Quantum Topology of Molecular Charge Distributions. 1

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Abstract: The primary concepts of descriptive chemistry, of an atom in a molecule with its own set of properties, and of a chemical bond, yield to precise definitions in terms of quantum mechanics and the observed topological properties of the charge distribution. The notion of a molecule as a collection of bonded atoms with a definite structure and shape is one which has meaning in real, Euclidean space. It should therefore be a consequence of a property of the system which is itself manifest in real space. It is shown that a particular topological property of the charge density, $\rho(\mathbf{r})$, defines the boundaries between pairs of bonded atoms (it defines an atom) and the network of bonds which link them (it defines structure). The definition of the boundary is universal and it defines the boundary of the molecule, as well as of the atoms within it (it defines molecular shape). These definitions apply to both stationary and dynamic systems. Thus the notions of the making and breaking of chemical bonds are also precisely defined. The boundary defined in the usual formulations of quantum mechanics is the one at infinity where the boundary condition on the variation of ψ is satisfied. These approaches are necessarily restricted in their applications to a total, isolated system. One may obtain a formulation of quantum mechanics which does define the physical subspaces of a system and yields a prediction and description of their average properties. The boundaries of these subspaces are found to be identical with the physical boundaries defined by the topological properties of $\rho(\mathbf{r})$. The observational and theoretical basis for these definitions is presented and illustrated for the diborane molecule. This paper serves as an introduction to a theory of bonding and molecular structure which is entirely determined by the observed properties of the charge density.

I. Introduction

Chemical observations made on a system are determined by the morphology of the system's charge distribution and by its evolution with time. This thesis may be demonstrated by first determining the universal properties of molecular charge distributions and then establishing the existence of a mapping of the experimentally determined concepts of chemistry onto this set of universal properties. We distinguish between those primary concepts which have evolved as a direct result of, and as necessary for the understanding of, chemistry and the models which have evolved to rationalize these concepts. The concepts we hope to discover intact in the properties of the charge density; the models may survive totally, partially, or not at all.

The primary concepts, those without which there would be no correlation and no prediction of the observations of descriptive chemistry, are (1) the existence of atoms in molecules, (2) the ability to identify an atom (or a functional grouping of atoms) in a molecule by its characteristic properties, and (3) the concept of bonding—that molecular stability may be understood by assuming the existence of particularly strong interactions (bonded interactions) between atoms within the molecule. In addition, to understand the saturation of bonding, valency, and ultimately the geometrical structure of molecules, one must in general assume that certain pairs of atoms in a molecule are bonded to one another, while other pairs are not. An important example of a model, on the other hand, is that of the electron pair which serves as a model for a bond or for nonbonded charge. Closely associated with the electron pair model, through its mating with orbital or geminal theories, is the assumption of the localized nature of electron pairs.

On the basis of extensive studies of the properties of molecular charge distributions,[2,3] we have determined what we believe to be important universal properties of the molecular charge density, $\rho(\mathbf{r})$. Such a study is essentially a study of the topological properties of the charge density. We have found that the universal properties may be characterized in terms of the gradient vector field of the charge density, $\nabla\rho(\mathbf{r})$.[4,5] The properties of this field, and hence the principal characteristics of a charge distribution, are totally determined by the number and character of its *critical points*, points at which the field vanishes. The trajectories of $\nabla\rho(\mathbf{r})$, all of which terminate at particular critical points, define the atoms in a molecule.[6] Those which originate at the same critical points isolate the number, locations, and directions of lines throughout a charge distribution, linking particular pairs of atoms, along which the charge density is a maximum. This network of lines faithfully reproduces the features outlined above as being essential to the concept of bonding. *In this sense* these particular trajectories of $\nabla\rho(\mathbf{r})$, called bond paths, define the number, locations, and directions of chemical bonds in a molecule.[2a,5] The atoms so defined are also observed to behave in a manner consistent with the chemical concept of an atom in a molecule. In particular, such topologically defined atoms are, by their very definition, the most transferable pieces of a molecule in real space, i.e., at the charge density level, and, further, their degree of transferability is found to coincide with chemical expectations.

Of equal importance to this charge density based approach to chemistry is the finding that the same topological property of the charge density which defines the boundary of an atom in a molecule also defines the boundary of a subspace in a total system whose variational properties exhibit maximum correspondence with the expressions of all space quantum mechanics.[3,7,8] We shall outline this link with quantum mechanics and show how it allows one to provide quantum definitions of both the atom in a molecule and of all of its properties.

Collard and Hall[9] have demonstrated the utility of orthogonal trajectories, that is, of the paths traced out by the gradient vectors of a scalar field and their associated critical points, in the analysis of scalar functions of several variables. Their analysis is used in the present study to classify the general topological properties of charge distributions of molecules in their equilibrium geometries. Specifically, this quantum topological approach to the development and use of a theory of bonding and molecular structure will be illustrated through a study of $\rho(\mathbf{r})$ for a selected set of boranes, beginning in this paper with diborane, B_2H_6. This theory is model independent and is determined entirely by the observed properties of the charge density. The boranes typify those substances whose structures cannot be rationalized in terms of the two-center electron pair bond model and the bonding in these molecules has been the subject of much discussion.[10-13]

The boranes are themselves representative of a larger class of compounds called clusters,[14] in which each atom appears to be bound to most of the other atoms in the molecule. A

