

Atoms in Molecules

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Approximate quantum mechanical state functions have recently been obtained for the norbornyl cation.¹ These calculations have yielded the energy of its equilibrium geometry and the relative energies of neighboring geometries. It is the purpose of this account to illustrate that more chemical information than simply energies and their associated geometries can be obtained directly from a state function. A state function contains the necessary information to both define the atoms in a molecule and determine their average properties.² It also enables one to assign a structure, that is, determine the network of bonds linking the atoms in a molecule and determine whether or not the structure is stable.³ The state function further determines where electronic charge is locally concentrated and depleted. Quantum mechanics can be used to relate these properties to local energy contributions,⁴ thereby providing an understanding of the geometry and reactivity of a molecule.⁵

The norbornyl cation provides a clear illustration of how quantum mechanics can be used to obtain this kind of information. The protracted discussion concerning the possible structures of this ion and their relationship to its chemistry have been the subject of a recent issue of *Accounts*.⁶ The possibility of unambiguously assigning a structure to the norbornyl cation demonstrates the usefulness of the theory.

Atoms in Molecules

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 from the state function through the action of a corresponding operator on Ψ . Thus quantum mechanics is concerned with observables, that is, with operators corresponding to physical properties. Depending on the nature of the state function some observables yield "sharp" values, others yield "average" values. The manner in which the value of each observable changes with time is given by a corresponding equation of motion, called a Heisenberg equation of motion. The theorems of quantum mechanics that yield relationships between various average values, such as the virial theorem and Ehrenfest relations, are derived from such equations. 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 of course, to the total system. An understanding of chemistry requires answers of a more regional nature. The notion that a molecule can be viewed as a collection

of atoms linked by a network of bonds is the operational principle underlying our classification and present understanding of chemical behavior. Therefore, it would appear that to find chemistry within the framework of quantum mechanics one must find a way of determining the values of observables for pieces, that is, subsystems, of a total system. But how is one to choose the pieces? Is there only one or are there many ways of dividing a molecule into atoms and its properties into atomic contributions? If there is an answer to this problem then the necessary information must be contained in the state function, for Ψ tells us everything we can know about a system.

Thus the question "Are there atoms in molecules?" is equivalent to asking two equally necessary questions of quantum mechanics: (a) Does the state function predict a unique partitioning of a molecule 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 principle that directly determines the observables, their values, and equations of motion for a quantum system. Such is Schwinger's principle of stationary action,⁷ the power and elegance of which derives from its unified approach—a single principle providing a complete development of quantum mechanics. The approach is also a very general one, so general that one can, within its framework, seek answers to questions a and b.⁸ It is found that the *same principle* does apply to a subsystem of a total system if the subsystem is bounded by a surface which satisfies a particular physical condition. The condition is stated in terms of a property of the electronic charge density, as determined by the state function of the total system. Thus the state function does predict that a system can be uniquely partitioned into subsystems. Since the principle of stationary action applies to these particular subsystems, the values and corresponding subsystem equations of motion for each observable are also uniquely determined. Thus

(1) Goddard, J. D.; Osamura, Y.; Schaefer, F., III, *J. Am. Chem. Soc.* 1982, 104, 3258.

(2) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* 1981, 14, 63.

(3) Bader, R. F. W.; Nguyen Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* 1981, 44, 893.

(4) Bader, R. F. W.; Essén, H. *J. Chem. Phys.* 1984, 80, 1943.

(5) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* 1984, 106, 1594.

(6) Grob, C. A. *Acc. Chem. Res.* 1983, 16, 426. Brown, H. C. *Acc. Chem. Res.* 1983, 16, 432. Olah, G. A.; Surya Prakash, G. K.; Saunders, M. *Acc. Chem. Res.* 1983, 16, 440. Walling, C. *Acc. Chem. Res.* 1983, 16, 448.

(7) Schwinger, J. *Phys. Rev.* 1951, 82, 914.

(8) In fact, the search for a quantum definition of an atom in a molecule leads in a natural way to the principle of stationary action. This principle is obtained through a general variation of the quantum action integral. In varying the action integral for a subsystem one must necessarily retain the variations in Ψ on the boundaries of the subsystem and this leads to their inclusion at the time end points of the action integral. This is precisely the step that transforms the usual action principle into Schwinger's more general principle of stationary action. It is the variations in Ψ at the time end points that are identified with and determine the properties of the observables of a quantum system.

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one has a quantum mechanics for a subsystem. The same theorems derivable from the Heisenberg equations of motion for the total system may be derived for a subsystem. The virial theorem and Ehrenfest relationships for example, apply to these subsystems. The virial theorem yields a definition of the electronic energy of a subsystem. It has been demonstrated that this energy faithfully reflects the near constancy or change in the distribution of charge over the subsystem when it is observed in different molecules.⁹

At this point one has a quantum definition of a subsystem stated in terms of a particular property of the charge distribution. One has next to determine whether or not a molecular charge distribution exhibits the properties demanded by this definition and whether the resulting subsystems, if they are so defined, correspond to the chemical atoms. Thus one is led to study the topology of a molecular charge distribution.

