS(\Omega, \mathbf{r}) \mathbf{j}_{\mathbf{r}, \mathbf{p}} \cdot \mathbf{n}(\mathbf{r}) + \text{cc} \right\} = -(N\hbar^2/4m) \left\{ \oint dS(\Omega, \mathbf{r}) \int d\tau' [\psi^* \nabla(\mathbf{r} \cdot \nabla \psi) - \nabla \psi^*(\mathbf{r} \cdot \nabla \psi) + \psi \nabla(\mathbf{r} \cdot \nabla \psi^*) - \nabla \psi(\mathbf{r} \cdot \nabla \psi^*)] \cdot \mathbf{n}(\mathbf{r}) \right\} - \oint dS(\Omega, \mathbf{r}) \mathbf{r} \cdot \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) - (\hbar^2/4m) \oint dS(\Omega, \mathbf{r}) \nabla \rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \quad (65)$$

where the final line is obtained through the use of the identity $\nabla(\mathbf{r} \cdot \nabla \psi) = \nabla \psi + \mathbf{r} \cdot \nabla \nabla \psi$. The negative of the first term on the right-hand side of eq 65 is labeled $\mathcal{V}_s(\Omega)$ and is the virial of the Ehrenfest forces exerted on the surface of the atom. The quantity $\vec{\sigma} \cdot \mathbf{n}$ is the outwardly directed force per unit area of surface and $\mathbf{r} \cdot \vec{\sigma} \cdot \mathbf{n}$ is the virial of this force

$$\mathcal{V}_s(\Omega) = \oint dS(\Omega, \mathbf{r}) \mathbf{r} \cdot \vec{\sigma}(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \quad (66)$$

The second term in eq 65 is $L(\Omega)$ as defined in eq 63. Equating the commutator and surface results followed by some rearranging of terms yields

$$-2T(\Omega) = \mathcal{V}_b(\Omega) + \mathcal{V}_s(\Omega) + L(\Omega) \quad (67)$$

Since the atom Ω is bounded by a surface of zero flux, $L(\Omega) = 0$ and one obtains the atomic statement of the virial theorem

$$-2T(\Omega) = \mathcal{V}_b(\Omega) + \mathcal{V}_s(\Omega) \quad (68)$$

or

$$-2T(\Omega) = \mathcal{V}(\Omega) \quad (69)$$

where $\mathcal{V}(\Omega)$, the sum of the surface and basin terms, is the total virial for the atom. While the partitioning of the virial into basin and surface contributions is dependent upon the choice of region (an origin can always be found which causes the surface virial to vanish), the value of the total virial $\mathcal{V}(\Omega)$ is, as evident from its equality with twice the kinetic energy, independent of this choice.

Equation 69 is identical in form with the virial theorem for a total system—the negative of twice the average kinetic energy of the electrons, equals the virial of the forces exerted on them. It is worthwhile here to summarize the ways in which this result is dependent upon the zero flux boundary condition (eq 1): (a) The use of the principle of stationary action to obtain a variational derivation of this theorem is restricted to a region satisfying eq 1. (b) Satisfaction of eq 1 insures the vanishing of the term $L(\Omega)$ which arises from the surface flux of the current density $\mathbf{j}_{\mathbf{r},\mathbf{p}}$. (c) The vanishing of $L(\Omega)$ is also necessary for the kinetic energy $T(\Omega)$ to be well defined. There is no statement corresponding to eq 69, variational or otherwise, for a subsystem with arbitrary boundaries.

For a stationary state, a local statement of the virial theorem can be obtained by using the identity

$$\nabla \cdot (\mathbf{r} \cdot \vec{\sigma}) = Tr \vec{\sigma} + \mathbf{r} \cdot \nabla \cdot \vec{\sigma} \quad (70)$$

The trace of the stress tensor is given in terms of the kinetic energy densities defined in eq 63 by

$$Tr \vec{\sigma}(r) = -K(r) - G(r) \quad (71)$$

or equivalently as

$$Tr \vec{\sigma}(r) = -2G(r) - L(r) \quad (72)$$

and substituting this final result into eq 70 and rearranging yields

$$-2G(r) = -\mathbf{r} \cdot \nabla \cdot \vec{\sigma} + \nabla \cdot (\mathbf{r} \cdot \vec{\sigma}) - (\hbar^2/4m) \nabla^2 \rho(r) \quad (73)$$

For a stationary state the local virial $-\mathbf{r} \cdot \nabla \cdot \vec{\sigma}$ equals the virial of the Ehrenfest force density $F(\mathbf{r})$ as can be seen by taking the virial of eq 55:

$$\mathbf{r} \cdot F(\mathbf{r}) = N \int d\mathbf{r}' \psi^* (-\mathbf{r} \cdot \nabla \hat{V}) \psi = -\mathbf{r} \cdot \nabla \cdot \vec{\sigma} \quad (74)$$

Thus the local statement of the virial theorem is term for term, the differential form of the integrated theorem in eq 67. Because of this correspondence, one can define the density corresponding to the total virial $\mathcal{V}(\Omega)$ as and

$$\mathcal{V}(\mathbf{r}) = -\mathbf{r} \cdot \nabla \cdot \vec{\sigma} + \nabla \cdot (\mathbf{r} \cdot \vec{\sigma}) \quad (75)$$

the local form of the virial theorem can be written as

$$(\hbar^2/4m) \nabla^2 \rho(\mathbf{r}) = 2G(\mathbf{r}) + \mathcal{V}(\mathbf{r}) \quad (76)$$

The kinetic energy density $G(\mathbf{r})$ is necessarily positive and eq 76 demonstrates that in those regions where electronic charge is locally concentrated, i.e., where the Laplacian of the charge density is negative, the electronic potential energy density $\mathcal{V}(\mathbf{r})$ is in local excess over the ratio of 2:1 for the average value of T to \mathcal{V} in the virial theorem. Equation 76 is unique in relating a property of the electronic charge density to the local components of the total energy. It will be used extensively in the characterization of bonding and in the prediction of the mechanisms of generalized Lewis acid-base reactions.

From eq 75 it is clear that the virial of the electronic forces, which is the electronic potential energy, is totally determined by the stress tensor $\vec{\sigma}$ and hence by the one-electron density matrix. The atomic statement of the virial theorem provides the basis for the definition of the energy of an atom in a molecule.

B. Energy of an Atom in a Molecule

The method of averaging an operator over the state function to obtain the corresponding atomic average is dictated by the mode of integration defined by the atomic statement of the principle of stationary action: summation over all spins and integration over the spatial coordinates of all electrons but the one whose coordinates appear in generator and which are integrated over the atomic basin. This imparts a basic one-electron nature to an atomic property, as each is determined by the integration of a corresponding property density over the basin of the atom, as previously indicated in eqs 36 and 37 for the determination of the atomic averages of the generator \hat{F} . This remains true even for many-electron operators, as illustrated in eqs 54 and 55 for the atomic force $F(\Omega)$ and in eqs 59 and 74 for the electronic potential energy density, the virial of the Ehrenfest force.

The most important consequence of the definition of an atomic property is that the average value of an observable for the total system $\langle \hat{A} \rangle$ is given by the sum of its atomic contributions $A(\Omega)$. Equation 77 is true

$$\langle \hat{A} \rangle = \sum_{\Omega} A(\Omega) \quad (77)$$

for both one-particle and two-particle operators. It states that each atom makes an additive contribution to the value of every property for a total system. *This is the principle underlying the cornerstone of chemistry—that atoms and functional groupings of atoms make recognizable contributions to the total properties of a system.* In practice, we recognize a group and predict its effect upon the static and reactive properties of a system in terms of a set of properties assigned to the group. In the limiting case of a group being essentially the same in two different systems, one obtains a so-called additivity scheme for the total properties, for in this case the atomic contributions as well as being additive in the sense of eq 77 are transferable between molecules.

Even a property not represented by a linear Hermitian operator can be expressed as a sum of atomic

contributions, as in eq 77. The polarizability of a molecule for example, which is determined by the first-order response of the charge density to an electric field, is not directly expressible as an average over a corresponding operator. This is not to say however, that the polarizability cannot be expressed as an additive atomic property, as is indeed done empirically. The atomic contributions to the molecular polarizability and magnetic susceptibility are defined and discussed in refs 15 and 22.

The theory of atoms in molecules is founded upon two important observations that resulted from the study of molecular charge distributions.⁵ First, the atoms of theory are the most transferable pieces of a system that can be defined in real space *and which exhaust the space of the system*. They therefore, maximize the transfer of atomic information between molecules at the level of the charge density. Second and most important, the constancy in the average values of an atom's observables, including its contribution to the total energy of a system, is found to be directly determined by the constancy in its distribution of charge. As a consequence of this observation and eq 77, when the distribution of charge over an atom is the same in two different molecules, i.e., when the atom or some functional grouping of atoms is the same in the real space of two different systems, then it makes the same contribution to the total energy in both systems. It is because of the direct relationship between the spatial form of an atom and its properties that we are able to identify them in different systems. Thus whether the form of an atom changes by a little or by a lot, its energy and other properties change by corresponding amounts. This observation has obvious consequences for density functional theory and these have been discussed in ref 23.

Along with the discovery that the most transferable atomic unit of the charge density is a region of space bounded by a zero flux surface⁵ was the observation that when the charge density was nearly unchanged over such a fragment in two different systems, the kinetic energy density exhibited a corresponding degree of transferability. Thus transferability of the distribution of charge over an atom leads to a corresponding constancy in its kinetic energy. If one postulated the existence of the virial theorem for such an atom, then this observation implies that when the charge distribution of an atom is identical in two different systems, the atom will contribute identical amounts to the total energies of both systems. This postulate has been proven true by the atomic statement of stationary action, and the atomic virial theorem yields the definition of an energy in an atom.

The electronic energy of an atom in a molecule, the quantity $E_e(\Omega)$, is defined as

$$E_e(\Omega) = T(\Omega) + \mathcal{V}(\Omega) \quad (78)$$

Because of the atomic virial theorem (eq 69), the atomic energy $E_e(\Omega)$ satisfies the following relationships which are the direct analogues of the all space results:

$$E_e(\Omega) = -T(\Omega) = (1/2)\mathcal{V}(\Omega) \quad (79)$$

Because of eq 69 and the vanishing of the Laplacian of the charge density over an atomic basin, the following identities hold:

$$E_e(\Omega) = -K(\Omega) = -G(\Omega) = (1/2) \int_{\Omega} Tr\sigma(r)d\tau \quad (80)$$

It is to be emphasized, that all of the above relationships, together with the atomic statements of the virial theorem (eq 79) remain true when Ω refers to the total system. It is in this sense that an atom is a quantum subsystem.

From its definition it is clear that like other atomic properties, the sum of the energies of the atoms in a system equals the total electronic energy E_e :

$$E_e = \sum_{\Omega} E_e(\Omega) = T + \mathcal{V} \quad (81)$$

and when there are no forces acting on any of the nuclei in the system, this sum equals the total molecular energy E as obtained by averaging the Hamiltonian in eq 23.

As emphasized above, it is the energy $E_e(\Omega)$ defined in terms of the virial theorem that possesses the property of paralleling the constancy exhibited by the charge distribution of an atom when it is transferred between systems. This theorem equates the electronic potential energy to the virial of the Ehrenfest forces acting on the electrons in the basin of the atom, and it is this step which makes possible the partitioning of the total energy into a sum of atomic contributions. It is the potential energy of interaction between particles and eventually between subsystems that is the stumbling block to obtaining a nonarbitrary and physical partitioning of a total energy. How, for example, does one partition the energies of repulsion between pairs of electrons and between pairs of nuclei appearing in the Hamiltonian in eq 23? As discussed in detail in refs 1 and 2, the use of the virial to define a potential energy overcomes this difficulty. A force is local, and as illustrated in eq 55, it is possible to define the force exerted on an electron by all of the other particles in the system, a result that is given deeper physical significance by the fact that the same force is expressible in terms of the quantum stress tensor. By taking the virial of this force density, one obtains a local potential energy density (eq 75) one which is also expressible locally in terms of the stress tensor. Thus the definition of the energy of an atom proceeds not through a spatial partitioning of the Hamiltonian, which would violate the indistinguishability of the electrons, or of the elements of the abstract Hilbert space on which the Hamiltonian acts, but rather through a partitioning of the Hamiltonian into a sum of effective one-electron contributions by using the virial operator.^{1,2} In summary, forces unlike energies, are local and by defining the potential energy in terms of the virial of a force, one obtains a local expression for the potential energy. All of the expressions are obtained directly from quantum mechanics and it is not necessary to rationalize or justify the resulting equations or their consequences. The above discussion is simply to make clear how physics does provide an answer to a long standing problem.

IV. Transferability of Atomic Properties

A. Energy Additivity in Normal Hydrocarbons

The above discussion emphasized that the use of the zero flux surface for the definition of an atom or functional grouping of atoms maximizes the extent of the transferability of its properties between systems,

a characteristic essential to the role of the atomic concept in chemistry. By defining a group and its properties and thereby enabling one to determine the effect of its presence on the properties of another group, the theory of atoms in molecules parallels the most important of all chemical codifiers, the substituent effect. Studies have illustrated the ability of the theory to quantify and make understandable the effects of a range of substituents on the properties of the ethyl, formyl, and phenyl groups,^{24,25} for example. It is the purpose of the present discussion to explore the limiting case where a group is transferable with little or no change in its properties and correspondingly, its perturbation of the remainder of the system is minimized.

It is possible to experimentally measure the energy of an atom in a molecule as an additive contribution to the molecule's heat of formation in those instances where a class of molecules exhibits an additivity scheme for the energy. Essential to the theoretical prediction and understanding of this experimental observation is the property of the atoms expressed in eq 77 that their properties, including their energies, be additive to yield the total property value for a molecule. It is demonstrated here that the energies of the methyl and methylene groups as defined by theory, predict the *additivity and transferability* of the group energies as is observed experimentally in normal hydrocarbon molecules. Their properties also predict and account for the deviations in this additivity scheme that are observed for small cyclic molecules, deviations which serve to define the strain energy. The ultimate test of any theory is its ability to predict what can be experimentally measured. By appealing to the limiting case of near transferability of atomic properties, one can demonstrate that the atoms of theory are the atoms of chemistry.²⁶⁻²⁸

The study of the molar volumes of the normal hydrocarbons by Kopp in 1855 provided the earliest example of the additivity of group properties. The experimentally determined heats of formation for the same homologous series of molecules, $\text{CH}_3(\text{CH}_2)_m\text{CH}_3$, also obey a group additivity scheme.²⁹⁻³² It is possible to fit the experimental heats of formation for this series, beginning with $m = 0$, with the expression

$$\Delta H_f^\circ(298) = 2A + mB \quad (82)$$

where A is the contribution from the methyl group and B that from the methylene group. The generally accepted values for A and B at 25 °C are -10.12 and -4.93 kcal/mol, respectively. The group enthalpy corrections from 298 to 0 K are additive for the n -alkanes,³³ as are the group zero point energy corrections.³⁴ Thus the calculated energies of the vibrationless molecules in their equilibrium geometries should exhibit the same additivity of the energy as represented by eq 82 and the additivity is indeed mirrored by the single determinantal SCF energies at both the 6-31G*/6-31G* and 6-31G**/6-31G* levels of approximation. The calculated molecular energies E for the n -alkanes satisfy the relationship

$$E = 2E(\text{CH}_3) + mE(\text{CH}_2) \quad (83)$$

The quantity $E(\text{CH}_3)$ is one-half the energy of ethane, equal to -39.619 12 au, and $E(\text{CH}_2)$ is the energy increment per methylene group equal to -39.037 79 au, when the 6-31G**/6-31G* calculated results were used.

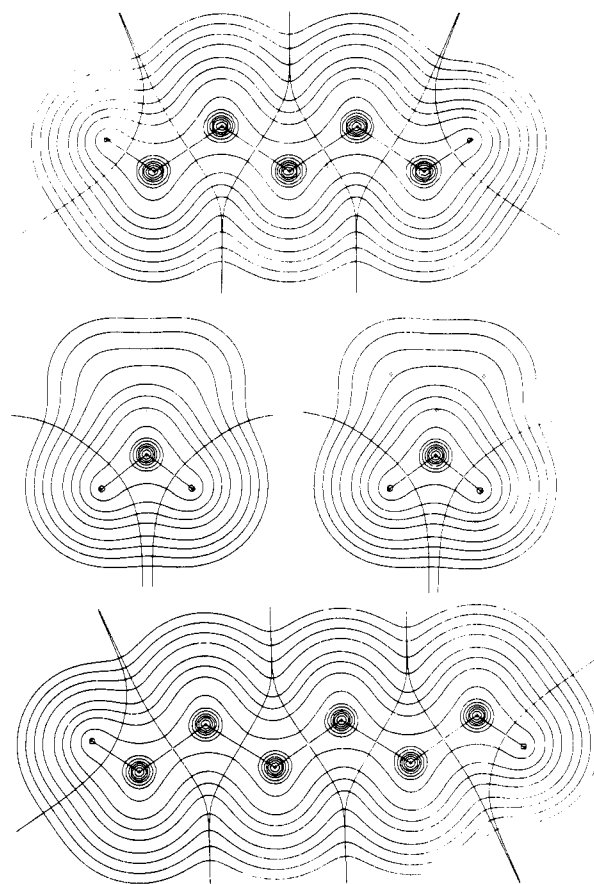


Figure 2. Contours of the charge density for the minimum energy geometries of the pentane (top) and hexane (bottom) molecules in the plane containing the carbon nuclei and the two terminal methyl protons. The projected positions of the out-of-plane symmetrically equivalent pairs of protons are indicated by open crosses. The central maps are for a (perpendicular) symmetry plane containing the C and H nuclei of the central methylene group in pentane (left-hand side) and for one of two equivalent such groups in hexane (right-hand side). The bond paths are shown, as are the positions of the interatomic surfaces. The position of out-of-plane nuclei are indicated by open crosses. The contour displays of the charge distributions of the methyl and corresponding methylene groups are superimposable on one another.