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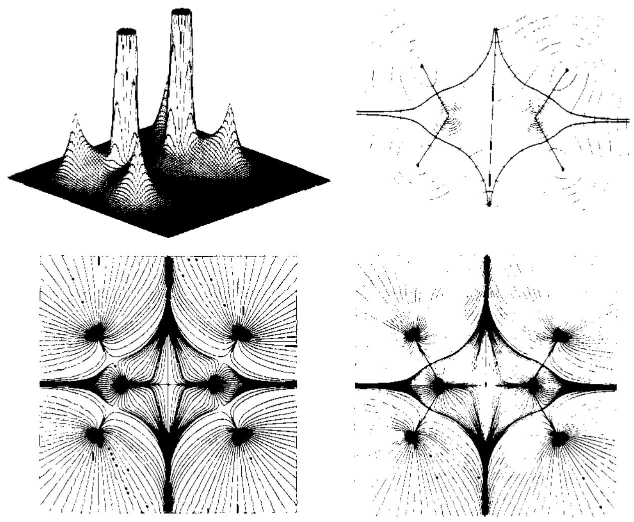

Figure 1. Representations of $\rho(\mathbf{r})$ and of the trajectories of its gradients in the B_2H_4 plane of diborane. There are four (3,−1) saddle points, one between each proton and its neighboring boron, and a (3,+1) or ring saddle point at the molecular center. In this plane (see three-dimensional display) all five critical points behave as (2,0) saddle points. All the trajectories shown in the left-hand side gradient path map originate at infinity and terminate at one of the nuclei except for two which terminate at the ring saddle point and two more which originate at this point. The trajectories associated with the (3,−1) critical points are not shown in this left-hand side map to emphasize the manner in which the gradient paths terminating at a given nucleus define a corresponding region of space by their avoidance of a (3,−1) saddle point in $\rho(\mathbf{r})$. These missing trajectories are shown in the right-hand map, and, again, superimposed on the contour map of $\rho(\mathbf{r})$. The two unique gradient paths which originate at infinity and terminate at a (3,−1) saddle point define the boundary between a pair of neighboring B and H fragments. The same fragments are linked together by the two unique vectors originating at the saddle point—the bond path. Also indicated on the contour plot are the two vectors which terminate at the ring saddle point—the unique axis of the (3,+1) critical point. Contour values (au), in this and the following figures, are 2×10^n, 4×10^n, and 8×10^n where n starts at −3 and increases in steps of unity.

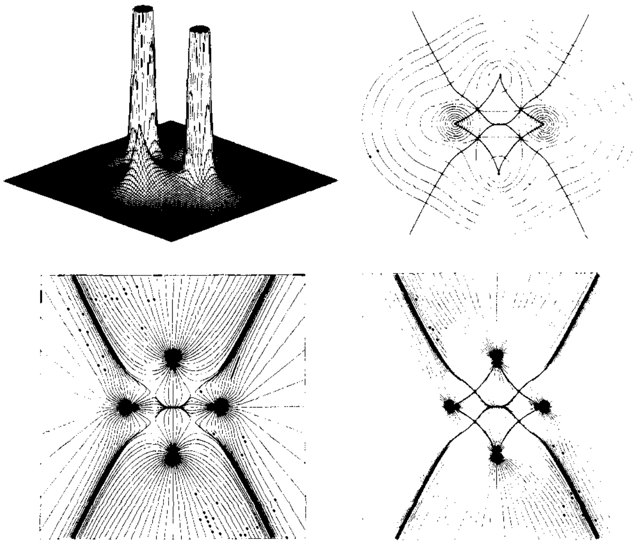

Figure 2. Representations of $\rho(\mathbf{r})$ and of the paths of $\nabla\rho(\mathbf{r})$ in the bridging plane of diborane. There are five saddle points in this plane—four (3,−1) bridging saddle points and (another view of) the (3,+1) ring saddle point. In this plane the ring saddle point appears as a minimum in $\rho(\mathbf{r})$, a (2,+2) critical point. Two maps of the gradient paths are shown, one omitting, the other including, the gradient paths associated with the (3,−1) saddle points. Transfer of these particular gradient paths to the contour map of $\rho(\mathbf{r})$ yields a definition of the boundaries between the hydrogen and boron fragments in this plane and of the bond paths which link these fragments. One extra contour of $\rho(\mathbf{r})$ is indicated in this diagram. Its value, 0.1195 au, is the value of $\rho(\mathbf{r})$ at a bridging saddle point. The value of $\rho(\mathbf{r})$ at the (3,+1) saddle point is 0.1059 au.

knowledge of the properties of the borane charge distributions should be of value in understanding the structures of cluster compounds in general. Finally, the charge distributions of the more complex boranes possess all four of the possible kinds of critical points which characterize a molecule in its equilibrium configuration.

While the present paper is concerned primarily with establishing the definitions of basic chemical concepts through a study of the properties of the charge distributions of molecules in equilibrium geometries, the same definitions apply to a dynamic system. Collard and Hall[9] have pointed out that the analysis of the discontinuous change in the topological characteristics of a molecular charge distribution resulting from the continuous change in its nuclear coordinates is given by the catastrophe theory of Rene Thom.[15] The extension of the present theory to the dynamic case to provide precise meanings to the concepts of the making and breaking of chemical bonds—these are the catastrophes of chemical change—is the subject of a companion study.[16]

II. Topological Properties of Charge Distributions

The universal properties of molecular charge distributions, their observational basis, their classification, and their role in defining chemical concepts are presented and illustrated through an analysis of the charge distribution of diborane. A succeeding paper, using the concepts introduced here, will provide a detailed discussion of the structure and bonding of the boranes.