Topology of Molecular Charge Distributions

The condition defining the quantum subsystem is stated in terms of a property of the gradient vector of the charge density ρ . This is most fortunate, for the gradient vectors of ρ (collectively called the gradient vector field of ρ) are precisely what one studies to obtain both a qualitative and quantitative understanding of the topology of ρ . Indeed, if one assumes that a molecular charge density contains the information necessary for the definition of molecular structure, then there already exists a complete mathematical theory that defines both structure and the stability of this structure in terms of the properties of the gradient vector field associated with a scalar field such as ρ .^{10,11}

The quantum condition of the subsystem is simply stated: the surface bounding the subsystem shall not be crossed by any gradient vectors of ρ . Figure 1a shows the intersection of an arbitrarily defined surface with a contour map of ρ . Since the gradient vector of ρ , denoted by $\nabla\rho$ always points in the direction of greatest increase in ρ , it must always be perpendicular to lines of constant density. Thus an arbitrarily constructed surface will not satisfy the quantum condition since it will in general be crossed by vectors $\nabla\rho$. Also shown on the diagram are unit vectors normal to the surfaces denoted by \vec{n} . If the scalar product $\nabla\rho \cdot \vec{n}$ vanishes then $\nabla\rho$ has no component through the surface. Thus the quantum condition is more compactly stated as

$$\nabla\rho \cdot \vec{n} = 0 \quad (1)$$

for every point on the surface of the subsystem. A surface satisfying this condition is known as "a zero flux surface" since there is no flux in $\nabla\rho$ through the surface. This condition is not satisfied by the surface in Figure 1a. It is satisfied by the one in Figure 1b. In this latter case the surface passes through a point with particular

(9) Every property is expressed in terms of a corresponding three-dimensional density distribution which is then integrated over the subsystem to obtain its average value. Thus the value of a given observable averaged over an atom yields, when summed over all the atoms in a molecule, the corresponding average value for the total system. This additivity relationship of atomic properties is true even for the Ehrenfest force and the energy as these many-electron properties are given in terms of the quantum stress tensor which is expressible in terms of the single-particle density matrix.

(10) Palis, J.; Smale, S. *Pure Math.* 1970, 14, 223.

(11) Thom, R. "Structural Stability and Morphogenesis"; Benjamin: Reading, MA, 1975. Poston, T.; Stewart, I. N. "Catastrophe Theory and its Applications"; Pitman: London, 1978.

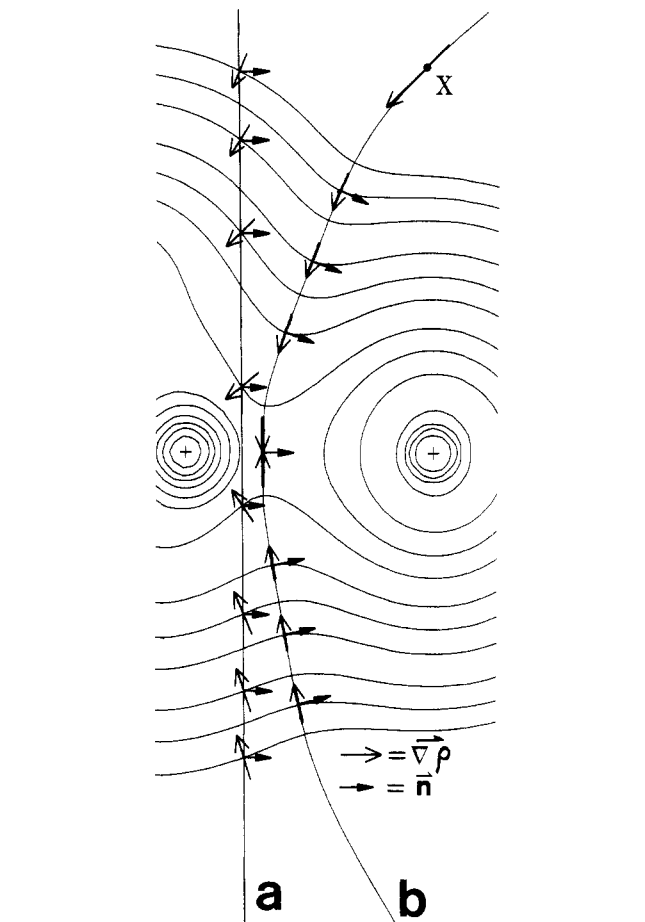


Figure 1. A portion of a contour map of a charge distribution showing its intersection with two partitioning surfaces. The line of intersection for surface a is crossed by the vectors $\nabla\rho$. The vector $\nabla\rho$ is tangent to the line of intersection of surface b at each point on the surface. The two aims of surface b meet at a point where $\nabla\rho = 0$, a critical point.

properties, a point where $\nabla\rho = 0$, called a *critical point*. Each of the arms indicating the intersection of the surface with the plane shown in Figure 1b is the path (or trajectory) traced out by $\nabla\rho$ starting at a particular point removed from the critical point. For example, start at the point labeled X in Figure 1b and calculate $\nabla\rho$. Move a very small distance away from X in the direction indicated by $\nabla\rho$ at X and again calculate $\nabla\rho$. If one repeats this procedure many times one will arrive at the critical point. The path generated by this procedure is called a gradient path—the path traced out by following the gradient vector of ρ from some initial point.¹² Gradient paths always originate at a critical point (which may be at infinity) and terminate at another critical point. By displaying the gradient vector field of ρ in terms of such gradient paths one can immediately determine whether or not a molecular charge distribution is partitioned into subsystems, i.e., atoms, bounded by zero flux surfaces.

