

nm (ϵ 5820) and 401 nm (ϵ 6530), respectively. This technique proved to be sufficiently sensitive to allow very small conversions (typically 0.01%) of dianthracene to be monitored. The absorptions due to the local excitation of the anthracene partially overlapped with those of the EDA complex so that the products competitively absorbed the incident light at 405 nm and (to a very small extent) at 436 nm. For this reason the conversions were kept below 0.1% for the determinations at 405 nm; and under these conditions the products absorbed $\leq 10\%$ of the incident light. However, agreement within experimental error was obtained with 436-nm excitation (or longer) when the analysis was performed either spectrophotometrically to 0.1% conversion (by monitoring product absorptions) and to $< 1\%$ conversion (by monitoring the disappearance of the EDA complex) or by ^1H NMR analysis to $< 10\%$ conversion.

The monomers, 9-cyano-, 9-formyl-, 9-methoxy-, and 9-acetoxy-anthracene, reacted sufficiently slowly with TCNE for them to be detected by UV or ^1H NMR spectrophotometry. Anthracene and 9-methylanthracene reacted with TCNE too rapidly under experimental conditions to detect as such, and only the Diels-Alder adduct was found. In every case the product (either the anthracene or its TCNE adduct) was formed quantitatively (200% yield), based on the conversion of the dianthracene. On standing for longer times, the anthracene monomers derived from the formyl and the acetoxy derivatives slowly reacted with TCNE to form the respective Diels-Alder adducts. The products and stoichiometries of the photochemical reactions were independent of the wavelength of the CT excitation.

The quantum yields for the disappearance of the dianthracenes were determined by Reinecke actinometry.⁵⁵ The values of Φ in Table II represent the average of three independent determinations and are re-

producable to within $\pm 10\%$. The quantum efficiencies at 436 and 480 nm were checked with ferrioxalate actinometry.⁵⁵ The light intensity from the xenon source was shown to be essentially independent ($3.2 \pm 0.3 \times 10^{-8}$ einstein) of the monitoring wavelengths used. Owing to the limited solubilities of the dianthracenes, the absorptions arising from the EDA complexes were low. Thus a correction for incomplete light absorption was applied to the quantum yields based upon the transmittance of the solution at each excitation wavelength. This correction varied essentially linearly with the absorbance, but it was appreciable especially at the long wavelengths for the dicyanoanthracene and dianthraldehyde donors. Although greater error limits must be associated with the quantum yields in these cases, standard deviations of $\approx 10\%$ were still obtained. The high reactivity of the dicyanoanthracene complex at 577 nm was attested to by the observation of substantial reaction after brief (~ 30 min) irradiation of the solution under conditions in which no reaction was detected for the unsubstituted dianthracene complex under identical conditions despite its much greater absorbance at this wavelength.

The electronic spectra were measured with a Hewlett Packard 8450A diode-array spectrometer capable of 0.1 s time resolution. The NMR spectra were recorded on a Nicolet NT360 (360 MHz) spectrometer.

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Toward a Theory of Chemical Reactivity Based on the Charge Density

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Abstract: This paper presents a theory of chemical reactivity based upon the properties of the electronic charge distribution and the changes in this distribution as induced by vibrational motions. The initial approach of the reactants is determined by aligning local charge concentrations with regions of charge depletion as determined by the Laplacian of their charge distributions, the quantity $\nabla^2\rho$. The energetically most favored nuclear motion of this combined system is the one which induces the largest and most facile relaxation in the charge distribution. This relaxation is approximated by the transition density obtained by mixing in the lowest energy excited state of the combined system. It is found here that the relative approach of the reactants as determined by the properties of their Laplacian distributions leads to the formation of a complex in which the most facile relaxation of the charge density is one that leads to further motion along the reaction coordinate defined by this approach. For example, CO and BH_3 may act as donors or acceptors in terms of their Laplacian distributions and in their addition this distribution requires the approach of C to B along the symmetry axis of BH_3 . The transition densities corresponding to both donor-acceptor possibilities have nearly equal excitation energies and are of the same symmetry: one is π -like and transfers charge to CO and the other is σ -like and transfers charge to BH_3 . In many cases the regions of space where HOMO and LUMO are most concentrated coincide respectively with the regions of charge concentration and depletion in the Laplacian distribution. Thus the requirements of the frontier orbital model correspond physically to aligning regions of charge concentration with regions of charge depletion. The examples given in this paper demonstrate that the Laplacian distribution provides a bridge between the density and orbital approaches to the understanding of chemical reactivity.

In a chemical reaction there is a continuous change in the distribution of electronic charge from that of the reactants to that of the products. Thus a primary prerequisite for predicting the course of chemical change is a knowledge of how the charge distribution changes for a given displacement of the nuclei. Electronic excitation can also effect a change in the charge distribution, but the ensuing chemistry of the excited or charged state is again governed by the accommodation of this essentially instantaneous change in the charge distribution to the field of the nuclei.

It has been previously shown how second-order perturbation theory can be used to predict the essential features of the change

or relaxation in the electronic charge density ρ for a given displacement of the nuclei.^{1a,2} This is done by approximating the relaxation in ρ by the transition density obtained by a mixing-in of the lowest energy excited state function of appropriate symmetry, the symmetry being determined by the symmetry of the perturbing nuclear displacement. Assuming that the largest re-

(1) (a) Bader, R. F. W. *Mol. Phys.* **1960**, *3*, 137. (b) This application is a direct test of the assumption that the vibrational mode that causes a mixing-in of the lowest energy excited state has the lowest force constant within the set of bond stretching constants of a given molecule.

(2) Bader, R. F. W. *Can. J. Chem.* **1962**, *40*, 1164.

laxation in ρ is caused by mixing in the excited state of lowest energy, one is able to determine the nuclear displacement that results in the smallest energy increase. This method has been used to predict the signs of interaction constants in vibrational potential functions,^{1b} the dissociative pathways of unimolecular reactions,² and the symmetries of equilibrium geometries.³

If one wishes to apply this method to predict the possible course of a reaction between two molecules, then one must in addition have a means of determining the preferred relative alignment of the reactants. This information is provided by the properties of the Laplacian of the electronic charge distribution, the quantity $\nabla^2\rho(r) = \partial^2\rho/\partial x^2 + \partial^2\rho/\partial y^2 + \partial^2\rho/\partial z^2$. This quantity determines where electronic charge is locally concentrated and depleted.^{4,5} The relative orientations of functional groups within a crystal structure and the initial orientation of reactants can be determined by aligning local concentrations of charge with local regions of charge depletion as determined by the Laplacian of their charge distributions. What is demonstrated in this work is that for a geometry of approach of the reactants determined in this manner the lowest energy transition density of the combined system is in general of a symmetry such that the energetically favored nuclear motion is the one that leads to the formation of the observed products.

Within the orbital model of electronic structure the approximation to the relevant transition density will generally be given as the product of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of the reactants. Fukui⁶ has argued that the relative orientation of the reactants is determined by requiring that the overlap of HOMO and LUMO be a maximum. In the present work, the properties of the Laplacian of ρ are used to predict the relative orientation of the reactants. The resulting HOMO-LUMO overlap for the combined system determines the transition density and hence the forces exerted on the nuclei by this energetically most favored relaxation in ρ .