Calculation of the Charge Density. The charge density for diborane was calculated from a single-determinantal SCF approximation to the ground-state function. The molecular orbitals were expanded in terms of an [11s, 6p, 2d (on B)|6s, 1p (on H)] basis set of GTOs contracted to a (5s, 3p, 1d|4s, 1p) set. The composition of the final basis set was obtained after extensive examination of various contraction schemes (with and without the presence of polarizing functions) and of the exponents. The principal properties of the derived charge density, the nature, and number of its critical points are predicted to be invariant to a further increase in basis set size. The actual values of $\rho(\mathbf{r})$ at the critical points and the geometric location of these critical points are predicted to be within 1 or 2% of the Hartree-Fock result. This study of the detailed dependence of $\rho(\mathbf{r})$ and its derived gradient field on basis set size and composition, together with a corresponding study for B_5H_9, will be reported in detail elsewhere. The state function employed in this study yields an average energy of −52.831 78 au compared to the best previous estimate of −52.7758 au obtained by Brundle et al.[17] The geometry used in the calculation is that determined by the electron diffraction experiments of Bartell and Carroll.[18]

The Charge Density and Its Gradient Field. The scalar charge density $\rho(\mathbf{r})$ is portrayed in the plane containing the terminal hydrogens, Figure 1; in the plane containing the bridging hydrogens and the borons, Figure 2; and in the plane containing the bridging hydrogens, perpendicular to the previous plane, Figure 3. The derived vector field, $\nabla\rho(\mathbf{r})$, is also illustrated via the gradient paths, the paths traversed by the vectors $\nabla\rho(\mathbf{r})$.

The direction of a gradient path is in the direction of increasing $\rho(\mathbf{r})$. Only a single gradient path traverses any given point in space. Their trajectories are orthogonal to isodensity (contour) lines. All gradient paths originate and terminate at critical points, points where $\nabla\rho(\mathbf{r}) = 0$.[4,5] (Critical points were previously referred to by us as stationary points.)

Collard and Hall[9] point out that the properties of a critical point may be uniquely classified by two numbers, labeled rank and signature. We have found this classification very useful and recommend that it be adopted for classifications of charge distributions. We review only briefly the theory behind rank and signature, as their meaning is made clear by their application. The properties of a critical point are determined by diagonalizing the second derivative or Hessian matrix of the scalar field, in this case $\rho(\mathbf{r})$, in the region of the critical point.[9,19] The dimensions of this matrix and the number of its eigenvalues equal the dimensionality of the scalar function, which is three for a distribution in real space. The rank denotes the number of nonzero eigenvalues. With only a single exception to be discussed later, all charge distributions for molecules in equilibrium configurations so far investigated in this laboratory exhibit critical points of rank three, i.e., there are no zero eigenvalues. The three eigenvalues determine three orthogonal eigenvectors or gradient paths which either terminate or originate at the critical point. If the eigenvalue is positive its associated eigenvector or gradient path originates at the critical point; it is directed away from the critical point. If the eigenvalue is negative, the associated gradient path terminates at the critical point; it is directed toward the critical point. The signature is the number of excess positive over negative eigenvalues. For critical points of rank three, only four values for the signature are possible: +3, +1, −1, and −3.

When all three eigenvalues are of the same sign, signature +3 or −3, it is possible to construct an infinity of sets of three mutually orthogonal gradient paths all of which originate or terminate at the critical point. Thus, a (3,+3) critical point is a minimum in $\rho(\mathbf{r})$. The charge density increases for motion in *any* direction away from the point. A (3,−3) critical point is a maximum in $\rho(\mathbf{r})$. The charge density decreases for motion in *any* direction away from this point. The collection of gradient paths which terminate at a maximum in $\rho(\mathbf{r})$ defines a volume of space in a molecular system.

When only two eigenvalues are of the same sign, signature +1 or −1, it is possible to construct an infinity of sets of two mutually orthogonal gradient paths all of which originate or terminate, respectively, at the critical point and which therefore define a surface perpendicular to the unique axis defined by the gradient path associated with the eigenvalue of unique sign. If the eigenvalue of unique sign is greater than zero, two oppositely directed gradient paths will originate at the critical point and define a unique axis in space along which $\rho(\mathbf{r})$ increases for motion away from the critical point. The infinity of gradient paths generated by the two negative eigenvalues, all of which terminate at the critical point, define a surface perpendicular to this axis. Motion in this surface in any direction away from the critical point leads to a decrease in the value of $\rho(\mathbf{r})$. These are the characteristics of a (3,−1) saddle point in $\rho(\mathbf{r})$.

The remaining possibility describes a (3,+1) saddle point. In this case, motion along the unique axis away from the critical point leads to a decrease in $\rho(\mathbf{r})$. Motion in the surface perpendicular to this axis in any direction away from the critical point leads to an increase in $\rho(\mathbf{r})$. Thus, a (3,−1) saddle point has associated with it a path along which $\rho(\mathbf{r})$ is a maximum with respect to a motion in any direction perpendicular to this path. It defines a line of maximum charge density. Correspondingly, a (3,+1) saddle point defines a path along which $\rho(\mathbf{r})$ is a minimum with respect to a motion in any direction perpendicular to this path.