These group values fit the calculated energies to within $\pm 0.000 14$ au, an average deviation smaller than the experimental one. The calculated results indicate that the corrections to the energy arising from the correlation of the electronic motions, a contribution neglected in a single determinantal calculation, should also obey a group additivity scheme. This indeed appears to be the case, as is demonstrated and discussed later.

The distributions of charge for the five- and six-carbon members are illustrated in Figure 2 in the form of contour maps of ρ . The maps show the bond paths linking the nuclei and indicate the intersection of the interatomic surfaces with the plane of the diagram. The diagrams show qualitatively what the atomic properties will demonstrate quantitatively: that the methyl and methylene groups in this series of molecules are transferable with little change in their form and, hence, with little change in their properties.

The physical properties of the n -alkanes indicate that the molecules are nonpolar and this is reflected in the small magnitudes of the net charges of the carbon and hydrogen atoms and of the molecular moments. Hydrogen is slightly more electronegative than carbon in

saturated hydrocarbons, and the order of group electron-withdrawing ability in hydrocarbons without geometric strain is $H > CH_3 > CH_2 > CH > C$. In ethane, methyl is bonded to methyl while in the other molecules of the *n*-alkanes it is bonded to methylene from which it withdraws charge. To within the accuracy of the numerical integrations of the atomic properties (which in general are $\pm 0.001e$ and ± 1 kcal/mol), one finds (see refs 1, 27 or 28) the energy and population of the methyl group to be constant when it is bonded to a methylene group. Thus the methyl group is essentially the same in all the members of the homologous series past ethane. This transferable methyl group is more stable relative to methyl in ethane by an amount $\Delta E = -10.5 \pm 0.5$ kcal/mol and its electron population is greater by an amount $\Delta N = 0.0175e$.

The charge and energy gained by the methyl group is taken from the methylene group. What is remarkable, and what accounts for the additivity observed in this series of molecules, is that the energy gained by methyl is equal to the energy lost by methylene. In propane, where the methylene group transfers charge to two methyl groups, its energy relative to the increment in eq 83 is $E(CH_2) - 2\Delta E$, and its net charge is (necessarily) $+2\Delta N$ where ΔE and ΔN the quantities defined above for the methyl group. Thus the energy as well as the charge is conserved relative to the group energies defined in eq 83. In butane, a methylene group is bonded to a single methyl group and correspondingly its energy is $E(CH_2) - \Delta E$ and its net charge is $+\Delta N$. The corresponding methylene groups in pentane and hexane, those bonded to a single methyl group, have the same energies and net charges as a methylene group in butane. Thus the charge transfer to methyl is damped by a single methylene group, and the central methylene group in pentane and the two such groups in hexane (see Figure 2) should have a zero net charge and an energy equal to the increment $\Delta E(CH_2)$. This is what is found to within the uncertainties in the integrated values, their calculated net charges being $0.0005 \pm 0.0002e$ and the maximum deviation on the energy from the standard value being within the integration error of ~ 1 kcal/mol. (It should be kept in mind that the total energy of a methylene group is $\sim 25 \times 10^3$ kcal/mol). Therefore, methylene groups bonded only to other methylenes, as found in pentane, hexane, and all succeeding members of the series possess a zero net charge and contribute the standard increment $E(CH_2)$ to the total energy of the molecule. The underlying reason for the observation of additivity in this series of molecules is the fact that the change in energy for a change in population, the quantity $\Delta E/\Delta N$, is the same for both the methyl and methylene groups. The small amount of charge shifted from methylene to methyl makes the same contribution to the total energy.

It is to be emphasized that the energies assigned to the methyl and methylene groups are independently determined by the theory of atoms in molecules. The fact that this assignment leads to an energy for the transferable methylene group equal to the value $E(CH_2)$ in eq 83, an equation which mirrors the experimental additivity of the energy eq 82, confirms that the theoretically defined atoms are responsible for the experimentally measured increments to the heat of formation, and that quantum mechanics predicts the properties

of atoms in molecules just as it does the properties of the total molecule. It is a straightforward matter to use quantum mechanics to relate a spectroscopically determined energy to the theoretically defined difference in energy between two states of a system. In a less direct, but no less rigorous manner, quantum mechanics also relates the difference in the experimentally determined heats of formation of butane and pentane to the corresponding theoretically defined energy of the methylene group.

The additivity of the energy in the *n*-alkanes is obtained in spite of small differences in group properties, differences which necessarily result from a change in the nature of the bonded neighbor. Thus there are two kinds of methyl groups: the one unique to ethane and the transferable methyl group which is bonded to a methylene group. There are three kinds of methylene groups: the one unique to propane and two transferable forms, one bonded to a methyl and the other bonded only to other methylene groups. Other properties of these groups exhibit the same pattern of transferable values as do their energies and populations. This has been illustrated^{1,28} for the atomic first moments, the atomic volumes, and the atomic contributions to the electronic correlation energy as determined by density functional theory. This latter result indicates that each of the transferable methyl and methylene groups should make a characteristic and essentially constant contribution to the total correlation energy of a normal hydrocarbon molecule, a result anticipated on the basis of the ability of the SCF calculations to recover the experimental additivity of the energy. It has also been demonstrated that the methyl and methylene groups contribute characteristic contributions to the mean molecular polarizabilities of normal hydrocarbons.³⁵

It must be considered remarkable that a methyl group with a total energy in excess of 25 000 kcal/mol, can be transferred between molecules—in reality and in theory—with changes in its energy of approximately 1 kcal/mol. It is still more remarkable when it is realized that the individual contributions to the energy of a carbon atom change by 2–5000 thousand kcal/mol between members of the series.^{1,23,27}

B. Origin of Strain Energy in Cyclic Hydrocarbons

The hybridization model predicts that the smaller bond angles found in a molecule with angular strain should result in an increase in the p character of the strained C–C bonds and hence in an increase in the s character of the associated C–H bonds.³⁶ Orbital models relate an increase in electronegativity of a carbon atom relative to that of a bonded hydrogen to an increase in the s character of its bonding hybrid orbital. Thus it follows that the presence of geometric strain in a hydrocarbon molecule should result in an increase in the electronegativity of carbon relative to hydrogen. In their classic study of strain in the cyclopropane molecule, Coulson and Moffitt³⁷ emphasized this point by showing that the bond lengths and bond angles of the methylene group in cyclopropane resemble those for ethylene. The argument for an increase in electronegativity with increasing s character is based on energy, an s electron being more tightly bound than a p electron. The theory of atoms in molecules shows that the

electronegativity of a carbon atom does indeed increase and its energy decreases as the extent of geometric strain increases.

Relative to its population in the standard methylene group, each hydrogen in cyclopropane transfers 0.045e to carbon, reducing the net charge on the carbon atom from +0.196e to +0.106e. While this charge transfer leads to an increase of 15.6 kcal/mol in the stability of the carbon atom, it results in a decrease of 12.5 kcal/mol in the stability of each hydrogen atom. Thus the methylene group in cyclopropane is calculated to be 9.4 kcal/mol less stable than the standard transferable methylene group. This yields a total strain energy for the molecule three times this or 28.2 kcal/mol, in good agreement with the generally accepted value based on the experimental heats of formation of 27.5 kcal/mol. The methylene group in cyclopropane is more stable than the same group in ethylene by only 2.1 kcal/mol. In terms of the charge transfer within the group and its energy, it resembles more closely the ethylene fragment (where $q(\text{C}) = +0.080e$) than it does the standard methylene group.

In the less strained cyclobutane, the transfer of charge from hydrogen to carbon relative to the populations in the standard methylene group is reduced to 0.014e for axial H and 0.012e for the other and the charge on carbon is +0.170e. The hydrogens are destabilized by 9.0 kcal/mol, and the carbon stabilized by only 2.5 kcal/mol, to give an energy increase of 6.5 kcal/mol for each methylene group. This yields a predicted strain energy of 26.1 kcal/mol, a value which again is in agreement with the experimental value of 26.5 kcal/mol. Experimentally, the heat of formation of cyclohexane is found to be six times the heat of formation of the standard methylene group and to possess no strain energy. An axial hydrogen in this molecule is calculated to possess 0.007 more electrons, ($N(\text{H}) = 1.099e$) and be more stable by 1.6 kcal/mol than an equatorial hydrogen. The atomic populations and energies of a methylene group in cyclohexane differ little from their values in the standard group and the energy of the group differs by only 0.0001 au or 0.06 kcal/mol from the standard value. Thus in agreement with experiment, cyclohexane is predicted to be strain free when its energy is compared with six times the energy of the standard methylene group. The reader is referred to ref 27 for further examples of the relation between increasing strain energy and an increasing degree of charge transfer from H to C in bicyclic systems and the propellane molecules. The few examples discussed here are introduced to emphasize that the strain energies calculated for cyclopropane and cyclobutane, and the predicted absence of strain in cyclohexane, all of which are in agreement with experiment, are predicted by the theory of atoms in molecules. The energy of the standard transferable methylene group, as defined by the zero flux boundary condition and as found in the pentane and hexane molecules, serves as the basis for the determination of these results. Not only does theory predict the transferability of atoms and groupings of atoms without change, it also correctly predicts the measured changes in their energies when these groups are perturbed.

While the excellence of the agreement of the relative energies of the methylene group in the cyclic molecules

with the measured strain energies may be to some extent due to the fortuitous cancellation of errors in the contributions not specifically considered, namely the correlation energy, the zero point energy, and $\Delta(\Delta H_f^\circ)$ between 0 and 298 K, the nature of the results leaves no doubt as to the correctness of the interpretation that has been given: the atoms of theory recover the experimentally measured properties of atoms in molecules.

V. Molecular Structure and Structural Stability

A. The Notion of Structure in Chemistry

The essential understanding and original intent associated with the notion of structure in chemistry is that it be a generic property of a system. Structure implies the existence of a particular network of bonds which was presumed to persist over a range of nuclear displacements until some geometrical parameter attained a critical value at which point bonds were assumed to be broken and/or formed to yield a new structure. However, the word "structure" has over the years acquired a duality of meanings. This has occurred for two reasons. The first was a result of our inability to unambiguously assign a network of bonds to a given system. The second was a result of our ever-increasing ability to experimentally measure the geometrical parameters which characterize the minimum energy nuclear configuration of a system within the Born-Oppenheimer model.

It is most important to distinguish clearly between molecular geometry and the original intent and use of the notion of structure in the molecular structure hypothesis. Geometry is a nongeneric property since any infinitesimal change in a set of nuclear coordinates, denoted collectively by \mathbf{X} , results in a different geometry. Molecular structure, on the other hand, was assumed to be a generic property of a system. Any configuration of the nuclei \mathbf{X}' in the neighborhood of a given configuration \mathbf{X} , while it has a different geometry, should possess the same structure, that is, the same nuclei should be linked by the same network of bonds in both \mathbf{X} and \mathbf{X}' . Difficulties ascribed to the notion of molecular structure are the inability to assign a single geometrical structure, average or otherwise, to rotation or inversion-related isomers, to a molecule in an excited vibrational state, or to a molecule in a "floppy" state wherein the nuclear excursions cover a wide range of geometrical parameters. In reality these are shortcomings of attempts to impose the classical idea of a geometry on a quantum system. The nuclei, like the electrons, cannot be localized in space and instead are described by a corresponding distribution function. The definition of structure proposed here recognizes this essential point and associates a molecular structure with an open neighborhood of nuclear configuration space, with a corresponding average being taken over the nuclear distribution function.

It has been shown⁶ that the topological properties of a system's charge distribution enable one to assign a molecular graph to each point \mathbf{X} in the nuclear configuration space of a system. This assignment corresponds to defining a unique network of atomic interaction lines to each molecular geometry. The charge distribution can be obtained from a wave function be-

yond the Born–Oppenheimer approximation by the generator coordinate method for example, to yield a wave function which, while no longer associated with a specific geometry, is associated with a specific structure.^{6b} A molecular structure is then defined as an equivalence class of molecular graphs. This definition associates a given structure with an open neighborhood of the most probable nuclear geometry, and removes the need of invoking the Born–Oppenheimer approximation for the justification or rationalization of structure in a molecular system.⁶ By defining all possible structures for a given system, the theory shows that a change in structure must be an abrupt and discontinuous process, one which is described in terms of the mathematical theory of dynamical systems and their stabilities. The reader is referred to the original papers⁶ or to ref 1 for full discussions of this aspect of the theory.

B. Molecular Graphs

The principal topological properties of an electronic charge distribution—maxima, which are topologically homeomorphic to $(3,-3)$ critical points at the positions of the nuclei and $(3,-1)$ critical points between atoms whose basins share a common surface—were introduced in section II.E. The first of these critical points defines an atom and its basin while the second defines the interatomic surface and atomic interaction line. The nuclei of two atoms which share a common interatomic surface are linked by a line along which the charge density is a maximum with respect to any neighboring line.

The existence of a $(3,-1)$ critical point and its associated atomic interaction line indicates that electronic charge density is accumulated between the nuclei that are so linked. This is made clear by reference to the displays of the charge density for such a critical point, as given in Figure 1 for example, and particularly in Figure 3, which emphasizes the fact that the charge density is a maximum in an interatomic surface at the position of the critical point. This is the point where the atomic interaction line intersects the interatomic surface and charge is so accumulated between the nuclei along the length of this line. Both theory and observation concur that the accumulation of electronic charge between a pair of nuclei is a necessary condition if two atoms are to be bonded to one another.¹ This accumulation of charge is also a sufficient condition when the forces on the nuclei are balanced and the system possess a minimum energy equilibrium internuclear separation. Thus the presence of an atomic interaction line in such an equilibrium geometry satisfies both the necessary and sufficient conditions that the atoms be bonded to one another. In this case the line of maximum charge density linking the nuclei is called a “bond path” and the $(3,-1)$ critical point referred to as a “bond critical point”.^{8,17}

For a given configuration X of the nuclei, a “molecular graph” is defined as the union of the closures of the bond paths or atomic interaction lines. Pictorially the molecular graph is the network of bond paths linking pairs of neighboring nuclear attractors. The molecular graph isolates the pair-wise interactions present in an assembly of atoms which dominate and characterize the properties of the system be it at equilibrium or in a state of change.

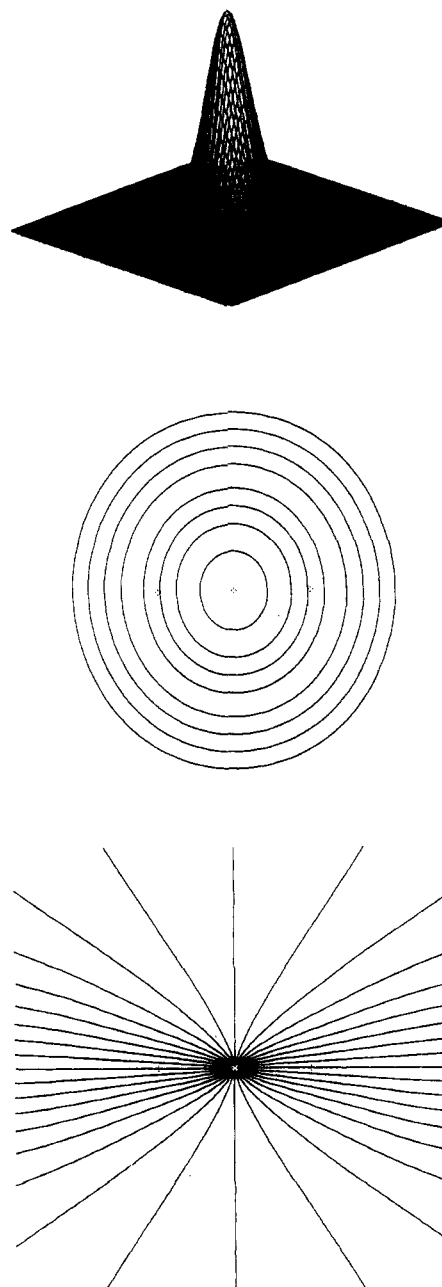


Figure 3. Relief and contour maps of the charge density and a display of the associated gradient vector field for the plane containing the C–C interatomic surface in ethene i.e., the plane bisecting and perpendicular to the C–C bond path. In this plane the $(3,-1)$ critical point appears as a two-dimensional attractor. Note the elliptical nature of the contours with the major axis perpendicular to the plane containing the nuclei. (The projected positions of the nuclei on this plane are indicated by open crosses.) This property of a charge distribution is measured by the bond ellipticity (section VI.A). The less rapid rate of falloff in ρ in the “ π ” plane is reflected in a corresponding paucity of trajectories in the display of the gradient vector field of ρ .