Laplacian of the Charge Density

The electronic charge density exhibits a local maximum only at the position of a nucleus and a local minimum only in the interior of a cage structure and lines, linking the nuclei of neighboring atoms, along which the charge density is a maximum with respect to all neighboring lines. These properties of ρ provide a faithful mapping of the models of atoms, bonds, and structure.^{7,8} The topology of ρ does not, however, provide any indication of the presence of shell structure in an atom or of maxima in a molecular charge distribution corresponding to bonded or nonbonded pairs of electrons as is anticipated on the basis of the Lewis model or the model of localized electron pairs—models that play an important role in our understanding of chemical reactivity and molecular geometry. These models are, however, recovered in the properties of the Laplacian of ρ . The form of this function for an isolated atom reflects its shell structure by exhibiting a corresponding number of pairs of spherical shells of charge concentration and charge depletion. Upon chemical combination, local centers of charge concentration and charge depletion are created within the valence shell. The number, locations, and magnitudes of the charge concentrations are found to be in general agreement with the properties that are ascribed to the bonded and nonbonded electron pairs in models of electronic structure.⁵

Sites of electrophilic and nucleophilic attack in a molecule correlate respectively with the sites of maximum charge concentration and charge depletion. The sites are not determined

by corresponding local maxima and minima in the charge distribution itself but rather by corresponding extrema in its Laplacian distribution. The Laplacian of ρ at a point r provides a measure of the difference between the average value of ρ at points neighboring r and its value at r . When $\nabla^2\rho(r) < 0$, $\rho(r)$ is greater than its average value at neighboring points and when $\nabla^2\rho(r) > 0$ the opposite is true. This difference between the local value and the average value of ρ is a maximum at the extrema in $\nabla^2\rho$. It is useful to think of the Laplacian as providing a measure of the pressure of ρ at a given point, the density being compressed in regions where $\nabla^2\rho < 0$ and expanded in regions where $\nabla^2\rho > 0$.

The Laplacian of ρ is directly related to the local contributions to the electronic energy of a system via the equation^{4,5}

$$(\hbar^2/4m)\nabla^2\rho(r) = V(r) + 2G(r) \quad (1)$$

$V(r)$ is the potential energy density (its integral over all space yields the total electronic potential energy V) and $G(r)$ is the kinetic energy density (its integral over all space yields the total kinetic energy of the electrons, T). Since $V(r) < 0$ and $G(r) > 0$ for all r , eq 1 states that the lowering of the potential energy dominates the total energy in regions where electronic charge density is concentrated or compressed, that is, where $\nabla^2\rho < 0$. The integral of the Laplacian of ρ vanishes for an isolated atom

$$\int \nabla^2\rho(r) d\tau = \int dS \nabla\rho(r) \cdot n(r) = 0 \quad (2)$$

because of the vanishing of $\nabla\rho$ on the surface of the atom at infinity. Thus the concentration of charge at certain distances from the nucleus (where $\nabla^2\rho < 0$) results in an equivalent depletion of charge at other distances (where $\nabla^2\rho > 0$) as demanded by the vanishing of the integral in eq 2. The corresponding alternation in the preponderance of either the potential or kinetic energy contributions in each shell, eq 1, also averages out on integration over an atom to yield the average values demanded by the virial theorem

$$V + 2T = 0 \quad (3)$$

From the local point of view afforded by eq 1, the virial theorem is obtained as a consequence of the Laplacian of ρ vanishing over an isolated atom or over an entire molecule. An atom in a molecule, as defined by the topological properties of ρ , is also bounded by a surface through which the flux in the gradient of ρ is zero as in eq 2. Thus the integral of the Laplacian of ρ over a bound atom Ω also vanishes and the virial theorem is again obtained

$$(\hbar^2/4m) \int_{\Omega} \nabla^2\rho d\tau = V(\Omega) + 2T(\Omega) = 0 \quad (4)$$

When an isolated atom enters into chemical combination the surface of zero flux in $\nabla\rho$ and its attendant physical consequences are preserved. The creation of local concentrations of bonded and nonbonded charge within the valence shell of an atom upon chemical combination must, therefore, result in the formation of equivalent regions of charge depletion (eq 2). The reaction of a nucleophile with an electrophile or of a base with an acid 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 of excess potential energy with one of excess kinetic energy (eq 1) 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 (eq 4).

Structure of the Laplacian Distribution

The locations of maxima, minima, or saddle points in a scalar function such as the charge density or its Laplacian are determined by the positions of critical points in these functions, points where either $\nabla\rho = 0$ or $\nabla(\nabla^2\rho) = 0$. Whether the function is a maximum, minimum, or saddle at a given critical point is determined

(3) Pearson, R. G. "Symmetry Rules for Chemical Reactions"; Wiley: New York, 1976. Bartell, L. S. *J. Chem. Educ.* **1968**, *45*, 754.

(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) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

(7) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *J. Chem. Phys.* **1979**, *70*, 4316. Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893.

(8) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.

by the curvatures of the function at that point.⁹ Since charge is concentrated where $\nabla^2\rho < 0$, it is more convenient to work with the function $-\nabla^2\rho$, a maximum in this function being a maximum in charge concentration.

The valence shell of charge concentration (VSCC) of an atom possesses a spherical surface over which the charge is maximally compressed or concentrated, i.e., $\nabla(\nabla^2\rho) = 0$ for every point on the surface. Thus the curvature of $-\nabla^2\rho$ normal to this surface, the radial curvature, is negative. The two remaining curvatures, those tangential to the surface, are equal to zero. In general this surface persists when the atom is in chemical combination (the derivative of $-\nabla^2\rho$ normal to the surface is still zero and the corresponding curvature is negative), but the surface is no longer one of uniform concentration as the tangential curvatures assume either positive or negative values. The topology of the Laplacian of ρ on this surface is equivalent to the description of the hills and valleys of a surface terrain. If a local maximum is formed on the surface, then the two tangential curvatures of $-\nabla^2\rho$ are negative while in the formation of a local minimum these same two curvatures assume positive values. A saddle point may also be formed on the surface in which case one of the tangential curvatures will be negative and the other positive.

The structure exhibited by the Laplacian of ρ through its collection of valence shell critical points is characteristic for a given type of atom with a given number of bonded neighbors. This structure corresponds to the atom's Lewis structure and it determines its overall chemical behavior. In methane (Figure 1) there is a maximum in the valence shell of charge concentration (VSCC) of the carbon atom along each of the C-H bond paths. Each maxima is linked to the other three by unique pairs of trajectories of the gradient of the Laplacian of ρ which originate at intervening saddle points on the surface of charge concentration. These lines are the analogues of the bond paths defined by the corresponding trajectories of the gradient of the charge density. This network of lines, called an *atomic graph*, partitions the surface of charge concentration into four segments and the basic structure is that of a tetrahedron with curved faces. In the center of each face there is a local minimum in the surface of the VSCC. Thus the uniform spherical surface of charge concentration of a free carbon atom is transformed in methane into one with four tetrahedrally arranged concentrations of charge with charge depletions in the center of each of the resulting triangular faces. The surface in the molecule is no longer spherical, the different critical points lying at slightly different distances from the nucleus, but all within the range 0.54 to 0.55 Å. The average radius of the surface increases slightly from that found in the free atom where it is 0.50 Å.

