The likely involvement of dinitrosyls in the above catalytic cycle receives support from the report by Ibers and Haymore[47] in which catalysis of reaction 16 by $Ir(NO)_2(PPh_3)^+$ and other dinitrosyl complexes is observed. However, no mechanistic studies have been made as yet on these systems.[50a] With a view to understanding the interrelationship of structure and reactivity, we have investigated the catalytic properties of various phosphine– and diolefin–rhodium complexes in Me_2SO[55] and find promotion of the reduction of NO by CO to be a rather general phenomenon. Included in this study were $[RhL_2Cl]_2$, $RhBrL_3$, $RhClL_3$, $RhCl(CO)L_2$, $[Rh(NBD)Cl]_2$, $[Rh(COD)Cl]_2$, and $Rh(NO)L_3$ (L = PPh_3; NBD = norbornadiene; COD = 1,5-cyclooctadiene). While none of the systems is as active as $[RhCl_2(CO)_2]^-$–(EtOH)–HCl, they all exhibit rapid product formation within the first 20 hr and approach the same slow limiting rate thereafter. Initial rapid product formation could *not* be reproduced on recharging these systems.

Recently Stanko and coworkers[54] have observed the catalyzed disproportionation of NO using ethanolic solutions of $RhCl_3$ to give N_2O and ethyl nitrite. A mechanism proposed by Stanko[54] involves the formation of a Rh^{III}–$(NO^+)(NO^-)$ intermediate followed by NO^- assisted attack of ethanol on NO^+ to give ethyl nitrite and the nitrosyl hydride ligand, HNO, which upon displacement and dimerization decomposes to give N_2O and H_2O. Alternative possibilities can be formulated, and the catalyzed disproportionation and reduction reactions may actually have steps in common.

Finally, Nunes and Powell[56] reported in 1970 the Cu(I)-catalyzed reduction of NO by $SnCl_2$. The reduction products were N_2O and hydroxylamine in ratios strongly influenced by Cu(I) and Sn(II) concentrations. The kinetic results were interpreted in terms of the formation of the catalytic intermediates Cl_3Sn–$Cu(NO)Cl_2{}^{2-}$, Cl_3Sn–$Cu(N_2O_2)Cl_2{}^{2-}$, and $[Cu_2(SnCl_3)_2Cl_4(N_2O_2)]^{4-}$, with the immediate precursors of both products being two-nitrogen species.

Concluding Comments

Studies in the coordination chemistry of nitric oxide over the last few years have been numerous, and significant progress has been achieved in establishing the structural systematics of metal nitrosyls, in developing a comprehensive bonding description of them, and in elucidating and exploring the reaction chemistry of coordinated NO.

A most intriguing aspect of nitrosyl chemistry which will command attention in the future will be the more complicated reactions of nitric oxide with metal complexes which go beyond the synthesis of M–NO bonds. That complexes in solution have been used as promoting agents and true catalysts for NO disproportionation and reduction seems only a beginning. Understanding how these reactions occur and applying that knowledge to the design of new, more efficient catalyst systems will be the goals of more exhaustive studies. Other avenues of inquiry will include extension to catalytically active complexes of the first transition series, the homogeneously catalyzed reduction of NO by other gaseous species, and perhaps the simultaneous reduction of NO and SO_2 by CO.

(55) C. D. Meyer, J. Reed, and R. Eisenberg, unpublished results.

(56) T. L. Nunes and R. E. Powell, *Inorg. Chem.*, **9**, 1912 (1970).

Molecular Fragments or Chemical Bonds?

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The atom played the central role in early chemical theories. The properties of a molecule were related to those of its constituent atoms. Early additivity schemes were expressed in terms of atomic contributions.[1] Pauling's[2] electronegativity scale is an atomic concept, based on the premise that one can assign a relative value to the ability of an atom to attract electrons to itself when in chemical combination with another.

With extraordinary perception, Lewis[3] introduced the concept of an electron pair *bond,* and in doing so focussed attention on the interactions between atoms responsible for chemical binding. Quantum mechani-

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(1) P. Pascal, *Ann. Chim. Phys.*, **19**, 5 (1910); **25**, 289 (1912); **180**, 1596 (1925).

(2) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.

(3) G. N. Lewis, *J. Amer. Chem. Soc.*, **38**, 762 (1916).

cal interpretations and calculations were directed at explaining *the chemical bond*. With the formulation and extended application of molecular orbital theory, the transition in thinking from "atoms" to "bonds" was completed. The basic notion of the molecular orbital is to provide a description of the motion of an electron in the field of all the nuclei. Only in the study of ionic lattices have we retained the concept of relating properties to the individual ions comprising the crystal. In all other systems the bond is paramount. Consider a glossary of presently used terms: ionic or covalent bonds, bond energy, bond moment, bond order, localized or delocalized bonds, etc.