Chemical Significance of Critical Points. Reference to the diagrams depicting the gradient paths shows that the maxima in $\rho(\mathbf{r})$ at the positions of the nuclei behave as do (3,−3) critical points; all gradient paths in the vicinity of a given nucleus terminate at that nucleus. Actually, because of the nuclear-electron coalescence cusp condition on the state function[20] and hence on the charge density,[21,22] $\nabla\rho(\mathbf{r})$ is undefined at a nuclear position. Thus, a maximum in $\rho(\mathbf{r})$ at the position of a nucleus is not a true critical point,[4,5] as $\nabla\rho(\mathbf{r})$ does not vanish. However, the topological behavior of $\rho(\mathbf{r})$ in the region of a nuclear cusp is the same as if it were a true (3,−3) critical point.[9]

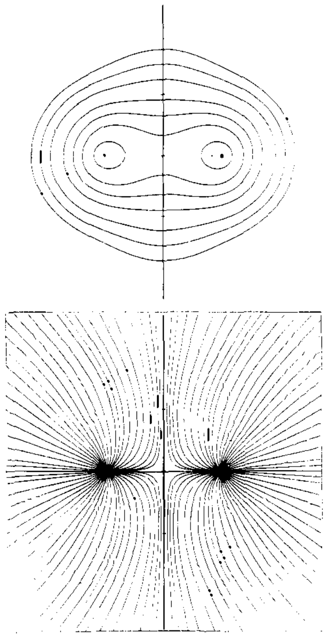

Figure 3. Contour plot of $\rho(\mathbf{r})$ and a map of its associated gradient paths in the plane containing the two bridging hydrogens. This plane contains only one nonnuclear critical point—the (3,+1) ring saddle point. In this plane, as in Figure 1, the ring saddle point has the characteristics of a (2,0) critical point. The two gradient paths which terminate at this critical point are indicated in both maps by a heavy line. They define the unique axis of this (3,+1) saddle point. This axis, which also appears in Figure 1, is the line of intersection of the four ring fragments. All remaining gradient paths in this plane terminate at either one or the other of the protons.

With only one exception, we have never observed a maximum in $\rho(\mathbf{r})$ other than at the position of a nucleus for a many-electron atom or molecule in its ground state or in an excited state when the charge distribution is obtained from a state function close to the Hartree-Fock limit.[23] The single exception found so far is for $\mathrm{Li_2}(\mathrm{X}^1\Sigma_g{}^+$, R = 5.051 au),[26,27] for which a charge density, close to the Hartree-Fock limit, exhibits a small maximum in $\rho(\mathbf{r})$ at the midpoint of the internuclear axis.[28] In all other cases, the critical point between bonded atoms is found to be a (3,−1) saddle point.[4,5,30]

As a consequence of the occurrence of maxima in $\rho(\mathbf{r})$ being restricted to nuclear positions, each nucleus acts as a sink for all the gradient paths which traverse the region of space associated with that nucleus. This behavior is a reflection of the dominance of the nuclear field in determining $\rho(\mathbf{r})$ in each such atomic region. The interaction between two such nuclear dominated regions of space results in the formation of a (3,−1) saddle point in $\rho(\mathbf{r})$ and the boundary between the regions is determined by the properties of this critical point.

There is a (3,−1) saddle point located between each boron and its two neighboring terminal hydrogens (Figure 1). In the two-dimensional display of $\rho(\mathbf{r})$ in this symmetry plane, these critical points reduce to (2,0) saddle points (two nonzero roots of opposite sign). Thus each of these saddle points is avoided by all gradient paths except for two which originate at infinity and terminate there, and two which originate there and terminate at each of the two nuclei, one at boron and one at hydrogen. Each pair of gradient paths which terminates at a (2,0) saddle point defines a boundary between the boron and hydrogen atomic fragments in this plane. Each boundary line denotes the intersection with the plane of the full three-dimensional surface defined by that collection of gradient paths, all of which terminate at a (3,−1) saddle point, i.e., the unique surface of such a critical point. At the saddle point, this surface is orthogonal to the axis defined by the two gradient paths which originate at the same point and terminate, one to each, at the neighboring nuclei. This pair of gradient paths defines the unique axis of a (3,−1) saddle point. Thus both boron nuclei are joined to each of their neighboring terminal protons by lines of maximum charge density.

Transfer of the unique gradient paths associated with the (3,−1) saddle points onto the contour map of $\rho(\mathbf{r})$ in Figure 1 defines the spatial boundaries of the hydrogen fragments in this plane, and lines through the charge distribution along which $\rho(\mathbf{r})$ is a maximum, the bond paths.[5] The boundary lines denote the intersection of the full three-dimensionally defined partitioning surfaces with this plane. Also shown are the two gradient paths which terminate at the central (3,+1) critical point between the borons. This *line*, as discussed below, results from the intersection of four partitioning surfaces and defines the boundary between the borons in this plane.