The values of the Laplacian of ρ at the maxima and minima in the VSCC of the atoms in a number of molecules are given in Table I along with the net charges on the atoms in these molecules. The effect of a charge-withdrawing substituent on the atomic graph and reactivity of the carbon atom is illustrated by CH_3F . While the general structure of the atomic graph is left unchanged by the substantial charge transfer from carbon to fluorine, it does cause major changes in the extent of charge concentration and charge depletion (Figure 1). As a result of the charge transfer, the minimum in the charge density along the bond path from C to F is found only 0.43 Å from the C nucleus and the associated bonded charge concentration is located within the boundary of the fluorine atom. If the loss of this charge concentration and its associated excess of potential energy was not compensated for, the energy of the carbon atom would increase significantly. Consequently, the three remaining bonded maxima, those linking the protons, double in magnitude as do the values of $-\nabla^2\rho$ at the intervening saddle points. As a result of this increase in the concentration of charge about the perimeter of the face of the VSCC opposite the F, the extent of charge depletion in this

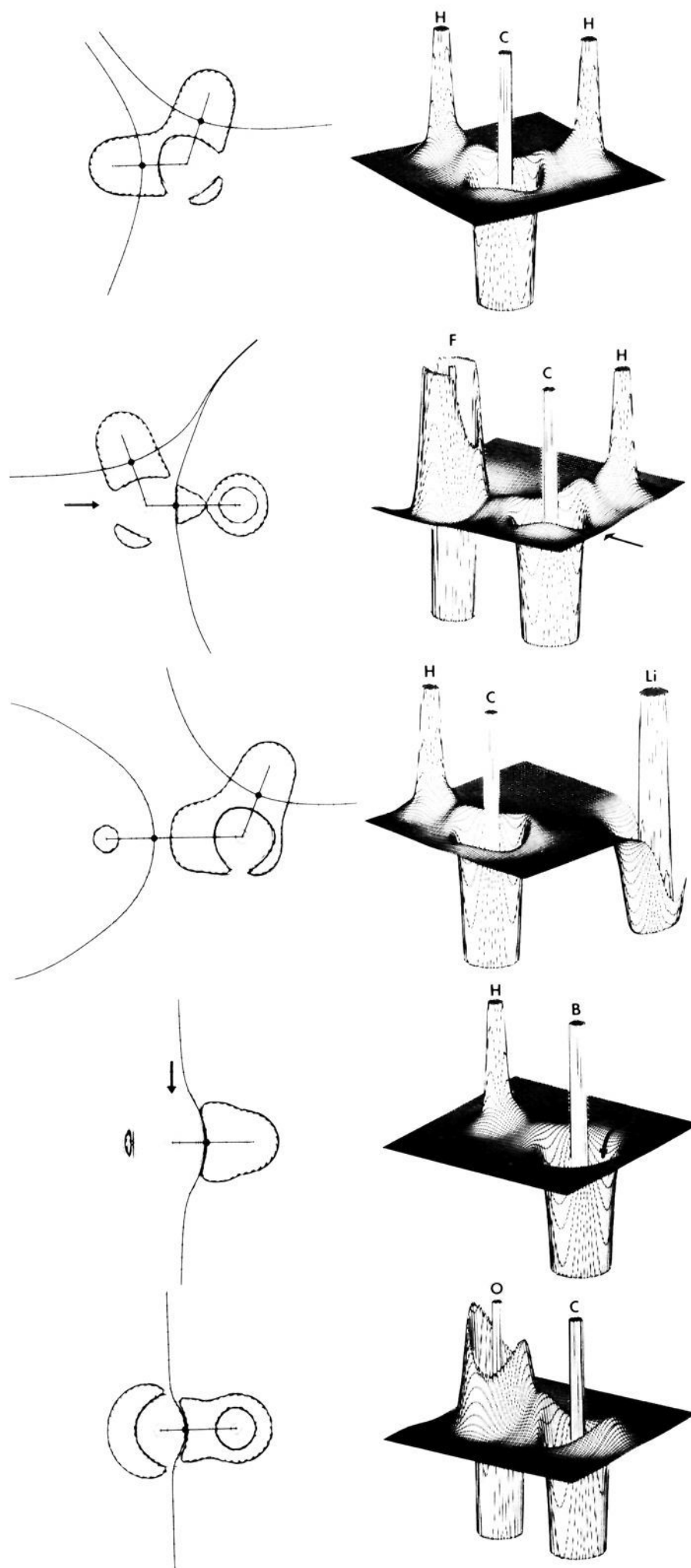


Figure 1. Contour plots of the Laplacian distribution $\nabla^2\rho$ and mirror image relief maps of $-\nabla^2\rho$ for the molecules CH_4 , CH_3F , CH_3Li , BH_3 , and CO . Solid contours denote positive and dashed contours negative values of $\nabla^2\rho$. The arrow in CH_3F indicates the region of charge depletion in the face of the VSCC of carbon opposite the fluorine. The curved arrow reaching into the core of boron in the relief map of BH_3 indicates the presence of holes in the VSCC of this atom. The values of $\nabla^2\rho$ at the bonded and nonbonded maxima and the local minima in the VSCC's are listed in Table I. The contour values in au are ± 0.002 , ± 0.004 , and ± 0.008 increasing in powers of 10 to ± 8.0 . The outermost contour in each plot is 0.002. The interatomic surfaces and bond paths are indicated on the contour plots.

(9) If all three curvatures are negative at a critical point, the function is a maximum, and if all three are positive, it is a minimum. Saddle points are obtained when the critical point is viewed in a plane where one curvature is negative and the other positive. The third curvature in these cases may be of either sign.

face is greatly increased (Table I). Thus carbon in methyl fluoride is more susceptible to nucleophilic attack than is carbon in methane. Methanol exhibits behavior similar to that found for

Table I. Atomic Properties of Reactants^a

reactant	Ω	$q(\Omega)^c$	A-B	$\rho_b(\text{A-B}),^b$ au	extrema in VSCC of Ω		
					Ω	type of extremum	$\nabla^2\rho$, au
CH ₄	C	+0.24	C-H	0.286	C	bonded maxima to H	-0.72
	H	-0.06			C	minima opposite H	+0.12
CH ₃ F	C	+0.87	C-H	0.301	C	bonded maxima to H	-1.42
	H	-0.04	C-F	0.237	C	bonded maximum to F	-0.44
	F	-0.74			C	minimum opposite F	+0.31
CH ₃ Li	C	-0.51	C-H	0.269	C	minima opposite H	+0.20
	H	-0.13	C-Li	0.042	C	bonded maxima to H	-0.98
	Li	+0.90			C	bonded maximum to Li	-0.87
					C	minimum opposite Li	-0.08
BH ₃	B	+2.16	B-H	0.184	B	only critical point is saddle point linking H nuclei	-0.01
	H	-0.72					
CO	C	+1.40	C-O	0.500	C	bonded maximum to O	-1.92
	O	-1.40			C	nonbonded maximum	-1.45
					C	toroidal minimum	+0.08
					O	nonbonded maximum	-6.23
OH ⁻	O	-1.38	O-H	0.371	O	nonbonded torus	-5.28
	H	+0.38			O	bonded maximum to H	-1.07
H ₂ CO	C	+1.36	C-H	0.297	C	bonded maxima to H	-1.46
	O	-1.30	C-O	0.431	C	bonded maximum to O	-1.57
	H	-0.03			C	p-like minima in VSCC	+0.13
					O	nonbonded maxima	-7.09

^aAll results calculated by using the 6-31G** basis set. ^b $\rho_b(\text{A-B})$ is defined as the minimum value that $\rho(r)$ attains along the bond path connecting atoms A and B. ^c $q(\Omega)$ is net charge on Ω , $q(\Omega) = -\int_{\Omega} \rho \, d\tau + Z_{\Omega} = -N(\Omega) + Z_{\Omega}$.

methyl fluoride, the value of $\nabla^2\rho$ at the face critical point opposite the oxygen being only slightly less positive than that for methyl fluoride.