All these concepts are based on the two- or many-center picture. The one point they have in common is that none can be given a rigorous definition in the general case. By a rigorous definition we imply one which can be stated in terms of physical quantities, real space, and the forces operating within the system and one which is independent of any model. For example, is it reasonable to ask where the C=O bond ends and the C–H bonds begin in the formaldehyde molecule, or, what is the C=O bond energy in this same system? While there are many answers to such questions, there is no *one* answer to any of them.

While one cannot deny the important role played by the bond concept, we propose, as an alternative, a return to what is essentially the "atoms in molecules" approach to chemistry. Specifically, one seeks to understand or predict the properties of a total system in terms of the properties of its parts. Rather than bonds, we choose as our fundamental parts mononuclear fragments of the system with boundaries defined in real space. We do so for two reasons: (a) *all* of the properties of such a fragment may be rigorously defined, and (b) theory and comparison with experiment indicate that such fragments are the fundamental building blocks for a total system.

The Spatial Partitioning of a Molecular System

The Partitioning Surfaces. The boundaries of the fragments of a molecular system are defined in a natural way. Starting from the point of minimum density between a pair of adjacent nuclei, a line in the partitioning surface follows the path of steepest descent through the distribution of charge. The definition is made quantitative by demanding that the charge distribution $\rho(\mathbf{r})$ be partitioned by those closed surfaces through which the flux of $\nabla\rho(\mathbf{r})$ is everywhere zero. Thus, if $S(\mathbf{r})$ denotes such a surface, then

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

where $\mathbf{n}(\mathbf{r})$ denotes a unit vector normal to $S(\mathbf{r})$ at the point $\mathbf{r}$. From the topography of the charge distribution it follows that the only surfaces which satisfy condition 1 are those which contain stationary points in the charge distribution—points at which $\nabla\rho(\mathbf{r}) = 0$. Most stationary points in charge distributions occur as saddle points between each pair of what would normally be considered as "bonded" nuclei. Occasionally, one encounters stationary points which correspond to relative minima in $\rho(\mathbf{r})$. The
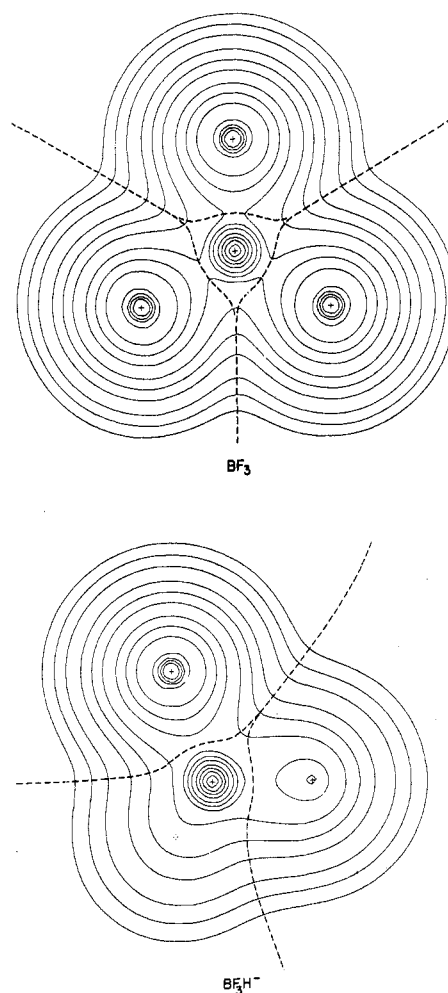

Figure 1. Contour plots of the electronic charge distributions in (a) the σ_h symmetry plane of $BF_3(X(^1A_1'))$ and (b) a plane containing a fluorine and the boron and hydrogen nuclei in $BF_3H^-(X(^1A_1))$. The intersections of the zero-flux partitioning surfaces with these planes are indicated by the dashed boundary lines. The density contours in this and the following figures increase in value from the outermost contour inwards in steps of 2×10^n, 4×10^n, 8×10^n. The smallest contour value is 0.002 au with n increasing in steps of unity to yield a maximum contour value of 20. The fragment populations in BF_3 are: $N(B) = 2.41$ e, $N(F) = 9.86$ e, and in BF_3H^-, $N(B) = 2.50$ e, $N(F) = 9.91$ e, and $N(H) = 1.76$ e.

density minimum in the center of a ring compound is an example of such a point. Examples of such partitioning surfaces are illustrated in Figure 1.

If we define a *gradient path* through a point $\mathbf{r}$ as the combination of the path of steepest ascent from that point, as traced by $\nabla\rho(\mathbf{r})$, and the path of steepest descent, as traced by $-\nabla\rho(\mathbf{r})$, then a partitioning surface is defined by *the collection of all gradient paths which both originate (generally at infinity) and terminate (generally at a saddle point) at stationary points in the charge distribution*. This definition is sufficient to unambiguously partition any molecular system of finite or infinite size. The surfaces themselves are unique. Since every gradient path which does not terminate at a stationary point in $\rho(\mathbf{r})$ terminates at a nucleus (where $\nabla\rho(\mathbf{r})$ is undefined), a given internuclear saddle point is contained in one and only one zero-flux surface.