A molecular graph is the direct result of the principal topological properties of a system’s charge distribution: that local maxima, $(3,-3)$ critical points, occur at the positions of the nuclei thereby defining the atoms, and that pairs of trajectories which originate at $(3,-1)$ critical points are found to link certain, but not all pairs of nuclei in a molecule. The network of bond paths thus obtained is found to coincide with the network generated by linking together those pairs of atoms which are assumed to be bonded to one another on the basis of

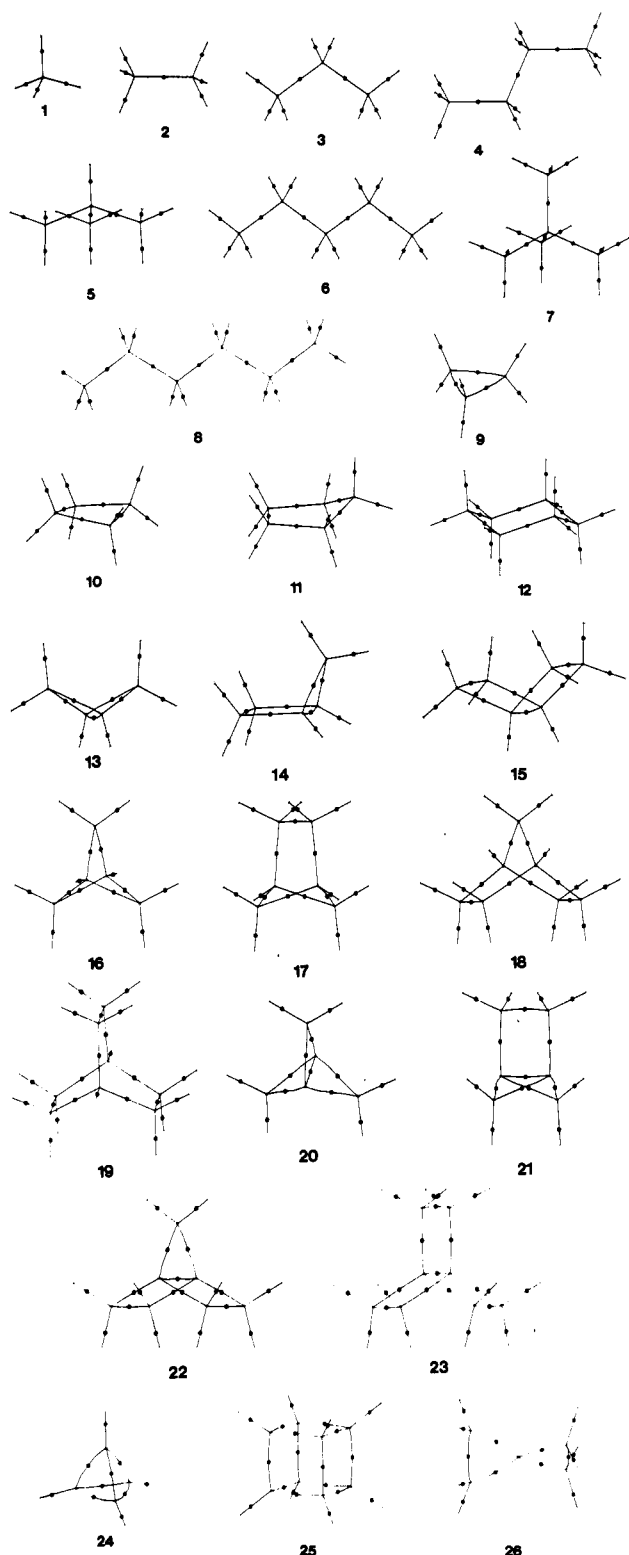


Figure 4. Molecular graphs for hydrocarbons. Bond critical points are denoted by black dots.

chemical considerations. Molecular graphs for a sampling of hydrocarbon molecules in equilibrium geometries are illustrated in Figure 4. The existence and position of a bond or $(3,-1)$ critical point in this and other figures is indicated by a black dot. The recovery of a chemical structure in terms of a property of the system's charge distribution is a most remarkable and important result. The representation of a chemical structure by an assumed network of lines has evolved

through a synthesis of observations on elemental combination and models of how atoms combine, particularly models of chemical valency. A great deal of chemical knowledge goes into the formulation of a chemical structure and, correspondingly, the same information is successfully and succinctly summarized by such structures. The demonstration that a molecular structure can be faithfully mapped onto a molecular graph imparts new information to them—that nuclei joined by a line in the structure are linked by a line through space along which electronic charge density, the glue of chemistry, is maximally accumulated. Finding the physical basis for a molecular structure also leads to a broadening of the concept—that the dominant interactions between atoms, by they attractive or repulsive, have a common physical representation. This is not an entirely surprising result since the ever present nuclear excursions from an equilibrium separation between a pair of atoms force a sampling of these same portions of a potential surface even though the atoms are considered to be bonded to one another. It is in answer to the closely related questions of what is meant by the making and breaking of chemical bonds that leads one to consider the most important extension of the molecular structure concept. As discussed in the following section, the dynamic behavior of the molecular graphs as caused by the relative motions of the nuclei forms the basis for the definition of structural stability and the analytical description of the mechanisms of structure change.

It is to be stressed that a bond path is not to be understood as representing a "bond". The presence of a bond path linking a pair of nuclei implies that the corresponding atoms are bonded to one another. As demonstrated later, the interaction can be characterized and classified in terms of the properties of the charge density at its associated $(3,-1)$ critical point. The complete description of the interaction, however, requires the evaluation of operators over the associated interatomic surface. We continue the identification of the elements of molecular structure with the topological properties of the remaining stable critical points, $(3,+1)$ and $(3,+3)$ critical points.

These remaining critical points of rank three occur as consequences of particular geometrical arrangements of bond paths and they define the remaining elements of molecular structure—rings and cages. If the bond paths are linked so as to form a ring of bonded atoms, as found in the cyclic and bicyclic molecules shown in Figure 4 for example, then a $(3,+1)$ critical point is found in the interior of the ring. The eigenvectors associated with the two positive eigenvalues of the Hessian matrix of ρ at this critical point generate an infinite set of gradient paths which originate at the critical point and define a surface, called the ring surface. This behavior is illustrated by the gradient paths in the bridging plane of the diborane molecule as shown in Figure 5. All of the trajectories, which originate at the critical point at the center of the ring of nuclei, the $(3,+1)$ or ring critical point, terminate at the ring nuclei, but for the set of single trajectories each of which terminates at one of the bond critical points whose bond paths form the perimeter of the ring. These bond paths are noticeably inwardly curved away from the geometrical perimeter of the ring, a behavior characteristic

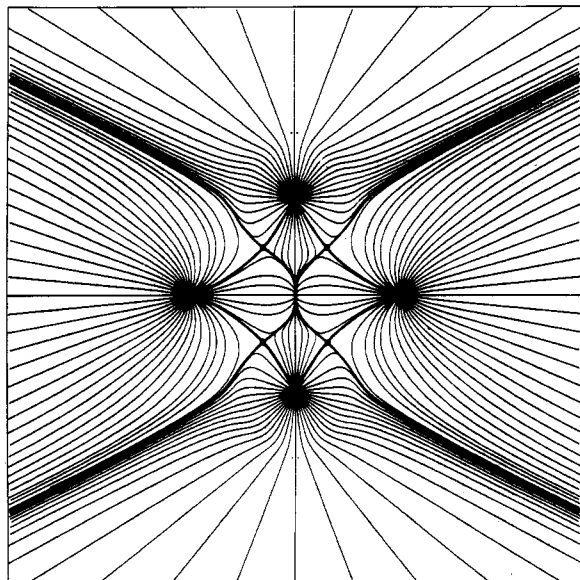


Figure 5. Display of the gradient vector field of the charge density in the plane of the bridging hydrogen atoms in diborane. The two protons (on the horizontal axis) are linked by bond paths to two boron nuclei to form a ring. The ring surface is defined by the trajectories which originate at the central ring critical point and terminate at the ring nuclei and the four bond critical points. The four latter trajectories define the boundaries of the atomic basins within the perimeter of the ring.

of systems which are electron deficient. The remaining eigenvalue of a ring critical point, its single negative eigenvalue, generates a pair of gradient paths which terminate at the critical point and define a unique axis perpendicular to the ring surface at the critical point. In diborane this axis is perpendicular to the plane shown in Figure 5. It represents the intersection of the boundaries of the basins of the hydrogen and boron atoms forming the ring. A ring, as an element of the structure, is defined as part of a molecular graph which bounds a ring surface.

If the bond paths are so arranged as to enclose the interior of a molecule with ring surfaces then a (3,+3) or cage critical point is found in the interior of the resulting cage. Cage structures are illustrated in Figure 4. The charge density is a local minimum at a cage critical point. Trajectories only originate at such a critical point and terminate at nuclei, and at bond and ring critical points, thereby defining a bounded region of space. A cage, as the final element of molecular structure, is a part of a molecular graph which contains at least two rings, such that the union of the ring surfaces bounds a region of R^3 which contains a (3,+3) critical point.

C. A Theory of Molecular Structure

The ideas underlying the definition of structure and structural stability are first introduced in a qualitative manner with the aid of examples. The basic idea makes use of an equivalence relationship of gradient vector fields of the charge density as a function of nuclear configurations \mathbf{X} , equivalent vector fields possessing the same molecular graph. The reader is referred to ref 1 for a full discussion.

Consider the thermal isomerization of HCN to the isocyanide, CNH. The gradient vector fields of the charge density, the fields $\nabla\rho(\mathbf{r},\mathbf{X})$ and the associated

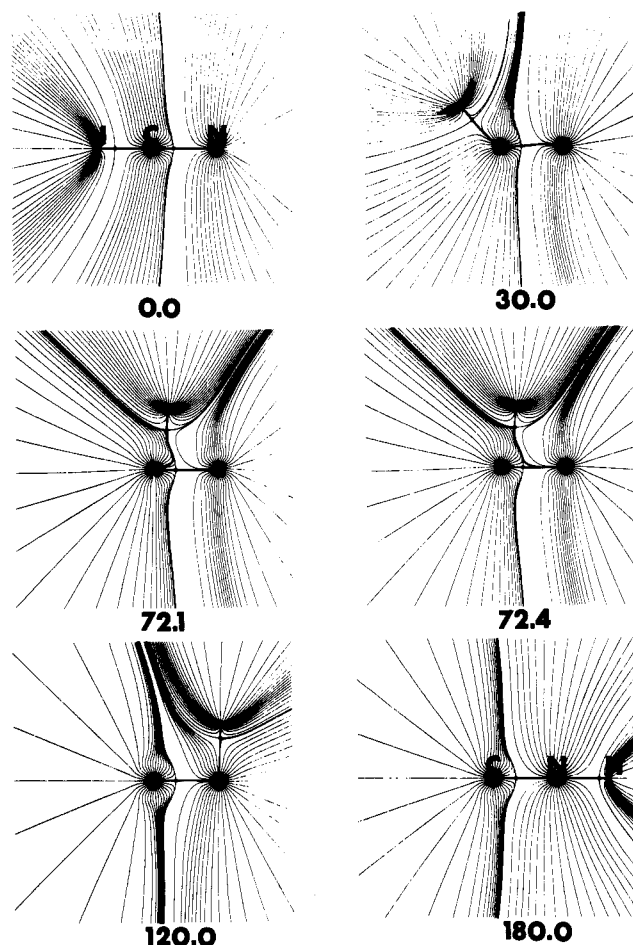


Figure 6. Displays of the gradient vector field of the charge density for points along the reaction path for the conversion of HCN to CNH. The first three gradient vector fields are homeomorphic and define equivalent molecular graphs and the stable structure HCN. Similarly, the final three maps are also homeomorphic and define equivalent molecular graphs for the stable structure CNH. These two stable structural regimes are separated by an unstable conflict structure.

molecular graphs for points \mathbf{X} in nuclear configuration space along the reaction coordinate are illustrated in Figure 6. The transition state occurs between values of the parameter $\theta = 72.1$ and 72.4° . The gradient vector fields of all configurations up to the transition state are equivalent—the gradient paths for one configuration \mathbf{X} can be mapped onto those for another—and they all have the same molecular graph corresponding to the structure H-C-N. This molecular graph is obtained for any and all arbitrary displacements of the nuclei in the vicinity of the equilibrium geometry of HCN. The structure denoted by one of the equivalent molecular graphs is a stable structure, as it occurs throughout an open region of nuclear configuration space. The gradient vector fields obtained after passage of the system through the transition state, while belonging to a single equivalence class, are not equivalent to those which preceded the transition state. They correspond to the new structure C-N-H, which is also a stable structure, since it also persists for arbitrary nuclear motions. At some point in the neighborhood of the transition state there is an abrupt and discontinuous change in structure, from H-C-N to C-N-H, as a result of the system passing through a configuration \mathbf{X}_c for which the gradient vector field and molecular

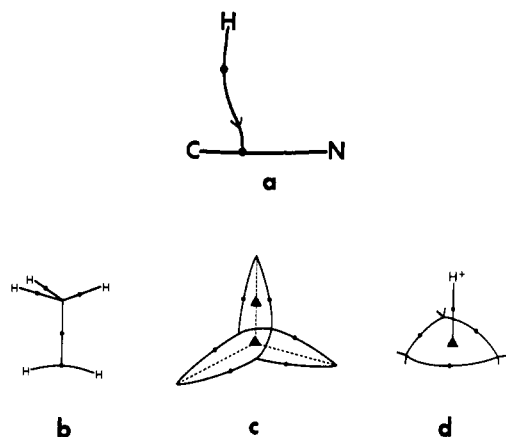


Figure 7. Diagram a is the conflict structure for the transfer of a hydrogen from C to N in the isomerization of HCN displayed in Figure 6. Diagrams b, c, and d illustrate the three possible types of conflict structures: (b) in CH_5^+ the bond path of one (3,-1) intersects the surface manifold of another such critical point, the same instability as found in a; (c) the unique ring axis of a (3,+1) critical point intersects the surface manifold of another such critical point in a structure of [1.1.1]propellane which neighbors the energetically stable structure; (d) the unique ring axis of a (3,+1) critical point intersects the bond path of a (3,-1) critical point in protonated cyclopropane.

graph are structurally unstable, i.e. they exist for but one configuration on the reaction path. The structure corresponds to one in which the bond path from the hydrogen does not terminate at either the carbon or the nitrogen nucleus, but rather at the (3,-1) or bond critical point of the C-N bond path. This arrangement of bond paths, illustrated in Figure 7, is unstable as it corresponds to the two-dimensional manifold of the bond critical point acting as an attractor in three-dimensional space. Such an intersection of manifolds of two (3,-1) critical points is mathematically unstable and is termed a conflict catastrophe, as the two attractors are in competition for a line of maximum charge density, the bond path to the proton. There are three such possible unstable intersections of manifolds of critical points in the charge density, and they are illustrated in Figure 7.

The conflict mechanism represents one way in which a stable structure can be changed into another and it occurs by passage of the system through a catastrophe point \mathbf{X}_c , a configuration of the nuclei for which the associated gradient vector field of the charge density is unstable to nuclear motions. There is only one other type of possible instability of a gradient vector field, and it is termed a bifurcation catastrophe. It is illustrated by the opening of the ring structure in cyclopropane, as shown in Figure 8. The change in ρ which accompanies an extension of a C-C bond causes the (3,+1) or ring critical point to migrate toward the (3,-1) or bond critical point of the extended bond. The charge density in the plane of the ring has a positive curvature at the ring critical point and a negative curvature at the bond critical point, the axes for both curvatures lying along a common C_2 axis. For some particular extension of the C-C separation, the two critical points coalesce to form a single, new critical point and the gradient vector field undergoes an abrupt change into one which is no longer equivalent to those which preceded it. At coalescence, the original positive and negative curvatures lying on the C_2 axis must vanish and the result is a critical point

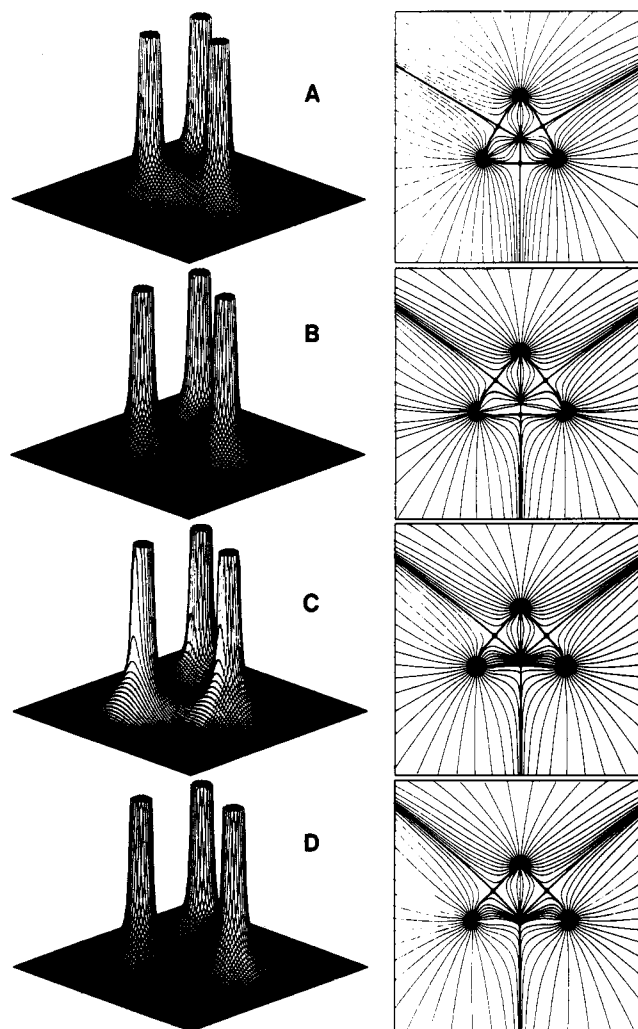


Figure 8. Relief maps of the charge density and displays of their associated gradient vector fields for the opening of a three-membered ring. Structure C is at, or close to, the bifurcation catastrophe point wherein a degenerate critical point is formed between the two carbons of the extended bond by the coalescence of the ring and bond critical points.

of rank two, a degenerate critical point. Such a critical point is mathematically unstable with respect to the changes in ρ caused by nuclear motions. It exists only for this one configuration of the nuclei along the reaction coordinate. Further extension of the C-C separation causes the unstable critical point vanish, the C-C bond has been broken and the ring structure has been transformed into the open structure. These changes are summarized by the profiles of ρ along the direction of approach of the two critical points shown in Figure 9.