The CH₃Li system illustrates the effect of charge donation on the VSCC of the methyl carbon. There is a transfer of 0.90 e⁻ from Li to the methyl group (Table I). While the negative charge is delocalized over the whole of the methyl group, the properties of the C-Li bond are characteristic of an ionic interaction. The value of ρ at the bond critical point is relatively small, 0.05 au (Table I), and the value of $\nabla^2\rho$ at the bond critical point is positive, indicating that the charge density is depleted in the interatomic surface and contracted toward the two nuclei.^{4,5} The Laplacian for CH₃Li shows that Li has but a single quantum shell as anticipated for a Li⁺ ion. The structure of the atomic graph for carbon is unchanged from that for methane, but more charge is concentrated at all of the critical points with the exception of those in the three faces adjacent to Li. In a covalent or shared interaction, $\nabla^2\rho$ exhibits a single contiguous concentration of charge extending over the basins of both atoms as, for example, in a C-H bond.^{4,5} The charge concentration on the C-Li bond path is, however, totally localized within the boundary of the carbon atom. Thus, as is typical of an ionic interaction, the bonded charge concentration of the C-Li bond is not shared but is instead localized on carbon and radially contracted toward the C core. It is also laterally more diffuse than a shared charge concentration. These are the characteristics one associates with a bond that has little directional character, and the bonded maximum can in such a case serve as a center of electrophilic attack, the electrophile laterally displacing the Li⁺ ion.

The VSCC of a Lewis acid is exemplified by that of the boron atom in BH₃. The surface of charge concentration on the boron atom has been punctured on either side of the plane of the nuclei, reducing the VSCC to a belt of charge concentration. This behavior is made evident in the relief map of the Laplacian by the absence of a "lip" at the corresponding positions of the core (see Figure 1). The Lewis model of an incomplete valence shell or the orbital model of a vacant p π orbital on boron appears in the Laplacian distribution as two holes in the shell of charge concentration. These holes provide direct access to the region of charge depletion in the core of the boron atom making it very susceptible to nucleophilic attack. The carbon atom of a carbocation exhibits similar behavior.

The CO molecule is characteristic of a class of molecules wherein the donor atom has more valence electrons than the acceptor has vacancies.¹⁰ Because of the large negative field exerted on the donor atom as a result of the charge transfer (Table I), its remaining valence density is strongly polarized into its nonbonded region where it forms a diffuse extended distribution.¹¹ Correspondingly, the Laplacian distributions of such molecules exhibit nonbonded charge concentrations on both donor and acceptor atoms. The concentration on O is large in magnitude and tightly bound, while that on C is of smaller magnitude and more spread out, both radially and laterally. Both atoms also possess a bonded charge concentration. Most important is the presence of a torus of charge depletion in the VSCC of carbon encircling the internuclear axis. In terms of its Laplacian distribution, the carbon atom of CO may act as an electron acceptor or electron donor.

From the examples given here and others given previously^{12,13} it is clear that regions of charge concentration and depletion in the Laplacian distribution coincide respectively with the regions where HOMO and LUMO are concentrated. In general, there is more than one local concentration of charge and HOMO will be associated with the least tightly bound of these. By eq 1 this is the charge concentration with the least negative value for $\nabla^2\rho$ and correspondingly the most diffuse distribution. In CO, for example, HOMO (5 σ) is strongly localized in the nonbonded region of carbon and correspondingly the nonbonded charge concentration on carbon is the least tightly bound (Table I) and most diffuse (Figure 1) of the charge concentrations in this

(10) Bader, R. F. W.; Beddall, P. M.; Cade, P. E. *J. Am. Chem. Soc.* **1971**, *93*, 3095.

(11) The result of this "back-polarization" of the charge density of the donor atom is the creation of a large atomic dipole. In CF, CO, and CN⁻, for example, the magnitudes of the atomic dipole on C are 1.47, 1.70, and 1.92 au, respectively.

(12) MacDougall, P. J.; Bader, R. F. W. *Can. J. Chem.*, submitted for publication.

(13) In cases where many low-lying virtual orbitals are closely spaced, in molecules containing third-row atoms, for example, it is questionable to assume that just the lowest of this dense set of orbitals dominates the reactivity of the system toward nucleophiles. The Laplacian of ρ , on the other hand, clearly defines the centers of charge depletion even in these cases. See, for example, $\nabla^2\rho$ for S₄²⁺ in the following: Tang, T.-H.; Bader, R. F. W.; MacDougall, P. J. *Inorg. Chem.* **1985**, *24*, 2047.

molecule. LUMO (π^*) is also localized on carbon as is the π -like region of charge depletion in $\nabla^2\rho$. LUMO in CH_3F is C-F antibonding and localized on the nonbonded side of carbon as is the region of charge depletion in the VSCC of carbon. The holes in the VSCC of boron and the B-H bonded concentrations in BH_3 correspond respectively to LUMO and HOMO of this molecule. Thus the properties of the Laplacian distribution demonstrate that the requirements of the frontier orbital model¹⁴ correspond physically to aligning regions of charge concentration with regions of charge depletion in the VSCC's of the reacting atoms. This statement is accounted for and documented below with use of the examples of nucleophilic addition and displacement reactions.

The Model

The change in energy correct to second order for a nuclear displacement Q_i from some given initial geometry that in general is not an energy minimum is given by

$$E(Q_i) = E(0) + [V_{nn}^i + V_{oo}^i]\delta Q_i + \frac{1}{2}[V_{nn}^{ii} + V_{oo}^{ii} + 2\sum_k |V_{ok}^i|^2 / (E_o - E_k)]\delta Q_i^2 \quad (5)$$

The terms linear in the displacement are the nuclear and electronic contributions to the Hellmann-Feynman forces exerted on the nuclei that are displaced in the mode Q_i . They are determined by the unperturbed charge density ρ_{00} . Thus V_{nn}^i is $\partial V_{nn}/\partial Q_i$ where V_{nn} is the nuclear-nuclear potential energy and

$$V_{oo}^i = - \int (\partial V_{ne}/\partial Q_i)\rho_{00} d\tau$$

where V_{ne} is the nuclear-electron potential energy operator. The quadratic terms determine the second derivatives of E . When evaluated at an equilibrium geometry they determine the force constant k_i for the model Q_i . The first term is a nuclear field gradient, $\partial^2 V_{nn}/\partial Q_i^2$. The second term represents the contribution to k_i when the nuclei are displaced in the presence of the unperturbed charge distribution ρ_{00} ,

$$V_{oo}^{ii} = \int (\partial^2 V_{ne}/\partial Q_i^2)\rho_{00} d\tau$$

The final term in eq 5 expresses the contribution to k_i from the change in ρ which is caused by the displacement of the nuclei. Thus

$$V_{ok}^i = \int (\partial V_{ne}/\partial Q_i)\rho_{ok} d\tau$$

where ρ_{ok} is a transition density—the change in ρ_{00} as described by “mixing-in” with the ground-state function Ψ_0 the singly excited state function Ψ_k . The term V_{ok}^i is the force exerted on the nuclei by the contribution to the change in ρ_{00} from the transition density ρ_{ok} .