The surfaces bisect what are normally considered to be chemical bonds, and the result of the partitioning procedure is to divide a molecule into a collection

of single-center or atomic-like fragments. The surfaces are called zero-flux surfaces and the fragments referred to as virial fragments. The basic premise underlying this partitioning is that the distribution of charge in any one fragment is governed primarily by the nucleus of that fragment. Indeed, the theoretical justification of this approach amounts to showing that the fragments possess properties and definitions in common with an *isolated* atomic or molecular system.

Partitioning of Molecular Properties. Of fundamental importance is the partitioning of the energy of a system.[4,5] We shall first give the definitions of the contributions to the energy of a virial fragment and then show that these particular definitions have a special theoretical significance.

The value of any one-electron property for a virial fragment is determined by the distribution of $\rho(\mathbf{r})$ (or the one-electron density matrix $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$) only within the domain of the fragment. As an elementary example, the electron population of a fragment (Ω), $N(\Omega)$, is

$$N(\Omega) = \int_\Omega \rho(\mathbf{r})d\mathbf{r} \qquad (2)$$

where the subscript on the integral signifies that the integration is performed only over the domain of (Ω). The kinetic energy of a fragment enjoys the same twofold definition as does the kinetic energy of an isolated or total system (eq 3).[4] The equality of the

$$T(\Omega) = -\tfrac{1}{2}\int_\Omega [\nabla_\mathbf{r}^2 \Gamma^{(1)}(\mathbf{r},\mathbf{r}')]_{\mathbf{r}=\mathbf{r}'}d\mathbf{r} =$$
$$\tfrac{1}{2}\int_\Omega [\nabla_\mathbf{r}\cdot\nabla_{\mathbf{r}'}\Gamma^{(1)}(\mathbf{r},\mathbf{r}')]_{\mathbf{r}=\mathbf{r}'}d\mathbf{r} \qquad (3)$$

two definitions in eq 3 is the result of the zero-flux condition defining the fragment boundary given in eq 1.

The nuclear–electron attractive potential energy is equal to the interaction of the charge density in (Ω) with all the nuclei in the system (eq 4). $V'(\Omega)$ may be

$$V'(\Omega) = -\int_\Omega \left(\sum_\alpha Z_\alpha/\mathbf{r}_\alpha\right)\rho(\mathbf{r})d\mathbf{r} \qquad (4)$$

broken down into the interaction of the nucleus (or nuclei) in (Ω) with the charge density in (Ω), $V'_\Omega(\Omega)$, and the interaction of the nuclei in the remainder of the system (Ω') with this same charge density, $V'_{\Omega'}(\Omega)$

$$V'(\Omega) = V'_\Omega(\Omega) + V'_{\Omega'}(\Omega)$$

The electron–electron repulsive contribution to the energy of (Ω) is

$$V''(\Omega) + \int_\Omega d\mathbf{r}_1 \int d\mathbf{r}_2 \Gamma^{(2)}(\mathbf{r}_1,\mathbf{r}_2)/\mathbf{r}_{12} \qquad (5)$$

which may be written as

$$V''(\Omega) = V''_\Omega(\Omega) + V''_{\Omega'}(\Omega) \qquad (6)$$

Equation 6 indicates that $V''(\Omega)$ may be expressed as the sum of the self-repulsion of the electrons in (Ω) plus one-half of the repulsions of the electrons in (Ω) with the electrons in the remainder of the system (Ω').

The remaining contribution to the total energy of a system is the nuclear repulsive potential

$$V'_\mathrm{n} = \sum_{\alpha<\beta} Z_\alpha Z_\beta/R_{\alpha\beta}$$

It would at first appear that an unambiguous spatial partitioning of V'_n is not possible since this quantity appears to depend upon the internuclear coordinates $\mathbf{R}_{\alpha\beta}$ and not upon the spatial coordinate $\mathbf{r}$ used to define a volume element of a fragment. However, in the case where all the nuclei are in stable or metastable equilibrium positions, the total nuclear repulsive *force* is equal and opposite to the *forces* $\mathbf{F}_\alpha^e$ exerted on the nuclei by the charge distribution $\rho(\mathbf{r})$. Furthermore, under these same conditions the virial of the electron–nuclear forces

$$-\sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha^e$$

is equal to the virial of the nuclear repulsive forces, a quantity which in turn equals V'_n. Since the forces $\mathbf{F}_\alpha^e$ are (*via* the Hellmann–Feynman theorem) determined by $\rho(\mathbf{r})$, one may spatially partition V'_n by determining what fraction of the force exerted on each nucleus α is exerted by the charge density in the fragment (Ω), *i.e.*

$$V_\mathrm{n}(\Omega) = -\sum_\alpha \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha^e(\Omega) \qquad (7)$$

$\mathbf{F}_\alpha^e(\Omega)$ is just the value of the force operator for nucleus α averaged over the charge distribution in the fragment (Ω).[6] If the nuclei are not in their equilibrium positions, that is, if an external force is acting on the system, then $V_\mathrm{n}(\Omega)$ includes the contribution to the energy of the fragment arising from the action of these external forces.