The single most striking observation regarding the form of ρ is that it exhibits local maxima only at the positions of nuclei. A local maximum means that electronic charge is most dense at the position of a nucleus and becomes less dense as one moves away from the nucleus in *any* direction. Thus in a diagram that

(12) While exact in the limit of small displacements this procedure is equivalent to approximating a function $f(x)$ by its tangent line at x .

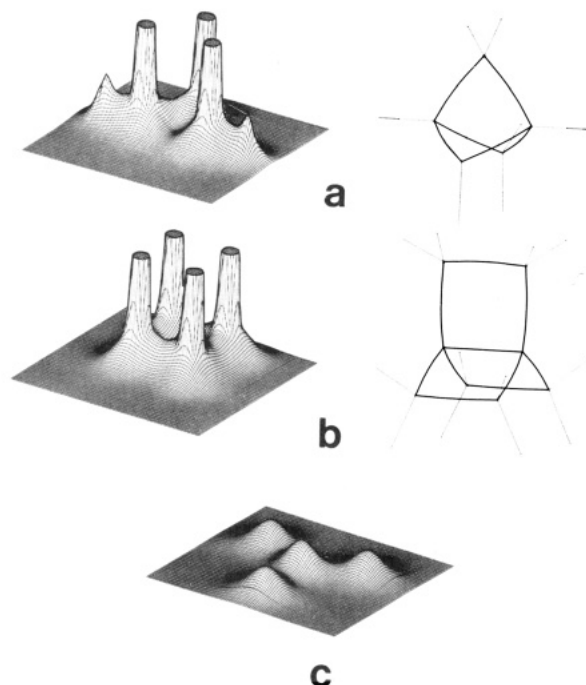


Figure 2. Displays of the charge density for (a) one plane of bicyclo[1.1.1]pentane and (b) and (c), two planes of [2.2.2]propellane. Also shown are the molecular graphs as determined by their respective charge distributions. The very large value attained by ρ at each carbon nucleus is not shown. (a) is for a plane containing the two bridgehead carbon nuclei and their bonded protons and one of the bridging carbon nuclei. (b) is for a plane containing the carbon nuclei in one of the 4-membered rings of [2.2.2]propellane. (c) is for a plane bisecting the bridgehead and the three outer C-C bonds of [2.2.2]propellane. It demonstrates that ρ attains a maximum value at the (3,-1) cp in each interatomic surface.

portrays ρ in a given plane (Figure 2), ρ will exhibit a maximum at a nuclear position for any plane containing that nucleus. Correspondingly in a display of the gradient vector field of ρ , all the gradient paths in the vicinity of a nucleus will terminate at the nucleus.¹³ A nucleus is said to behave as an *attractor* in the gradient vector field and *nuclei are the only attractors in the field* $\nabla\rho$. The region of three-dimensional space traversed by all gradient paths that terminate at a given attractor defines the *basin* of the attractor. Thus this single, dominant observation regarding the form of ρ yields a complete partitioning of the real space of a molecular system. The system is partitioned into a set of basins and each basin contains a single attractor, i.e., nucleus. This is illustrated in Figure 3. Since every gradient path in a given basin terminates at the attractor of that basin, it necessarily follows that no trajectories of $\nabla\rho$ will cross the surface separating neighboring basins—this partitioning satisfies the zero flux surface condition of quantum mechanics. From this point on, *each attractor and its associated basin will be called an atom*. By studying the behavior of the remaining gradient paths we can define an interatomic surface and show that it satisfies the quantum subsystem condition, eq 1.

Reference to Figure 2 illustrates that ρ exhibits a saddle point between some but not all pairs of nuclei in a molecule—it does between the bridgehead nuclei

(13) The gradient vector of ρ is not defined at a nuclear position because of the cusp condition on Ψ .³