The ground-state charge distribution of diborane exhibits four more (3,−1) saddle points which are displayed in the diagrams for the bridging plane, Figure 2. There is a (3,−1) saddle point between each boron and each of the bridging hydrogens. In this symmetry plane, each such point again behaves as does a (2,0) saddle point. The pair of gradient vectors which terminates at each such point defines the boundary between a hydrogen and a boron. In this instance, one gradient path originates at infinity, the other at the central critical point, which is a (3,+1) saddle point. All other gradient paths terminating at the bridging saddle points originate at infinity on either side of the plane. Two sets of such gradient paths terminating at the bridging saddle points associated with one proton define the surface of a bridging hydrogen fragment which is trough-like in shape. The unique axis belonging to each of these (3,−1) saddle points lies in the bridging plane and together they define four bond paths linking each bridging hydrogen to both borons. These bond paths are noticeably curved toward the interior of the molecule. Thus the borons, or alternatively the two (BH_2) fragments, are linked together, via the bridging protons, by two lines through the charge distribution along which $\rho(\mathbf{r})$ is a maximum.

The remaining critical point in B_2H_6 is a (3,+1) saddle point located at the center of the ring formed by the borons and the bridging hydrogens. The unique axis of this saddle point, along which $\rho(\mathbf{r})$ *decreases* for motion away from the saddle point, is perpendicular to the plane of the ring. It constitutes a boundary line along which the four surfaces of the ring fragments intersect. The surface associated with this saddle point lies in the plane of Figure 2. In this plane, the critical point has the properties of a (2,+2) critical point, that is, of a minimum in $\rho(\mathbf{r})$. The charge density *increases* for motion away from this point in all directions in the bridging plane.

When viewed in the two planes perpendicular to the bridging plane, (Figures 1 and 3), the (3,+1) saddle point exhibits the characteristics of a (2,0) stationary point. However, the pair of gradient paths which originates at this stationary point and terminates at the two boron nuclei (Figure 1) and the corresponding pair which terminates at the bridging protons (Figure 3) do not define bond paths, that is, ridges in the charge density. While $\rho(\mathbf{r})$ does decrease for motion perpendicular to these two axes in the two designated planes, these same axes represent lines of *minimum* values of $\rho(\mathbf{r})$ for motion in the plane perpendicular to the designated planes. Reference to Figure 2 shows that these axes are but two of an infinity of gradient paths which originate at the (3,+1) saddle point and terminate at one of the four ring nuclei. They lie in the surface associated with this saddle point. A bond path, on the other hand, is defined by the *unique* axis associated with a (3,−1) saddle point. In the plane perpendicular to this axis, a (3,−1) saddle point has the properties of a (2,−2) critical point, that is, of a two-dimensional maximum in $\rho(\mathbf{r})$. Thus all of the gradient paths which define the unique surface of a (3,−1) saddle point terminate at the point of maximum density in the surface. Starting at this point of maximum density the bond path then maps out the line of corresponding points at which $\rho(\mathbf{r})$ is a local maximum in the succession of planes passed through as one moves away from the saddle point.

The set of surfaces generated by the (3,−1) critical points contained within a molecular charge distribution partitions the space of a molecule into a collection of chemically identifiable atomic-like regions. Thus the diborane molecule is partitioned into two boron fragments and six hydrogen fragments in agreement with its chemical composition, B_2H_6. The partitioning surfaces are clearly unique because of the topological properties of a (3,−1) critical point. Their unique character may be expressed in another way: they are the only closed, continuous surfaces, $S(\mathbf{r})$, within a molecular charge distribution which satisfy the boundary condition of zero flux.[4,6]

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

The vector $\mathrm{n}(\mathbf{r})$ is the vector normal to the surface at $\mathbf{r}$. An arbitrarily drawn surface will be traversed by gradient paths and hence will not satisfy eq 1. Any gradient path which terminates at a nucleus does not satisfy eq 1 at the position of the nucleus as $\nabla\rho(\mathbf{r})$ is undefined there. Since all but a finite number of the gradient paths which define the surface of a (3,+1) or ring saddle point terminate at the ring nuclei, such a surface is not a zero flux surface. Thus only a surface unique to a (3,−1) critical point satisfies eq 1 for all points on the surface. (It should be recalled that the two vectors which define the bond path originate at the saddle point where $\nabla\rho(\mathbf{r}) = 0$.)

The existence of a (3,−1) saddle point in $\rho(\mathbf{r})$ between a pair of nuclei implies that the two associated fragments are *neighboring* fragments as they share a common surface. In addition, two such nuclei are connected by a line along which the charge density is a maximum—the bond path. *Thus neighboring fragments are bonded to each other.*

The network of bond paths defined by the presence of (3,−1) saddle points within a molecular system coincides with the network generated by linking together those pairs of atoms which are considered to be bonded to one another on the basis of chemical considerations.[5] This is illustrated in Figure 4, which depicts the number and location of (3,−1) critical points and their associated bond paths in a number of representative systems. In the hydrides AH_n (A = Li through to F), neutral or charged (e.g., BH_4^-), the number of (3,−1) critical points equals n, so located that a bond path links A to each of the n hydrogens. The hydrogens are not linked to one another, nor are they neighbors.

The number of bond paths equals the number of chemical linkages; it does not equal the assumed number of "electron pair bonds" where such a description assigns multiple linkages to bonded pairs of atoms.[32] Thus in ethylene a single bond path links the carbons and in formaldehyde a single bond path links carbon to oxygen. Bond order in the present scheme is determined primarily by the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ at the saddle point.[5] Thus the value of $\rho(\mathbf{r})$ at the carbon-carbon saddle point in acetylene exceeds that found for ethylene, which exceeds that found for ethane.