The contribution of the nuclear repulsive potential to the total energy of a fragment is, therefore, determined by the virial of the forces which the nuclei exert on the charge density *within* the fragment. As shown below, *all* of the potential energy contributions to the energy of a fragment are equal to the virials of the corresponding forces exerted on the charge distribution of the fragment.

Any property determined as the expectation value of a one- or two-electron operator may be defined for a fragment in a similar manner. One may also assign dimensions and volumes to these spatially bound fragments.[7]

(4) R. F. W. Bader and P. M. Beddall, *J. Chem. Phys.*, **56**, 3320 (1972).
(5) R. F. W. Bader, P. M. Beddall, and J. Peslak, Jr., *J. Chem. Phys.*, **58**, 557 (1973).

(6) Equation 7 for $V_\mathrm{n}(\Omega)$ refers to a fragment bounded by but one continuous surface of zero flux. For fragments such as (B) in BF_3 (Figure 1), bounded by three such surfaces, the nuclear contribution to the virial is obtained by subtracting from V_n for the total system the contribution from each neighboring fragment.
(7) For example, the bonded radius is taken as the distance from the nucleus of the fragment to an internuclear stationary point where $\nabla\rho(\mathbf{r}) = 0$. The nonbonded radius is defined as the distance from the nucleus to a particular contour value of $\rho(\mathbf{r})$ in the nonbonded direction. Usually the 0.002 au contour is taken (this contour envelopes 98 to 99% of the total charge density) as this yields nonbonded sizes and shapes for molecules which agree with experimental values.[8] A large number of bonded and nonbonded radii and values of $\rho(\mathbf{r})$ at the internuclear stationary point are tabulated in ref 9.

The Fragment Virial Theorem. It has recently been demonstrated[10] that if a certain theoretical restraint is satisfied, the virial theorem is obeyed over a fragment of a total system *when the kinetic and potential energies of the fragment are defined as above,* thereby yielding

$$-2T(\Omega) = V'(\Omega) + V''(\Omega) + V_n(\Omega) = V(\Omega) \quad (8)$$

As stated in eq 8 $V(\Omega)$, the virial of all the forces exerted on the fragment (Ω), is equal to the electron–nuclear potential, the electron–electron potential, and what we have called the nuclear virial $V_n(\Omega)$. When there are no external forces acting on the system (so that $V_n = V'_n$), one obtains the further virial relationship

$$-T(\Omega) = E(\Omega) \quad (9)$$

where $E(\Omega)$, the *total* energy of the fragment, is given by

$$E(\Omega) = T(\Omega) + V'(\Omega) + V''(\Omega) + V_n(\Omega) \quad (10)$$

It should be noted that any fragment property, when summed over all fragments, yields the corresponding value of the property for the total system.

It has also been shown[10] that if a particular restraint is satisfied by the surface defining a fragment of a molecular system, the hypervirial theorem for the virial operator, $-\mathbf{r} \cdot \nabla$, will be obeyed over the domain of the fragment. This result again applies to fragments with energies defined as above. The existence of regional forms of the hypervirial theorem was recently demonstrated by Epstein.[11] Thus, it is possible to define a fragment of a molecular system such that the virial theorem and the hypervirial theorem (for the virial operator) are simultaneously obeyed if two conditions are satisfied. One condition determines the position of the origin which must be defined to fix the value of $V_n(\Omega)$ and the second condition, the surface restraint, requires that the fragment be bounded by a surface with particular properties. Numerical evidence indicates that a fragment bounded by a surface satisfying the zero-flux condition of eq 1 simultaneously satisfies both theoretical restraints.[10]

The virial partitioning method thus divides a total system into subsystems which possess theoretical properties and definitions in common with a total, isolated system. These properties are: (a) the virial theorem is obeyed; (b) the hypervirial theorem for the virial operator $-\mathbf{r} \cdot \nabla$ is obeyed; (c) the kinetic energy is defined as the expectation value of either of the two possible kinetic energy operators; and (d) when there are no external forces acting on the system, one may rigorously define a total energy for the fragment (eq 10) with the property that

$$\sum_{\Omega} E(\Omega) = E \quad (11)$$

The spatial partitioning of the total energy given in eq 10 and 11 has a theoretical basis, is applicable to any system, and is model independent.

Chemical Significance of Virial Partitioning

One of the cornerstones of chemistry is the observation that fragments or groups of fragments in different molecular systems, or ions in various crystal environments, can have characteristic sets of properties which vary between relatively narrow limits. This retention of properties is, in many instances, so close as to give rise to additivity schemes for the properties, including the energy. The fragment virial theorem can be used to provide the physical condition which must be obeyed if a fragment of a molecular system is to possess an identical energy and population in two different systems.