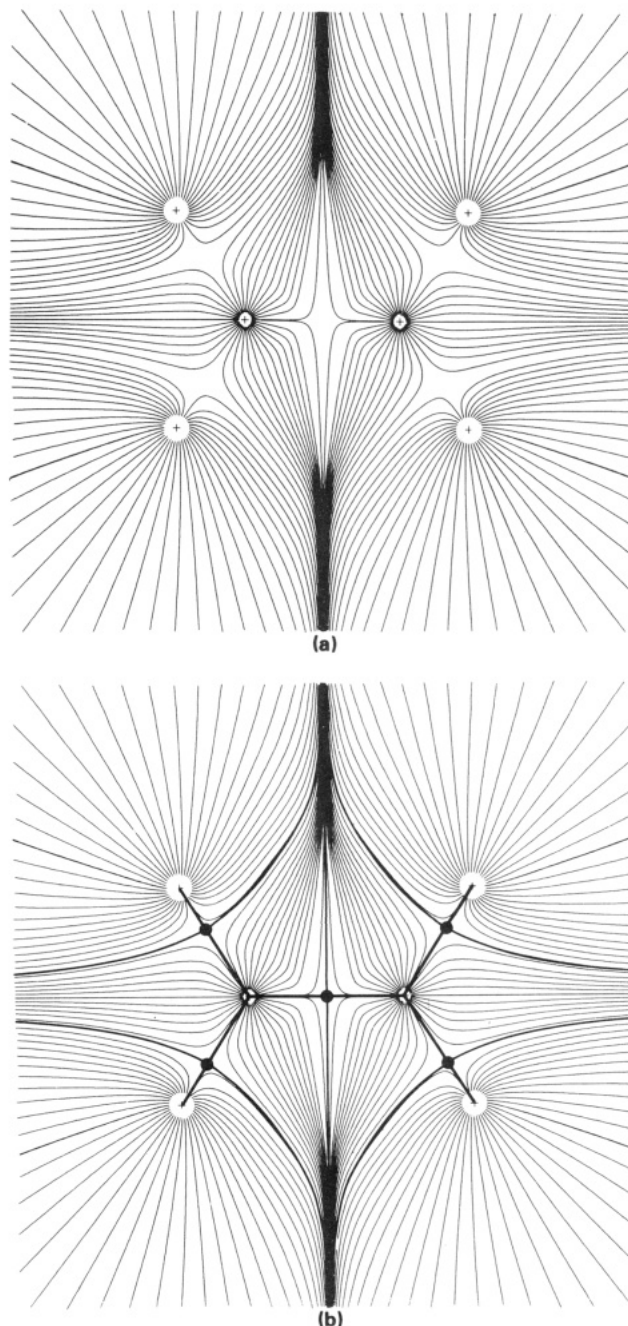


Figure 3. (a) Displays of the gradient paths traced out by the vectors $\nabla\rho$ for the plane containing the nuclei in C₂H₄. The paths have been arbitrarily terminated at the boundary of a small circle centered on each nucleus. Only trajectories that terminate at a nucleus are shown. This diagram illustrates the partitioning of space into atomic basins. (b) includes as well the pairs of trajectories which in this plane terminate at each (3,-1) cp in ρ (denoted by a black dot). Each such pair denotes the intersection of an interatomic surface with this plane. Also shown are the unique pairs of trajectories which originate at a (3,-1) cp and terminate at the neighboring nuclei. Each pair defines a bond path and collectively they define the molecular graph.

in [2.2.2]propellane for example, but not between the corresponding nuclei in bicyclo[1.1.1]pentane. If ρ retains this form when viewed in every plane containing the internuclear axis then it contains a critical point at which ρ is a minimum with respect to one direction (along the line of the nuclei) and a maximum with respect to all directions perpendicular to this line. This is true of the saddle points appearing in Figure 2. One notes that the presence of such a critical point [called

a (3,-1) cp since it has *three* curvatures, one positive and two negative, $+1-1-1 = -1$] between a pair of nuclei indicates that electronic charge is accumulated between them. If one displays ρ in a plane perpendicular to the internuclear axis then ρ exhibits a maximum at the position of a (3,-1) cp (figure 2). Since ρ is a maximum in two-dimensions at such a critical point a set of gradient paths will terminate at this point and define a surface—the interatomic surface separating the basins of two neighboring atoms. A (3,-1) cp is found between every pair of *neighboring atoms*. Thus the basin of each atom is bounded by one or more interatomic surfaces as generated by the sets of trajectories of $\nabla\rho$ that terminate at the corresponding (3,-1) critical points. Surfaces defined by trajectories of $\nabla\rho$ are necessarily surfaces of zero flux as illustrated in Figure 3 and as previously illustrated in Figure 1b. The quantum condition governing the definition of a subsystem is fulfilled in a natural way by the form of a molecular charge distribution, the condition yielding a partitioning of space into distinct nonoverlapping regions, each region containing a single nucleus.

Definition of Molecular Structure

The same properties of the gradient vector field of ρ that yield the definition of an atom as a quantum subsystem contain the necessary information for the definition of molecular structure and for the application of the theory of structural stability.

The charge density in an interatomic surface is a maximum at the (3,-1) cp. The value of ρ is also a minimum at this same point along a line perpendicular to the surface at the critical point that links the two neighboring nuclei. This line is defined by the two and only two gradient paths that originate at a (3,-1) cp. Each terminates at one of the neighboring nuclei. The presence of these two gradient paths indicates the existence of a line linking the nuclei along which the charge density is a maximum with respect to any neighboring line. These lines are called *atomic interaction lines* because they exist only between atoms which share a common surface. The network of such lines is called a *molecular graph*. If the nuclei are linked by interaction lines so as to form a ring, then a critical point called a ring cp is found in the interior of the ring. The charge density is a minimum at this point in the ring surface.¹⁴ The [2.2.2]propellane molecule, Figure 2, contains three rings and the minimum in ρ at the center of one of these ring surfaces is evident in the display of ρ shown in this figure. If the nuclei are linked so as to enclose the interior of the molecule with ring surfaces then another and final kind of critical point is found in the interior of the resulting cage. The charge density is a local minimum at a cage critical point. This is exemplified by the display of ρ for the bicyclo[1.1.1]pentane molecule in Figure 2.¹⁵ The interior of this molecule is bounded by the surfaces of three four-membered rings and one view of the local minimum attained by ρ at the cage critical point located midway between the two bridgehead carbon nuclei is

(14) A ring critical point is a (3,+1) cp. It exhibits two positive curvatures in the ring surface and a negative curvature along an axis perpendicular to the ring surface.

(15) A cage critical point is a (3,+3) cp since it exhibits three positive curvatures. The minimum in ρ observed between the bridgehead carbons of bicyclopentane (Figure 2) will be observed in every plane containing this cp.

illustrated. Thus the topology of ρ is such that its critical points allow for the definition of atoms and the network of lines that shows how the atoms are linked to one another. They further indicate the presence of rings or cages in the structure so defined.

