

Electrostatic Force Theory for a Molecule and Interacting Molecules. I. Concept and Illustrative Applications

Hiroshi Nakatsuji

*Contribution from the Department of Hydrocarbon Chemistry,
Faculty of Engineering, Kyoto University, Kyoto, Japan.*

Received May 8, 1972

Abstract: *The electrostatic force (ESF) theory in which chemical phenomena are studied through the force concept (not through energetics) on the basis of the electrostatic theorem of Hellmann and Feynman is presented. Taking advantage of the physical simplicity and visuality of this theorem, we derived three pictorial concepts called atomic dipole (AD) force, exchange (EC) force, and gross charge (GC) force. The AD force represents the attraction between the concerned nucleus A and the weighted center of the polarized electron distribution belonging to the AO's of atom A. The EC force represents the attraction between nucleus A and the electron distribution piled up in the region between nucleus A and its neighboring atom B through electron exchange. The GC force represents the electrostatic interaction between nucleus A and the gross charge on atom B. The relative importance of these forces in usual molecules is AD force > EC force (triple > double > single bond) >> GC force. The AD force is important for lone-pair electrons, and the EC force depends on bond multiplicity. In order to extend the applicability of the theory to a wide variety of molecules, the influences induced on these forces by the changes of atom A and substituent B are also studied. The change in these forces following the change in electronic structure (e.g., by electron excitation, ionization, electron attachment, etc.) is also discussed. From these, a simple qualitative measure about the shapes of usual molecules is obtained. For some illustrative examples it is shown how the ESF theory works actually in predicting shapes of molecules in both the ground and excited states and in understanding natures of chemical reactions and structures of products. The present theoretical concept is shown to be wide enough to be able to apply to both of these fundamental problems in chemistry.*

Theoretical chemists have searched for conceptual models which enable us to grasp the essential features of the apparently complicated chemical phenomena. For the problems which include the movements of nuclei in a molecule and interacting molecules, such as molecular structure, vibrational force constant, chemical reaction, etc., almost all of the models have been built up on the *energetic* considerations (e.g., by drawing potential energy surface, etc.). However, these phenomena can also be studied by examining the *forces* acting on the constituent nuclei. Among several methods giving these forces,^{1,2} the electrostatic theorem due to Hellmann and Feynman¹ has been most frequently used. Berlin³ gave a very pictorial concept of intramolecular binding and antibinding regions. Bader and Jones⁴ noted the advantage of the electrostatic interpretation of chemical binding. They discussed also the relations between electron density distributions and molecular shapes for some simple hydrides.^{4b} Moreover, Bader and his coworkers and Ransil, *et al.*, calculated these forces from considerably accurate wave functions of diatomic molecules in order to obtain deeper understanding of the nature of chemical binding.⁵ The origin of the internal rotation barrier about

the single bond was also studied from this standpoint.⁶ On the other hand, Parr, *et al.*, derived the integral Hellmann-Feynman theorem⁷ and applied it extensively.⁸ The physical meaning of this theorem is very similar to that of the usual differential form.

In this series of papers, we are attempting to develop these force concepts on the basis of the electrostatic theorem of Hellmann and Feynman. The main purpose is to interconnect these forces with the electronic structures of molecules and with the nature of interactions of the interacting systems, and at the same time, to give predictive pictures for the phenomena such as molecular structure, vibrational force constant, chemical reaction, etc. The theoretical concept is named *electrostatic force (ESF) theory*.

In the present first report, the concept of the ESF theory will be explained in detail and some pictorial concepts will be derived. In order to extend the applicability of the theory to a wide variety of molecules, we will examine the influences induced by the changes of the concerned atoms and their neighboring substituents. The change in force following the change in electronic structure will also be discussed. For some illustrative examples, we will show how the ESF theory actually works in predicting shapes of molecules in both the ground and excited states and in understanding the nature of chemical reactions and structures of the products. From these, the possibility is shown that the present theoretical concept is wide enough to be

(1) H. Hellmann, "Einführung in die Quantenchemie," Deuticke, Leipzig, 1937; R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

(2) A. C. Hurley in "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., p 161; *Proc. Roy. Soc., Ser. A*, **226**, 170, 179 (1954).

(3) T. Berlin, *J. Chem. Phys.*, **19**, 208 (1951).

(4) (a) R. F. W. Bader and G. A. Jones, *Can. J. Chem.*, **39**, 1253 (1961); (b) *ibid.*, **41**, 586 (1963); (c) *J. Chem. Phys.*, **38**, 2791 (1963).

(5) (a) R. F. W. Bader and W. H. Henneker, *J. Amer. Chem. Soc.*, **88**, 280 (1966); (b) R. F. W. Bader, W. H. Henneker, and P. E. Cade, *J. Chem. Phys.*, **46**, 3341 (1967); (c) R. F. W. Bader, I. Keaveny, and P. E. Cade, *ibid.*, **47**, 3381 (1967); (d) R. F. W. Bader and A. D. Bandrauk, *ibid.*, **49**, 1653, 1666 (1968); (e) P. E. Cade, R. F. W. Bader, W. H. Henneker, and I. Keaveny, *ibid.*, **50**, 5313 (1969); (f) P. E. Cade, R. F. W. Bader, and J. Pelletier, *ibid.*, **54**, 3517 (1971); (g) B. J. Ransil and J. J. Sinai, *ibid.*, **46**, 4050 (1967).

(6) J. Goodisman, *ibid.*, **45**, 4689 (1966); O. J. Sovers, C. W. Kern, P. M. Pitzer, and M. Karplus, *ibid.*, **49**, 2592 (1968).

(7) R. G. Parr, *ibid.*, **40**, 3726 (1964); H. J. Kim and R. G. Parr, *ibid.*, **41**, 2892 (1964); S. T. Epstein, A. C. Hurley, R. E. Wyatt, and R. G. Parr, *ibid.*, **47**, 1275 (1967).

(8) R. E. Wyatt and R. G. Parr, *ibid.*, **41**, 3262 (1964); **43**, S217 (1965); **44**, 1529 (1966); E. F. Hayes and R. G. Parr, *ibid.*, **44**, 4650 (1966); A. Mazziotti and J. P. Lowe, *ibid.*, **50**, 1153 (1969); M. T. Marron and R. G. Parr, *ibid.*, **52**, 2109, 3600 (1970).

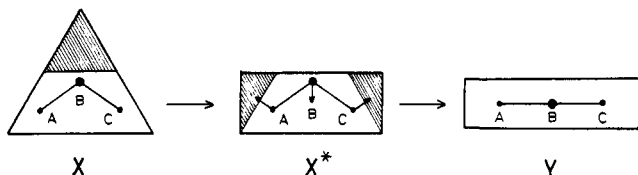


Figure 1. Schematic illustrations of the forces and electron clouds.

able to apply to both of these fundamental problems in chemistry. More detailed applications of this theory and comparison with other molecular structure theories such as the Walsh rule,⁹ the valence-shell electron-pair repulsion (VSEPR) theory,¹⁰ and the second-order¹¹ (or pseudo-¹²) Jahn-Teller (SOJT) theory¹³ will be given in succeeding papers of this series.¹⁴

Background of the ESF Theory. As in classical mechanics, the force concept is sometimes more convenient to understand the motions of nuclei than the traditional potential surface treatments. From the electrostatic theorem,^{1,2} the force acting on nucleus A of a system is given in atomic units by

$$F_A = -\partial W/\partial R_A = -(\partial/\partial R_A)\langle\Psi|\mathcal{H}|\Psi\rangle = -\langle\Psi|\partial\mathcal{H}/\partial R_A|\Psi\rangle = Z_A \left\{ \int \rho(\mathbf{r}_1) \mathbf{r}_{A1}/r_{A1}^3 d\mathbf{r}_1 - \sum_{B(\neq A)} Z_B \mathbf{R}_{AB}/R_{AB}^3 \right\} \quad (1)$$

where W is the total energy, \mathcal{H} the Hamiltonian

$$\mathcal{H} = \sum_{\nu} \left(-\frac{1}{2} \Delta_{\nu} - \sum_A Z_A/r_{A\nu} \right) + \sum_{\mu>\nu} 1/r_{\mu\nu} + \sum_{A>B} Z_A Z_B/R_{AB} \quad (2)$$

Ψ the electronic wave function of the system for which the Hellmann-Feynman theorem holds ("stable" wave functions¹⁵ such as exact or Hartree-Fock wave functions),² and Z_A the nuclear charge; \mathbf{r}_{A1} and \mathbf{R}_{AB} are the vectors pointing from nucleus A to electron 1 and nucleus B, respectively. $\rho(\mathbf{r}_1)$ is the density of electron cloud

$$\rho(\mathbf{r}_1) = N \int \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) ds_1 d\mathbf{x}_2, \dots, d\mathbf{x}_N \quad (3)$$

where \mathbf{s} and \mathbf{x} are the spin and spin-space variables, respectively N is the number of electrons of the system. When the third equality of eq 1 does not hold by approximations,² the correctness of the force calculated by the last expression depends on the correctness of the density of electron cloud $\rho(\mathbf{r}_1)$. Note that electron cloud

(9) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2301, 2306, 2321 (1953).