Assuming both systems in which the fragment (Ω) occurs are in electrostatic equilibrium, then because of the fragment virial theorem, the requirement that $E(\Omega)$ be the same in both systems requires that $T(\Omega)$ and hence *the virial $V(\Omega)$ of all the forces exerted on (Ω) be identical in the two systems.*[4] A more detailed statement of this restraint is possible. The total virial of a fragment may be equated to the virial of the forces which originate within the fragment, the inner virial $V^{(i)}(\Omega)$, plus the virial of the forces exerted on the fragment by the nuclei and charge density outside the fragment, the outer virial $V^{(o)}(\Omega)$. Thus

$$E(\Omega) = -T(\Omega) = \tfrac{1}{2}(V^{(i)}(\Omega) + V^{(o)}(\Omega)) \quad (12)$$

The interesting point is that $T(\Omega)$ and the inner virial $V^{(i)}(\Omega)$ are determined solely by the distribution of charge and quantum properties within the fragment (Ω). Requiring the fragment to be identical in all respects in both systems will result in the inner virial $V^{(i)}(\Omega)$ being the same in both systems. Thus, *for a given fragment to possess identical properties in two different systems, the virial of all the external forces exerted on the fragment must be identical in the two systems.*[5] It is important to note that while the various contributions to the external forces exerted on a fragment (electron–nuclear, electron–electron, nuclear–nuclear) must necessarily be different in different systems, the requirement for the retention of properties of the fragment is only that the *sum* of the virials of all the external forces remain the same.

The above result is true as a result of the fragment virial theorem. What we give now is evidence that a fragment bounded by a surface of zero flux, a virial fragment, maximizes the possibility of meeting the above requirement for the retention of the properties of a fragment in different systems, *i.e.*, that fragments defined by a particular topological property of $\rho(\mathbf{r})$ are the fundamental building blocks of a system.

We have observed that when a fragment is defined by a surface of zero flux, the constancy in its kinetic and total energy is paralleled by a corresponding constancy in the distribution of the electronic charge within the fragment.[4,5] In particular, it is found that the charge density $\rho(\mathbf{r})$ and the kinetic energy density are the same throughout a given fragment in different systems to the extent that the virial of all the forces exerted on each element of $\rho(\mathbf{r})$ remains unchanged. The extent to which the properties of a

(8) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967).

(9) R. F. W. Bader, P. M. Beddall, and P. E. Cade, *J. Amer. Chem. Soc.*, **93**, 3095 (1971).

(10) S. Srebrenik and R. F. W. Bader, *J. Chem. Phys.*, **61**, 2536, (1974).

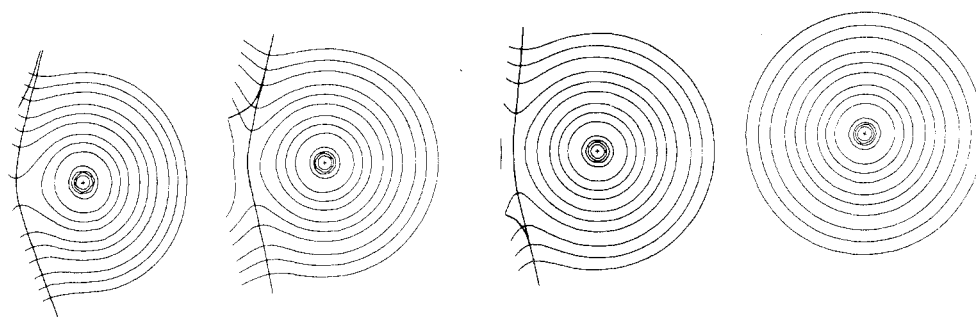(11) S. T. Epstein, *J. Chem. Phys.*, **60**, 3351 (1974).

Figure 2. Contour plots of the charge distribution of just the (F) fragments in (from left to right) $CH_3(F)$, the transition states $[F-CH_3-(F)]^-$, $[N-C-CH_3-(F)]^-$ and the fluoride ion. Note the increase in the number of contours which encompass only the fluorine nucleus through the series of fragments.

Table I
Comparison of Charge and Kinetic Energies of (H) Fragments^a in AH and AH$_n$

	$N(H)$, e	$\Delta N(H)$, e	$T(H) = E(H)$, kcal/mol	$\Delta T(H)$, kcal/mol
$BeH-BeH_2$	1.868	-0.007	484	+6
$BH-BH_3$	1.754	-0.042	557	+7
$NH-NH_3$	0.677	+0.041	310	+8
$OH-H_2O$	0.415	+0.022	230	+9

^{a} $N(H)$ and $T(H)$ refer to populations and kinetic energies of (H) in AH. $\Delta N(H)$ and $\Delta T(H)$ are the differences between (H) in AH and an (H) fragment in AH$_n$, $\Delta N(H) = N(H)_{AH} - N(H)_{AH_n}$. $E(H)$ for a free H atom is -314 kcal/mol.

fragment remain unchanged in different systems is, therefore, determined by the extent to which $\rho(\mathbf{r})$ remains unchanged. Based on the above observations, if $\rho(\mathbf{r})$ of a virial fragment remains unchanged on transfer, so does its total virial $V(\Omega)$ and, since the fragment obeys the virial theorem, $T(\Omega)$ and $E(\Omega)$ are conserved as well. Thus, it is assumed that $\rho(\mathbf{r})$ is the fundamental carrier of the information in a system.[12]