The atomic interaction lines enable one to give the necessary and sufficient conditions for the existence of a chemical bond. A necessary requirement for the existence of a bond between a pair of nuclei is that they be linked by a line along which the charge density is a maximum with respect to any neighboring line as illustrated in Figure 2. The existence of such a line indicates that electronic charge is accumulated between the nuclei of every pair of neighboring atoms. If electronic charge is accumulated between every such pair of nuclei to the extent that it balances the forces of repulsion acting on the nuclei for some particular geometry and exerts a net restoring force on any nucleus when displaced from its position of equilibrium, then the system is bound; the energy increases for any displacement from the equilibrium configuration. This statement regarding the necessity of charge accumulation between bonded nuclei is a consequence of the Hellmann-Feynman and virial theorems.⁴ In a bound system an atomic interaction line is called a *bond path*. Thus the existence of a bond path is both a *necessary* and *sufficient* condition for the existence of a bond.

The network of bond paths is found to coincide with the network of chemical bonds that are assigned to define a chemical structure, as exemplified in Figures 2 and 3. In general, a molecular graph remains unchanged as the nuclei undergo their vibrational motions. A molecular graph with these properties is said to represent a stable structure. The whole of nuclear configuration space for a molecular system (this is a space in which every point represents a unique geometrical arrangement of the nuclei) can thus be partitioned into regions. Associated with each region is a given structure with a representative molecular graph. This definition of structure partitions all of nuclear configuration space into open nonoverlapping regions that are separated by surfaces—hypersurfaces in this many-dimensional case. It immediately follows that the structure associated with a nuclear geometry corresponding to a point contained in such a hypersurface must be unstable. Since it lies on the boundary separating different stable structures it must be stable to some *but not all* of the possible nuclear motions. There will be at least one nuclear motion which carries it into one or the other of the neighboring stable structural regions. Thus a change in molecular structure is an abrupt and discontinuous process and the intervening unstable structure will possess a molecular graph that is in some sense intermediate between those of the initial and final structures.¹⁶

The mathematical theory of structure makes precise statements regarding structural stability.¹⁰ In the

(16) It is important that one distinguish between molecule structure and molecular geometry. Structure is generic and persists over nuclear motions. The present definition of structure prevails beyond the Born-Oppenheimer approximation. A state function not associated with a specific molecular geometry is still associated with a specific structure. Molecular geometry on the other hand is not generic—any change in position of a nucleus gives a new geometry. The notion of a molecular geometry does not survive beyond the fixed nucleus approximation to Ψ . (Bader, R. F. W.; Tal, Y.; Anderson, S. G.; Nguyen-Dang, T. T. *Isr. J. Chem.* 1980, 19, 8.)

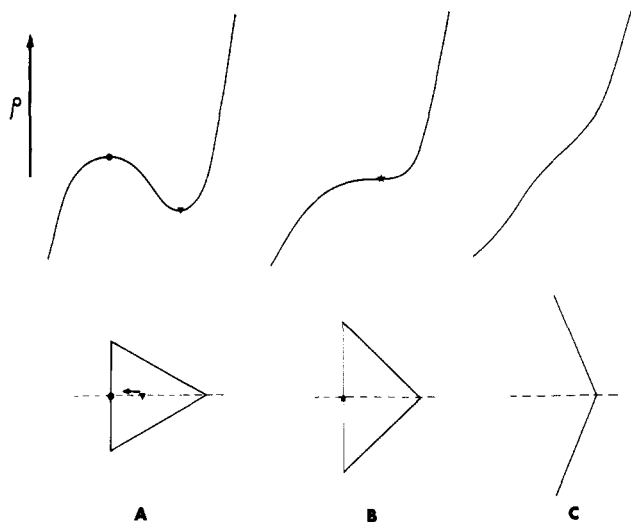


Figure 4. Profiles of ρ along the indicated (dashed) line of a three-atom system to illustrate the opening of a ring structure. (A) Ring structure showing the position of the bond (\cdot) and ring (\blacktriangle) critical points and their respective ρ values on the profile. (B) The two critical points coalesced to yield an unstable critical point (*). Both the first and second derivatives of ρ with respect to the coordinate of the dashed line vanish. (C) A further extension of the system annihilates the unstable critical point, the bond is broken and the open structure is obtained.

particular case of a molecular structure defined in terms of the charge density the requirements for structural stability are (a) Every critical point in ρ must have three non-zero curvatures (i.e., ρ must be either a maximum or a minimum with respect to three orthogonal axes—it cannot be “flat” or possess a zero curvature along any axis). (b) The critical points of a charge distribution are linked by trajectories of $\nabla\rho$. The theory predicts that certain of these possible ways of linking the critical points are inherently unstable. Thus the mathematical analysis of the properties of ρ demonstrates that there are just two basic ways in which bonds can be made and/or broken to bring about a change in structure.