The discussion so far has demonstrated that the definition of structure is inextricably bound up with the definition of structural stability. The result of applying the equivalence relationship to the field $\nabla\rho(\mathbf{r};\mathbf{X})$ is a partitioning of nuclear configuration space R^Q into a finite number of nonoverlapping regions, each of which is characterized by a unique molecular structure. These structurally stable, open regions are separated by boundaries, hypersurfaces in the space R^Q . A point on a boundary possesses a structure which is different from but transitional to the structures characteristic of either of the regions it separates. Since a boundary is of dimension less than R^Q , arbitrary motions of the nuclei will carry a point on the boundary into neighboring

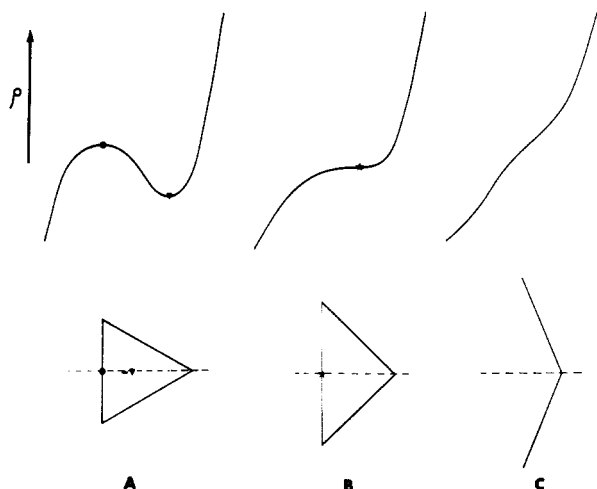


Figure 9. Profiles of the charge density along the indicated 2-fold axis for the opening of a three-membered ring, an example of a fold catastrophe.

stable structural regions and its structure will undergo corresponding changes. The boundaries are the loci of the structurally unstable configurations of a system. In general, the trajectory representing the motion of a system point in R^Q will carry it from one stable structural region through a boundary to a neighboring stable structural region. The result is an abrupt and discontinuous change in structure as illustrated in the above examples. A change in structure is catastrophic and for this reason the set of unstable structures is called the catastrophe set. A point in a structurally stable region of nuclear configuration space is termed a "regular point", and a point on one of the structurally unstable boundaries is termed a "catastrophe point".

A knowledge of the stable structural regions and their boundaries as defined by the catastrophe set enables one to construct a structure diagram, a diagram which determines all possible structures and all mechanisms of structural change for a given chemical system. Figure 10 is a two-dimensional cross section of the structure diagram for an ABC system. (The reason for the particular form shown there is justified in terms of catastrophe theory, see ref 6.) The letters may stand for atoms or functional groupings of atoms. The full lines, denoting the catastrophe set, partition nuclear configuration space into its structural regions. The hypocycloid portion denotes the loci of the bifurcation catastrophes, of the type illustrated in Figure 8, and the three semiaxes, the loci of the conflict catastrophes, as illustrated in Figure 7.

We now give a concise mathematical development of the ideas of structure outlined and illustrated above. The resulting theory of molecular structure is obtained by the application of a general mathematical theory of structural stability. This work has evolved under the general headings of differential topology and qualitative dynamics, a theory of dynamical systems and their stabilities. Contributions of particular importance to the present work are the theory of elementary catastrophes as developed by Thom³⁸ and the general statement of the theorem of structural stability given by Palis and Smale.³⁹ The possibility of using the theory of elementary catastrophes to describe changes in molecular structures was first pointed out by Collard and Hall.⁴⁰

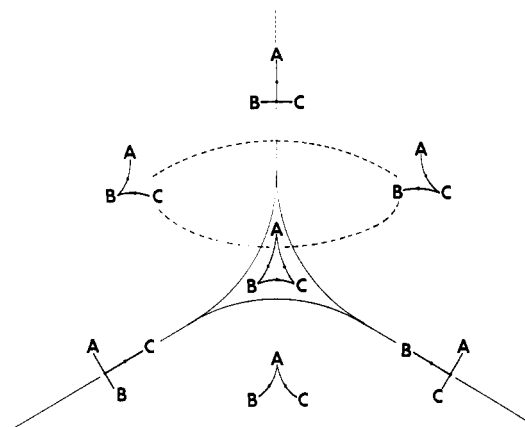


Figure 10. Two-dimensional display of the structure diagram for an A-B-C system. It details all possible stable structures for this system together with the mechanisms for structural change via unstable transitional structures. The form of this diagram is determined by the unfolding of the elliptic umbilic catastrophe.⁶

The ideas are to be applied to the dynamics of the gradient vector field of the charge density as caused by the motions of the nuclei. It should be recalled that the study of the gradient vector field of the charge density has its basis in quantum mechanics for it is in terms of this field that the boundary condition for an open quantum system is stated.

The equivalence relation of vector fields over R^3 is defined as follows: two vector fields v and v' over R^3 are said to be equivalent if and only if there exists a homeomorphism, i.e., a bijective and bicontinuous mapping of R^3 into R^3 , which maps the trajectories of v onto the trajectories of v' . By applying this definition to the gradient vector fields $\nabla\rho(\mathbf{r},\mathbf{X})$, $\mathbf{X} \in R^Q$, one obtains an equivalence relation operating in the nuclear configuration space R^Q which states: two nuclear configurations \mathbf{X} and $\mathbf{X}' \in R^Q$ are equivalent if and only if their associated gradient vector fields $\nabla\rho(\mathbf{r},\mathbf{X})$ and $\nabla\rho(\mathbf{r},\mathbf{X}')$ are equivalent. We further say that the nuclear configuration $\mathbf{X} \in R^Q$ is structurally stable if \mathbf{X} is an interior point of its equivalence class. In other words, one can always find a neighborhood V of a structurally stable configuration \mathbf{X} , such that V is totally contained in the equivalence class of \mathbf{X} . All configurations in V possess the same molecular graph as does the stable configuration \mathbf{X} .

Indeed for any point \mathbf{X}' of V one can find a homeomorphism, $h_{\mathbf{X}\mathbf{X}'}$, which maps the gradient paths of $\nabla\rho(\mathbf{r},\mathbf{X})$ into those of $\nabla\rho(\mathbf{r},\mathbf{X}')$. It is easily seen that through $h_{\mathbf{X}\mathbf{X}'}$ a critical point of type (ω,σ) in $\rho(\mathbf{r},\mathbf{X})$ is mapped onto a critical point of the same type in $\rho(\mathbf{r},\mathbf{X}')$. Moreover, a gradient path connecting a pair of critical points $(\mathbf{r}_c, \mathbf{r}_c')$ in $\rho(\mathbf{r},\mathbf{X})$ is transformed into a corresponding path of $\nabla\rho(\mathbf{r},\mathbf{X}')$, which connects the images of \mathbf{r}_c and \mathbf{r}_c' . Since the distance between \mathbf{X}' and \mathbf{X} can be made arbitrarily small, and since all nuclear configurations in V are equivalent, one finds that the molecular graphs associated with the points of V consist of the same number of bond paths linking the same nuclei. These molecular graphs represent a single structure, and the maximal neighborhood which is contained in the equivalence class of \mathbf{X} is called the structural region associated with \mathbf{X} .

An equivalence relation for molecular graphs is defined as follows: two molecular graphs are equivalent

if and only if they are associated with two points of the same structural region. An equivalence class of molecular graphs is called a molecular structure. It is then seen that a unique molecular structure is associated with a given structural region and that molecular structure, as defined above through the equivalence of molecular graphs, necessarily fulfills the requirement of being generic.

The application of the notion of structural stability to the topological study of the molecular charge distribution leads to a partitioning of the nuclear configuration space into a finite number, ℓ of non-overlapping regions, the structural regions, W_i , $i = 1, \dots, \ell$ each of which is characterized by a unique molecular structure. These structural regions form a dense open subset of the nuclear configuration space, i.e.

$$\overline{\bigcup_{i=1}^{\ell} W_i} = R^Q \quad (84)$$

where the symbol \bar{A} denotes the closure of the set A and \cup denotes the set-theoretic union. A point which belongs to the union of the W_i belongs to some structural region and is called a regular point. A nuclear configuration belonging to the complementary of the set of regular points is called a catastrophe point. The catastrophe set, C , is the collection of all structurally unstable points of nuclear configuration space. Let ∂W_i denote the boundary of the structural region W_i . Since $\bigcup_{i=1}^{\ell} W_i$ is dense in R^Q , we have

$$C = \bigcup_{i=1}^{\ell} (\partial W_i) \quad (85)$$

i.e. the catastrophe set is the union of the boundaries of all the ℓ structural regions W_i . Equation 85 denotes the catastrophe set C as the loci of structural changes. Indeed, according to eq 85, a catastrophe point $Y \in C$ belongs to ∂W_i , for some $i \in \{1, \dots, \ell\}$. Any neighbourhood of Y in R^Q thus has nonempty intersections with W_i and at least one structural region W_j , with $j \neq i$. Consequently, the slightest displacement of the system from the nuclear configuration Y will cause the molecular graph to change from the graph associated with Y to one which represents either the structure over W_i or that over W_j . Thus, the molecular graph associated with a catastrophe point denotes a discontinuous change in structural which results from a continuous variation in the set of control parameters, the nuclear coordinates.

The partitioning of nuclear configuration space obtained as a result of the definition of molecular structure leads to the concept of a structure diagram. The space R^Q is partitioned into a finite number of structural regions with their boundaries, as defined by the catastrophe set, denoting the configurations of unstable structures. This information constitutes a system's structure diagram, a diagram which determines all possible structures and all mechanisms of structural change for a given chemical system.

By appealing to the theorem of structural stability of Palis and Smale³⁹ one can show that only two kinds of structural instabilities or catastrophe points can arise and that there are therefore, only two basic mechanisms for structural change in a chemical system.

Palis and Smale's theorem of structural stability when used to describe structural changes in molecular system predicts a configuration $\mathbf{X} \in R^Q$ to be struc-

turally stable if $\rho(\mathbf{r}, \mathbf{X})$ has a finite number of critical point such that: (a) each critical point is nondegenerate, and (b) the stable and unstable manifolds of any pair of critical points intersect transversely.

The immediate consequence of the theorem is that a structural instability can be established through one of two possible mechanisms which correspond to the bifurcation and conflict catastrophes previously described. A change in molecular structure can only be caused by the formation of a degenerate critical point in the electronic charge distribution or by the attainment of an unstable intersection of the submanifolds of bond and ring critical points, as described above.

Thom³⁸ has developed a classification of elementary catastrophes based upon their codimension, the dimension of the control (nuclear) space and their corank, the number of behavior coordinates for which only third or higher order terms appear in the Taylor series expansion of ρ in the neighborhood of a degenerate critical point. The latter are called the essential variables and for each catastrophe type, Thom gives a function f of the essential variables, whose unfolding from the origin of control space describes all possible deformations which the function can undergo. It has been shown that this theory correctly predicts all of the stable structures and the intervening catastrophe sets in the neighborhood of a catastrophe point in nuclear configuration space which arise from the presence of a degenerate critical point in the electronic charge density.^{1,6} That is, Thom's theory correctly predicts the form of the structure diagram in the neighborhood of a catastrophe point.

VI. Applications of the Quantum Theory of Molecular Structure

A. Bond Order, Bond Path Angle, Bond Ellipticity, and Structural Stability

The properties of a given structure are usefully characterized in terms of the properties of the charge density at the (3,-1) or bond critical points. For bonds between a given pair of atoms one may define a bond order whose value is determined by ρ_b , the value of the charge density at the bond critical point.⁴¹⁻⁴³ The extent of charge accumulation in the interatomic surface and along the bond path increases with the assumed number of electron pair bonds and this increase is faithfully monitored by the value of ρ_b . The ρ_b values of the C-C bonds in hydrocarbons can be fitted to an expression to obtain bond orders of 1.0, 1.6, 2.0, and 3.0 for ethane, benzene, ethylene, and acetylene, respectively.⁴³ In a hydrogen bond AH-BX, obtained when an acid AH binds to a base atom B of a base BX, the value of ρ_b is relatively small and only slightly greater than the sum of the unperturbed densities of the H and B atoms of the acid and base molecules at the degree of penetration found in the dimer. The strength of the hydrogen bond is found to parallel this degree of penetration of the van der Waals envelopes of the acid and base molecules and to exhibit an increase with an increase in ρ_b .⁴⁴⁻⁴⁶ The variation of ρ_b with the equilibrium internuclear separation R_e has also been investigated.⁴⁷ Particularly useful relationships between ρ_b and R_e have been developed by Boyd and co-workers.^{45,46,48,49} A related property is the bonded radius of

an atom, the distance from the nucleus to the associated bond critical point, a quantity closely paralleling the relative electronegativity of two bonded atoms.⁵⁰⁻⁵² Boyd and co-workers have used this quantity in the classification of bonds in diatomic hydrides and mixed halides of Al, Si, and P.^{53,54}

A bond path, unless dictated to be so by symmetry, is not necessarily coincident with the internuclear axis and when it is not, the bond path length R_b is greater than the internuclear separation R_e . Such bent bond paths are present in those systems where classical structural arguments predict the presence of strain such as in the small ring hydrocarbons.^{17,43,47} In these instances the bond paths in general, are outwardly bent from the geometrical perimeter of the ring, as illustrated by the molecular graphs for ring structures in Figure 4. In molecules which are electron deficient, such as the boranes, the bond paths linking the bridging hydrogen atoms are strongly bent toward the interior of the ring so as to maximize the binding from a minimum amount of electron density (see Figure 5). Wiberg and co-workers have shown that the presence of bent bond paths is more prevalent than anticipated and that the degree of bending is a useful parameter in understanding structural effects in molecules. This property of bond paths is, however, more usefully catalogued by using the idea of a bond path angle rather than of the bond path length. The bond path angle, α_b , is the angle subtended at a nucleus by the pair bond paths linking it to the two nuclei which define the corresponding geometrical bond angle α_e .⁴³ The difference $\Delta\alpha = \alpha_b - \alpha_e$ provides a measure of the degree of relaxation of the charge density away from the geometrical constraints imposed by the nuclear framework. In general, for a strained molecule $\Delta\alpha > 0$ and in these cases the bonds are less strained than the geometrical angles α_e would suggest. In cyclopropane for example, the bond path angle exceeds the 60° C-C-C bond angle by 18.8° . Wiberg and Murcko⁵⁶ have discussed the significance of the $\Delta\alpha$ values found in H_2O , H_2S , NH_3 , and PH_3 while Wiberg and Breneman⁵⁵ have found large negative values for $\Delta\alpha$ for the H-C-X angle in a variety of methyl derivatives CH_3X when X is more electronegative than C, and positive values when X is less electronegative. They have related these changes in $\Delta\alpha$ to both steric and electronic effects. Wiberg and Laidig,⁵⁷ in a study of the origin of the rotational barriers adjacent to double bonds have used the bond path angle to determine the degree of p character in the bonds to a carbonyl carbon. They find the angle opposite the more electronegative atom to have the larger bond angle and the orbital directed to it has high p character. The geometrical angles do not reflect the anticipated changes in hybridization that are revealed through the study of the bond path angles.

The charge density along a bond path attains its minimum value at the bond critical point and the associated curvature or eigenvalue of the Hessian of ρ at \mathbf{r}_e , λ_3 , is thus positive. The charge density in an interatomic surface on the other hand, attains its maximum value at the bond critical point and the two associated curvatures of ρ at \mathbf{r}_e , λ_1 and λ_2 , those directed along axes perpendicular to the bond path, are thus negative. In a bond with cylindrical symmetry, these two negative curvatures of ρ at the bond critical point

are of equal magnitude. However, if electronic charge is preferentially accumulated in a given plane along the bond path (as it is for a bond with π -character, for example), then the rate of falloff in ρ is less along the axis lying in this plane than along the one perpendicular to it, and the magnitude of the corresponding curvature of ρ is smaller. If λ_2 is the curvature of smallest magnitude, then the quantity $\epsilon = [\lambda_1/\lambda_2 - 1]$, the ellipticity of the bond, provides a measure of the extent to which charge is preferentially accumulated in a given plane.⁴¹ The axis of the curvature λ_2 , the major axis, determines the relative orientation of this plane within the molecule (see Figure 3). The ellipticities of the C-C bonds in ethane, benzene, and ethylene are 0.0, 0.23, and 0.45, respectively, for densities calculated from basis sets containing proper polarizing functions and the major axis of the ellipticity in each of the latter two molecules is perpendicular to the plane of the nuclei. The bond ellipticities faithfully recover the anticipated consequences of the conjugation and hyperconjugation models of electron delocalization.⁴¹

The chemistry of a three-membered ring is very much a consequence of the high concentration of charge in the interior of the ring relative to that along its bond paths, a fact which is reflected in substantial bond ellipticities.^{41,58} The values of ρ_r , the value of the charge density at a ring critical point, is generally only slightly less than, and in some cases almost equal to, the values of ρ_b for the peripheral bonds in the case of a three-membered ring of carbon atoms. In four-membered and larger rings of carbon atoms the values of ρ_r are considerably smaller, as the geometrical distance between the bond and ring critical points is greater than in a three-membered ring. Because electronic charge is concentrated to an appreciable extent over the entire surface of a three-membered ring, the rate of falloff in the charge density from its maximum value along the bond path toward the interior of the ring is much less than its rate of decline in directions perpendicular to the ring surface. Thus the C-C bonds have substantial ellipticities, and their major axes lie in the plane of the ring. The ellipticity of a C-C bond in cyclopropane is actually slightly greater than that for the "double bond" in ethylene, indicating that the extent to which charge is preferentially accumulated in the plane of the ring is greater than that accumulated in the π -plane of ethylene. This property accounts for the well-documented ability of three-membered rings to act as an unsaturated system with the charge distribution in the plane of the ring exhibiting properties characteristic of a π -like system, one that is able to conjugate with a neighboring unsaturated system. Such conjugation is illustrated by the interaction of the cyclopropyl group with the (formally) vacant 2p orbital in CH_2^+ . The major axis of the ellipticity induced in the C- CH_2 bond has an overlap of 0.97 with the corresponding axes of the neighboring C-C bonds of the cyclopropyl group. (The overlap is determined simply by taking the scalar product of the eigenvectors defining the major axes of the two bond critical points.) Such conjugating ability of the cyclopropyl group is rationalized by using molecular orbital models through the choice of a particular set of orbitals, the so-called Walsh orbitals. Theory shows that the " π -like" nature of a three-membered ring is a property of its total charge distribution, one that

results from the proximity of its ring and bond critical points. Understanding the physical basis of this effect enables one to predict its appearance and consequences in other systems.