(10) (a) N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **176**, 153 (1940); (b) C. E. Mellish and J. W. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954); (c) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); (d) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); (e) H. A. Bent, *ibid.*, **40**, 446, 523 (1963); **45**, 768 (1968).

(11) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 1252, 4947 (1969); *J. Chem. Phys.*, **52**, 2167 (1970); **53**, 2986 (1970); *Chem. Phys. Lett.*, **10**, 31 (1971).

(12) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968).

(13) (a) R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960); *Can. J. Chem.*, **40**, 1164 (1962); (b) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969).

(14) Paper II: H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 354 (1973); paper III: H. Nakatsuji, *ibid.*, to be submitted for publication.

(15) G. G. Hall, *Phil. Mag.*, **6**, 249 (1961).

is conceptually independent of the approximation method of electronic structure (*e.g.*, molecular orbital (MO) method, valence bond method, configuration interaction method, etc.). This is not like the "orbital energies" in the MO theory which are extensively used in the Walsh rule,⁹ SOJT theory,¹¹⁻¹³ etc.

Equation 1 is a rigorous, quantum mechanical consequence and still has unique physical simplicity and visuality; it describes classical electrostatic coulomb forces between nucleus A and a portion of the electron cloud, $\rho(\mathbf{r}_1)d\mathbf{r}_1$, and the other nuclei. For example, in Figure 1, when the shaded portion of the electron cloud of a stable molecule X is transferred (*e.g.*, by electron excitation) to the shaded portion of molecule X* (*e.g.*, as in the Franck-Condon state), the forces shown by arrows should be exerted on nuclei A, B, and C and induce the movements of these nuclei accompanying a change in electron distribution, until these forces die away in the structure Y (in this case, the structures of the ground and excited states are different). Furthermore, in a reacting system, the interaction between reactants will function to pile up an electron density between their reaction sites, which induce the movements of the constituent nuclei along reaction coordinate.

Concepts of the ESF Theory. In order to obtain quantitative insight on the relation between forces and the electron cloud, it is convenient to develop the density of the electron cloud, $\rho(\mathbf{r}_1)$, by means of an atomic orbital set $\{\chi_r\}$ as

$$\rho(\mathbf{r}_1) = \sum_{r,s} P_{rs} \chi_r(\mathbf{r}_1) \chi_s(\mathbf{r}_1) \quad (4)$$

where P_{rs} is the (generalized) density matrix element between AO's χ_r and χ_s . Then, eq 1 is rewritten as

$$F_A = Z_A \left\{ \sum_{r,s} P_{rs} \langle \chi_r | \mathbf{r}_A/r_A^3 | \chi_s \rangle - \sum_{B(\neq A)} Z_B \mathbf{R}_{AB}/R_{AB}^3 \right\} \quad (5)$$

Although the following considerations are developed mainly on the basis of eq 5, some formulations based on the single-determinant MO theory are useful. When an MO set is given by $\{\varphi_i\}$ and their occupation numbers by $\{m_i\}$ ($m_i = 0, 1, \text{ or } 2$), the density of electron cloud is written as

$$\rho(\mathbf{r}_1) = \sum_i m_i \varphi_i^*(\mathbf{r}_1) \varphi_i(\mathbf{r}_1) \quad (6)$$

By defining the MO contribution to force as

$$f_{Ai} = \langle \varphi_i | \mathbf{r}_A/r_A^3 | \varphi_i \rangle \quad (7)$$

eq 1 is rewritten as

$$F_A = Z_A \left\{ \sum_i m_i f_{Ai} - \sum_{B(\neq A)} Z_B \mathbf{R}_{AB}/R_{AB}^3 \right\} \quad (8)$$

Note that the electronic contribution to force (the first term) is the simple sum of orbital contributions. This is very simple compared with the potential energy treatment in which electronic energy is not expressed by the simple sum of orbital energies. This simplicity offers a possibility to interconnect the present theory with the Walsh diagram.¹⁶ In the LCAO (linear combination of atomic orbitals) MO approximation, an MO is expressed by $\varphi_i = \sum_r C_{ir} \chi_r$ and then the density matrix P_{rs} defined in eq 4 is written simply as

$$P_{rs} = \sum_i m_i C_{ir} C_{is} \quad (9)$$

(16) C. A. Coulson and B. M. Deb, *Int. J. Quantum Chem.*, **5**, 411 (1971).

Now, let us return to eq 5. In order to derive conceptual pictures on the relation between forces and the electron cloud, some modifications are necessary for the integrals appearing in eq 5. They are grouped to one-, two-, and three-center integrals. Hereafter, we designate the center of AO by a suffix, like χ_{rA} . For the one-center integrals, the coulombic integrals of the type $\langle \chi_{rA} | \mathbf{r}_A / r_A^3 | \chi_{rA} \rangle$ are zero from symmetry. The most important nonzero term is of the type $\langle ns_A - |\alpha_A / r_A^3| np_{\alpha A} \rangle$ ($\alpha = x, y, \text{ or } z$). For the two-center coulombic integrals, we introduce the approximation¹⁷

$$\langle \chi_{sB} | \mathbf{r}_A / r_A^3 | \chi_{sB} \rangle \simeq \mathbf{R}_{AB} / R_{AB}^3 \quad (10)$$

and for the two-center exchange integrals, we introduce the net-exchange force integral¹⁸ defined by

$$\langle \chi_{rA} | (\mathbf{r}_A / r_A^3)_0 | \chi_{sB} \rangle \equiv \langle \chi_{rA} | \mathbf{r}_A / r_A^3 | \chi_{sB} \rangle - \frac{1}{2} S_{rAsB} \langle s_B | \mathbf{r}_A / r_A^3 | s_B \rangle \quad (11)$$

where S_{rAsB} is the overlap integral and s_B is the s-type AO of atom B belonging to the same shell as χ_{sB} .¹⁸ Other two- and three-center integrals are calculated by the Mulliken approximation

$$\langle \chi_{rB} | \mathbf{r}_A / r_A^3 | \chi_{sC} \rangle \approx \frac{1}{2} S_{rBsC} \{ \langle \chi_{rB} | \mathbf{r}_A / r_A^3 | \chi_{rB} \rangle + \langle \chi_{sC} | \mathbf{r}_A / r_A^3 | \chi_{sC} \rangle \} \quad (12)$$

Then, eq 5 becomes

$$\mathbf{F}_A = Z_A \left\{ \sum_{r(\neq s)}^A \sum_s^A P_{rAsA} \langle \chi_{rA} | \mathbf{r}_A / r_A^3 | \chi_{sA} \rangle + 2 \sum_{B(\neq A)}^A \sum_r^A \sum_s^B P_{rAsB} \langle \chi_{rA} | (\mathbf{r}_A / r_A^3)_0 | \chi_{sB} \rangle - \sum_{B(\neq A)} (Z_B - N_B) \mathbf{R}_{AB} / R_{AB}^3 \right\} \quad (13)$$

where \sum_r^A means the summation over the AO's belonging to atom A, and $N_B = \sum_r^B \sum_s^{all} P_{rs} S_{rs}$ is the gross atomic population¹⁹ and $\delta_B \equiv Z_B - N_B$, the gross charge on atom B.¹⁹

Equation 13 has very simple physical meanings. The first term, composed of only one-center integrals, represents the attraction between nucleus A and the weighted

(17) Equation 10 corresponds to the *point charge approximation* which approximates the interaction between nucleus A and the electron belonging to the AO centered on nucleus B by the interaction between nucleus A and the unit charge on nucleus B. That is, eq 10 approximates the shielding of nuclear charge Z_B by the electrons belonging to the AO's of atom B to be complete. Although this approximation always overestimates the true value, the better it is, the larger the AB distance. For important bond-length regions, the error due to eq 10 is less than 10% for the atoms except hydrogen. But for C-H pair, the error is as large as 30%. This is due to the relatively small C-H bond distance and small orbital exponent of hydrogen 1s AO. From these reasons, we do not use this approximation in the actual calculations of forces. We will calculate all types of integrals exactly.