Consider the first of these, called the bifurcation mechanism. The critical points already discussed, those which denote the presence of atoms, bonds, rings, and cages are stable critical points. Their characteristics do not change as ρ is changed by a displacement of the nuclei. Hence the structure they define is itself stable (assuming they are properly connected). Consider however, what must happen when two or more stable critical points coalesce such as occurs in the opening of a ring structure for example. When a bond of a ring structure is extended the resulting change in ρ causes the ring critical point to migrate towards that of the bond. The charge density has a positive curvature at the ring critical point (in the ring surface) and a negative curvature at the bond critical point (ρ is a maximum in the interatomic surface at the bond critical point). A profile of ρ along the direction of approach of the two critical points is shown in Figure 4a. At coalescence the two curvatures must be equal and hence the curvature of ρ at the new critical point resulting from their coalescence is zero, (Figure 4b). This new critical point with one zero curvature is unstable—it exists only for this particular value of the bond extension and at this extension the bond is broken. A further infinitesimal extension of the nuclei causes the unstable critical point to vanish. Motion of the system along this

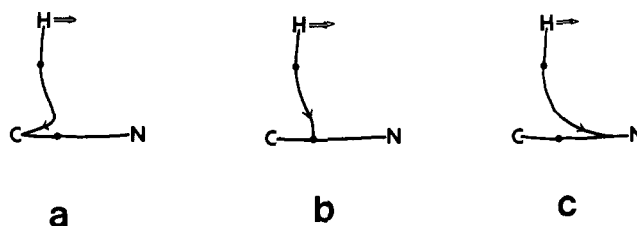


Figure 5. Molecular graphs illustrating the conflict mechanism in the isomerization of $\text{HCN} \rightarrow \text{CNH}$. Molecular graphs a and c are obtained for geometries immediately preceding and following the unstable conflict structure (b). The structures represented by a and c persist for motion along the reaction path before and after respectively, the transition state (b).

particular reaction coordinate has resulted in the loss of a bond and a ring critical point and the original ring structure has changed into an open structure. One may use the mathematical theory to predict all possible stable structures that can be obtained from a given type of instability.¹¹

The second of the two basic ways of changing structure is given by the conflict mechanism. In this case the unstable structure has the same number and kind of critical points as do the two stable structural regions it connects but the manner in which the critical points are linked by gradient paths is unstable. Examples are provided by the isomerization of CH_3CN or HCN to their corresponding isocyanides. The structure associated with the transition-state geometry is one in which the H atom of HCN for example, is not bonded to either the C or N atoms, but is instead linked by a bond path to the (3,-1) or bond critical point of the C-N bond, (see Figure 5). This intersection of gradient paths is unstable and with a further motion of H the bond path abruptly switches to the N atom to yield the stable structure CNH . The name conflict mechanism derives from the competition that exists between the attractors of the C and N basins to attract and hold the line of maximum charge density linking the proton.

One easily becomes adept at recognizing the potential for structural change within a system. In the norbornyl cation for example, the distribution of charge over a portion of the surface defined by nuclei 1, 2, and 6 (Figure 6) is relatively flat, and the near vanishing of a curvature of ρ between carbon atoms 2 and 6 forewarns one of the facile structural changes this system is found to undergo.

Structure and Reactivity of Norbornyl Cation

Goddard et al.¹ have determined the minimum energy geometry of the norbornyl cation using the 4-21G basis set in an SCF calculation. The corresponding structure of this ion as determined by the properties of the derived charge distribution is shown in Figure 6a. By imposing a plane of symmetry on the ion, but otherwise optimizing the geometry, structure b was obtained (Figure 6b). The energy of this geometry was found to be 0.2 kcal/mol greater than the energy of a. Yoshimine et al.¹⁷ found that all basis sets above 4-31G yield only a single minimum energy geometry corresponding to the symmetrical structure b. Using the 4-21G geometries obtained by Goddard et al.¹ they found the energy of a (which is no longer an energy minimum) to be higher

(17) Yoshimine, M.; McLean, A. D.; Liu, B. *J. Am. Chem. Soc.* 1983, 105, 6185.

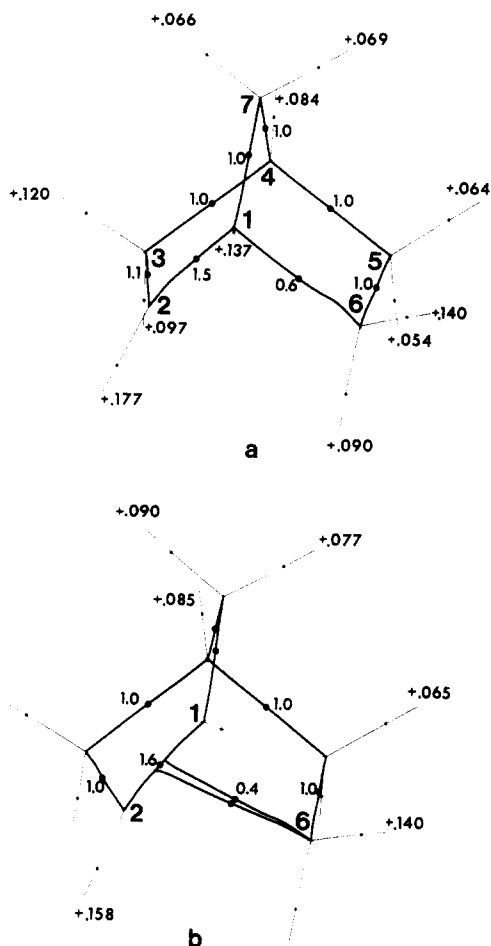


Figure 6. Molecular graphs for the norbornyl cation representative of the open or classical structure a and of the bridged or nonclassical structure b. Also indicated on the diagram are the net charges on the H atoms and the C-C bond orders. Carbons 4, 5, and 6 define a symmetry plane in b.

in energy than that of b by 0.5 kcal/mol in a large basis set SCF calculation and for this value to increase to 2.0 kcal/mol with the inclusion of electron correlation.