A virial fragment, therefore, maximizes the possible transfer of properties between systems because the zero-flux surface—by the nature of its definition in terms of $\rho(\mathbf{r})$—maximizes the extent to which the distribution of charge of the fragment is transferrable between systems. That is, any other choice of surface will either include part of the neighboring fragment, which may change radically or transfer, or will omit a portion of the charge density, which changes little on transfer. The same zero-flux condition, eq 1, defines a fragment which obeys the virial theorem, has its own set of definable properties, and behaves maximally as an isolated system, acting as a single unit in response to changes in the external forces exerted on it.[13]

(12) A theorem by Hohenberg and Kohn [P. Hohenberg and W. Kohn, *Phys. Rev. B*, **136**, 864 (1964)] proves that the total energy and the kinetic energy are, in principle, uniquely determined by $\rho(\mathbf{r})$ for the total system in a nondegenerate ground state. What we are postulating is that the same functional relationship between $\rho(\mathbf{r})$ and the kinetic energy (and hence the virial) be valid over some properly defined fragment of the system as well.

(13) It is not meant to be implied that the definition of a virial fragment is useful only in those cases where its properties remain nearly unchanged. It is the limiting case of near transfer which points to the relations between $\rho(\mathbf{r})$, $T(\Omega)$ and $V(\Omega)$, but the relationships remain true whether the fragment changes by small or relatively large amounts. Any changes in the properties of a fragment may always be related to a change in its virial and ultimately to the changes in the individual potential contributions which compose the virial.

To illustrate the properties of virial fragments described above, and in particular their apparent ability to adjust to new environments with a minimum of change, we compare in Table I the populations and kinetic energies of the (H) fragments in a number of diatomic AH and polyatomic AH$_n$ systems. Each entry gives the population $N(H)$ and kinetic energy $T(H) = -E(H)$ in AH and the changes in these quantities when AH is changed to AH$_n$. The three-dimensional distribution of electronic charge in the (H) fragment is very similar in any of the AH-AH$_n$ pairs of systems, as evidenced by the small differences in their populations (see Figure 2 in ref 5, for example, which compares (H) in BeH and BeH$_2$). Correspondingly, the kinetic energies and hence total energies of the (H) fragments for a given pair of systems differ by only small amounts.

These relatively small changes in $\rho(\mathbf{r})$, $N(H)$, and $T(H)$ are found in spite of large changes in the individual forces exerted on the (H) fragment as the system changes from AH to AH$_n$. For example, the change in the electron–nuclear attractive potential exerted on the (H) fragment in passage from BeH to BeH$_2$ is -228 kcal/mol. However, the sum of the changes in the electron–electron and nuclear repulsive contributions is of almost equal magnitude and opposite sign and hence the change in the total virial of (H) is relatively small.

As discussed above, the fragment virial theorem requires an equality in the virials of just the external forces exerted on a fragment if the fragment is to be identical in two systems. This requirement is closely obeyed in the case of (H) in BeH and BeH$_2$, for example. The virial of the forces exerted on (H) by (Be) in BeH, the outer virial $V^{(o)}(H)$, is -0.7174 au while the virial of the forces exerted on (H) by the (BeH) fragment in BeH$_2$ is -0.7196 au, a difference of $\sim$2 kcal/mol. In this way, the virial definition of a fragment accounts for the fact that the properties of a hydrogen in BeH are similar to those in BeH$_2$. Since the outer virials for the virial fragments often change by only small amounts, the definition of such fragments accounts for the observation that fragments or groups of fragments in molecular systems can have characteristic sets of properties which vary between relatively narrow limits.

Interpretation of Chemistry in Terms of Fragments

Fragment Populations. Studies of the populations and energies of the (H) fragments in combina-

tion with various (A), A = Li to Cl, provide a quantitative probe of the relative bonding of (A).[14,15] The charge distribution of (H) is a maleable one and sensitive to changes in the virial of the external forces exerted on it. The populations and values of the electron–nuclear attractive interactions for (A) and (H) in AH parallel one's chemical intuition and notions based on concepts such as electronegativity. These same populations of (H) in combination with (A) have been used to order the first- and second-row elements, neutral and charged, in their abilities to abstract or denote charge relative to hydrogen.[15] This ordering is of general interest as the population of (H) in AH changes little on passage to the general (most stable) polyatomic AH_n.