The primary change in the charge density that accompanies a nuclear displacement corresponds to a rigid following of the nuclear motion. This rigid following does not contribute to the change in energy, or to the force constant for displacement from an equilibrium configuration.¹⁵ The electronic contribution to the change in energy or to a force constant is determined entirely by the relaxation of the charge density which accompanies a nuclear displacement.¹⁶ By the relaxation in ρ we mean the difference between the total change in ρ and that which corresponds to rigid following. Since most of the density change corresponds to a rigid following of the nuclei there is a very large degree of cancellation between the term V_{oo}^{ii} —moving the nuclei in the static distribution ρ_{00} —and the summation over the excited state terms wherein the transition densities enable the charge density to catch-up with the displaced nuclei.¹⁷ The core density

mostly follows the motion of the nuclei, and this will be described by excited states Ψ_k derived from Ψ_0 by excitations from the core and inner-shell orbitals. On these grounds and on the basis of the valence density being the least tightly bound, the dominant contributions to the relaxation in ρ , i.e., that part of the total change in ρ which determines the change in energy, will be described by the transition densities arising from the lowest lying of the excited states. The integral V_{ok}^i vanishes unless Q_i and ρ_{ok} have identical symmetries and the relaxation in ρ for a given nuclear motion will be approximated by the single ρ_{ok} of appropriate symmetry. Because of the energy difference $E_0 - E_k$ appearing in the denominator of each term of the summation in eq 5, one anticipates that the largest relaxation in ρ will occur for the mode Q_i which is of the appropriate symmetry to mix in the lowest of the excited states Ψ_k .

The transition density is defined as

$$\rho_{ok}(r) = N \int d\tau' \Psi_k \Psi_0$$

where $\int d\tau'$ implies a summation over all spins and an integration over the coordinates of all the electrons but the one whose position coordinate is denoted by r . Because of the orthogonality of the state functions Ψ_0 and Ψ_k

$$\int \rho_{ok}(r) d\tau = 0$$

Thus ρ_{ok} does not represent an absolute amount of charge but rather it describes a change in the charge distribution, charge being removed from regions where $\rho_{ok} < 0$ and being placed in regions where $\rho_{ok} > 0$. If we use a single determinantal function to approximate Ψ_0 for a closed-shell system and if we further assume that Ψ_k may be expressed in terms of the occupied and virtual set of orbitals obtained in the calculation of Ψ_0 , then ρ_{ok} reduces to a simple product of molecular orbitals, those that are singly occupied in Ψ_k . For large initial separations of the reactants the state function is approximated by the antisymmetrized product of the state functions of the reactants. With Ψ_0 approximated in this manner, the orbitals used to approximate ρ_{ok} will, in general, be the HOMO of the base or nucleophile and the LUMO of the acid or electrophile.

The working model that is to be used to determine the initial relative alignment of the reactants and the subsequent motion of the nuclei that leads to the lowest energy pathway is as follows: (1) The terms linear in the displacement in eq 5, the forces acting on the nuclei, are assumed to be made maximally attractive by aligning the charge concentrations on one reactant with the regions of charge depletion on the other as determined by the Laplacians of their charge distributions. This step determines the symmetry of the combined system. (2) All of the second-order changes in E are replaced by the single contribution arising from the mixing-in of the lowest of the excited states of the combined system. The form of the associated transition density ρ_{ok} is meant to determine the major contribution to the relaxation of the charge density. The symmetry of ρ_{ok} determines the symmetry of the vibrational motion Q_i which results in the largest relaxation in the distribution of charge and to the smallest increase in energy.

The pathway predicted in this manner is the energetically favored one, as both the force of attraction between the reactants as determined by ρ_{00} and the rate of increase in this force of attraction as determined by the relaxation density ρ_{ok} are maximized by this approach.

Calculations

A single-determinant SCF calculation with the approaching atoms of the reactants separated by 2.0 or 2.1 Å and with each reactant in its equilibrium geometry was made for each reaction. For the addition of BH_3 to CO the 6-31G** basis set was used. For reactions involving the negatively charged bases F^- and OH^- the 6-31G* basis augmented with a set of diffuse s and p functions on all of the second-row atoms was used.¹⁸

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(17) In N_2 , for example, moving the nuclei in the static charge distribution contributes +6007.6 au to the force constant while the contribution obtained by allowing the charge density to both follow and relax (the last term in eq 5) equals -6017.2 au. The nuclear field gradient contribution is 11.1 au and the value of k_i is 1.5 au.