In summary, theory predicts that the bridged structure b is the only minimum energy structure in this region of the potential energy surface. However, the open structure a obtained from b for some *finite* displacement of C6 away from the symmetry plane toward either of the equivalent carbons C1 or C2, is so close in energy as to be accessible by thermal motions. As a result of these motions the ion will constantly undergo structural changes with the bond from C6 switching back and forth from C1 to C2 to yield a structure equivalent to b as the vibrationally averaged structure. Spectroscopic measurements such as the ^{13}C NMR experiments of Saunders and Kates¹⁸ will reflect the properties of the average structure associated with the energy minimum, structure b.

The value of ρ at a bond or (3,-1) cp, ρ_b , can be used to define a C-C bond order n ($n = 1.0, 2.0, 3.0$, respectively for C_2H_6 , C_2H_4 , and C_2H_2) that provides a relative measure of the extent to which electronic charge is accumulated between the pairs of bonded nuclei.¹⁹

(18) Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6868.
 (19) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061. Cremer, D.; Kraka, E.; Slee, T. S.; Bader, R. F. W.; Lau, C. D. H.; Nguyen-Dang, T. T.; MacDougall, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 5069.

The values of n are given in Figure 6, parts a and b. The net charges on the H atoms are also given. These are obtained by integrating ρ over the basin of an atom and then subtracting this average number of electrons from the nuclear charge. Positive charge is delocalized over all the hydrogens in both structures. In a the hydrogen attached to the methine carbon C2 has the largest net charge. The next largest net charges are on the H of C1 and one H of C6. The charge density along the long ($R = 1.753 \text{ \AA}$) C1-C6 bond path is much reduced from that of a normal C-C bond yielding a bond order of 0.6 while that of the C1-C2 bond is increased to yield $n = 1.5$. There is a delocalization of charge extending from the C6-C1 bond to the C1-C2 bond as evidenced by the relatively low values of ρ and its lack of significant curvatures in the C6-C1-C2 plane in the neighborhood of the C1-C6 bond critical point. As a consequence, the atomic surfaces of C6 and C2 are on the verge of forming a common interatomic surface through the formation of a singularity (an unstable critical point) in ρ . This occurs as C6 is displaced towards C2 and the singularity bifurcates to yield a new bond and ring critical point. The formation of the bridged structure b is the reverse of the ring-opening mechanism described above. The bridging bonds, each of order 0.5, are very curved and their gradient paths that terminate at C1 and C2 are *nearly* coincident with the bond path between C1 and C2. The integrated path length of a bridging bond is 2.46 \AA compared to the geometrical internuclear separation of 1.940 \AA . The newly formed ring critical point lies between the critical points of the two bridging bonds and the value of ρ at this point is almost identical to the ρ_b values for the bridging bonds. Thus the curvature of ρ along this line of critical points in the ring surface is close to zero. This signifies that the bridged structure is very unstable and easily changed by a coalescence of the ring critical point with the critical point of one of the bridging bonds. This same structural transformation is found for the 1-propyl cation but in this case the bridged structure (corner protonated cyclopropane) is less susceptible to a change in structure and the interaction between the two C-C bonds in the open structure is less pronounced. (The two bond orders are 1.3 and 0.7 as compared to 1.5 and 0.6 in structure a. In both ions the two bond orders sum to ~ 2.0).

The position of preferred nucleophilic attack in the norbornyl cation can be predicted in terms of the properties of the Laplacian of ρ , the quantity $\nabla^2\rho$. This quantity determines where electronic charge is locally concentrated ($\nabla^2\rho < 0$) and depleted ($\nabla^2\rho > 0$) within a molecular system.⁵ It recovers the shell structure of an atom by displaying a corresponding number of pairs of shells of charge concentration and charge depletion. On bonding, the uniform valence shell of charge concentration of a free atom is distorted so as to form "lumps" and "holes" in this shell. The maxima in $-\nabla^2\rho$ recover in a most satisfying way the "lumps" in a molecular charge distribution as anticipated in terms of the Lewis electron-pair model or as surmised to exist in Gillespie's VSEPR model of molecular geometry.²⁰ These local concentrations of charge determine the sites of electrophilic attack. The points where $-\nabla^2\rho$ attains

(20) Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold: London, 1972.

its minimum values locate the "holes" in the valence-shell charge concentration. These holes, since they give direct access to the core of the atom are the sites of nucleophilic attack.