The principal reason for assigning populations to various centers in a molecule is to obtain some measure of the potential field generated by the system, thereby enabling one to predict or rationalize its reactivity. Since the populations of the virial fragments are determined by the distribution of charge in real space, one anticipates that they provide physically meaningful numbers in this regard. For example, the fragment populations and moments may be used to obtain rapid approximations to the potential maps of Bonaccorsi, Scrocco, and Tomasi.[16,17] These authors have shown that the product of a reaction, which is dominated by the properties of the reactants, may be predicted through a knowledge of the electrostatic potential $V(\mathbf{r}_0)$ generated by the reactant charge distribution. The value of $V(\mathbf{r}_0)$ at any one point in space requires an integration over the whole distribution. An alternative is to expand the electronic contribution to $V(\mathbf{r}_0)$ by a multipole expansion in terms of the fragment moments. It is found that $V(\mathbf{r}_0)$ is rapidly approximated to within ± a few kcal/mol using this expansion.[18]

The usefulness of the fragment moments to predict the form of $V(\mathbf{r}_0)$ goes beyond providing a rapid method for its evaluation. The nature of a system's electrostatic potential map is readily understood and qualitatively predictable in terms of the fragment multipole moments. For example, the carbon monoxide molecule has never been protonated. The very weak basicity of CO is surprising when compared to that of the carbonyl fragment and in terms of the expected transfer of charge from (C) to (O) in CO. Virial partitioning does indeed predict net charges of ±1.347 for the (C) and (O) fragments, respectively.

However, the charge distribution of CO possesses characteristics which are found to be general for any system in which the number of valence electrons on the donor exceeds the number of vacancies on the acceptor.[9,14] The unshared valence density on the donor fragment in such a molecule is localized in its nonbonded region in the form of a diffuse distribution, being repelled there by the net negative charge on the acceptor. Similarly, the charge distribution of the acceptor fragment is polarized toward the donor

as a result of the positive charge on the latter fragment. The result is that both fragments, particularly the donor, possess large fragment dipoles which generate a field acting in opposition to the charge-transfer field.[9,15] Thus, at a point on the internuclear axis 5 au from the oxygen nucleus in the nonbonded region, the contribution to $V(\mathbf{r}_0)$ from the monopoles is −0.0805 au. The contribution to $V(\mathbf{r}_0)$ from the fragment dipoles is, however, of almost equal magnitude and opposite sign, +0.0759 au, and the net field is very small. (The quadrupolar contribution is +0.0009 au.)

At a similar point located on the nonbonded side of (C), the monopole contribution is of equal magnitude but of positive sign. In this region of space, the dipole contributions dominate $V(\mathbf{r}_0)$ with a value of −0.0889 au giving, together with a quadrupolar contribution of −0.0019 au, a net field of −0.0102 au. Thus, in CO both ends of the system exert a negative potential, but its magnitude is very small. In H_2CO or $(CH_3)_2CO$, there is no unshared valence density on (C), the fragment dipole is greatly reduced, and the field in the region of (O) is dominated by the monopole contribution arising from the charge transfer from (C) → (O).

A knowledge of fragment multipole moments for elements in common bonding situations could be used to provide a more quantitative relationship between the electronic structure of a system and its chemical properties. There is also the possibility, based on the transferrability of the charge distribution and moments of a virial fragment, of predicting the potential fields generated by large molecular systems through the use of tabulated values for fragment multipole moments in an expansion of $V(\mathbf{r}_0)$. The moments of fragments in various bonded situations could be calculated theoretically with high accuracy in small molecular systems. This possibility is presently being investigated.

Fragment Energies. The change in energy for any process may be partitioned into a sum of fragment energy differences. The virial equations

$$-2\Delta T(\Omega) = \Delta V'(\Omega) + \Delta V''(\Omega) + \Delta V_n(\Omega) \quad (13)$$

$$-\Delta T(\Omega) = \Delta E(\Omega) \quad (14)$$

have been used to relate the kinetic energy of binding in the first- and second-row diatomic hydrides to the changes in the potential energies and total energies of each fragment.[14,15] While the total kinetic energy must increase in the formation of a chemical bond, the change in kinetic energy for any given fragment may be greater or less than zero. Thus, from the sign of $\Delta T(\Omega)$ in eq 14, one may determine whether a given fragment is stabilized or destabilized in the formation of a molecule. Equation 13 relates the change in $\Delta T(\Omega)$ to the change in the virial of all the forces, attractive and repulsive, exerted on the fragment, and hence allows one to relate a change in the fragment's stability to changes in the individual potential energy contributions.

Changes in the nuclear potential energy of a fragment are readily related to changes in the polarizations of $\rho(\mathbf{r})$, eq 7. Viewing the nuclear potential as a quantity determined by the distribution of charge in

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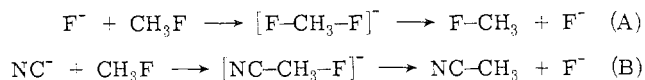
(18) R. R. Messer and R. F. W. Bader, unpublished results.

the system provides a rationalization of the existence of lone pairs. Unshared valence charge density is invariably projected into nonbonded regions in the form of relatively diffuse distributions. The description given previously for the nonbonded charge on (C) in CO is a good example, but the property is a general one. The accumulation of charge density in antibinding (nonbonding) regions of space is very evident in density difference maps ($\Delta\rho(\mathbf{r})$ maps) which illustrate the changes in atomic densities incurred on formation of a molecule.[8] The $\Delta\rho(\mathbf{r})$ maps for H_2 and H_2^+ (and supposedly those for other one- and two-electron systems) are the only exceptions to this otherwise general behavior.