(18) The net-exchange force integral defined by eq 11 has the following physical meaning. As the electrons belonging to atom B shield the nuclear charge Z_B (eq 10), the electrons in the overlap region between χ_{rA} and χ_{sB} also shield Z_B . This effect may be represented by the Mulliken approximation of the first term, namely $\frac{1}{2} S_{rAsB} \langle \chi_{sB} | \mathbf{r}_A / r_A^3 | \chi_{sB} \rangle$. However, since this term destroys the invariance of the integral value for the rotation about coordinate axis, it is substituted for $\frac{1}{2} S_{rAsB} \langle s_B | \mathbf{r}_A / r_A^3 | s_B \rangle$, where s_B is the s-type AO of atom B belonging to the same shell as χ_{sB} . Thus, the net-exchange force integral may be considered to represent the attractive force induced only by the electron exchange effect between χ_{rA} and χ_{sB} . The above physical meaning will become clear by noting further that the second term of eq 11 is incorporated later in the gross charge force. In other words, the introduction of the net-exchange force integral becomes necessary for natural introduction of the gross charge force.

(19) R. S. Mulliken. *J. Chem. Phys.*, 23, 1833 (1955).

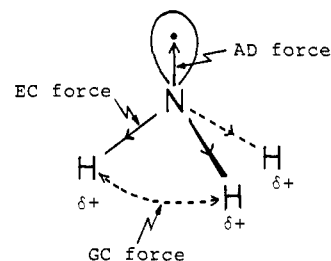
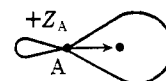
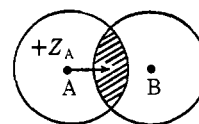


Figure 2. Examples of the forces acting in ammonia.

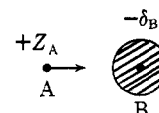
(by \mathbf{r}_A / r_A^3) center of the polarized electron distribution belonging to the AO's of atom A. Typical example of the polarized electron distribution is the hybrid orbital distribution illustrated by



Since this kind of polarized electron distribution plays an important role in the calculation of the dipole moment as atomic dipole, we call this force the *atomic dipole (AD) force* from similarity. The second term represents the attraction between nucleus A and the electron distribution piled up in the region between nuclei A and B through electron exchange,¹⁸ and may be illustrated as



We call this force the *exchange (EC) force*.²⁰ The last term represents the electrostatic interaction between nucleus A and the gross charge δ_B on atom B as illustrated by



which may be called the *gross charge (GC) force*.²¹

Now we see how these forces operate in real molecules. In Figure 2, an example is given for NH_3 . Since lone-pair electron distribution is usually polarized in the above sense, *the AD force is especially important for lone-pair electrons*. In NH_3 , *the AD force operates to make the molecule nonplanar*. Note that *the AD force is small for hydrogen atom*, since the mixing of the 1s and 2p AO's is small for this atom. On the other hand, the NH bond electrons attract the nitrogen nucleus. *These EC forces operate as a restoring force to planar structure*,

(20) The exchange force defined in the present ESF theory is different from that used in the field of intermolecular forces. The latter term is usually used to denote the short-range repulsive energy (rather than force) between closed shell atoms (see for example E. A. Mason and L. Monchick, *Advan. Chem. Phys.*, 12, 329 (1967)). However, the present EC force can also include this kind of short-range repulsive force. The details will be given in the succeeding paper¹⁴ as the *overlap effect* on the EC force.

(21) Although the AD and EC forces can be exact concepts, the GC force is only approximate due to eq 10 and 12. However, if we extend to define it as the rest of the total force subtracted by the AD and EC forces, all three forces can be exactly defined. This may be called *extended gross charge (EGC) force*. Its physical behavior should be similar to that of the GC force but the value be slightly different in that the nuclear-nuclear repulsion term is more stressed in the EGC force than in the GC force.

opposing the function of the AD force. Moreover, the EC force plays a very important role in determining the shapes of molecules which have scarcely any atomic dipole (e.g., CH_3^+ , CH_4 , C_2H_6 , etc.). In these molecules, the structures are such that all the EC forces balance. The structure of maximum symmetry is the most frequent example. Furthermore, for the chemical reaction, the EC force should be the most important driving force of reaction. This may be understood from the definition of the EC force. The GC force in NH_3 between the proton and other hydrogens also operates as a restoring force to the planar structure, since δ_{H} is positive in NH_3 . However, this force is small as shown later.

Some notices are necessary about the EC force on hydrogen. Namely, due to the crudeness of eq 10 for the hydrogen atom ($A = \text{H}$),¹⁷ eq 13 cannot be applied to the hydrogen atom in the usual bond length region. In other words, since the error included in the third term of eq 13 (GC force) amounts to cancellation of the second term (EC force) if $A = \text{H}$,²² it is convenient to assume that approximately no EC force is exerted on the hydrogen atom in the usual bond length region. This is obvious if we apply eq 13 to the hydrogen molecule.²³ However, when the A-B distance becomes larger, eq 10 and then eq 13 become more valid and can be applied even to the hydrogen atom. For example, the EC force should be the most important force in the middle stage of hydrogen molecule formation.²³

(i) **Relative Importance.** In Table I, the values and the relative importances of the AD, EC, and GC forces are summarized for AA and AH pairs ($A = \text{boron}$,

Table I. The AD, EC, and GC Forces (au) Acting on Nucleus A and Their Relative Importances^{a,b}

A =	Boron	Carbon	Nitrogen
(i) AD Force			
sp^3	0.56 (100)	0.88 (100)	1.27 (100)
sp^2	0.61 (100)	0.96 (100)	1.38 (100)
sp	0.65 (100)	1.02 (100)	1.46 (100)
(ii) EC Force			
A-A ^c			
A-A (sp^3)	0.32 (57)	0.45 (51)	0.51 (40)
A=A (sp^2)	0.34 (56)	0.62 (65)	0.74 (54)
A≡A (sp)	0.41 (63)	0.78 (77)	0.98 (67)
A-H ^c			
$\text{sp}^3\text{-H}$	0.29 (51)	0.40 (46)	0.51 (40)
$\text{sp}^2\text{-H}$		0.40 (42)	0.50 (36)
sp-H		0.38 (37)	0.47 (32)
(iii) GC Force			
Complete ionic bond	$\text{C}^{+1.0}\text{-C}^{-1.0}$, 1.5 Å		0.12 (12)
Polar bond	$\text{C}^{+0.2}\text{-C}^{-0.2}$, 1.5 Å		0.03 (3)
Nonbonded interaction	$\text{C}^{+0.2} \dots \text{C}^{-0.2}$, 2.5 Å		0.01 (1)

^a Bond lengths are chosen or assumed from representative molecules (e.g., ethane, ethylene, and acetylene for C-C and C-H bond lengths). ^b Values in parentheses are the relative importances defined as the ratios to the corresponding AD forces in percentage.

(22) If we use the extended GC force²¹ in spite of the GC force, it can be shown approximately that the EC force cancels the EGC force for the hydrogen atoms in equilibrium bond length.