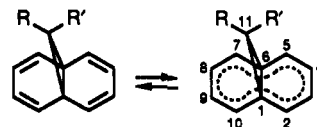
Cremer and Kraka^{59,60} and Cremer and Gauss⁶¹ have used these properties of the density together with those of the Laplacian distribution to great advantage to obtain a predictive understanding of the structure and reactivity of three-membered ring systems. The important role of the concentration and delocalization of electronic charge in the surface of these structures is brought to the fore through the introduction of the concept of σ -aromaticity. The continuous change in the nature of the interaction of a substituent X with an ethylene fragment from one yielding a regular three-membered ring structure to one yielding a π -complex, i.e., a conflict structure, is monitored through the changes in the corresponding molecular graphs as the electron-donor ability of X is increased. The changes in structure induced by the resulting perturbations of the charge density are as predicted by the structure diagram for a three-membered ring system Figure 10 with the π -complex being identified with the conflict structure obtained when the bond path from X terminates at the C-C bond critical point. The reader is referred to the original papers for a detailed discussion of the results and of the manner in which they may be applied to the prediction of the chemistry of three-membered ring systems.

It was shown that the opening of a ring structure resulted from the coalescence of the ring and a bond critical point, the positive curvature of the ring point annihilating the in-plane negative curvature λ_2 of the bond point to yield a zero curvature characteristic of an unstable or degenerate critical point, Figures 8 and 9. The decrease in the magnitude of λ_2 and its eventual disappearance means the ellipticity of the bond which is to be broken increases dramatically and becomes infinite at the geometry of the bifurcation point. Thus a structure possessing a bond with an unusually large ellipticity is potentially unstable. The two equivalent ring bonds of the cyclopropylcarbanyl cation, $C_4H_7^+$, provide an example of this behavior.⁵⁸ The two long bonds of the three-membered ring of this are of order 0.6 and exhibit ellipticities equal to 6.7. Their corresponding paths are very inwardly curved and their bond path length exceeds the internuclear separation by 0.20 Å. The structure verges on instability since either of the bond critical points of the long bonds can be annihilated by coalescence with the ring critical point. The curvature of ρ at the ring critical point which lies almost on the line joining the two bond critical points, is close to zero and correspondingly, the associated negative curvature, λ_2 , of each of the neighboring bond critical points is equally small in magnitude. As anticipated for long bonds, the positive curvature of ρ along their bond paths is relatively large, as is the second and parallel positive curvature of ρ at the ring critical point. The values of ρ at the bond and ring critical points differ by only 0.001 au. Thus there is a nearly flat-bottomed trough in the distribution of charge linking these three critical points and little energy is required to cause a migration of the ring point along the trough to coalesce with a bond point and yield a ring-opened structure. It is a general observation that

little energy is required for the nuclear motions which result in a migration of a critical point along an axis associated with vanishing by small curvature of the charge density. Thus the energy surface in the neighborhood of this structure is very flat for such a motion of the nuclei and the open structure differs from it in energy by less than a kcal/mol.⁵⁸

Further examples of potentially unstable structures being revealed through exceptionally high bond ellipticities are provided by the propellanes, particularly [2.1.1]propellane, structure 21 in Figure 4. The bridgehead bond critical point and each of the ring critical points of the two three-membered rings in this molecule are separated by only 0.07 Å and the value of $\rho_b = 0.197$ au exceeds that of ρ_r by only 0.001 au. The close proximity and nearly equal values for the bond and ring critical points results in a near zero value for the curvature of the density at the bond critical point in the direction of the three-membered ring critical points. The result is a very large ellipticity, equal to 7.21, for the bridgehead bond in this molecule. The bridgehead bonds in both [2.2.1]- and [2.1.1]propellane are predicted to be the most susceptible to rupture by the bifurcation mechanism and both molecules readily undergo polymerization at 50 K. The bifurcation catastrophe undergone by the [1.1.1]propellane molecule has been used to illustrate the mathematical modeling of a structural instability.¹⁶ Bachrach⁶² has shown that [1.1.1]propellane with the bridgehead carbons replaced with phosphorus atoms possesses a relatively large P-P separation of 2.485 Å and no bridgehead bond path. It is a cage structure. In the dication obtained by the removal of two electrons from antibonding HOMO, this distance is reduced to 2.181 Å and a bridgehead bond path is present. The structure however, is close to an instability as the ring critical points are extremely close in value and position to these same properties of the bridgehead bond critical point.

These properties of a charge distribution have been applied to a study of the position of the equilibrium dinorcaradiene = [10]annulene as a function of the substituents R.⁶³ While X-ray diffraction studies yield the geometries of the relevant species, and in particular the C1-C6 internuclear separation, they do not enable one to determine whether or not carbons C1 and C6 are bonded to one another and hence to determine which of the two structures is the correct one for a given set of substituents R and R'. Gatti⁶³ et al. determined the



topological properties of the theoretically determined charge distributions at the experimentally measured geometries for combinations of substituents R and R' = CN, CH₃, H, and F yielding C1-C6 separations ranging from 1.543 Å for R = R' = CN to 2.269 Å for R = R' = F. The study determined which of the systems possesses a C1-C6 bond. The dimethyl derivative in one of the two crystallographically distinct unit cells and with a C1-C6 separation of 1.770 Å is the last member of the series to possess the [10]annulene structure. The bond order of the C1-C6 bond and the separation between its critical point and the ring critical

point of the three-membered ring undergo a continuous decrease and, correspondingly, the C1–C6 bond ellipticity exhibits a continuous increase through the series of molecules until the bond is ruptured. A display of the gradient vector field of the next member in the plane of the three-membered ring, which possesses a C1–C6 separation only slightly greater at 1.783 Å, indicated that this separation is past the geometry of the bifurcation point created by the coalescence of the ring and bond critical point, as both critical points are absent from the display.

It has been shown⁵⁸ that the topological theory of molecular structure can also be used to treat in an unambiguous manner the corresponding problem of determining whether or not homoaromatic conjugation is present in a given system, a property which is also determined by the properties particular to a cyclopropyl ring. Further applications have been made by Cremer et al.⁶⁴ to 1,2-dihydroborete and by Barzaghi and Gatti to the homotropylium cation⁶⁵ and to a number of related hydrocarbons, all of which potentially have six π -electrons and which differ by the number of basal carbon atoms and the formal charge.⁶⁶ The latter study considered the relative importance of mobius aromaticity and homoaromaticity as a source of stabilization in these compounds. The topological parameters supported the conclusion that the mobius aromaticity rather than homoaromaticity is the principal stabilizing interaction in the compounds studied. The topological parameters of the charge density have been used by Cremer and Schmidt⁶⁷ in a direct determination of the degree of electron delocalization in the compound bicyclo[6.2.0]decapentaene. They concluded that the compound is weakly aromatic with the charge being delocalized primarily over the periphery of the ring system, as opposed to its separate delocalization over each ring to result in an antiaromatic destabilization.

Ritchie et al.⁶⁸ have used the parameters of ρ_b to assign structures and properties to the bonds for three states of the C_4 system using correlated densities in their analysis. They conclude that there is bond path between the inverted sp^2 carbon atoms in the rhombus geometry of the 1A_g state, which is predicted to be marginally more stable than the linear geometry of the $^3\Sigma_g^-$ state. The charge density at the corresponding bond critical point, however, exhibits a very large ellipticity, equal to 24, and the structure is clearly unstable with respect to any motion which increases the distance between these two carbon nuclei.

The above applications of the theory have demonstrated that the properties of the charge density at the bond critical points, together with the related concept of structural stability, enable one to determine the presence or absence of the predicted electronic effects of orbital theories and, when found to be present, to translate these predictions into observable consequence in the charge distribution. An excellent further example is provided by the application of the theory of atoms in molecules to one of the problems most intensively studied by orbital theories, that of the regioselectivity and chemoselectivity that is observed in pericyclic reactions. Gatti et al.⁶⁹ have provided a detailed analysis of the properties of the structures at number of stationary points along the synchronous and nonsynchronous pathways of the thermal cycloaddition of two ethylenes

and of the Diels–Alder addition of ethylene to butadiene. This analysis is significantly aided by the ability of the theory to determine for the first time the points on the potential energy surface where the new C–C bonds are first formed.

Most of the above applications of the theory have also included a tabulation and discussion of the value of the Laplacian of the charge density at the bond critical point, the quantity $\nabla^2\rho_b$. The present discussion of this quantity, which is invaluable in providing a classification of chemical bonding, is presented in the section dealing with the properties of the Laplacian distribution function.

The topological analysis of the charge density can be applied directly to an experimentally measured charge distribution and this is being increasingly done by experimentalists. Some time ago Stewart^{70a} pointed out that one can obtain a direct mapping of the electrostatic potential, electric force field, electric field gradient, gradient of the charge density, and the Laplacian of the charge density from X-ray structure factors. Stewart^{70b} has recently located and identified all of the critical points in the unit cells of paramagnetic (298 K) and antiferromagnetic (11 K) phases of MnF_2 from charge densities obtained from X-ray data. All of the Mn–F and F–F bonded interactions are determined. Ozerov and co-workers⁷¹ have measured the properties of ρ at the experimentally determined bond critical points in a number of crystals, including crystals of ethane, ethylene, and acetylene, and classified the bonding accordingly. Destro et al.⁷² have performed careful low-temperature measurements on crystals of glycine and alanine. These data have been used to obtain a classification of the bonding in these crystals⁷³ by using the topological parameters of ρ . In particular, they find the hydrogen-bonded proton to be linked to the acid by a bond with a relatively large value of ρ_b and with $\nabla^2\rho_b < 0$ and to the base by a bond with a relatively low value for ρ_b and with $\nabla^2\rho_b > 0$, as predicted by theory. Downs⁷⁴ has determined the Laplacian distribution of a crystal of BeO and confirms the ionic nature of this substance.

Guo et al.⁷⁵ have extended the topological analysis to the densities derived from local density, self-consistent field, discrete variational $X\alpha$ calculations. They have applied the technique to a study of various approaches of H_2 to a Ni_4 tetrahedron and are able to determine not only the new bonds formed to the hydrogen but also determine that in the face and bridge approach these bonds are formed at the expense of breaking Ni–Ni bonds, a process which accounts for the enhanced mobility of H in a metal.

Orbital models of atomic properties may also be related to the theory. Slee⁷⁶ has used a Taylor series expansion of the charge density about the bond critical point to determine the effect of substituents on the position of the bond critical point and to predict the accompanying shift in the interatomic surface and the ensuing changes in the atomic populations. He was able to show that the trends found in the position and properties of the bond critical point can be understood in terms of perturbational molecular orbital methods. The effects of fluoro substitution in the ethyl, vinyl, and carbonyl groups are used to illustrate the model. Ritchie^{77a} has used the topological parameters of the charge

density to analyze the effects of vinyl and allylic fluorine substitution in isobutylene. He is able to show that a vinylic fluorine acts as a σ -acceptor by electron transfer into the C-F bond and as a π -repeller by polarization of the adjacent π -bond while an allylic fluorine acts as a π -attractor. Ritchie and Bachrach^{77b} have assigned structures and determined bond and atomic properties for a series of 23 organolithium compounds. The Li atoms are found to exhibit coordination numbers ranging from one to four but no bond paths linking one Li atom to another are observed. In another study, Ritchie et al.^{77c} have used the theory to determine the structure of the diaminoguanidinium cation. Rather than the anticipated internal hydrogen bonds, a base nitrogen in this structure is linked to the nitrogen bearing two hydrogens by a curved bond path. Bachrach finds that the values of ρ_b for bonds to phosphorus provide excellent measures of bond order and bond length in the phosphines, phosphoalkanes, and phosphoalkynes,^{77d} as well as in phosphirane and phosphetane.^{77e} These papers provide good examples of how structures and properties throughout a series of compounds can be systematically characterized in terms of parameters which summarize the important physical features of the observable charge density.

A number of papers have recently appeared, all of which use the theory to assign a structure and characterize the interactions in systems with unusual bonding. Tang^{78a} has assigned structures to π -bonded hydrogen complexes of HF with acetylene, ethylene, and benzene, and also with cyclopropane. In the benzene complex, the H is linked to all six carbon nuclei by bond paths which exhibit large in-plane ellipticities. The complexes with acetylene and ethylene possess conflict structures. Lammertsma and Leszczynsk^{78b} found the topological properties of ρ to provide a concise description of the structure present in digallane, Ga₂H₄, clearly delineating the ionic nature of the linkage of Ga⁺ to the covalently bonded hydrido-bridged anion GaH₄⁻. Cioslowski,^{78c} in a theoretical investigation of the lowest energy geometries of Li₂C₂O₂, finds each Li to be bonded to an oxygen and a carbon in a bicyclic structure which is the most stable structure next to the linear one. Cioslowski^{78d} has also investigated the behavior of the nonnuclear attractors found in Li₂ as a function of the internuclear separation using Thom's catastrophe theory.³⁸ He finds this system to exhibit two cusp and two-fold catastrophes. Bachrach and Ritchie^{78e} have used the connectivity determined by the molecular graph and the values of ρ_b and $\nabla^2\rho_b$ for the bonds to Li in a study of the coordination effects in organolithium compounds. With the sole exception of lithioacetamide, the Li is found to be linked to both the carbanion carbon and to the oxygen of the amide group to yield a cyclic structure. A discussion and comparison of the C-Li and O-Li interactions is also given.

B. Atomic Populations and Moments

The average electron population $N(\Omega)$ of atom Ω is obtained by an integration of $\rho(\mathbf{r})$ over the basin of the atom. The charge on atom Ω with nuclear charge Z_Ω , $q(\Omega)$, is given by $Z_\Omega - N(\Omega)$. The atomic first moment is obtained by weighting the basin integration of $\rho(\mathbf{r})$ by \mathbf{r}_Ω , the electronic position vector with the nucleus of atom Ω as origin. Atomic populations and moments

have been determined in many systems and no attempt is made to list them here. Instead we review some of the applications of charges and moments that have been made to specific problems.

The contribution to an atom's population from orbitals of π -symmetry or pseudo- π -symmetry found in systems with axial or planar symmetry, respectively, is easily determined by the separate integration of their corresponding densities over an atomic basin.⁷⁹ The resulting σ - and π -populations are frequently found to undergo opposing polarizations. Examples of this in a familiar context are provided by the Hückel π -populations predicted for a system of conjugated double bonds as compared to the total atomic populations as determined by theory. The π -populations of the carbon atoms in the allyl⁸⁰ and pentadienyl cations, starting from a terminal carbon atom, are 0.48 and 0.97 in allyl and 0.63, 1.00, and 0.61 for pentadienyl. These values are very similar to the predicted Hückel populations of 1/2 and 1 for allyl and 2/3, 1, and 2/3 for pentadienyl. However, the atoms with the smallest π -populations bear the smallest net positive charges because of an opposing polarization of the σ -density. The net charges on the atoms in the same order as the π -populations given above are +0.09 and +0.22 for allyl and +0.09, +0.16, and +0.01 for pentadienyl. Thus atomic net charges cannot be assigned on the basis of Hückel π -populations as is done in models based on an assumed relationship between the π -density at a carbon nucleus and the ¹³C chemical shift observed in nuclear magnetic resonance spectra.

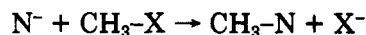
As pointed out by Libit and Hoffmann,⁸¹ arguing on the basis of orbital models, polarization of the π -density is of particular importance when an unsaturated system is bonded to a π -electron donor or abstractor group. This is illustrated by the polarization of the atomic π -densities of the carbonyl group as caused by a substituent X bonded to carbon of the carbonyl group in the substituted formyl compounds HXC=O.²⁴ A π -donating group causes the π -population of the oxygen atom, rather than that of the carbon atom, to increase while a π -withdrawing group causes the π -population of oxygen to decrease relative to that found for X = H. Examples of opposing polarizations of the σ - and π -density distributions which result in an alternation in the corresponding atomic populations are provided by the substituted benzenes.²⁵ The amino group, for example, is π -donating and, as in the substituted carbonyls, the polarization of the π -density in the bonds to the carbon atom bearing the substituent causes its π -populations to decrease and that of the atoms attached to it, the ortho carbon atoms, to increase. This effect alternates around the ring, producing the pattern of charge increase at ortho and para carbon atoms and its decrease at the meta atoms characteristic of ortho-para directing groups. The σ -populations change in just the opposite way with the σ -charge becoming more negative at the meta carbon atoms. The nitro group is π -electron withdrawing and thus the π -population of the carbon bearing the substituent is increased and the accompanying alternation causes corresponding increases at the meta position and decreases at the ortho and para positions, as is characteristic of meta directing groups. The σ -populations again change in just the opposite way. The amino group increases the π -population of

the phenyl group by 0.084 e and activates the ring toward electrophilic aromatic substitution relative to benzene, while the nitro group decreases the π population by 0.099 e and deactivates the ring.