A nonbonded accumulation of charge and the antibinding force it exerts on its associated nucleus is not understandable in terms of a Berlin-type electrostatic analysis of molecular binding. Nor is it understandable in energy terms as to why charge is not accumulated solely in the internuclear regions (as it is in H_2 and H_2^+) where the electron–nuclear attractive forces are maximal. However, the requirement that the sum of the nuclear repulsions must equal the virial of the electrostatic forces which $\rho(\mathbf{r})$ exerts on the nuclei imposes a restraint on the distribution of charge in the system which makes this behavior understandable.

A binding force yields positive contributions to the nuclear virial, while an antibinding force yields a negative contribution and hence contributes to the stabilization of the system through a local lowering of the total energy. An overaccumulation of charge density in the binding region corresponds to a value for the nuclear virial in excess of just the nuclear repulsive forces. The same accumulation causes a local increase in the kinetic energy of the system. This is just the description of a highly compressed system with net repulsive forces acting on the nuclei. The equilibrium situation is instead obtained only when charge density is also accumulated in the antibinding regions, thereby yielding negative contributions to the nuclear virial and to the total energy. Simultaneously, the kinetic energy of the system is lowered as a result of the diffuse nature of the distribution. Thus, the formation of lone pairs lowers the total energy of the system by contributing negative values to the nuclear virial and through a lowering of the kinetic energy.[19]

The energetic consequences of a change in the charge distribution of a fragment caused by or during a reaction are quantitatively determined by the change in its kinetic energy. For example, in a calculation of the potential surfaces for the two reactions[21]

$$F^- + CH_3F \longrightarrow [F\text{--}CH_3\text{--}F]^- \longrightarrow F\text{--}CH_3 + F^- \quad (A)$$

$$NC^- + CH_3F \longrightarrow [NC\text{--}CH_3\text{--}F]^- \longrightarrow NC\text{--}CH_3 + F^- \quad (B)$$

the change in the charge distribution and energy of each fragment in the system from reactant to transition state to products was monitored *via* the kinetic energy changes. Considering just the (F) fragment as an example (Figure 2), one sees that its charge density in CH_3F and the two transition states exhibits a progressive change toward that of the product F^- ion. (The C–F bond is found to be more extended in the transition state of reaction B than A). The net charge of (F) in CH_3F is -0.717, in the transition state of reaction A it is -0.864, in that of reaction B it is -0.954 and -1.00 in the product F^-. By the virial partitioning method one determines that the energy of the bound (F) in CH_3F is more stable than that of a free F^- ion by 199 kcal/mol. As the separation of (F) increases, its total charge and kinetic energy approach those of F^-. Thus, (F) in the transition state of reaction A is only 60 kcal/mol more stable than F^- and in reaction B the near separation of (F) as F^- in the transition state is reflected in the fragment energy being increased to within 36 kcal/mol of F^-. Thus, during reaction B, the changes incurred in the leaving (F) fragment contribute 163 kcal/mol to a total activation energy of 22 kcal/mol.

It is important to realize that the energy changes obtained in this way are the *net* changes in energy necessary to account for the observed changes in the charge distribution of the fragment. Any one of the potential energy contributions to the energy of the (F) fragment in the above reactions, for example, changes by thousands of kcalories/mol from bound (F) to F^-. The changes in the charge distribution of (F), however, are governed by the change in its total virial, that is, by the *sum* of the changes in $V'(F)$, $V''(F)$ and $V_n(F)$, a sum which is measured by $\Delta T(F)$.

Another observation of general applicability was made in the partitioning study of reactions A and B. The (H) fragments of the methyl groups were found to be compressed and reduced in volume in the corresponding transition states. The net result is the storage, in the form of potential energy, of ~ 45 kcal/mol in the (H) fragments of the transition state. The release of this energy serves as a driving force for further motion of the system along the specific reaction coordinate. Thus, one may, *via* the virial partitioning method, isolate those *spatial* regions or fragments of a reacting system in which potential energy is at first accumulated and then later released, either to drive the same reaction to completion or to initiate a subsequent one. This ability to identify spatially the "energy rich" regions of a molecular system can be used to quantify the concept of "high-energy bonds" and the role they are assigned in biochemical reactions.

Conclusion

The existence of a quantum mechanical virial theorem for a fragment of a molecule signifies that a molecular system may be spatially partitioned in a way which is both unique and physically meaningful. A virial fragment, with its natural and physically obvious definition in terms of topographical minima in the charge distribution, appears to be the embodiment of this partitioning scheme.

(19) In just those systems where no lone pairs exist, H_2 and H_2^+, the accumulation of charge density in the internuclear region (which in these examples occurs to an unusually high degree) results in an actual decrease in the local kinetic energy.[20] Thus, a relatively large positive V_n may be tolerated (*i.e.*, a short equilibrium bond length is obtained). In a system with more than two electrons this behavior is not observed.

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