(23) Due to Hirschfelder and Eliason (*J. Chem. Phys.*, **47**, 1164 (1967)), the van der Waals force between two hydrogen atoms originates from the AD force. But, in the middle stage of the reaction, the EC force should be a main driving force of reaction. However, at the equilibrium bond distance, the force acting on the proton must die away. But eq 13 still gives the EC force acting to bind two protons further. This is obviously incorrect and due to the inapplicability of eq 10 for hydrogen atoms in usual bond-length region;¹⁷ see also ref 22.

carbon, and nitrogen). In these, typical hybrid orbitals (sp^3 , sp^2 , and sp) are assumed and the bond orders between them are supposed to be $P_{\tau_A\tau_A} = 2.0$ and $P_{\tau_A\tau_B} = 1.0$. The EC forces given for double bond ($\text{A}=\text{A}$) and triple bond ($\text{A}\equiv\text{A}$) are the sums of the σ and π contributions. From Table I, we see the following. (1) Although the AD and EC forces increase from boron to nitrogen, their relative importances (shown in parentheses) are roughly constant within the atoms belonging to the same period. The AD force is always most important and the next is the EC force. The GC force is small except for the complete ionic pair. (2) The EC force increases with increasing bond multiplicity. For a single bond, the EC force on A along the A-H bond is approximately equal to that along the A-A bond. Summing up these points, we obtain the following sequence of relative importance

$$\text{AD force} > \text{EC force (triple} > \text{double} > \text{single)} \gg \text{GC force} \quad (14)$$

$$100 \qquad \qquad 70 \qquad 60 \qquad 50$$

$$5-1$$

where the values show the rough relative ratios (in per cent) of these forces to the AD force obtained for the typical hybrid orbitals assumed in Table I.

(ii) **Influence on the AD Force.** The polarized one-center electron distribution causing the AD force arises through the hybridization of one-center AO's. Of the two types of hybridization schemes, namely s-p and p-d hybridizations, we consider here only the s-p hybridization. From the simple numerical check on SH_2 molecule with the CNDO/2 MO's,²⁴ the AD force on the S atom comes primarily from the s-p hybridization and the p-d hybridization functions to diminish slightly the total AD force.

It is convenient to divide the influences on the AD force into two origins. The first is the nature of the central atom A and the second is the substituent effect due to the neighboring atom or group B. About the nature of atom A, it is convenient to subdivide further; one is the nature varying within the same family of periodic table (*central atom effect*) and the other is concerned with the local symmetry of the electron cloud near atom A and related to the number of valence electrons of atom A (*central symmetry effect*).

Central Atom Effect. Generally speaking, the smaller the difference between the levels of valence s and p AO's, the larger the extent of hybridization. In Figure 3, the differences in the Mulliken orbital electronegativity $\chi_{\text{M}} (=Ip + E_{\text{A}}$, where Ip and E_{A} are the valence-state ionization potential and electron affinity, respectively)²⁵ between the valence s and p AO's are plotted for the elements from the first to fourth rows in periodic table. These values are obtained from the tables given by Hinze and Jaffé.²⁵ From Figure 3, we can expect that *within the same family, the extent of s-p hybridization and hence the AD force increase with sliding down the rows of the periodic table.* Hereafter, we call this effect the *central atom effect*. Important exceptions are found in the third and fifth families from Al

(24) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967); J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(25) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1962).

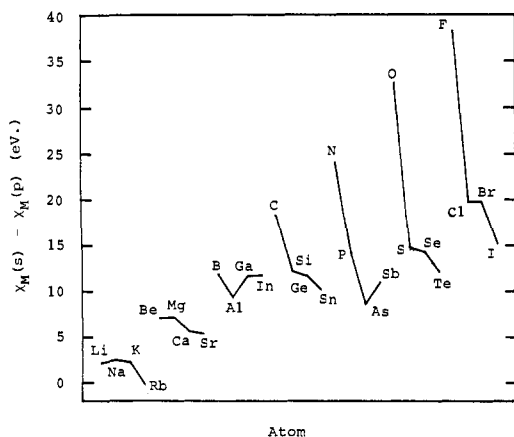


Figure 3. Differences in the Mulliken orbital electronegativity between the valence s and p AO's for the elements from the first to fourth rows in the periodic table.

to Ga and from As to Sb. Furthermore, note that from the fourth to the seventh families the gaps between first- and second-row elements are surprisingly large. *This causes the frequent sharp differences in valence angles between the first- and second-row elements.*

(2) Central Symmetry Effect. The valence-electron population near atom A and especially their density distribution in space vary from molecule to molecule and from state to state (e.g., cation, radical, anion, and excited states). This is one of the most important reasons for the variety of molecular shapes, as will be fully discussed later in this and succeeding papers. Nevertheless, the number of valence electrons near atom A is primarily determined in usual molecules by the core charge of atom A (the family of atom A). For hydrogen atom and alkaline, alkaline-earth, and boron cation families, if no s-p promotion occurs through molecular formation, the AD force cannot be produced on these atoms, since the valence electrons are in the spherical s-type orbitals around nucleus A. Likewise, for halogen anion and noble gas families, if no electrons are withdrawn from these atoms through molecular formation, the AD force cannot also be produced, since the fully occupied valence shell is also spherical around the nucleus. The unimportance of inner-shell electrons is due to the same reasons.

In actual problems, we are frequently interested in the AD force along a special direction, say x direction. In this case, the problem is the symmetry of electron distribution near nucleus A along the $\pm x$ axes, the origin being nucleus A. Similar to the above discussions, *if only s_A AO is partially or completely filled and p_{zA} AO is empty, or if both s_A and p_{zA} AO's are completely filled, the electron distribution near nucleus A is symmetric about nucleus A along the $\pm x$ axes. For both cases, the AD force along the x axis cannot be produced.* This effect is called hereafter the *central symmetry effect*.

(3) Inductive Substituent Effect. Here, we consider the fragment A-B, where A is the concerned atom and B is the substituent. The extent of hybridization of the AO's of atom A depends on the natures of both s_A and p_A AO's in the A-B fragment. The off-diagonal element of density matrix, $P_{s_A p_A}$, shows the extent of hybridization. Thus, two types of substituent effects, namely σ - and π -inductive effects, are considered.

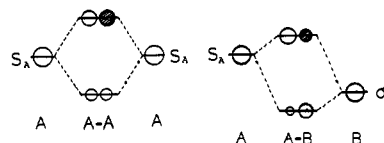


Figure 4. Bond orbital levels and coefficients of the A-A and A-B bonds, where B is more σ attractive than A. Larger circle shows larger coefficient.

Since the AD force is most important for lone-pair electrons, the effect on the coefficients of s_A and p_A AO's of the lone-pair (or $n-$) MO becomes most important. For the π -inductive effect, the π -donating substituent B functions to enlarge the coefficient of $p_{\pi A}$ AO and then the AD force, and *vice versa*. For the σ -inductive effect, the effect is more roundabout than the π effect. When B is more σ attractive than A, the levels and coefficients of the AB bond orbitals will become as illustrated in Figure 4. The left-hand side shows the homopolar A-A case. The important feature is that for the antibonding orbital, its level is lowered and the coefficient of s_A AO is enlarged. Therefore, the mixing of this antibonding orbital into the lone-pair MO is facilitated and then the coefficient of s_A AO in this MO is enlarged. Then, the AD force increases by this effect. Summing up the above statements, we obtain Table II. Since the π effect is

Table II. Substituent Effect on the AD Force

Effect	AD force
π donating	Increase
π attractive	Decrease
σ donating	Decrease
σ attractive	Increase

more direct than the σ effect, and since the s electron is more tightly bound than the p electron (see Figure 3), *the π -inductive effect is usually more effective than the σ -inductive effect.*

(iii) Inductive Substituent Effect on the EC Force. The substituent effect on the EC force is more complicated than that on the AD force. From eq 13, the EC force exerted on atom A along the AB bond is given by

$$2Z_A \sum_T^A \sum_S^B P_{TASB} \langle \chi_{TA} | (\mathbf{r}_A / r_A^3) | \chi_{SB} \rangle$$

which depends on both P_{TASB} and the net-exchange force integral. Although both are the functions of the substituent B and the A-B distance, we consider first the effect of substituent B at a fixed A-B distance. For the case where B is more electropositive than A, the electron distribution in the AB-bond region becomes