The Laplacian of ρ plays a dominant role in the theory of atoms in molecules. Because of the quantum condition for the definition of an atom, eq 1, the atomic average of the Laplacian of ρ must vanish. Thus while there is no constraint on the moment of electronic charge contained within the boundaries of an atom there is a constraint on the relative extents of concentration and depletion of charge. If charge is concentrated in some regions of an atom it must be depleted to a corresponding extent in others. This property is common to all atoms, free or bound. The quantum mechanical theory of atoms in molecules yields relationships between local values of properties as well as between their average values. In particular the local expression for the virial theorem is

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

where $V(\mathbf{r})$ and $G(\mathbf{r})$ are the potential and kinetic energy densities, respectively. Since the integral of $\nabla^2\rho$ vanishes over an atom as well as over the total system, the integration of eq 2 over an atom Ω to yield the corresponding average values gives the virial theorem $V(\Omega) + 2T(\Omega) = 0$. Since $G(\mathbf{r}) > 0$, eq 2 demonstrates that the lowering of the potential energy dominates the energy in regions of space where electronic charge is concentrated, i.e., where $\nabla^2\rho < 0$.⁴

In summary, the reaction of a nucleophile with an electrophile is the combination of a center of charge concentration with one of charge depletion within the valence shells of the respective atoms. Their reaction corresponds to the combination of a region with excess potential energy with another of excess kinetic energy to yield a linked pair of atoms for which the virial theorem is satisfied for each atom separately as well as for the combined pair.

Figure 7 illustrates the Laplacian of ρ for the C1-C2-C6 face of structures a and b of $C_7H_{11}^+$. The open structure a exhibits two sites of charge depletion in the valence shell of C1 (or equivalently of C2). There is however, a remarkably large rearrangement of charge density associated with the change in structure a \rightarrow b and in the bridged ion, charge is concentrated over the entire valence shells of both C1 and C2 except for a small area in each where $\nabla^2\rho \sim 0$ and a local minimum exists in the valence shell of charge concentration. Thus on vibrational averaging over b and the two equivalent open structures the most pronounced "holes" in the valence shells of C1 and C2 will be found on the side opposite C6. The reaction of either of these holes with the charge concentration of a nucleophile will yield the mirror-image *exo*-norbornyl end products as is observed.

Conclusion

In 1975 an Account²¹ appeared giving observations and arguments in support of the thesis that regions of a molecule bounded by surfaces of zero flux in $\nabla\rho$ could be identified with the chemical atom. A restricted proof of an atomic statement of the virial theorem was dis-

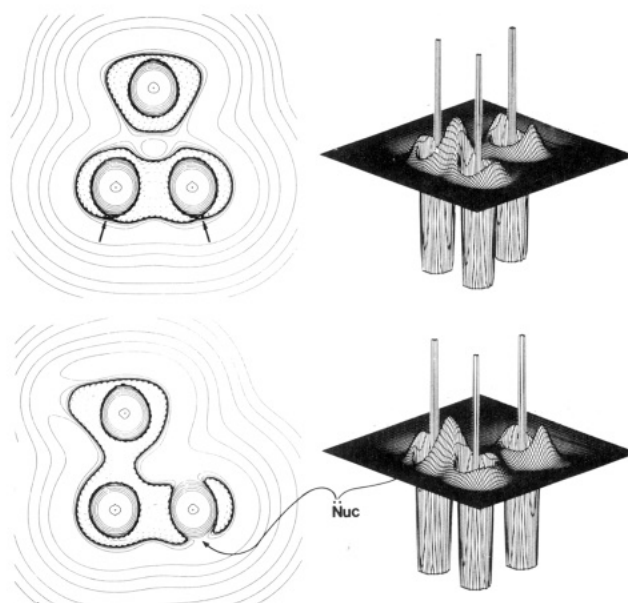


Figure 7. Displays of $\nabla^2\rho$ for the C1-C2-C6 plane for geometries b and a of $C_7H_{11}^+ \cdot C_6$ is the uppermost nucleus. In the contour displays dashed lines denote $\nabla^2\rho < 0$ (charge is locally concentrated) and solid lines denote $\nabla^2\rho > 0$ (charge is locally depleted). The Laplacian is also negative within the region bounded by the innermost solid contour enclosing each nucleus. The quantity $-\nabla^2\rho$ is plotted along the third axis in the diagrams on the RHS. A maximum in these diagrams is a maximum in the concentration of electronic charge. Mirror-image planes are shown for the nonclassical structure. The arrows denote the "holes" in the charge distribution—the points of nucleophilic attack.

cussed in relation to the definition of the energy of an atom in a molecule. We now have a quantum definition of these atomic regions and of their properties. All theorems derivable from the Heisenberg equation of motion, not just the virial theorem, apply to the atom in a molecule. In terms of these relationships and their corresponding local expressions one has a quantum mechanical description of an atom in a molecule. This study has led in a natural way to a definition and understanding of molecular structure. One point must be emphasized, however. It is the atom and its properties that are defined by quantum mechanics. The bond paths and the structure they define just mirror and summarize in a convenient way what the atoms are doing. Nonetheless the theory now offers the possibility of relating the properties of atoms to the properties of their bonds. The atomic statement of the principle of stationary action relates the atomic average of the commutator of the Hamiltonian \mathcal{H} and some observable \mathcal{A} to an integral over the surface of the atom. This surface integral is in turn composed of a sum of interatomic surface integrals—one integral for each bonded neighbor. Thus the *atomic* statement of the principle of stationary action offers a way of using quantum mechanics to define properties that can be associated with individual bonds. It is not impossible that among these properties will be a quantum definition of a bond energy.

I wish to thank Professor K. Wiberg of Yale University for kindly supplying SCF state functions at the corresponding (6-31G) optimized geometries for bicyclo[1.1.1]pentane and [2.2.2]propellane.*

(21) Bader, R. F. W. *Acc. Chem. Res.* 1975, 8, 34.