Unless so demanded by symmetry, the bond path will not in general be coincident with the corresponding internuclear axis. Instead, it exhibits a curvature which reflects the existence of stabilizing or destabilizing forces acting within the system. Thus in cyclopropane (Figure 4) the bond paths of the carbon ring are strongly bent away from its perimeter[5] in agreement with the chemical concept of strain. In benzene (Figure 4) the bond paths defining the ring are curved slightly inward. The binding force exerted on the nuclei of the ring is maximized by concentrating electronic charge within the ring thereby yielding an increased stability toward rupture of the ring. In B_2H_6 (Figures 2 and 4) the bridging bond paths are strongly curved toward the interior of the ring. The angle formed by a boron and its two bridging critical points, the bond path angle $\angle C_HBC_H$, is 33.1° smaller than the corresponding geometrical or "bond" angle, $\angle HBH = 97.0°$. As discussed more fully in the following paper of this series, the bridging structure achieves stability by concentrating charge density in the interior of the ring. The value of $\rho(\mathbf{r})$ at a bridging saddle point (the lowest value of $\rho(\mathbf{r})$ in the perimeter of the ring) is 0.1195 au, only 0.0136 au greater than that at the position of the (3,+1) saddle point at the ring center. The linkage between boron and a terminal hydrogen requires the density equivalent of two electronic charges, while a *single* bridging link requires the density equivalent of one electronic charge. Thus the value of $\rho(\mathbf{r})$ at the position of a terminal (3,−1) saddle point, 0.1847 au, is greater than that found at a bridging saddle point. The terminal linkages are found to be individually spatially localized (in the physical, not orbital, sense[32]). Correspondingly, the bond path angle for the terminal hydrogens $\angle C_HBC_H$ exceeds the bond angle $\angle HBH = 119.0°$ by only 2.8°.

The number of bond paths terminating at a given nucleus, defined to be the atom's coordination number, is model independent and is instead determined by the topological properties of the charge distribution. These properties are in turn determined by the nature of the forces acting between the various nuclear dominated regions of space. Thus in pentaborane, B_5H_9 (Figure 4), the apical boron is found to be the terminus for five bond paths, bonding it to a terminal hydrogen and four borons. The remaining borons are bonded to four centers: a terminal hydrogen, two bridging hydrogens, and the apical boron. Also shown in Figure 4 is an example of a five-coordinated carbon atom as found[33] for the transition state of an S_N2 displacement reaction of F^- with CH_3F.

The use of the bond path to identify the nature and location of the dominant bonded interactions within a molecule allows one to extend the application of such an analysis to systems where the usual notions of bonding either fail or are inapplicable because of their model dependence. As an example of the generality of the present approach consider the change in the nature of the bonding encountered when $O(^1D)$ reacts with $H_2(^1\Sigma_g^+)$ in the minimum energy C_{2v} approach. The precise description of the catastrophes—the making and breaking of bonds—encountered during the course of a chemical reaction is the subject of the companion paper.[16] We discuss here only the qualitative aspects of the physical picture so obtained. At large separations of O from H_2 (Figure 4) there are two (3,−1) critical points and two bond paths, one linking the two hydrogens, the other denoting weak bonding (weak as determined by the properties of the associated critical point) of the O with the hydrogen molecule. Upon closer approach a catastrophe occurs (a (3,−1) saddle point is transformed into one (3,+1) and two (3,−1) saddle points) and a bonded ring is formed. Thus in this approach oxygen bonds with the two hydrogens separately before the bond between the hydrogens is broken. Continued motion along this path leads to a second catastrophe, the simultaneous merging and annihilation of the (3,+1) ring saddle point and the H-H (3,−1) bond saddle point to yield water in its normally bonded state.

From this example, it is clear that passage of the system through a point in nuclear configuration space at which a catastrophe occurs will involve the making or breaking of bonds.[16] Thus one does not anticipate equilibrium charge distributions to exhibit catastrophes, that is, critical points of rank less than three. Some examples do exist, however, and they all result from the presence of a proton and from its lack of a core density.

The ions F^+ and Ne^+ are very strongly electron withdrawing. The reaction of a hydrogen atom with either of these ions results in a motion of the initially formed (3,−1) bond saddle point toward the proton, as charge density is progressively transferred to the A fragment. Eventually a catastrophe occurs when the (3,−1) critical point merges with the "pseudo"-(3,−3) critical point at the position of the proton. In this limit the bond path will be defined by a single gradient vector originating at the proton and terminating at the A nucleus. Such a catastrophe will not occur when both bonded atoms possess a core density.[32] The value of $\rho(\mathbf{r})$ at a (3,−1) saddle point as determined by the valence density will be smaller in value than that at the position of either nucleus, except possibly for extremely short internuclear distances between two nuclei with a marked disparity in their charges.