Thus, in this case, the EC force acting on nucleus A becomes larger than that in the homopolar AA bond. In Figure 5, the net-exchange force integrals centered on carbon and nitrogen are plotted for various substituent atoms to exemplify the above statement. To conclude, *at fixed A-B distance, the more electropositive the substituent B, the stronger the EC force acting on atom A.*

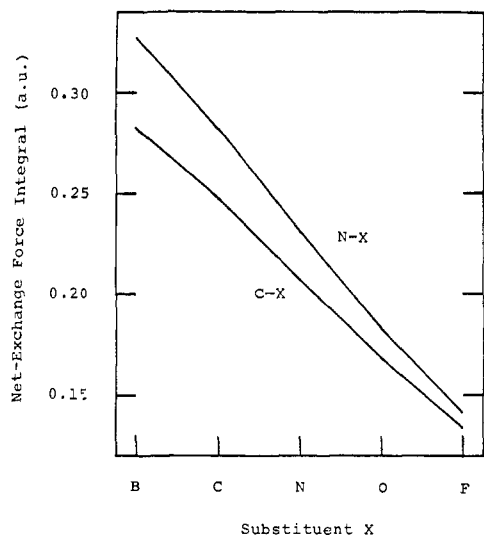


Figure 5. Substituent effect on the net-exchange force integrals centered on carbon and nitrogen. Bond length is 1.4 Å.

The second important effect is the one due to the bond multiplicity of A-B bond. This effect is already specified in eq 14. Namely, *with increasing bond multiplicity of AB bond, the EC force increases as expressed in eq 14.*

Changes in Electronic Structure. In order to discuss the changes in electronic structure, the molecular orbital theory is more suitable. From eq 8, if we neglect the changes of MO's following to the change in electronic structure ($\alpha \rightarrow \beta$), the change in the force acting on atom A is expressed by²

$$\Delta F_A^{\alpha \rightarrow \beta} = Z_A \sum_i (m_i^\beta - m_i^\alpha) f_{A_i} \quad (15)$$

where m_i^α is the occupation number of i th MO in state α . For example, for the excitation between the states with the same electronic configurations

$$\Delta F_A^{\alpha \rightarrow \beta} = 0 \quad (16a)$$

which implies that the differences between these states in the force-dependent properties such as the structures, force constants etc., are expected to be small.² For the excitation from i th to j th MO's

$$\Delta F_A^{\alpha \rightarrow \beta} = Z_A (f_{A_j} - f_{A_i}) \quad (16b)$$

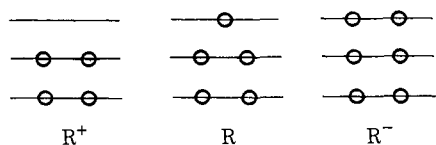
for the ionization from the i th MO

$$\Delta F_A^{\alpha \rightarrow \beta} = -Z_A f_{A_i} \quad (16c)$$

and for the electron attachment to i th MO

$$\Delta F_A^{\alpha \rightarrow \beta} = Z_A f_{A_i} \quad (16d)$$

Especially for the cations, radicals, and anions with the following electronic configurations



the force induced at the radical geometry (vertical state) satisfies

$$\Delta F_A(R \rightarrow R^+) = -\Delta F_A(R \cdot \rightarrow R^-) \quad (16e)$$

which implies that *the force-dependent properties of R should always be median between those of R⁺ and R⁻*

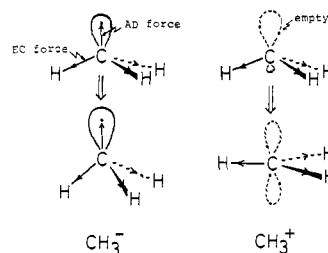


Figure 6. Important forces for the shapes of CH_3^- and CH_3^+ .

As seen from eq 9 and 13, the AD and EC forces are expressed by the simple sum of orbital contributions. f_{A_i} in the above equations includes these contributions from the i th MO. Then, the changes in the AD and EC forces are easily estimated by considering the orbital contributions to density matrix (see eq 9) for the MO's responsible for electron transition, ionization, etc. For example, the change in the AD force following the excitation from the i th to the j th MO is given from eq 9 and 13 as

$$Z_A \sum_{r(\neq s)}^A \sum_{\delta}^A (C_{jTA} C_{j\delta A} - C_{iTA} C_{i\delta A}) \langle \chi_{TA} | \mathbf{r}_A / r_A^3 | \chi_{\delta A} \rangle$$

The term in parentheses corresponds to the change in the density matrix, $P_{TA\delta A}$, due to the transition.

Illustrative Examples of the Applications of the ESF Theory. Although detailed applications of the ESF theory to the shapes of ground- and excited-state molecules and to chemical reactions will be given in the succeeding papers of this series,¹⁴ some illustrative examples are given below to explain how the present ESF theory works in the actual problems.

(i) **Shapes of the Ground- and Excited-State Molecules.** As a prototype, we first discuss the shapes of CH_3^- , CH_3 , and CH_3^+ . Illustrations of the important forces are given in Figure 6. In planar CH_3^- , the electrons in the p_π AO exert no force on the carbon atom from symmetry. However, when CH_3^- is slightly bent, the AD force due to the hybrid orbital generated rapidly on carbon atom attracts it in the direction shown in Figure 6. Three EC forces along the C-H bonds operate as a restoring force to planar structure. Although the GC force is minor, the negative gross charge on hydrogen attracts the other protons, to make the molecule nonplanar. Since the AD force is more important than the EC force, the molecule continues to bend until the vector sum of the EC forces cancels the AD force. Thus, CH_3^- is expected to be nonplanar.²⁶ Likewise, from the constancy in the relative importance between the AD and EC forces (Table I), NH_3 is also expected to be nonplanar, as it actually is. On the other hand, in CH_3^+ only the restoring EC forces act when it is slightly bent, since the hybrid orbital is empty.²⁷ The GC forces also act as a restoring force, although they are minor. Thus, CH_3^+ takes a planar D_{3h} structure,²⁶ where the three equivalent EC forces balance. Likewise, BH_3 and BeH_3^- take a planar D_{3h} structure.²⁸ CH_3 is median between CH_3^- and CH_3^+

(26) (a) C. Bugg, R. Desiderato, and R. L. Sass, *J. Amer. Chem. Soc.*, **86**, 3157 (1964); (b) R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **50**, 1443 (1969); (c) G. V. Bünau, G. Diercksen, and H. Preuss, *Int. J. Quantum Chem.*, **1**, 645 (1967).

(27) With reference to the INDO MO's,²⁴ a small hybrid orbital directed downward is generated on the carbon atom, but the AD force due to this hybrid orbital is small.

(28) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966).

and necessitates more detailed examinations, but it takes a planar D_{3h} structure from both experimental^{29,30} and theoretical³¹ studies. Likewise NH_3^+ ³² and BH_3^- ³³ take planar D_{3h} structures. Moreover, from the above discussions, the force constant of the out-of-plane bending vibration of CH_3^+ is expected to be larger than that of CH_3 .^{26b,30,34}

The above relations among CH_3^+ , CH_3 , and CH_3^- are also closely related to the prediction written under eq 16e. The p_π orbital in the planar structure or the hybrid orbital on carbon shown in Figure 6 is empty in CH_3^+ , singly filled in CH_3 , and doubly filled in CH_3^- . Other examples which also support this prediction are summarized in Table III.

Table III. Geometries of Cations, Radicals, and Anions^a

Radical	Geometrical parameter	Geometry		
		Cation	Radical	Anion
NO_2^b	$\angle \text{ONO}$	180	131.1	115.4
	R_{NO}	1.154	1.1934	1.236
CN^b	R_{CN}	1.1727	1.1718	1.09 ~ 1.15
OH^b	R_{OH}	1.0289	0.9706	0.944
$\text{O}_2^{b,c}$	R_{OO}	1.1227	1.2074	1.28
BH_2	$\angle \text{HBH}$	(180) ^d	131 ^e	(102) ^{d,f}

^a The interatomic distances, R_{AB} , are given in Å units and $\angle \text{ABC}$ are given in degrees. ^b Reference 35. ^c The value of R_{OO} in O_2^{2-} is 1.49 Å and is also larger than that of O_2^- (ref 35). ^d Theoretical value; ref 28. ^e Reference 30. ^f Theoretical value; L. M. Sachs, M. Geller, and J. J. Kaufman, *J. Chem. Phys.*, **52**, 974 (1970).