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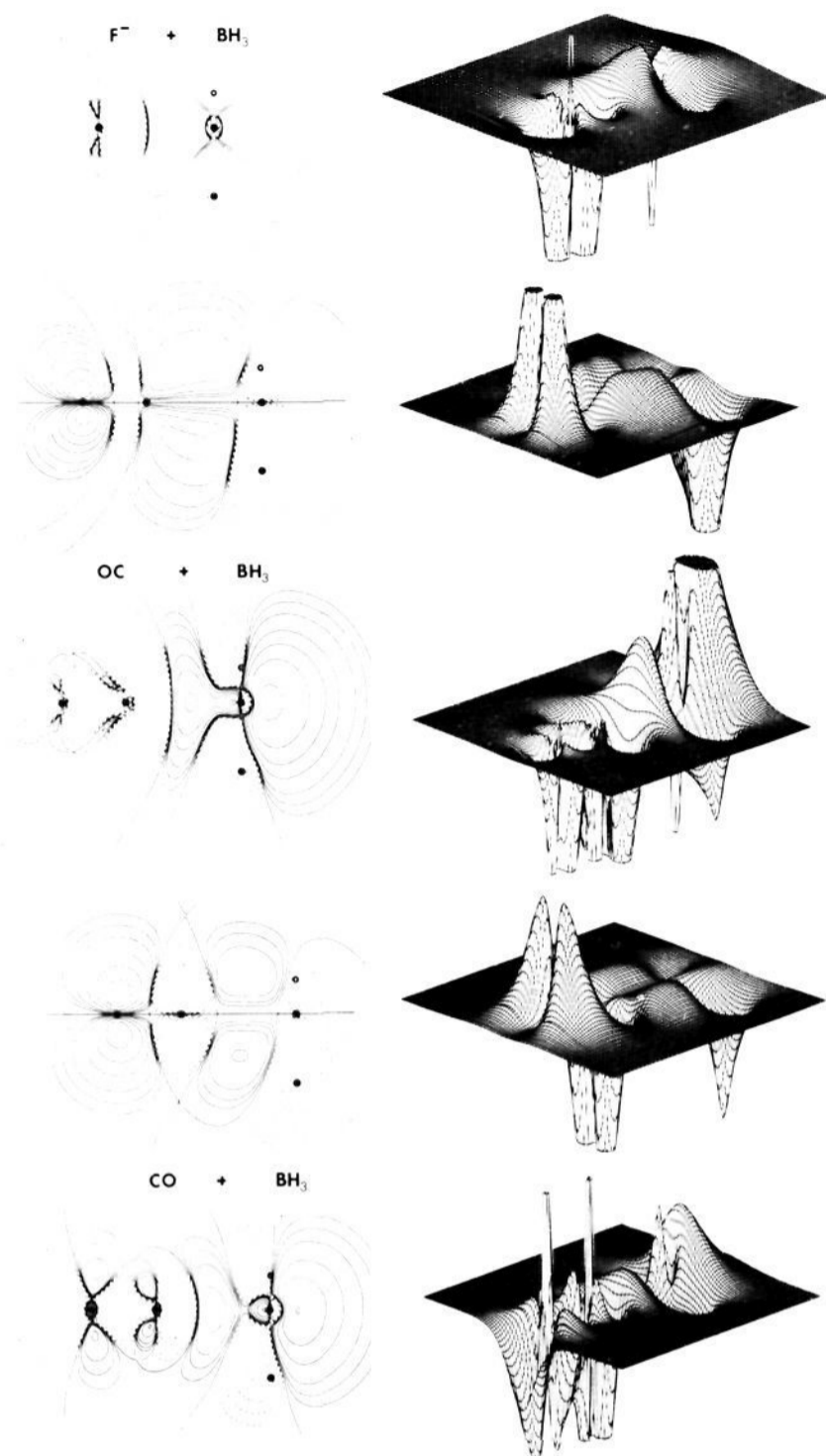


Figure 2. Contour plots and corresponding relief plots of transition densities for addition reactions. The contours begin with the values ± 0.0002 au and increase in the same series in powers of ten to the same final values as in Figure 1. There are pairs of diagrams for the approach of C and of O of CO to BH_3 . The upper diagram of each pair is for the lowest energy π -like transition density, the lower diagram showing the σ -like density of slightly higher excitation energy. All densities predict charge relaxations of A_1 symmetry. Positions of in-plane nuclei are indicated by solid circles and the projected positions of out-of-plane nuclei by open circles.

Applications

One anticipates that a Lewis acid–base adduct should be formed in a direct manner with an electron pair on the base filling the orbital vacancy of the acid. This expectation is fulfilled by the reaction of the base F^- with the acid BH_3 . The orbital model, when translated into the properties of the Laplacian, corresponds to aligning the valence shell of charge concentration of the fluoride ion with one of the holes in the corresponding shell of the boron atom. The relevant transition density of A_1 symmetry of the resulting adduct is as anticipated with HOMO being primarily a $2p$ orbital on F^- and LUMO mostly the vacant $2p$ orbital on boron.¹⁹ A plot of the transition density illustrates a simple transfer of charge from HOMO to LUMO (Figure 2). The form of the transition density is such as to draw the B and F nuclei together and exert forces on the protons drawing them out of their original planar arrangement and away from the approaching F^- ion.

(19) In the adduct, at a separation of 2.0 \AA , the $2p$ orbitals on F^- are slightly split (0.01 au) with $2p_x > 2p_y$. This gives a ρ_{ok} of e symmetry corresponding to a degenerate bending motion of the complex.

Table II. Atomic Properties of BH_3CO

Ω	$\Delta E(\Omega)^a$	$q(\Omega)$	$\Delta N(\Omega)^b$
B	-46.1	+2.09	+0.07
H	+27.6	-0.66	-0.05
C	-91.8	+1.27	+0.13
O	+46.1	-1.35	-0.05

^a $\Delta E(\Omega) = E(\Omega)_{\text{adduct}} - E(\Omega)_{\text{reactant}}$, kcal/mol. ^b $N(\Omega) = \int_{\Omega} \rho \, d\tau$, the average electron population of Ω ; $\Delta N(\Omega) = N(\Omega)_{\text{adduct}} - N(\Omega)_{\text{reactant}}$.

The reaction of CO with BH_3 is potentially more interesting than the above example since the carbon atom may act as a base or as an acid. In terms of the orbital model, if 5σ of CO is HOMO then it will act as a base with the vacant $2p$ on boron serving as LUMO. The vacant π^* orbitals of CO may, however, serve as LUMO with B–H bonding orbitals of like e symmetry in the complex acting as HOMO via a hyperconjugative electron release mechanism. This latter possibility was discussed by Chatt et al.²⁰ and by Mulliken and Person.²¹ It is also consistent with the Dewar–Chatt–Duncanson model of π back-donation frequently invoked in the description of bonding in organometallic complexes with the d_{π} orbitals of the metal serving as the electron donor.²²

In terms of the Laplacian distributions both mechanisms dictate that the bond axis of CO be aligned with the symmetry axis of BH_3 . The nonbonded charge concentration on either C or O will then be opposite a hole in the VSCC on B. For C approach the torus of charge depletion in the valence shell of C will be properly aligned to accept charge from the three concentrations of charge in the B–H bonds. For the approach of carbon a distance of 2.0 \AA from boron, the energy is found to decrease by 0.06 kcal/mol . HOMO is found to be the doubly degenerate set of B–H bonding orbitals and LUMO is π^* , largely localized on CO.²³ Both orbitals are of e symmetry and thus the lowest energy excited configuration is $e^3 e^*1$, yielding excited states and transition densities of E , A_1 , and A_2 symmetries. The transition density of relevant symmetry (A_1) is π -like and is shown in Figure 2. It exhibits a nearly uniform torus of charge accumulation about the carbon–boron axis as well as an accumulation on the oxygen, slightly polarized away from the carbon. Charge is removed primarily from the B–H bonds as anticipated for this mechanism of relaxation. Thus the most facile relaxation of the charge density is one in which charge is transferred from BH_3 to the π system of CO. Their donor–acceptor roles are reversed in the next transition density of A_1 symmetry. This density is obtained by a mixing-in of the excited state in which an electron is promoted from the a_1 orbital lying immediately beneath the e HOMO and correlating with the 5σ of CO to the a_1^* orbital lying immediately above the e^* LUMO and correlating with the vacant $2p$ orbital on boron. This excitation energy is only 0.1 au greater than the excitation of lowest energy. The resulting transition density (Figure 2) is σ -like and resembles in its general features the corresponding transition density for the BH_3F^- system. There is a charge transfer from CO to both the bonded and nonbonded regions of boron. In predicting the forces exerted on the nuclei by the charge relaxation one must consider both transition densities since they are of the same symmetry and have nearly equal excitation energies. The net forces exerted on the nuclei are such as to draw the C and B nuclei together and draw the protons back, away from the approaching CO molecule. The relaxations are largely cancelled in the region of the oxygen nucleus.