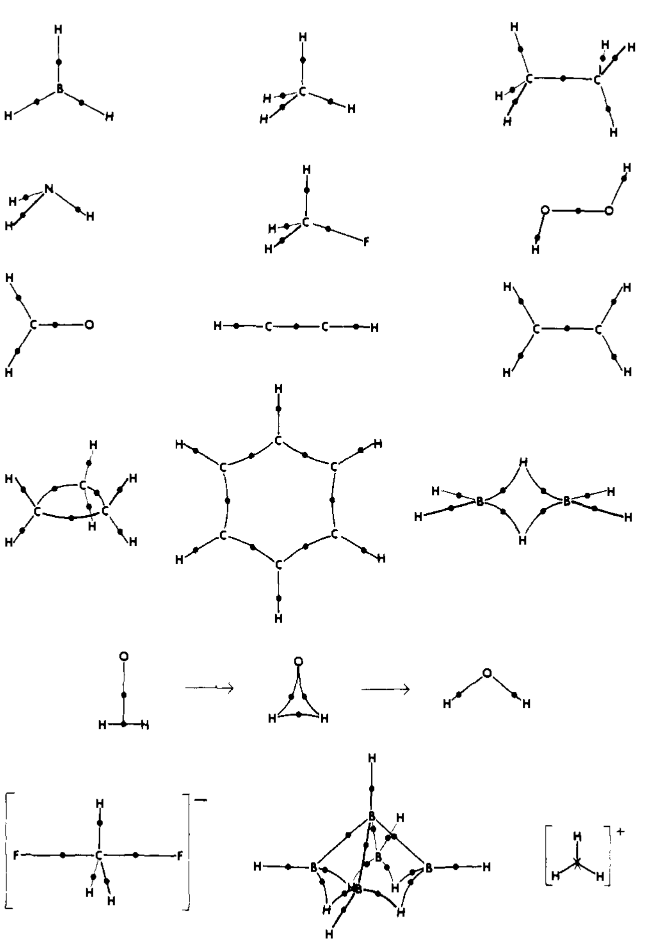

Figure 4. The bond paths defined by the unique axes of the (3,−1) saddle points found within the charge distributions of representative sets of molecules. The figures are drawn approximately to scale, including the relative positions of the saddle points, which are indicated by dots. Associated with each saddle point is a partitioning surface (not shown). Only those atoms whose nuclei are linked by a bond path share a common surface; they are neighboring nuclei. The single catastrophe in H_3^+ is indicated by a cross.

The only example so far found of an equilibrium charge distribution exhibiting a critical point of rank less than three is that for H_3^+.[9,16] The binding of three equivalent protons by the charge density of two electrons results in the formation of a plateau in the charge distribution in the center of the system.[34] The value of $\rho(\mathbf{r})$ in the plateau is exceeded only by that at the nuclear positions. The single critical point (aside from the nuclear cusps) located at the center of the molecule is a catastrophe point with two zero roots. It is characterized by the existence of three gradient paths which originate at this point and terminate one at each nucleus (Figure 4). The molecule is also partitioned into three atomic fragments by three surfaces symmetrically disposed between the bond paths and generated by the gradient vectors which terminate at the catastrophe point. Thus all three atoms are defined and linked by the gradient paths associated with the central critical point. This view of the bonding in H_3^+ is remarkably similar to that proposed by Christoffersen and Shull[34] in their investigation of the charge distribution for this system.

Clearly, whatever the topological properties of a charge distribution, the definition of a bond path enables one to identify the dominant interatomic interactions within a molecule, or between molecules. To provide a precise definition of the notion of a bonded pair of atoms, one must define an atom as well as the bond. Both definitions are contained within the properties of a (3,−1) critical point. The atoms and the bond are simultaneously defined, the former by the surface and the latter by the unique axis of such a critical point. Both definitions persist when one or more (3,−1) critical points are transformed into a catastrophe point, as illustrated for H_3^+.

III. Quantum Basis for Definition of Atomic Fragments

The general topological properties of the charge density define a partitioning of a molecular charge distribution which yields fragments identifiable as its atomic constituents. The zero flux surface condition, eq 1, which defines the topological boundary of an atom in a molecule, also defines the boundary of a subspace in a total system whose variational properties exhibit maximum correspondence with the quantum mechanical expressions which refer to the total system.[3,7,8] This result is obtained by first generalizing the variational principle of quantum mechanics through the *removal* of variational constraints on the state function ψ. One then finds that for a time-dependent or a time-independent system, the generalized variational expressions so obtained remain unchanged when the zero flux surface condition is imposed as an *added* variational constraint.[3,8]

As a result of the quantum description of an atomic fragment through the generalized variational principle, which applies only to a system bounded by a surface of zero flux in $\nabla\rho(\mathbf{r})$, any property of a molecule may be partitioned into a sum of atomic contributions, i.e., all of the properties of an atomic fragment are defined and their average values may be determined.[2,4,7] The single most important concept in the definition of the properties of a subspace is that they are all determined by a corresponding one-electron density distribution defined in real space.[8] Thus the average value of a subspace property is obtained by integration over a volume of space out to a surface of zero flux. The generalized variational principle yields a variational statement of the hypervirial theorem for stationary-state or time-dependent systems.[3,7] A particular, but fundamental, application of this result is to obtain a variational derivation of the subspace (or atom in a molecule) virial theorem. The subspace virial theorem leads to a unique spatial partitioning of the total energy of a molecule into a sum of atomic contributions by yielding a quantum prescription for the definition of a one-electron energy density in a many-electron system.