A manifestation of the relative importance expressed by eq 14 is seen, for example, in the shapes of NH_3 , $\text{CH}_2=\text{C}(\text{CH}_3)_2$, and C_2H_2 . With reference to Figure 2, since the AD force is more important than the EC force, the HNH angle in NH_3 is expected to be smaller than the tetrahedral angle, 109.47°. Indeed, the experimental angle is 107.8°. ³⁰ As to the dependence of the EC force on bond multiplicity, the structure of isobutene $\text{CH}_2=\text{C}(\text{CH}_3)_2$ offers a good example. Since the EC force acting on carbon along the CC double bond is larger than that along the single bond, the $\text{CH}_2=\text{C}-\text{CH}_3$ angle is expected to be larger than the $\text{CH}_3-\text{C}-\text{CH}_3$ angle. The experimental angles verify this prediction ($\text{CH}_2=\text{C}-\text{CH}_3$, 124.3°; CH_3CCH_3 , 111.5°). ³⁵ Moreover, in ethylene the $\text{C}=\text{C}-\text{H}$ angle (121.2°) is larger than the $\text{H}-\text{C}-\text{H}$ angle (117.6°). ³⁰ This is due to the similarity in the EC forces between the CC and CH single bonds (Table I).

As to the central atom effect on the AD force, the following hydrides offer good examples: ³⁰ Vth family, NH_3 (107.8°), PH_3 (93.3°), AsH_3 (92°); VIth family, OH_2 (105.2°), SH_2 (92.2°), SeH_2 (91°), TeH_2 (90.25°) (where the values in parentheses are the HAH angles).

(29) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(30) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1965.

(31) (a) K. Morokuma, L. Pedersen, and M. Karplus, *J. Chem. Phys.*, **48**, 4801 (1968); (b) T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, *Bull. Chem. Soc. Jap.*, **42**, 2437 (1969).

(32) T. Cole, *J. Chem. Phys.*, **35**, 1169 (1961).

(33) M. C. R. Symons and H. W. Wardale, *Chem. Commun.*, 758 (1967); M. C. R. Symons, *Nature (London)*, **222**, 1123 (1969).

(34) W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.*, **44**, 2527 (1966); D. E. Milligan and M. E. Jacox, *ibid.*, **47**, 5146 (1967).

(35) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

The above trend occurs due to the increase in the AD force with increasing period of the central atom within the same family in the periodic table. Moreover, note that sharp differences are seen between NH_3 and PH_3 and between OH_2 and SH_2 as expected from Figure 3.

Another example of the central atom effect is the structures of CH_3 , SiH_3 , GeH_3 , and SnH_3 .³⁶ From esr measurements, the HAH angles in SiH_3 , GeH_3 , and SnH_3 were reported to be 113.5, 115, and 117°, respectively.^{36c} The pyramidal structure of SiH_3 , GeH_3 , and SnH_3 is reasonable from the central atom effect on the AD force (see Figure 3). However, the trend in the changes in the HAH angles among SiH_3 , GeH_3 , and SnH_3 cannot be understood only from the central atom effect.

As an example of substituent effect, the shapes of fluoromethyl radicals are interesting.^{37,38} The experimentally estimated out-of-plane angles are 0° for CH_2 , smaller than 5° for CH_2F , about 12.5° for CHF_2 , and about 17.8° for CF_3 .³⁷ Since fluorine atom is π donating and σ attractive, the AD force on carbon atom is reinforced (see Table II). Since fluorine is more electro-negative than hydrogen, the EC force (the main restoring force to planar structure) diminishes. Although the GC force is small, the negative gross charge on fluorine attracts the nonbonded nuclei. Thus, all kinds of forces are affected by fluorine substitutions to make cooperatively the molecules nonplanar. Then, the total substituent effects are rather drastic as shown by experiments.³⁷ Note however that the structures of HBF_2 and BF_3 are planar.^{35,39} This is due to the fact that, in these molecules, the AD forces generated on borons by small bending are between those of BH_3 ²⁸ and BH_3^- ³³ and cannot overcome the restoring force to planar structure due to the EC force.

Like the fluorine substituent in the above example, if the substituent is bound by the single bond to the central atom A, the π -donating (π attractive) substituent is usually σ attractive (σ donating). In these cases, the σ - and π -inductive effects on the AD force and the inductive effect on the EC force are cooperative in affecting the shapes of the substituted molecules. Among these effects, the π -inductive effect on the AD force seems most important. This may be clear from eq 14 and from the discussions given in (3) of the previous section.

The above considerations suggest that *shapes of usual molecules are in close relation with the electron density in the p_π AO of the central atom A in planar or linear structure, which is designated as $D(p_{\pi A})$* . This fact allows us to draw up a qualitative measure shown in Figure 7. The difference between AXY and AXYZ molecules arises from the difference in the number of the EC forces. Although three EC forces are there in AXYZ , only two EC forces are there in AXY . Therefore, for example, although CH_3 is planar,³⁰ triplet CH_2 is bent.⁴⁰ ($D(p_{\pi C})$ is unity for both cases.) In Figure 7,

(36) (a) R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966); (b) G. S. Jackel, J. J. Christiansen, and W. Gordy, *ibid.*, **47**, 4274 (1967); (c) G. S. Jackel and W. Gordy, *Phys. Rev.*, **176**, 443 (1968); (d) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 3938 (1969).

(37) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(38) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, **48**, 4802 (1968).

(39) T. Kasuya, W. J. Lafferty, and D. R. Lide, *ibid.*, **48**, 1 (1968).

(40) G. Herzberg and J. W. C. Johns, *ibid.*, **54**, 2276 (1971).

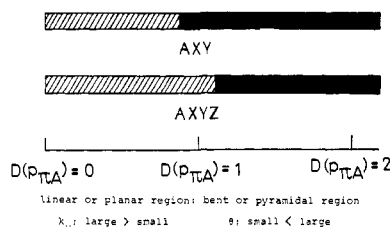


Figure 7. Qualitative measure about the shapes of AXY and AXYZ molecules (A is the central atom and X, Y, and Z are the substituents). $D(p_{\pi A})$, k_{ν} , and θ are the electron density of the $p_{\pi A}$ AO in planar or linear structure, the out-of-plane bending force constant, and the out-of-plane angle, respectively. About the limitations of this measure, see the text.

the critical values of $D(p_{\pi A})$ dividing linear (or planar) and bent (or pyramidal) regions are drawn from this example. However, *this value is affected if central atom A becomes heavier than the first-row atom* (remember the structures of SiH_3 , GeH_3 , and SnH_3 discussed above). In the planar or linear region, the bending force constant is expected to increase with decreasing $D(p_{\pi A})$ while in the pyramidal region the extent of bending is expected to increase with increasing $D(p_{\pi A})$. As shown later in this and succeeding papers,¹⁴ Figure 7 is very useful in predicting shapes of usual molecules in both the ground and excited states.