The ordering of the relevant occupied and lowest energy virtual orbitals and hence of their associated transition densities remain unchanged for the adduct in its equilibrium geometry. Thus the π mechanism of charge release from BH_3 to CO remains the most

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(23) For the adduct at 2.0 \AA , LUMO is e^* (π^*) and it lies 0.05 au below the next vacant orbital which is a^* ($2p$ on B). In the separated reactants this order is reversed with a^* on BH_3 lying 0.08 au below π^* on CO.

facile relaxation in the final adduct as well as for the approaching reactants. The excitation energy associated with the mixing-in of this transition density is significantly decreased in the formation of the adduct, from 0.62 to 0.58 au. The excitation energy for the σ mechanism of charge relaxation, on the other hand, is increased from 0.73 to 0.83 au. The atomic properties of the adduct (Table II), which is calculated to be 9.0 kcal/mol more stable than the reactants,²⁴ indicate that both transition densities contribute to the redistribution of charge associated with the formation of the adduct. The electron populations of both carbon and boron increase and they are energetically most stable in the adduct. The oxygen and the hydrogens lose electronic charge and they are energetically less stable in the adduct. The B–H bond length increases (by 0.014 Å) as anticipated on the basis of both transition densities. The weakening of the B–H bond is also reflected in the decrease in the value of ρ at the bond saddle point, from 0.184 au in BH₃ to 0.168 au in the adduct.

In terms of the simplified orbital model the extent of σ donation to BH₃ is given by integration of the density of the top a_1 orbital (originally 5σ on CO) over the BH₃ fragment. Similarly, the extent of π back-donation to CO is given by the integration of the top e orbital (originally the B–H bonding set in BH₃) over the CO fragment. The fragments are defined by the C–B interatomic surface of zero flux in $\nabla\rho$.⁸ These integrations show a σ transfer of 1.4 e to BH₃ and a π transfer of 0.33 e to CO, contributions that are quite different from the changes in the total atomic populations given in Table II. The differences are primarily accounted for by the very large transfer of charge from the bonding orbital of a symmetry of BH₃ to the 3σ and 4σ orbitals on CO. Bauschlicher and Bagus,²⁵ using the newly developed constrained space orbital variation method for assessing the relative energetic importance of various charge redistributions, have concluded that the metal to CO π donation in iron pentacarbonyl and nickel tetracarbonyl is more important than is the CO to metal σ donation. They find the σ donation to be largest for the iron complex, where there is a double vacancy in the d shell of iron.

Also included in Figure 2 are displays of the corresponding transition densities for the approach of the oxygen of CO toward the boron of BH₃. The same π and σ transition densities are found for this case as for the approach of carbon and the excitation energies are essentially unchanged for a separation of 2.0 Å. In this case, however, the energy is found to increase by 7.3 kcal/mol even at this large separation, a reflection of the fact that no stable BH₃OC adduct is formed. While the transition densities are of the same overall symmetry in the two cases there are important quantitative differences between them. In the lowest energy π transition density, charge is removed principally from the oxygen atom and accumulated primarily on the carbon atom. The torus of charge accumulation about the B–O axis is much less than the corresponding accumulation about the B–C axis, and the extent of charge removal from the B–H bonds is also less in the O than in the C approach. In the C approach the primary charge relaxation is a transfer of charge from the BH₃ fragment to a torus about the length of the B–C bond. In the approach of O, the primary charge relaxation is a transfer of charge from oxygen to carbon. Similarly in the σ relaxation, the approach of O rather than C results in a much reduced transfer of charge to the orbital vacancy on boron.

The charge relaxation associated with the addition of a nucleophile to an unsaturated system is similar in its gross characteristics to that for the Lewis acid–base addition. The example considered is addition of hydroxide ion to formaldehyde. The Laplacian distribution obtained for the reactants separated by 2.0 Å is illustrated in Figure 3. At this separation the properties of

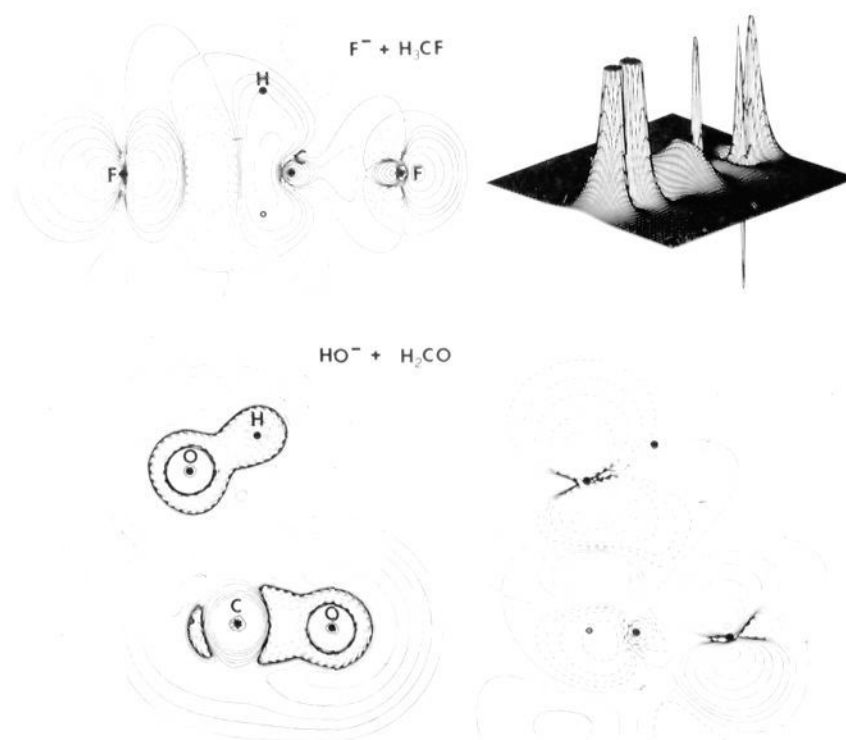


Figure 3. Contour and corresponding relief plots of the lowest energy transition density for the nucleophilic displacement reaction of F[−] with CH₃F. Note the region of charge removal between the approaching F[−] and the carbon atom. The lower diagrams are for the addition of OH[−] to formaldehyde. The diagram on the left is a contour plot of $\nabla^2\rho$ for the reactants at a separation of 2.0 Å. The OCO approach angle of 111° is determined by the angle made by the minimum in the surface of charge concentration on carbon with the C–O axis. Note that even at this relatively large separation the torus of charge on oxygen of OH[−] is polarized toward the region of charge depletion on carbon and the VSCC of the C atom is polarized away from the approaching O atom. The diagram on the right is a contour plot of the lowest energy transition density for this approach.

the atomic graphs are unchanged in all important respects from those of the separated reactants. The OH[−] ion has a nonbonded charge concentration in the form of a torus about the internuclear axis on the oxygen atom. The atomic graph of a carbonyl carbon consists of three bonded maxima in the plane of the nuclei and a region of charge removal—a local minimum in the VSCC—above and below this plane.⁵ Its presence mimics the localized model of the C–O π^* orbital. The initial angle of approach of a nucleophile to the carbonyl carbon is determined by the angle made by one of the local minima in the VSCC of carbon with the C–O axis. As previously shown,⁵ this angle in formaldehyde and a number of other carbonyl compounds is found to be $110 \pm 2^\circ$, in agreement with the results of crystallographic studies on compounds with carbonyl groups in the vicinity of a base in the crystal structure.²⁶ This is the approach shown in Figure 3. The HOMO of this combined system is the component of the 1π orbital of OH[−] in the OCO plane and largely localized on oxygen and LUMO is the C–O π^* orbital of the carbonyl group.²⁷ The HOMO–LUMO transition density for the complex is shown in Figure 3. There is a transfer of charge from the nucleophilic oxygen atom to the carbonyl oxygen and to a region between the carbon and the approaching oxygen. The transition density exerts a force drawing the keto oxygen out of what was a symmetry plane of formaldehyde and away from the approaching hydroxide ion. The hydroxide oxygen is in turn drawn toward carbon. The primary transfer of charge from one oxygen to the other is as anticipated for the formation of the product HOCH₂O[−].