The π -donating/withdrawing ability of a substituent X in the substituted phenyls Ph-X is found to be the same as that observed in the substituted formyl derivatives, XHC=O. The effect of most of the same group of substituents on the charge distribution and moment of the ethyl group has also been studied.²⁴ The ordering of the total charge withdrawal by X is found to be the same in all three series of molecules.

Information corresponding to the π -populations of the orbital model is recovered in the quadrupole polarization of the atomic charge densities, a property of the total charge density. A quadrupolar polarization of an atomic density along the z axis obtained by weighting the basis integration of $\rho(\mathbf{r})$ by the operator $(3z^2 - r^2)$, has the form of a d_{z^2} orbital, a removal of charge from a plane and its concentration in an axial direction perpendicular to the plane. In benzene and ethylene, with the z axis perpendicular to the plane containing the nuclei, $Q_{zz}(C) = -3.34$ and -3.38 au, respectively, corresponding to the presence of a single π -electron. With z taken as the internuclear axis in acetylene, $Q_{zz}(C)$ is large and positive, equal to +4.14 au corresponding to a torus-like concentration of π -density about the z axis as reflected in the negative values for $Q_{xx}(C) = Q_{yy}(C) = -2.07$ au. In the planar methyl cation molecule with a nearly vacant p_x orbital, $Q_{zz}(C) = +1.22$ au and the carbon atom appears as an oblate spheroid.²⁶ The quadrupolar polarizations of the ortho and para carbon atoms of substituted benzenes vary linearly with their atomic π -populations.²⁵ In forming a hydrogen bond, the quadrupolar polarizations of the hydrogen atom and of the base atom B along their axis of approach are both decreased in magnitude, corresponding in the orbital model to a σ - to π -promotion of their atomic densities.⁴⁴ Wiberg et al.⁸² have determined the σ - and π -populations of the atoms in benzene and the azines in a study of π -electron delocalization.

Wiberg and Laidig⁵⁷ also determined the charges and energies of the atoms in their study of the rotational barriers in esters and amides. Their results leave in doubt the resonance model of the origin of the barrier in these molecules. The same failure of the classical resonance model applies to the understanding of the relative acid strengths of esters compared to ketones^{83a} and of carboxylic acids compared to alcohols.^{83b} A study of the atomic charges in these systems and their corresponding anions shows that it is the inductive effect of the carbonyl group rather than a charge transfer to the carbonyl oxygen as anticipated on the basis of the resonance model that is responsible for the difference in acidities of the pairs of species. Wiberg and Breneman have presented an extensive investigation of the effect of substituents on the atomic properties of methyl⁵⁵ and *n*- and *tert*-butyl^{84a} derivatives. The atomic charges and the net charge induced on the methyl group are in good accord with the electronegativities of the substituents. Shi and Boyd^{84b} are conducting an extensive theoretical investigation of the S_N2 reaction for a wide range of nucleophiles N^- and leaving groups X in the reaction



As well as determining the energies of reaction and activation by using a high level of theory, the changes in the charge distribution between reactants, transition state, and products are monitored by the properties of ρ at the bond critical points and the charges on the atoms. The effects of electron correlation are found to be important in determining the geometry of and the atomic charges in the transition state. The values of ρ_b of the C-X bond and of the charge on X in the transition state are shown to be determined primarily by the position of the transition state along the reaction coordinate. Cao et al.^{84c} have used a large basis set to calculate the minimum energy geometries, atomic properties, and bond parameters for a set of 18 acyclic and cyclic molecules containing N-N bonds. A bond order based on the value of ρ_b for the N-N bond is given and found to yield useful correlations with observed properties. The N-N bond in N_2O_4 for example, is found to be 0.58. (The charge on F when combined with N is mistakenly reported as -1.4 rather than -0.4.)

Streitwieser and co-workers independently developed a method of defining an atomic charge which is also based upon a spatial partitioning of the electronic charge density. In their method, the density is first integrated in a direction perpendicular to a given plane. The resulting two-dimensional distribution is then partitioned by its two gradient paths which terminate at a (2,0) critical point, the two-dimensional analogues of an interatomic surface, and a (3,-1) critical point. The resulting populations are referred to as integrated projection populations. These authors have noted that such populations are computationally easier to determine than are the atomic populations of theory. They have also shown that the projected populations form approximations to and recover the trends in the values exhibited by the atomic populations. The method of integrated electron populations has been applied to a wide range of chemical problems.⁸⁶

Stutchbury and Cooper⁸⁷ have used atomic populations to study the acidities and basicities of aliphatic alcohols and amines. The gas-phase ordering of the acidities of alcohols and amines is the opposite of that anticipated on the basis of the operation of the inductive electron release from a methyl group in the reactant, the acidity and basicity both increasing with increasing methyl substitution. Corresponding results are obtained for substituted carbonium ions, their stability increasing with increasing methyl substitution. The atomic populations of the carbonium ions and their neutral counterparts have also been determined²⁶ and the same set of observations explains the observed results in all three systems. These observations are (1) Methyl substitution does not cause significant changes in atomic charges in the neutral saturated molecules. (2) The replacement of H by methyl in the anions and cations does cause significant changes in the atomic populations and always corresponds to a dispersal of the excess charge over the hydrogens of the methyl groups. (3) The hydrogen atoms of a methyl group may act very effectively as either a sink or a source of electronic charge.

Cooper and Allan⁸⁸ have shown how the densities obtained from spin-coupled wavefunctions may be partitioned according to the zero flux boundary con-

dition. Such functions faithfully reproduce the changes in charge density which accompany the formation of chemical bonds from separated reactants and the method was applied to a study of the changes in the atomic properties which accompany bond formation in LiH and BH. Changes in atomic energy, atomic population, and atomic moments have been used in a study of hydrogen-bond formation,⁴⁴ in the reactivity of substituted benzenes²⁵ and the energetics of their protonation⁸⁹ and in the formation of the Lewis adducts between HCN and NgF^+ , $\text{Ng} = \text{Kr}$ and Xe .⁹⁰

Cooper and Stutchbury^{91a} have shown that the electrostatic potential maps calculated by a distributed multipole moment method using the atomic monopole, dipole, and quadrupole moments can be successfully used to predict the conformations of hydrogen bonded van der Waals complexes formed with hydrogen fluoride. Breneman^{91b} has shown that one can construct the electrostatic map for a molecule using a standard transferable set of group moments calculated from statistically averaged multipole moments of the atoms of theory. The field predicted in this manner is encoded on the 0.002 au envelope of the charge density.

Through the use of the quantum definition of an atom and its properties, one can relate any chemical property or change to its atomic contributions and to any accompanying change in structure. Recent examples of such applications which make full use of the theory are a discussion of the origin of rotation and inversion barriers by Bader et al.,^{92a} an investigation of the importance of resonance stabilization in the allyl anion and cation by Wiberg et al.,^{92b} and work by Glaser^{92c} on the relation of the thermal stability of diazonium cations to the properties of the C-N linkage as determined by the variation in the atomic and bond properties observed in a series of such cations. All three of these investigations draw into question classical models of the related phenomena: the changes in the charge distribution accompanying the internal rotation in ethane are not consistent with the model of Pauli-like exchange repulsions between localized C-H bond orbitals,^{92a} little stabilization of the allyl anion can be attributed to electron delocalization or resonance,^{92b} and Glaser^{92c} shows how the Lewis resonance structures can be reinterpreted to bring their anticipated consequences into line with the observed properties of the charge distribution as brought to the fore by the theory of atoms in molecules. Ritchie and Bachrach^{92d} have used the atomic population on hydrogen, the bond path angle, and the values of ρ_b and $\nabla^2\rho_b$ in a discussion of the acidity of cubane relative to that of strained and unstrained hydrocarbons. The atomic population $N(\text{H})$ and $\nabla^2\rho_b(\text{C-H})$ are found to yield a better correlation with both observed and calculated deprotonation enthalpies than does the $J(^{13}\text{C-H})$ coupling constant.

VII. Properties of the Laplacian of the Electronic Charge Density

A full discussion of the Laplacian of the electronic charge density and its use in models of molecular geometry and reactivity is given in ref 1. These same topics are the subject of a recent review.⁹³ The present discussion is therefore, limited to an overview of the role which this function plays throughout the theory and of the physical basis it provides for the models based on

the electron pair concept of Lewis.⁷

A. Role of the Laplacian in the Theory of Molecular Structure

The Laplacian of the charge density appears as an energy density in the theory, that is as $L(\mathbf{r})$, the quantity

$$L(\mathbf{r}) = -(\hbar^2/4m)\nabla^2\rho(\mathbf{r}) \quad (86)$$

The integral of $L(\mathbf{r})$ over an atom Ω to yield $L(\Omega)$ van-

$$L(\Omega) = \int_{\Omega} L(\mathbf{r}) d\tau = (-\hbar^2/4m) \int_{\Omega} \nabla^2\rho(\mathbf{r}) d\tau = (-\hbar^2/4m) \oint dS(\Omega, \mathbf{r}) \nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad (87)$$

ishes because of the zero flux boundary condition (eq 1) which defines an atom in a molecule. The demonstration that an atom is an open quantum subsystem is obtained by a variation of Schrödinger's energy functional $\mathcal{G}[\psi, \Omega]$ for a stationary state and by a variation of the action integral for a time-dependent system. In each case the zero flux boundary condition is introduced by imposing the variational constraint that

$$\delta L(\Omega) = \delta \left\{ \int_{\Omega} \nabla^2\rho(\mathbf{r}) d\tau \right\} = 0$$

at every stage of the variation. The possibility of introducing the constraint in this manner is a consequence of the property of the functionals $\mathcal{G}[\psi, \Omega]$ and $\mathcal{L}[\Psi, \Omega]$, that at the point of variation where the appropriate Schrödinger equation is satisfied, they both reduce to an integral of the density $L(\mathbf{r})$. The property given in eq 87 is common for an atom and for the total system and it is this property which endows them with similar variational properties, thereby making possible the generalization of the principle of stationary action to an atom in a molecule.

The two kinetic energy densities $K(\mathbf{r})$ and $G(\mathbf{r})$ differ by $L(\mathbf{r})$ (eq 63) and it is because $L(\Omega)$ vanishes for an atom that $T(\Omega)$, the electronic kinetic energy of an atom, is well defined (eq 64). It was demonstrated in section III that the density $L(\mathbf{r})$ appears in the local expression for the virial theorem. This is an important result, since it relates a property of the charge density to the local contributions to the energy, and it is repeated here as eq 88. The electronic potential energy

$$(\hbar^2/4m)\nabla^2\rho(\mathbf{r}) = 2G(\mathbf{r}) + \mathcal{V}(\mathbf{r}) \quad (88)$$

density $\mathcal{V}(\mathbf{r})$, the virial of the forces exerted on the electrons, eqs 68 and 75, and the electronic kinetic energy density $G(\mathbf{r})$ (eq 61) define the electronic energy density $E_e(\mathbf{r})$

$$E_e(\mathbf{r}) = G(\mathbf{r}) + \mathcal{V}(\mathbf{r}) \quad (89)$$

Because $L(\Omega)$ vanishes for an atom, integration of eq 88 over the basin of an atom yields the atomic virial theorem

$$2T(\Omega) = -\mathcal{V}(\Omega) \quad (90)$$

and as a consequence, the electronic energy of an atom in a molecule satisfies the following identities:

$$E_e(\Omega) = \int_{\Omega} E_e(\mathbf{r}) d\tau = -T(\Omega) = (1/2)\mathcal{V}(\Omega) \quad (91)$$

It is a property of the Laplacian of a scalar function, such as the charge density $\rho(\mathbf{r})$, that it determines where

the function is locally concentrated, where $\nabla^2\rho(\mathbf{r}) < 0$, and locally depleted, where $\nabla^2\rho(\mathbf{r}) > 0$.⁹⁴ Electronic charge is concentrated in those regions of space where the Laplacian of the charge density is negative. The expressions "local charge concentrations" and "local charge depletions" will refer to maxima and minima in the function $-\nabla^2\rho(\mathbf{r})$, extrema which are to be distinguished from local maxima and minima in the charge density itself. This property of the Laplacian can be used to determine the dominant contributions to the local energy of the electronic charge distribution by using the local expression for the virial theorem.

The potential energy density $\mathcal{V}(\mathbf{r})$ is everywhere negative, while the kinetic energy density is everywhere positive. Thus the sign of the Laplacian of the charge density determines, via eq 88, which of these two contributions to the total energy is in excess over their average virial ratio of 2:1. *In regions of space where the Laplacian is negative and electronic charge is concentrated, the potential energy dominates the local total electronic energy $E_e(\mathbf{r})$ and the local virial relationship. Where the Laplacian is positive and electronic charge is locally depleted, the kinetic energy is in local excess.*

An energy density is dimensionally equivalent to a force per unit area or a pressure. Thus the Laplacian may alternatively be viewed as a measure of the pressure exerted upon the electronic charge density relative to the value of zero required to satisfy a local statement of the virial theorem, i.e., $\mathcal{V}(\mathbf{r}) + 2G(\mathbf{r}) = 0$. In regions where the Laplacian is negative, the charge density is tightly bound and compressed above its average distribution. In regions where the Laplacian is positive, the charge density is expanded relative to its average distribution, the pressure is positive and the kinetic energy of the electrons is dominant.

B. Laplacian of the Charge Density and the Lewis Electron Pair Model

Neither the electronic charge density nor the electronic pair density offer any evidence of the localized bonded and nonbonded pairs of electrons evoked in the Lewis model of electronic structure. The relatively simple topology exhibited by the charge density has already been described and while it accounts for the elements of molecular structure, it does not offer any suggestion of the existence of spatially localized pairs of electrons. The extent to which electrons are spatially localized is determined by the pair density, a distribution function whose properties are dominated by the so-called Fermi hole.⁹⁵ An electron can only go where its hole goes and thus an electron is localized to a given region of space only if its Fermi hole is correspondingly localized.⁹⁶ The Fermi hole is very localized for motion of an electron in the immediate vicinity of a nucleus. It is possible to define a core radius within which the contained Fermi correlation is maximized for one α and one β electron and the result is a region of space from which essentially all other electrons of both spins are excluded to yield a localized pair of electrons. The fluctuation in the average population of such a region of space is minimized when the contained Fermi correlation is maximized.⁹⁶ Such physical localization of electronic charge is not a general phenomenon, but is found in atomic cores and within the atomic boundaries

of ionic systems, such as the Na and Cl atoms in NaCl. In the atoms of these systems, the contained Fermi correlation approaches its limiting value, which is the negative of the average electron population, and the electrons are in excess of 90% localized within the separate atomic basins.^{1,93,96} What one does not find the pair population to predict are bonded or nonbonded pairs of valence electrons as envisaged by the Lewis model or as represented by individual localized orbitals.

The electron pairs of Lewis and the associated models of geometry and reactivity find physical expression in the topology of the Laplacian of the charge distribution. The Laplacian distribution recovers the electronic shell model of an atom by exhibiting a corresponding number of pairs of shells of charge concentration and charge depletion.^{5,8,97,98} For a spherical-free atom, the outer or valence shell of charge concentration, the VSCC, contains a sphere over whose surface electronic charge is maximally and uniformly concentrated. Upon entering into chemical combination, this valence shell of charge concentration is distorted and maxima, minima, and saddles appear on the sphere of charge concentration. The maxima correspond in number, location, and size to the localized pairs of electrons assumed in the Lewis model. The VSEPR model of molecular geometry⁹⁹ is a direct extension of the Lewis model and it predicts the geometries of closed-shell molecules about some central atom which contains from two to seven pairs of electrons in its valence shell. All of the properties postulated in this model for bonded and nonbonded pairs of electrons are recovered by the maxima in the valence shell of charge concentration of the central atom and the Laplacian of the charge density provides a physical basis for this most successful of models of molecular geometry.^{9,93,100} This mapping of the topology of the $\nabla^2\rho$ onto the Lewis model is illustrated in Figure 11 for the molecule ClF_3 whose T-shaped geometry can be deduced as a consequence of the behavior of the maxima in the VSCC of the Cl atom—the most stable geometry being the one which maximizes the separations between the maxima. It has been shown that positioning an electron at the critical point corresponding to a maximum in the Laplacian distribution maximally localizes its Fermi hole.¹⁰⁰

The discussion so far has focused on the properties of the local charge concentrations of the Laplacian distribution and on how they recover the Lewis and VSEPR models of electron pairs. The Lewis model, however, encompasses chemical reactivity as well, through the concept of a generalized acid–base reaction. Complementary to the local maxima in the VSCC of an atom for the discussion of reactivity are its local minima. A local charge concentration is a Lewis base or a nucleophile, while a local charge depletion is a Lewis acid or an electrophile. A chemical reaction corresponds to the combination of a "lump" in the VSCC of the base combining with the "hole" in the VSCC of the acid. In terms of the local virial theorem (eq 88) the reaction of a nucleophile with an electrophile is a reaction of a region with excess potential energy on the base atom with a region of excess kinetic energy on the acid atom. The accompanying rearrangement of the charge is such that at every stage of the reaction $L(\Omega)$ remains equal to zero for each atom. Thus reductions in the magnitudes of the local concentrations or depletions of charge

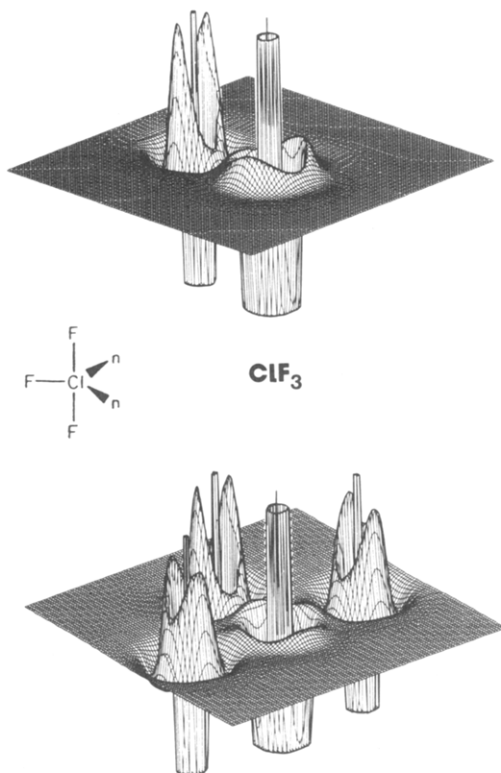


Figure 11. A display of the negative of the Laplacian distribution for ClF₃. The equatorial plane (top) shows the presence of two nonbonded and one bonded concentration of charge in the valence shell charge concentration of the Cl atom. (Note the presence of three quantum shells for Cl and of two such shells for F.) The plane containing the two axial as well as the equatorial F atoms exhibit three bonded charge concentrations in the VSCC of Cl and another view of the (3,-1) critical point which appears as a saddle point in $-\nabla^2\rho$ between the two nonbonded charge concentrations in the upper diagram. The Cl atom in ClF₃ exhibits two nonbonded and three smaller bonded charge concentrations in its VSCC.

requires opposing changes in other parts of the atom to satisfy the constraint on its charge distribution as given in eq 87.