Figure 7 has drawn from the considerations chiefly on the π effect on the AD force. Namely, the AD force increases with increasing $D(p_{\pi A})$. However, from the definition of the AD force, this is correct only when the nature (density, energy level, etc.) of s_A AO is approximately constant among the molecules containing atom A. The reason that this approximate constancy holds in usual molecules is that the s electron is usually more tightly bound than the p electrons. In other words, the levels of the MO's composed mainly of s_A AO are considerably deeper than those of the MO's composed mainly of p_A (both $p_{\pi A}$ and $p_{\sigma A}$) AO's (refer to Figure 3). However, when electrons begin to fill the $s_A - \sigma_X$ antibonding orbital, Figure 7 is not at all applicable. The reason is that when both s_A and $p_{\pi A}$ AO's are filled, no important AD force can be grown along the π direction due to the central symmetry effect stated in paragraph ii-2 of the previous section. For example, in ICl_2^- , I_3^- , lBrCl^- , Br_3^- ,³⁵ and XeF_2 ⁴¹ the s AO's of the central halogen and xenon atoms are completely filled, since in these the $s_A - \sigma_X$ antibonding orbital is doubly occupied. The $p_{\pi A}$ and $p_{\sigma A}$ AO's are also completely filled. Then, although $D(p_{\pi A})$ is larger than or equal to 2, the shapes of these molecules are all linear.^{35, 41}

Although the above examples are given only for the ground-state molecules, the present ESF theory is also applicable to the excited-state molecules. For example, in the ground state of H_2CO the density $D(p_{\pi C})$ is less than unity⁴² and the EC force increases due to the double bond character of $\text{C}=\text{O}$ bond (eq 14). Then, the molecule is expected to be planar. However, in the $n - \pi^*$ excited states $D(p_{\pi C})$ becomes larger than unity,⁴² since the transition transfers one electron from the lone-pair orbital on oxygen to the π MO which has a larger

(41) S. Reichman and F. Schreiner, *J. Chem. Phys.*, **51**, 2355 (1969); P. Tsao, C. C. Cobb, and H. H. Classen, *ibid.*, **54**, 5247 (1971).

(42) Due to the INDO MO's,²⁴ the values of $D(p_{\pi C})$ for the ground and excited states of H_2CO are 0.805 and 1.402, respectively.

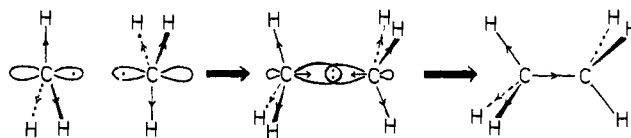


Figure 8. Important forces in the reaction $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$.

density on carbon. Then, the $n - \pi^*$ excited states of H_2CO becomes pyramidal. Experimentally, the out-of-plane angles of the singlet and triplet excited states are $\sim 20 - 31^\circ$ and 35° ,^{30, 43} respectively. For linearity, HCN is a good example, which is linear in the ground state but bent in the excited states.³⁰ The reasoning is quite similar to that in H_2CO .¹⁴

Other interesting examples are the Rydberg excited states of H_2O and NH_3 . As expected from Figure 7, the presences of lone-pair electrons make their ground-states bent and pyramidal, respectively.³⁰ By the Rydberg transition, one of the $2p_{\pi}$ electrons of H_2O is transferred to the Rydberg orbital which is mainly composed of $3p$ AO of oxygen.³⁰ Since both $2p_{\pi}$ and $3p$ electrons exert no force on the oxygen nucleus by symmetry, the geometries of both the ground and Rydberg excited states of H_2O are expected to be quite similar, which accords with experiments (ground state, 105.2° ; Rydberg excited state, 106.9°).³⁰ On the other hand, in NH_3 these transitions transfer one electron from the lone-pair orbital to approximately the $3s$ or $3p$ AO's of nitrogen. Thus, in these Rydberg excited states, the AD force diminishes considerably. The situations are very similar to that in NH_3^+ . Thus, from Figure 7, they are expected to be planar as experimentally ascertained.³⁰

(ii) Chemical Reaction and Structure of Product.

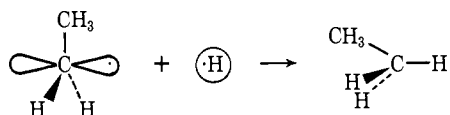
In this section we give the preliminary results obtained by applying the ESF theory to a chemical reaction. For the occurrence of the chemical reaction, the interaction between two reactants should cause an increase of electron density in the region between reacting sites of the reactants and, at the same time, should cause a decrease of the bond electron density of the old bond.⁴⁴ This suggests *the importance of the EC force in a chemical reaction. In the ESF theory, we can predict not only the reaction paths but also the shapes of products of the reaction.* Note that when interacting atoms or molecules are widely apart, the basic eq 13 becomes a good approximation.¹⁷

First, we discuss the formation of ethane from two methyl radicals. Important forces along this process are illustrated in Figure 8. When two radicals are widely apart, three equivalent EC forces are acting on the carbon atom balancing in a planar D_{3h} structure. However, in the intermediate region of reaction, two p_{π} orbitals on the carbons become overlapping (in valence bond language, electron exchange occurs between two p_{π} orbitals). As a consequence, the EC force begins to exert on each carbon atom making the approach shown in Figure 8 preferable. This force is literally a *driving force of reaction* and, at the same time, causes each methyl radical to become non-planar as in ethane. Namely, in the ESF theory, two phenomena, that the reaction proceed along the above

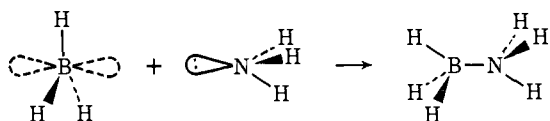
(43) D. E. Freeman and W. Klemperer, *J. Chem. Phys.*, **45**, 52 (1966).

(44) H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jap.*, **44**, 2936 (1971).

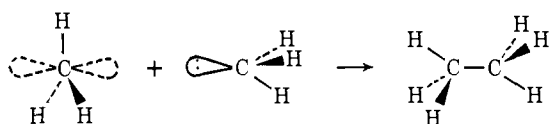
reaction path and that each methyl radical becomes nonplanar as in ethane, are just different manifestations of the same origin. At the final stage of reaction, the EC force along the C–C bond grows to the value nearly equal to that along the C–H bond (see Table I), resulting in an almost tetrahedral CH_3 fragment in ethane. Quite similar considerations are also true in the ethane formation reaction from ethyl radical and hydrogen atom



Although the above examples correspond to the formation of the covalent bond, the next is the formation of the coordinate bond. An example is the ammonia–boron trihydride system



The difference from the above examples is that the p_x orbital of the planar BH_3 molecule is vacant and the lone-pair orbital of the NH_3 molecule is doubly occupied. Thus, in the course of reaction, the EC force is produced on boron, and the AD force on nitrogen in free NH_3 is partially transformed to the EC force. From eq 14 and from the inductive effect on the EC force, it is expected that the BH_3 fragment in the BH_3 – NH_3 molecule becomes nonplanar, although the HBH angle is larger than the tetrahedral angle $109^\circ 28'$. Although no experimental geometry is found for BH_3 – NH_3 , the FBF angle in BF_3 – NH_3 is known experimentally to be 111° , although it is 120° in free BF_3 .³⁵ The HNH angle is not known.³⁵ Interestingly, from the similar considerations as above on the reaction $\text{CH}_3^+ + \text{CH}_3^- \rightarrow \text{C}_2\text{H}_6$



the HCH angle of CH_3^- is expected to be smaller than $109^\circ 45'$, the HCH angle in ethane.³⁵ The HCH angle of CH_3^- calculated by Kari and Csizmadia^{26b} is around this value, the uncertainty being due to the changes in the assumed CH bond length and in the computational method.

Discussion

In the present paper, we have presented the ESF theory in which chemical phenomena are investigated through *force concepts* on the basis of the electrostatic theorem of Hellmann and Feynman. Taking advantage of the physical simplicity and visibility of this theorem, we derived three pictorial concepts such as the AD, EC, and GC forces. Their roles and relative importances are studied and, at the same time, the influences on these forces induced by the changes of the concerned atoms and their neighboring substituents are investigated. The change in these forces

following the change in electronic structure is also discussed. Especially about the shapes of usual molecules, a simple qualitative measure shown in Figure 7 is obtained. For some illustrative examples, it is shown that these pictorial concepts are very intuitive and useful in predicting shapes of molecules in both the ground and excited states and in understanding natures of chemical reactions and structures of products.

The relative importances of the AD, EC, and GC forces shown in eq 14 correspond to the following order of the valence-shell electron-pair repulsion energies in the VSEPR theory:¹⁰ lone pair > triply bonded electron pairs > doubly bonded electron pairs > singly bonded electron pair. In the VSEPR theory, the nonbonded interactions are neglected.¹² Since the theoretical basis of the VSEPR theory seems rather weak, eq 14 may also be regarded as a theoretical reasoning of the above order in the VSEPR energies.