The subspace energies $E(\Omega)$ yield the chemically expected values. The changes in $E(\Omega)$ for motion from one point to another on a potential energy surface are the energy *changes* of chemical interest—partitioned into atomic contributions. The most important observation regarding the atomic fragments is that in those cases where the distribution of charge remains nearly unchanged upon transfer of the fragment between different chemical systems, the fragment energy exhibits the same degree of invariance. The fragment virial theorem provides a precise statement of the physical conditions which must be satisfied for the complete or partial retention of fragment properties when an atom or a functional group of atoms is transferred between different systems.[2b,4,7] Since the condition is a physically realizable one, demanding that the *net* virial of the external forces exerted on the atomic fragment remain unchanged or nearly unchanged, respectively, one has both an explanation and prediction of the existence of additivity schemes in chemistry and, more importantly, of the experimental observation that atomic fragments or polyatomic functional groups may exhibit characteristic sets of properties which vary between relatively narrow limits.

All of these properties of atoms in molecules are to be illustrated in this study of the boranes. For example, one anticipates that the terminal hydrogen fragment will not exhibit a wide variation in its properties throughout the series. One may bring the investigation even more into line with the existing chemical discussions of the boranes by considering the terminal hydrogen and its neighboring boron fragment as a single structural entity. In this way one may recover the discussion of the effect of different environments on the terminal H–B bond through a study of its associated bond path.

An atom or a molecule (a collection of strongly interacting atomic fragments) is always bounded by a zero flux surface. If the atom or molecule is an "isolated" system this surface is found at infinity and is uninteresting. As systems, atoms or molecules, approach one another their surfaces of zero flux persist, but they then define a shape and a volume for each system as determined by the forces of interaction between them. Of importance to descriptive chemistry is that at this level of observation the underlying quantum mechanics that generates the distribution of charge in real space does not distinguish, in its topological definition of a system, between an atom in a molecule and the molecule itself, or between a molecule in a collection of interacting molecules and the whole collection of molecules.

IV. Discussion

Diborane possesses three of the four types of critical points which characterize the charge distribution of a molecule in its most stable geometry. It is anticipated that the fourth type, a (3,+3) critical point denoting a minimum in $\rho(\mathbf{r})$, will be found in the interior of a bonded cage of nuclei.[9] Based on the observations and definitions given here one may identify the number of nuclei n with the number of pseudo- (3,−3) maxima in $\rho(\mathbf{r})$, the number of (3,−1) saddle points with the number of bond paths or bonds N, the number of (3,+1) saddle points with the number of rings r, and the number of (3,+3) minima with the number of cages c. The number and kind of critical points possessed by a molecular system with a finite number of nuclei are not arbitrary but determined by the Poincaré–Hopf relation. Collard and Hall[9] point out that, with the above identifications, this relation yields a restraint on this set of structural parameters, namely

$$n - N + r - c = 1 \qquad (2)$$

Clearly the set of numbers (n, N, r, c), which shall be referred to as the characteristic set, is a useful summary of the major topological properties of a molecular charge distribution. The structure of diborane is characterized as (8,8,1,0). While the relationship given in eq 2 is a topological one, as used here it contains physical information as a result of the association of each type of critical point with a given structural feature of the molecule. Aside from these associations, eq 2 is model independent. For a given number of nuclei and an assumed geometry, the number of bond paths, or bonds, associated with the proposed structure is fixed by eq 2. However, without further chemical or physical input its usefulness as a predictive tool is severely limited.

A topological-like set of rules for predicting the structures of the boranes has already been formulated by Lipscomb:[11] the "*styx*" rules. This set of rules is based upon a model, that is, the essential structural information of the boranes is reduced to a set of rules stated in terms of the model. The underlying assumption of this model is that each boron is involved in precisely four electron pair bonds, where the bonds may be of the two-center or three-center type. The set of letters *s*, *t*, *y*, and *x* signify respectively the number of three-center BHB bonds, the number of three-center BBB bonds, the number of BB bonds, and the number of BH bonds. With these model-based definitions, the rules consist of a number of equations of balance relating these numbers to the total number of electron pairs present in the system.

The network of bond paths found here for diborane is formally consistent with the description of the bonding as determined by the *styx* rules, the latter predicting four BH bonds, two three-center BHB bonds, and, as in the bond path description, no direct BB bonding. At this level of comparison the two approaches differ only in their description of the BHB bridges, the two three-center bonds of the *styx* model being replaced by four individual two-center linkages in the topological description. The two descriptions again predict the same bonded interactions for B_5H_9, but the *styx* rules, since they are tied to the tetravalent electron pair model, do not yield a single bond structure for this molecule. In the unique bond path structure[35] obtained for B_5H_9 (Figure 4), the apical boron is bonded to five centers (to the same centers as in the *styx* model). The presence of five bond paths, however, does not imply the participation of ten electrons. Instead, the properties of the charge distribution of B_5H_9 show that the density equivalent of only eight electronic charges is required.

From this discussion it is clear that the structural information implied by the characteristic set (n,N,r,c) could be used as a basis for predicting molecular structure if one could translate the information contained in N into some equivalent number of electronic charges. One may introduce an electron count, the chemical information most lacking in eq 2, by determining the *average* number of electrons necessary for the formation of each bond (as characterized by its bond path) observed to be characteristic of a given class of molecules. For any proposed structure, eq 2 will predict the number and type of bond paths. This information may then be translated into a predicted number of electrons, which is then compared with the available number of electrons. It appears that the observed structures of the boranes, for example, may be characterized in terms of the properties of just three different types of bond paths. The method of introducing the equivalent electron count in a manner dictated entirely by the observed properties of $\rho(\mathbf{r})$ will be illustrated in the second paper of this series.

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