The positions of the local charge concentration and depletion together with their magnitudes, are determined by the positions of the corresponding critical points in the VSCC's of the respective base and acid atoms. This information enables one to predict positions of attack within a molecule and the geometries of approach of the reactants. For example, a keto oxygen in the formamide molecule has two large nonbonded charge concentrations in the plane of the nuclei ($\nabla^2\rho = -6.25$ and -6.30 au) while the nitrogen atom exhibits two such maxima of lesser magnitude ($\nabla^2\rho = -2.14$ au) above and below this plane. On the basis of this information one correctly predicts that the formamide molecule will preferentially protonate at the keto oxygen,¹⁰¹ specifically at the position of the largest of the two charge concentrations and in the plane of the nuclei. There are holes in the VSCC of a carbonyl carbon and they determine the position of nucleophilic attack at this atom. These holes are above and below the plane of the nuclei of the keto grouping and the corresponding critical point for a number of ketones are positioned to form angles of $110^\circ \pm 1$ with respect to the C=O bond axis. This is the angle of attack predicted for the approach of a nucleophile to a carbonyl carbon.¹⁰²

Similar predictions have been made for the Michael addition reaction, specifically for the nucleophilic attack of an unsaturated carbon in acrylic acid, CH₂=CH-CO₂H, and methyl acrylic acid.¹⁰³ The properties of the Laplacian distribution correctly predict that the attack occurs at the terminal carbon of the methylene group, the carbon of the unsubstituted acid being most reactive, and that the approach of the nucleophile will be from above or below the plane of the nuclei along a line forming an angle of 115° with the C=C bond axis, the latter prediction being in agreement with calculations of the potential energy surface for this reaction. Bader and Chang²⁵ have given a discussion of the use of the Laplacian distribution in the prediction of the sites of electrophilic attack in a series of substituted benzenes.

Electrostatic potential maps have been used to make predictions similar to these.¹⁰⁴ Such maps, however, do not in general reveal the location of the sites of nucleophilic attack,¹⁰⁵ as the maps are determined by only the classical part of the potential. The local virial theorem (eq 88), which along with the kinetic energy density, determines the sign of the Laplacian of the charge density, involves the full quantum potential. The potential energy density $\mathcal{V}(\mathbf{r})$ (eq 75) contains the virial of the Ehrenfest force (eq 54) the force exerted on the electronic charge at a point in space (eqs 55 and 56). The classical electrostatic force is one component of this total force.

The Laplacian distribution has been used to predict the structures of a large number of hydrogen-bonded complexes by aligning the (3,+3) critical point, a local charge depletion on the nonbonded side of the proton in the acid HF, with the (3,-3) critical point of the base, a local concentration of charge, for which $-\nabla^2\rho$ attains its large value.¹⁰⁶ With only a few exceptions, the geometries of the complexes predicted in the SCF calculations (which agree with experiment where comparison is possible) are those predicted by the properties of the Laplacian as outlined above. Figure 12 illustrates the Laplacian distribution for three of the bases involved in this study. They form an interesting set, as the Lewis model of localized pairs fails for two of these molecules. The Laplacian, since it is model independent and instead reflects the properties of the charge distribution, correctly predicts the observed structures of the complexes. The oxygen in NNO possesses a torus of charge concentration (which appears as two maxima in the plane shown in Figure 12) for which $-\nabla^2\rho = 5.63$ au, while the single nonbonded charge concentration on the terminal N has a magnitude of 2.90 au. (This arrangement of nonbonded charges, as does that for the bonded charge concentrations, agrees with the Lewis model, :N::N::O:.) The Laplacian predicts the proton to bond with the oxygen and to form a bent structure with a bond angle of 103.1° compared to the calculated value of 104.4° . Contrary to the Lewis model, the oxygen in SCO exhibits only a single nonbonded maximum which is colinear with the internuclear axis. This maximum is also the largest of the charge concentrations in this molecule and one thus predicts a linear complex SCO-HF, as is both observed and calculated. In OCO, the nonbonded charge concentration on each O forms a torus about the molecular axis, in correspondence with the Lewis model. The value of $-\nabla^2\rho$ for the torus, which forms an angle with the internuclear

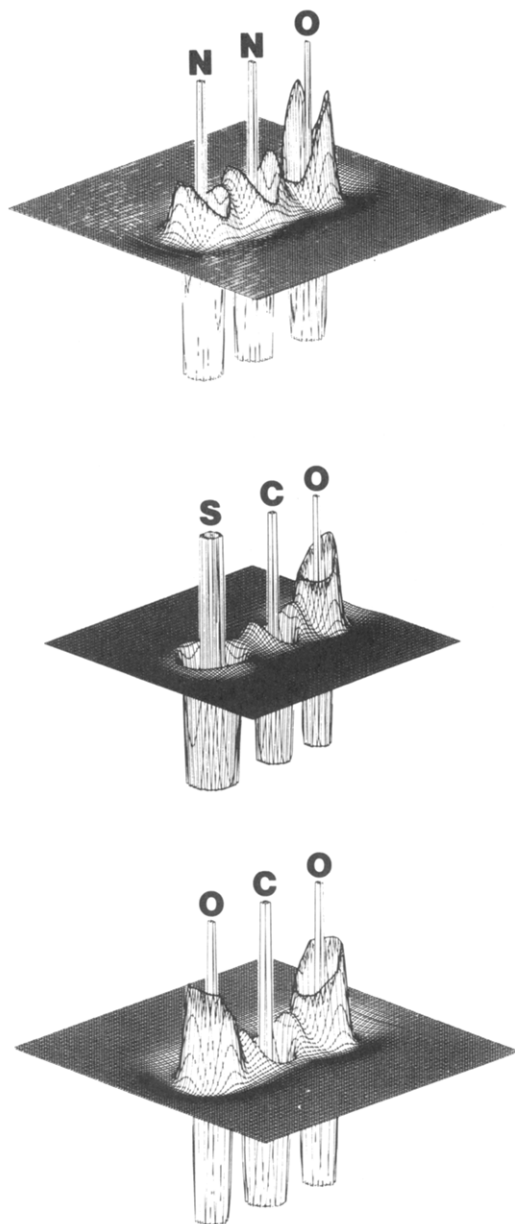


Figure 12. Relief maps of $-\nabla^2\rho$ for axial planes of N_2O , SCO and CO_2 . Note the presence of three quantum shells on sulfur.

axis of 149° , is 4.74 au. As is clear from the display of the Laplacian for OCO , however, each oxygen atom is capped by a nonbonded charge concentration which is of almost constant value and the value of $-\nabla^2\rho$ in the VSCC of oxygen on the internuclear axis equals 4.72 au. The properties of the Laplacian are thus consistent with the experimental result of a floppy complex with a bond angle within the range of $180^\circ \pm 30$. The calculated equilibrium structure is found to be linear, but its energy differs from that of a secondary bent structure with a bond angle of 165° by only 0.1 kcal/mol.

Tang et al.¹⁰⁷ have observed remarkably linear correlations between the magnitudes of the nonbonded charge concentration (the magnitude of the Laplacian at a (3,-3) critical point in $-\nabla^2\rho$) on the nitrogen atom and the gas-phase basicity for the series of methyl amines $NH_{3-n}Me_n$, $n = 0-3$, and for a set of cyano and pyridine compounds. Clearly, the size of a charge concentration or charge depletion as determined by the Laplacian of the charge density provides a measure of

the propensity of a given center toward reaction through a series of related compounds.

Aray and Murgich¹⁰⁸ have demonstrated a direct relationship between the maxima in the VSCC of a nitrogen atom and the components of the electric field gradient at the same nucleus in a series of nitriles. The largest diagonal component of the electric field gradient tensor was found to be determined by the combined effect of the bonded and nonbonded charge concentrations in the VSCC of nitrogen along the C-N axis. This work demonstrates that this tensor can be interpreted directly in terms of a property of the observable charge distribution and removes the necessity of invoking orbital models in the interpretation of this important quantity.

C. Classification of Atomic Interactions

The gradient vector field of the charge density identifies the set of atomic interactions within a molecule. These interactions, which define the molecular structure, can be characterized in terms of the properties of the Laplacian of the charge density. The local expression of the virial theorem (eq 88) relates the sign of the Laplacian of ρ to the relative magnitudes of the local contributions of the potential and kinetic energy densities to their virial theorem averages. By mapping those regions where $\nabla\rho^2 < 0$, the regions where electronic charge is concentrated, one is mapping those regions where the potential energy density makes its dominant contributions to the lowering of the total energy of the system.

As discussed in section II.E, the interaction of two atoms leads to the formation of a critical point in the charge density at which the Hessian of ρ has one positive eigenvalue labeled λ_3 and two negative eigenvalues labeled λ_1 and λ_2 , implying that ρ exhibits one positive and two negative curvatures at the point \mathbf{r}_c . Since the two perpendicular curvatures of ρ , whose eigenvectors define the interatomic surface, are negative, the charge density is a maximum at \mathbf{r}_c in the interatomic surface and charge is locally concentrated there with respect to points in the surface. The curvature of ρ along the interaction line is positive, charge density is locally depleted at \mathbf{r}_c relative to neighboring points along the line and ρ is a minimum at \mathbf{r}_c along this line. Thus the formation of a chemical bond and its associated interatomic surface is the result of a competition between the perpendicular contractions of ρ towards the bond path which lead to a concentration or compression of ρ along this line and the parallel expansion of ρ away from the surface which leads to its separate concentration in each of the atomic basins. The sign of the Laplacian of ρ at the bond critical point, the quantity $\nabla^2\rho(\mathbf{r}_c)$, determines which of the two competing effects is dominant and because of the appearance of $\nabla^2\rho(\mathbf{r}_c)$ in the local expression for the virial theorem (eq 88) its sign also serves to summarize the essential mechanical characteristics of the interaction which creates the critical point. There is therefore, an intimate link between the topological properties of $\rho(\mathbf{r})$ and its Laplacian, the trace of the Hessian of ρ , and through the properties of the Laplacian one may begin to bridge the gap between the form of the charge distribution and the mechanics which govern it. The reader is referred to ref 1 for a full discussion and for

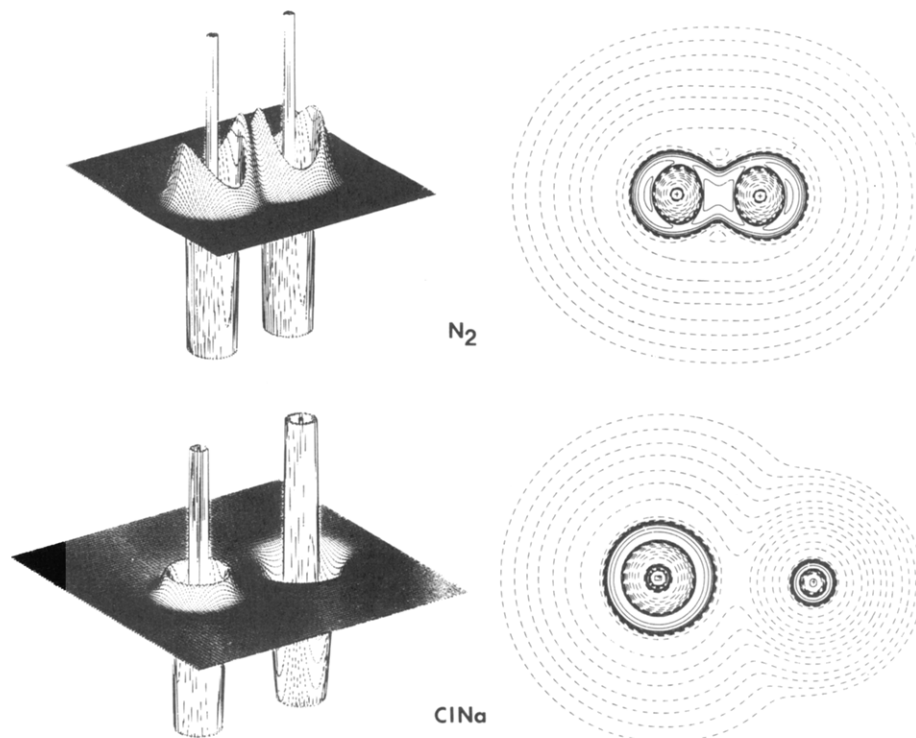


Figure 13. Relief maps of $-\nabla^2\rho$ for N_2 and NaCl and contour maps for the same axial planes with negative values of the Laplacian, the regions where electronic charge is concentrated, given by the solid contours. In N_2 , a shared interaction, the VSCC's of both atoms are joined by a concentration of charge in the internuclear region. In NaCl , the Laplacian distributions retain their atomic-like nature, with Cl exhibiting three quantum shells and Na two, as anticipated for a system in which nearly one electronic charge is transferred from one atom to the other. Note the polarization of the VSCC on Cl toward the Na. In N_2 the nuclei are bound by the shared concentration of charge (eq 88). In NaCl the nuclei are bound by the charge concentration localized within the VSCC of the Cl atom.

numerical and pictorial illustrations.

When $\nabla^2\rho(\mathbf{r}_c) < 0$ and is large in magnitude, electronic charge is concentrated in the internuclear region as a result of the dominance of the perpendicular contractions of ρ toward the interaction line, or equivalently in these bound systems, toward the bond path. The result is a sharing of electronic charge by both nuclei, as is found for interactions usually characterized as covalent or polar and they shall be referred to as "shared interactions". In shared interactions, as exemplified for N_2 in Figure 13, the region of space over which the Laplacian is negative and which contains the interatomic critical point, is contiguous over the valence regions of both atoms and the VSCC's of the two atoms form one continuous region of charge concentration. The interaction is dominated by the lowering of the potential energy associated with the formation of the (3,-1) critical point. In a shared interaction, the nuclei are bound as a consequence of the lowering of the potential energy associated with the concentration of electronic charge shared between the nuclei (eq 88). This concentration of electronic charge in the interatomic surface is reflected in relatively large values of $\rho(\mathbf{r}_c)$, the value of ρ at the (3,-1) critical point, for molecules with shared interactions and the ratio of the perpendicular contractions of ρ to its parallel expansion, as measured by the ratio $|\lambda_1/\lambda_3|$, is greater than unity.^{1,8}

The second limiting type of atomic interaction is that occurring between closed-shell systems, such as found in noble gas repulsive states, in ionic bonds, in hydrogen bonds, and in van der Waals molecules. One anticipates that such interactions will be dominated by the requirements of the Pauli exclusion principle. Thus for

closed-shell interactions, $\rho(\mathbf{r}_c)$ is relatively low in value and the value of $\nabla^2\rho(\mathbf{r}_c)$ is positive.⁸ The sign of the Laplacian is determined by the positive curvature of ρ along the interaction line, as the exclusion principle leads to a relative depletion of charge in the interatomic surface. These interactions are dominated by the contraction of charge away from the interatomic surface toward each of the nuclei. The Laplacian of ρ is positive over the entire region of interaction and the kinetic energy contribution to the virial from this region is greater than the contribution from the potential energy. The spatial display of the Laplacian of ρ given in Figure 13 for NaCl is atomic-like for this example of a closed-shell interaction. The regions where the Laplacian is negative are, aside from small polarization effects, identical in form with those of a free atom or ion. Thus the spatial regions where the potential energy dominates the kinetic energy are confined separately to each atom, reflecting the contraction of the charge toward each nucleus, away from the region of the interatomic surface. The ratio $|\lambda_1/\lambda_3| < 1$ in all the examples of closed-shell interactions.⁸

The almost complete interatomic transfer of one electronic charge found for ionic systems such as NaCl is verified by the nodal structure of the corresponding Laplacian maps. The cations Li^+ , Na^+ , and K^+ all lack the outer nodes associated with the valence density distribution of the isolated atom. Thus Li in LiCl has but one negative region rather than two, Na in NaCl has two rather than three, and K in KF has three rather than four.