Although the AD and EC forces defined in eq 13 can be the exact concept, the GC force is only approximate. However, if we introduce the *extended GC (EGC) force*²¹ in spite of the GC force, all three forces are exactly defined. Since the approximation 10 is not always good¹⁶ notwithstanding its simplicity, we will use the EGC force in the actual calculations of forces.⁴⁵

In the present ESF theory, we have only to consider the *electrostatic* interactions between the electron cloud and nuclei and between nuclei. This simplicity makes a marked contrast to the complexity of the energetic concept where many different kinds of terms appear: kinetic, electron–nuclear attraction, and electron–electron and nuclear–nuclear repulsion terms. Moreover, the concepts of the ESF theory are independent of the approximation methods of electronic structure (e.g., MO method, valence bond method, configuration–interaction method, etc.), since the electron cloud is conceptually independent of the models of electronic structure. This is not like the “orbital energies” in MO theory, which are extensively used in the Walsh rule and SOJT theory.^{9,11–13}

Although many past studies have shown that the magnitude of calculated electrostatic forces is very sensitive to the accuracy of the approximate wave functions used,^{5,6,8,46} we believe that the quantitative consequence will be improved with increasing accuracy of the wave function used,⁴⁷ *without changing* the underlying conceptual simplicity and visibility.

In the present paper, the possibility is shown that the present theoretical concept is wide enough to be able to apply to both problems of molecular structure and chemical reaction. These are certainly fundamental problems in chemistry. More detailed applications of the ESF theory to these problems will be published subsequently in this series of papers.¹⁴

(45) H. Nakatsuji, T. Kuwata, and A. Yoshida, to be submitted for publication.

(46) L. Salem and E. B. Wilson, Jr., *J. Chem. Phys.*, **36**, 3421 (1962); L. Salem and M. Alexander, *ibid.*, **39**, 2994 (1963); W. H. Fink and L. C. Allen, *ibid.*, **46**, 3270 (1967); J. Goodisman, *ibid.*, **47**, 334 (1967).

(47) In order to obtain good magnitude of electrostatic forces from *ab initio* wave functions, the floating Gaussian orbitals extensively used by Frost, *et al.*, will be useful, since for these orbitals, the Hellmann–Feynman theorem will be satisfied² (see A. A. Frost, *J. Chem. Phys.*, **47**, 3707, 3714 (1967), and the succeeding papers). Although in the present formulation we assumed implicitly that the center of AO coincide with the position of nucleus (nonfloating orbital), the removal of this constraint does not much affect the formulation of the AD, EC, and GC (or extended GC²¹) forces.

Acknowledgment. The author wishes to acknowledge Professors T. Yonezawa and H. Kato for encouragement and valuable discussions. He also thanks the

members of Quantum Chemistry Group of his department for useful discussions and the referee for some pertinent comments.

Electrostatic Force Theory for a Molecule and Interacting Molecules. II. Shapes of the Ground- and Excited-State Molecules

Hiroshi Nakatsuji

*Contribution from the Department of Hydrocarbon Chemistry,
Faculty of Engineering, Kyoto University, Kyoto, Japan.
Received May 8, 1972*

Abstract: The electrostatic force (ESF) theory developed in the previous paper was successfully applied to the shapes of both the ground and the excited states of a wide variety of molecules of the types AH_2 , AH_3 , HAX , XHY , H_2AX , and XAY . Indeed, among these molecules for which the shapes are known experimentally, no exceptions were found missing from this theory. In these, simple molecular orbitals were used in order to obtain qualitative features of electron density distributions. The relative importance of the atomic dipole (AD), exchange (EC), and gross charge (GC) forces and the various important effects on these forces (*e.g.*, the central atom effect, the central symmetry effect, and the inductive substituent effects on the AD and EC forces; etc.) summarized previously were shown very useful in understanding not only the trends within a type of molecule but also the relations among different types of molecules. Similar to the Walsh rule, the ESF theory also correlates shapes of molecules with the number of valence electrons, although the basic approaches are quite different between these two theories. Moreover, the ESF theory was able to give simple accounts even to the shapes of the molecules for which other theories of molecular structure such as the Walsh rule, the valence-shell electron-pair repulsion (VSEPR) theory, and the second-order Jahn–Teller (SOJT) theory found difficult to give straightforward explanations.

Many models have been developed for molecular geometries, especially for the shapes of molecules. In 1953, Walsh¹ gave the "orbital correlation diagrams" which interconnect the number of valence electrons and the shapes of molecules in their ground and lower excited states. Although his rule is very successful,² no firm theoretical bases are yet found for the simple effective one-electron energy.³ The valence-shell electron-pair repulsion (VSEPR) theory^{4,5} chiefly owed to Gillespie and Nyholm is very pictorial and successful, although restrictive only to the ground-state molecules and weak in its theoretical foundations. In conjunction with the Walsh rule, a device to allow the theory semiquantitative predictions of bond angles has recently been reported.⁶ The second-order⁷ (pseudo-⁵) Jahn–Teller (SOJT) theory developed by Bader,⁸ Bartell,⁵ Pearson,⁷ and Salem⁹

gave the symmetry rule of molecular structure. Similar formulation can also give a theoretical foundation of the symmetry rule of reaction path,^{9,10} such as the well-known Woodward–Hoffmann rule.¹¹

Aside from the details, the above three theories give, of course, similar and generally correct predictions and so should be different side views of physical reality. Theoretically, the Walsh and SOJT theories are based on the molecular orbital (MO) concept, and the VSEPR theory is close to the valence bond and localized orbital concepts.¹²

Although the above three theories are all based on the *energetic* considerations, the problems of molecular structure can also be studied by considering the *forces* acting on the constituent nuclei. In the previous paper,¹³ the *electrostatic force (ESF) theory* in which chemical phenomena are studied through the force concept is presented on the basis of the electrostatic theorem of Hellmann and Feynman.¹⁴ Taking ad-

(1) A. D. Walsh, *J. Chem. Soc.*, 2260, 2266, 2288, 2296, 2301, 2306, 2321 (1953).

(2) B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970); **93**, 593, 815 (1971).

(3) C. A. Coulson and B. M. Deb, *Int. J. Quantum Chem.*, **5**, 411 (1971), and references cited therein.

(4) (a) N. V. Sidgwick and H. M. Powell, *Proc. Roy. Soc., Ser. A*, **176**, 153 (1940); (b) C. E. Mellish and J. E. Linnett, *Trans. Faraday Soc.*, **50**, 657 (1954); (c) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); (d) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); (e) H. A. Bent, *ibid.*, **40**, 446, 523 (1963); **45**, 768 (1968).

(5) L. S. Bartell, *ibid.*, **45**, 754 (1968).

(6) (a) Y. Takahata, G. W. Schnuelle, and R. G. Parr, *J. Amer. Chem. Soc.*, **93**, 784 (1971); (b) H. B. Thompson, *ibid.*, **93**, 4609 (1971).

(7) R. G. Pearson, *ibid.*, **91**, 1252, 4947 (1969); *J. Chem. Phys.*, **52**, 2167 (1970); **53**, 2986 (1970); *Chem. Phys. Lett.*, **10**, 31 (1971).

(8) R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960); *Can. J. Chem.*, **40**, 1164 (1962).

(9) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969).

(10) (a) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5948 (1969); (b) R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970); *Accounts Chem. Res.*, **4**, 152 (1971).

(11) (a) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969, and their preceding papers cited therein; (b) K. Fukui, "Theory of Orientation and Stereoselection," Springer-Verlag, Heidelberg, 1970.

(12) (a) C. Edmiston and K. Ruendenberg, *Rev. Mod. Phys.*, **35**, 457 (1963); (b) L. C. Allen, *Theor. Chim. Acta*, **24**, 117 (1972).

(13) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345 (1973), preceding paper which is called paper I.

(14) (a) H. Hellmann, "Einführung in die Quantenchemie," Deuticke, Leipzig, 1937; R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939); see also (b) A. C. Hurley in "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 161; *Proc. Roy. Soc., Ser. A*, **226**, 170, 179 (1954).