Stone and Erskine²⁸ have used an SCF perturbation theory²⁹ to discuss nucleophilic attack on carbonyl groups. They also predict an approach angle in line with the experimental results²⁶ for the attack of OH[−] and find that the dominant term in de-

(24) The total energy of the adduct is calculated to be -139.14525 au and the geometrical parameters are $R(\text{O–C}) = 1.108$ Å, $R(\text{C–B}) = 1.626$ Å, $R(\text{B–H}) = 1.202$ Å, and $\angle\text{CBH} = 102.9^\circ$. The atomic properties of this adduct have been previously determined with use of a slightly larger basis set. (Runtz, G. R.; Bader, R. F. W. *Mol. Phys.* **1975**, *30*, 129.) The stabilization energy was found to be -6.3 kcal/mol. The atomic properties and their changes are very similar to the values found here.

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(27) In the isolated formaldehyde molecule LUMO is σ^* of C–O lying 0.002 au below π^* . However, in the complex with the reactants aligned according to the properties of the Laplacian distribution 2.0 Å apart, this order is reversed with π^* lying 0.024 au below σ^* .

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termining this angle is the exchange repulsion.

The reaction of two closed-shell systems is exemplified by the nucleophilic attack of methyl fluoride by fluoride ion. As noted above, the VSCC of carbon in methyl fluoride exhibits a region of charge depletion in the face opposite the fluorine and the Laplacian thus dictates that the F^- ion approach this face along the threefold symmetry axis. One anticipates that HOMO will be the 2p orbital on F^- directed along the symmetry axis and LUMO the antibonding C-F orbital on CH_3F . This is found to be the case when the reactants are 2.1 Å apart. Both orbitals are of a_1 symmetry and hence the lowest energy excited state and the associated transition density (Figure 3) are also of A_1 symmetry. The transition density does not show a simple transfer of charge from one reactant to the other as found for the addition reactions discussed above. Instead charge is transferred to the approaching F as well as to carbon and the departing fluorine. In addition, a region of charge removal is formed between the carbon and the approaching fluorine. Such a rearrangement of charge is similar to that found for the approach of two helium atoms³⁰ and is as anticipated for the approach of two closed-shell systems in general.

The charge relaxation in the neighborhood of the fluorine nucleus initially bonded to carbon is such as to draw this nucleus away from carbon. The relaxation of charge in the vicinity of the carbon and the approaching fluorine is such as to draw the nuclei of these two atoms together. Thus the lowest energy transition density exerts forces on the nuclei as required for a nucleophilic displacement. This reaction has been previously shown^{18b} to possess a symmetrical transition state 7 kcal/mol less stable than the reactants, a result which is consistent with gas-phase experimental measurements.³¹ The transition density pictured in Figure 3 changes to A_2'' symmetry in the transition state as originally predicted.² It was there pointed out that such a transition density could exert forces on the protons as required to achieve inversion about the carbon nucleus in the reaction. One notes in Figure 3 that even at 2 Å the charge relaxation in the vicinity of the protons is such as to lead to both inversion and to an initial shortening of the C-H bonds. The previous theoretical calculations show that the C-H bonds do indeed shorten by ≈ 0.04

Å in the formation of the transition state.^{18b}

The examples given in this paper illustrate that the relative approach of reactants as determined by aligning regions of charge concentration with regions of charge depletion in their Laplacian distributions leads to the formation of an initial complex in which the most facile relaxation of the charge density is one which leads to further motion along the reaction coordinate initiated by this approach. In these examples the local concentrations of charge present in the Laplacian of the base coincide with the properties associated with the HOMO orbital. Similarly, the local regions of charge depletion in the Laplacian of the acid or electrophile coincide with the properties associated with the LUMO orbital. Perhaps the most important information contained in the state function to be sacrificed in its reduction to the charge density is the information regarding its phase. In the orbital approximation, the relative phases of the orbitals determine their symmetry properties and their effective overlap. The Laplacian of a charge distribution, by recovering predictions based upon orbital phase information, provides not only a bridge between the density and orbital approaches but a step toward the development of a theory of reactivity based solely on the properties of the charge density.

Parr and co-workers^{32,33} have already shown that the principal ideas of frontier orbital theory can be related, in a formal manner, to density functional theory. They relate reactivity to a function, called the Fukui function, which determines the local contributions to the change in the electronic chemical potential. They argue that attack occurs where the Fukui function is largest and that this function can be approximated by HOMO, by LUMO, and by their average respectively in electrophilic, nucleophilic, and radical attack. Clearly, the Laplacian of the electronic charge density and the Fukui function of density functional theory contain similar information. It is possible that a pursuit of the connection between these two functions will facilitate the development of a density-based theory of chemical reactivity.

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The Ring Opening of Gas-Phase Cyclopropane Radical Cations

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Abstract: The possibilities of isomerization of gas-phase cyclopropane radical cations to propene or of ring opening to the trimethylene radical cation are addressed. Structural information was obtained by collisionally ionizing various C_3H_6 radical cations formed over a range of ionizing energies to give $C_3H_6^{2+}$ which fragments to give distinctive spectra of product ions. Confirmation of the conclusions drawn from these studies was found by measuring the reactivity of the C_3H_6 radical cations in ion-molecule reactions studied with use of Fourier transform mass spectrometry. The neutral reagents which react selectively with C_3H_6 radical cations are ammonia, propene- d_6 , and carbon disulfide. Collisionally stabilized adducts were delineated by obtaining their collisionally activated decomposition spectra with a tandem mass spectrometer. On the basis of the ammonia reaction studied here and by others, a structural change of activated cyclopropane radical cations can be clearly established. Structural isomerization to the propene radical cation can be ruled out, however, on the basis of several pieces of evidence: reactivity with propene- d_6 and carbon disulfide, the structure of the cyclopropane- CS_2 adduct radical cation, and the collisional ionization spectra. Ring opening to the trimethylene radical cation is consistent with the results of these studies, and this process is entirely analogous to the structural change of cyclopropane radical cations in condensed phases.

There is considerable evidence that small (3-5 carbon) cycloalkane radical cations isomerize in the gas phase to yield acyclic

structures prior to dissociating.¹ The ring opening of the simplest cycloalkane radical cation, cyclopropane, has been extensively