A hydrogen bond results from the interaction of two closed-shell systems, and the properties of ρ at the as-

sociated bond critical point reflect all of the characteristics associated with such interactions: a low value for $\rho(\mathbf{r}_c)$ and $\nabla^2\rho(\mathbf{r}_c) > 0$. The same characteristics, with even smaller values of $\rho(\mathbf{r}_c)$, are found for the bond to hydrogen formed in a van der Waals complex of an acid such as HF or HCl with an inert gas atom. A hydrogen bond, which includes the van der Waals complexes, is defined to be one in which a hydrogen atom is bound to the acid fragment by a shared interaction, $\rho(\mathbf{r}_c)$ large and $\nabla^2\rho(\mathbf{r}_c) < 0$, and to the base by a closed-shell interaction, $\rho(\mathbf{r}_c)$ small and $\nabla^2\rho(\mathbf{r}_c) > 0$. These are the very characteristics exhibited by the experimentally determined charge density at the bond critical points for the bond paths linking a proton in crystals of amino acids.⁷³

The kinetic energy density $G(\mathbf{r})$ (eqs 60 and 61) is expressible in terms of three contributions along orthogonal axes. The relative values of the component parallel to the internuclear axis (G_{\parallel}) and one of the components perpendicular to this axis (G_{\perp}) faithfully reflect the values of the corresponding curvatures of ρ at \mathbf{r}_c . For the shared interactions, $G_{\perp}(\mathbf{r}_c) > G_{\parallel}(\mathbf{r}_c)$, while just the reverse situation is found for the closed-shell interactions. In addition, as anticipated on the basis of the local virial theorem (eq 88) the kinetic energy per electronic charge, the ratio $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$, is less than unity for the shared interactions and greater than unity for the closed-shell interactions. Thus when the positive curvature of ρ is large and dominated by the contraction of the charge toward the nuclei, the kinetic energy per electron is absolutely large and the value of its parallel component exceeds that of a perpendicular component. In the shared interactions, the accumulation of charge in the internuclear region leads to a softening of the gradients of ρ and of the corresponding curvature of ρ along the interaction line, and the parallel component of $G(\mathbf{r})$ is correspondingly less than its perpendicular components. The dominance of these latter components again mirror the corresponding dominance of the perpendicular contractions of ρ toward the bond axis in shared interactions. Because of the concentration of charge and the concomitant negative values of the Laplacian of ρ over the same region, the potential energy is dominant and the kinetic energy per electron is absolutely small.

The same observations regarding the behavior of the parallel and perpendicular components of the kinetic energy and their relation to the gradients and curvatures of ρ in molecular systems were first made by Bader and Preston¹⁰⁹ for the molecules H_2 and He_2 . They studied the spatial properties of $G(\mathbf{r})$ and $K(\mathbf{r})$ and their relation to $L(\mathbf{r})$. The differing behavior of $G(\mathbf{r})$ in the binding region of a bound and an unbound system is made very clear by comparing the plots of this function they give for H_2 and He_2 . The correlation of the local behavior of the kinetic energy density with the gradients and curvatures of ρ are partially accounted for by theory through eq 88. When $\nabla^2\rho(\mathbf{r}) > 0$ and the Laplacian is dominated by the positive curvature of ρ (contraction of ρ toward each nucleus), the larger contribution to the Laplacian comes from the kinetic energy—and by observation, primarily from its parallel component. Correspondingly, when the Laplacian of ρ is negative and ρ is concentrated as a result of contractions perpendicular to the bond path, not only does

the potential energy make the dominant contribution to the virial but one observes the perpendicular components of $G(\mathbf{r})$ to dominate its parallel component. Thus one concludes that the kinetic energy dominates the contributions to the virial and to the energy in regions of space where its parallel component is dominant. This occurs in regions where $\nabla^2\rho(\mathbf{r}) > 0$. Conversely, in regions where the perpendicular components to $G(\mathbf{r})$ are largest, the potential energy makes the major contribution to the virial and to the energy of the system.

Extraordinarily small values of $G(\mathbf{r}_c)/\rho(\mathbf{r}_c)$, of the order of 0.03 au, are exhibited by the nonnuclear maxima, the pseudoatoms, in the metallic clusters of Li and Na atoms referred to in section II.E. The same small values of kinetic energy per electron are reflected in the ratio of the average values of $T(\Omega)$ to $N(\Omega)$ for the pseudoatoms and, in accordance with the Heisenberg uncertainty principle, they indicate that the charge density of the pseudoatoms is loosely bound and unconfined. The Laplacian distributions for these clusters show the metal atoms to be missing their outer charge concentrations, indicating that they are present primarily as ionic cores. The charge density of the cores is highly localized as indicated by values in excess of 90% for the contained Fermi correlation. The charge on the pseudoatoms, however, is very delocalized with values for the contained Fermi correlation being only 30% of that required for complete localization. Aside from the inner shell charge concentrations of the metallic cores, the negative values of the Laplacian distribution are confined within the boundaries of the pseudoatoms. The value of $\nabla^2\rho(\mathbf{r}_c)$ is positive at the bond critical point linking a pseudoatom to a metallic core, but negative at a critical point linking two pseudoatoms. The properties of ρ at the critical point linking two pseudoatoms are characteristic of a weak, shared interaction: $\rho(\mathbf{r}_c) = 0.0056$ au, $\nabla^2\rho(\mathbf{r}_c) = -2.6 \times 10^{-4}$ au, and $G(\mathbf{r}_c)/\rho(\mathbf{r}_c) = 0.10$ au. The ionic cores are linked to one another through the pseudoatoms and the study of these clusters gives a model of group I metals consisting of positively charged metal atoms with very localized charge distributions immersed in and bound by an intermeshed network of negatively charged pseudoatoms. Metallic binding is a result of the lowering of the potential energy associated with the charge concentrations of the valence density and these concentrations are confined within the boundaries of the pseudoatoms. These same charge concentrations have a very low kinetic energy per electron, and the potential energy lowering associated with the formation of the pseudoatoms is obtained without a large accompanying increase in the kinetic energy. As a consequence, the electron density of the pseudoatoms should be mobile under the influence of an electric field. The quantum mechanical current for a core density is simply the diamagnetic current circulating around the nucleus and the metal atoms in these clusters will not contribute appreciably to the electrical conduction. It is the highly delocalized density of the network of pseudoatoms which is responsible for the binding in a metallic system and for its conducting properties.

The examples so far considered have demonstrated the existence of two extremes of atomic interactions, one set being the opposite of the other in terms of the regions of charge concentrations and depletions and the

associated mechanical consequences. The whole spectrum of possible interactions lying between these two limiting extremes are found to occur for interactions that do and do not involve interatomic charge transfer. Some examples are given here but the reader is referred to ref 1 for a full discussion.

The C–O interaction of a carbonyl group, for example, is characterized by a transfer of charge of the order of 1.3 e from carbon to oxygen. Transfer of the order of one electronic charge or more does not imply the presence of an ionic interaction. The charge distributions and the properties of the atoms in the carbonyl group do not begin to approach those of closed-shell systems, a fact reflected in the properties of ρ at the bond critical point. The first observation for C=O interaction is that while $\nabla^2\rho(\mathbf{r}_c)$ is large in this case, the value of $\rho(\mathbf{r}_c)$ is also large in value, much greater than the values associated with the closed-shell or ionic limit. This in turn is a result of the large magnitude of the curvatures of ρ at \mathbf{r}_c , values which are much larger than those for the closed-shell limit, but comparable to those for the shared limit. They reflect the large stresses that are present in the interatomic charge distribution, stresses which lead to a large accumulation of charge in the interatomic surface and to the formation of a concentration of charge on the electronegative side of the interatomic surface and to a corresponding depletion of charge on the electropositive side. The large positive curvature, λ_3 , found for the C–O bond dominates the interaction and the properties of the bond. Such a bond is perturbed only slightly by substitution of a hydrogen, in formaldehyde, for example.^{76,77} When λ_3 is low in value, as for an ethylenic bond, atomic substitution can more readily lead to a shift in the interatomic surface, corresponding to a transfer of charge across the surface to a change in the physical characteristics of the bond.

The atomic interactions in C=O are clearly intermediate in character: there is a large accumulation of charge in the interatomic surface resulting from the considerable contractions of ρ toward the bond path, but the interaction is dominated by the still larger positive stress in ρ along the interaction line, giving a tight distribution with a large kinetic energy per electron. The ability to summarize the details of the mechanics of an interaction in terms of the properties of ρ at \mathbf{r}_c and the properties of the atoms whose nuclei are linked by the associated interaction line precludes the need to assign oversimplifying labels to describe the interaction. It is however, important to realize that the parameters which summarize an interaction do exhibit a continuous spectrum of values, linking limiting situations that can be classified as shared and closed-shell interactions.

It is also possible to observe behavior transitional between shared and closed-shell interactions in the absence of charge transfer. In the homonuclear series $B_2 \rightarrow F_2$ both $\rho(\mathbf{r}_c)$ and $|\nabla^2\rho(\mathbf{r}_c)|$ increase to a maximum at N_2 and decrease to minimum values at F_2 . Their behavior parallels the binding energies of these molecules, as it does the occupation of the $1\pi_u$ bonding orbital (fully occupied at N_2) and of the $1\pi_g$ antibonding orbital (fully occupied at F_2). Occupation of the $1\pi_g$ orbital leads to an increase in the localization of the charge on each atom and this has the expected conse-

quences on the properties of ρ at \mathbf{r}_c ; namely a decrease in $\rho(\mathbf{r}_c)$ and an increase in the positive curvature λ_3 and hence in $\nabla^2\rho(\mathbf{r}_c)$. In F_2 , the contraction of ρ toward each nucleus dominates the interaction and the VSCC of each F atom is localized in a near-spherical atomic-like shell, as is typical of the closed-shell limit. The characteristics of ρ at \mathbf{r}_c for F_2 are intermediate between those for O_2 and Ne_2 .⁸ The ratio of the perpendicular to parallel kinetic energy contributions at \mathbf{r}_c is 0.751, a value, while less than unit as typical of closed-shell interactions, is considerably greater than the value for Ne_2 .

Both the charge density and the pair density of the electrons of a F atom are very localized within its basin. There is only a 7% exchange of the electrons of a F atom in F_2 with the electrons on the neighboring atom. Thus the strong potential field exerted on the valence electrons in a fluorine atom, while providing the major source of binding in fluorides via charge transfer to the fluorine atom, is also the cause of the weak binding found in the F_2 molecule.

There is no suggestion that the atomic interaction in the F_2 molecule is at the closed-shell limit. It is however, demonstrated that the binding in this molecule is qualitatively different from that found in N_2 and that the differences are made quantitative by the properties of each system at the critical point in its charge density that is formed as a consequence of the interaction of the two atoms.

Frenking et al.^{110a} have used the properties of the charge density at its critical points and the Laplacian distribution in a study of the binding of helium in singly and doubly charged first-row diatomic cations. Bartlett^{110b} has also appealed to the properties of the Laplacian of the charge density in a general discussion of the bonding in helium containing compounds. Preston et al.⁹⁰ and Frenking et al.¹¹¹ have used the properties of the charge density in conjunction with those of its Laplacian distribution in a study of the bonding to noble gas atoms in positively charged species. Alcamí et al.¹¹² have used the Laplacian of the charge density to classify the interactions found in the complexes formed between the lithium ion and a number azines. Azines containing neighboring nitrogen atoms are found in general, to form a bonded ring structure with the lithium ion. The properties of the Laplacian distribution clearly demonstrate the closed-shell nature of these interactions and make clear the dominance of the electrostatic potential in determining their properties.

The electrostatic and virial theorems, coupled with the properties of the Laplacian of the charge density, also enable one to classify a given atomic interaction as belonging to a bound or unbound state. The regions of charge concentration as defined by the Laplacian can be used in conjunction with the electrostatic theorem to determine whether the forces on the nuclei will be attractive or repulsive. The electronic charge in these same regions makes the dominant stabilizing contributions to the potential and total energies of the system and in this way the Laplacian provides a link between the force and the energy. The reader is referred to ref 1 for this discussion.

Cremer and Kraka^{42,113} relabel an atomic interaction line as an MED (for maximum electron density) and state that a covalent bond exists between two atoms

when their nuclei are linked by an MED and when the energy density $E_e(\mathbf{r})$ defined in eq 89, which they relabel $H(\mathbf{r})$, is negative in value at the position of the associated (3,-1) critical point. Using eq 88, one finds that $H(\mathbf{r}) = -K(\mathbf{r})$, the kinetic energy density defined in eqs 60 and 61, and the behavior of this quantity in both the shared and closed-shell limits of atomic interactions has been previously discussed.¹⁰⁹ Their definition and its accompanying discussion in terms of charge accumulation in the internuclear region as determined by a density difference distribution, implies directly or indirectly, that the bonding between two atoms linked by an atomic interaction line for which $H(\mathbf{r}_c) > 0$, as found in ionic and hydrogen-bonded systems, for example, differs in some fundamental way.

This definition ignores the property that all bonded interactions have in common: two atoms are bonded if their nuclei are linked by an atomic interaction line in a minimum energy geometry, that is if they are linked by a bond path. The presence of such a line demonstrates the accumulation of charge between the nuclei in an absolute sense, and not relative to some arbitrary reference distribution. The observed range of properties exhibited by this line and its associated interatomic surface accounts for the observed diversity in chemical bonding. This same unified view of chemical bonding is what Lewis considered to be one of the major accomplishments of his electron pair model:⁷ "However, according to the theory which I am now presenting, it is not necessary to consider the two extreme types of chemical combination, corresponding to the polar and the very nonpolar compounds, as different in kind, but only different in degree." The different degrees of polarity were represented by the unequal or equal sharing of the electron pair between the "kernels" of the two atoms, corresponding to the localization of the charge concentration responsible for the binding within the basin of a single atom as in an ionic bond, or to its sharing between the basins of both atoms as in a covalent bond. The quantum theory of molecular structure through its ability to explicitly define interatomic interactions and their stability, broadens this concept still further, by demonstrating that all atomic interactions, both bound and unbound, have a common basis in the form they impart to the electronic charge distribution. The energetic and other mechanical consequences of this form are predicted and made understandable by theory.¹

VII. Conclusions

A fundamental principle of physics yields a unified theory of atoms, bonds, structure, and structural stability, in addition to providing predictive models of molecular geometry and chemical reactivity. It is to be emphasized that the theory of atoms in molecules evolved because it followed the necessary dictum of paralleling experiment in the recovery of observational concepts. It will continue to grow only if it proves useful in the study of the properties of all forms of matter. Eberhart et al.¹¹⁴ evoke a similar requirement in their development of a chemistry of cohesion and adhesion within and between materials in their bulk state. They deem as necessary for this development an appropriate representation of a bond and a measure for the competition for bond formation in network, ionic, covalent,

metallic, and van der Waals solids. Since the present theory of structure is based on the properties of the total charge density, these authors argue that it should be generalizable to different types of bonding in different classes of materials, and in particular to the description of bonding in condensed matter systems. Consequently, they have applied the topological aspects of the theory to an analysis of the charge densities of metals obtained using both the layer Korringa-Kohn-Rostaker method^{115,116} and the local density functional cluster method.^{117,118} It is to be noted that the zero flux boundary condition for a quantum subsystem (eq 1) corresponds to the conventional Wigner-Seitz cell in an elemental solid and they find that the occurrence of bond paths in both the fcc and bcc (face-centered and body-centered cubic) structures constrains the distribution of charge throughout this cell. The reader is referred to the paper for the extensive list of problems the authors are able to treat in this initial development of a chemistry of cohesion and adhesion. Among these, is the demonstration of relationships between the bulk properties of a metal and local properties of the charge density together with the important observation that in systems where the formation of a bond path to a second neighbor is not possible, the fcc structure is favored over the bcc structure.

Since physics predicts what can be observed, it should be possible to construct a molecule by using theory in the same manner that this is done in the laboratory, from pieces of other molecules. Chemists do not begin a synthesis starting with beakers full of nuclei and electrons, the step corresponding to the theoretical synthesis of a molecule starting with the correct Hamiltonian. The first step toward the development of the theoretical synthesis of a molecule, large or small, in a manner which parallels experiment, is the identification of the pieces, that is, the atoms and functional groups of chemistry, that the chemist uses to plan and execute a synthesis. With the theory of atoms in molecules this step is complete and what remains is to discover how to put the pieces together.

To do this it will be necessary to extend the quantum mechanics of an open system to include a prediction of how the properties of subsystem change when it is subjected to a changed environment, i.e., to develop a perturbation theory for an atom in a molecule. However, one does not have to await this extension of the theory to build a molecule from group fragments in all cases. As emphasized throughout this article, the theory of atoms in molecules enables one to take advantage of the most important postulate of the molecular structure hypothesis; that atoms and functional groupings of atoms exhibit characteristic and measureable sets of properties that vary between relatively narrow limits. There are many systems of interest, particularly biological macromolecules, that are composed of repeating structural units. Therefore, it is possible in these cases to construct a molecule from the atoms of theory and predict their properties with acceptably small errors even though one is not at the limit of nearly perfect transferability, as found in the hydrocarbons and discussed in section IV.A, for example.

It has been demonstrated¹¹⁹ that it is possible to synthesize a tripeptide from fragments defined in simpler systems and that the properties predicted for the

synthesized molecule, as obtained by summing the corresponding properties of the atoms in each fragment, are in excellent agreement with those obtained in a direct calculation. The energy of glycylglycine constructed from glycylamine and formylglycine for example, is predicted to within 3 kcal/mol of the calculated value. Other atomic properties such as multipole moments, volumes, and extrema in the Laplacian distribution are predicted with correspondingly small errors. The synthesis requires the matching of the C-N interatomic surfaces from two peptide fragments, a procedure which results in the prediction of the C-N bond length in the dipeptide as the sum of the bonded radii of the C and N atoms. In general peptide bond lengths are reproduced to within 0.001 Å by this method.

A most important advantage that the theoretical synthesis has over the experimental one is that it is not necessary to completely reproduce the whole of a large system. If interest is centered on a portion of a large molecule, an active site for example, just that portion of the molecule is synthesized, the outer interatomic surfaces of the end fragments being left exposed. The properties of a subsystem are determined by the shape of its bounding surface. It is not necessary that it be coupled to another fragment.

The ability to construct a molecule from functional groups will bring the theory of atoms in molecules into complete parallel with experiment and fulfill the purpose of the theory.

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