

Electron-Cloud Following and Preceding and the Shapes of Molecules

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Abstract: First, the present paper shows the importance of the electron-cloud incomplete following and preceding in determining the shapes of molecules. The results of the preceding paper imply that if the electron-cloud incomplete following or preceding occurs when the molecule is bent from the planar shape, the stable shape of the molecule would be planar or bent, respectively. Here, the electron-cloud incomplete following and preceding in AH_n molecules are depicted from the nonempirical SCF wave functions. They are found to appear as the formation of an atomic dipole on atom A and the distortion of the A-H bond electron cloud. The former induces the atomic dipole (AD) force on atom A and the latter induces the exchange (EC) force on proton. The functions of these forces are confirmed to be just as implied by the results of the preceding paper. The alternative perturbational treatment which corresponds to the density approach of the second-order Jahn-Teller theory is also given. Second, the generality of the "bent bond" in equilibrium structure is shown as a special example of the electron-cloud preceding in the bond region. Third, the characteristics of the electron-cloud incomplete following and preceding are shown to be represented by the localized orbitals obtained at the configuration apart from the equilibrium structure.

In the preceding paper,² two common features of the electron clouds of the systems under the changes in nuclear configuration are deduced from the Hellmann-Feynman³ and integral Hellmann-Feynman⁴ theorems

$$F_A^\alpha = \int \rho_\alpha(\mathbf{r}_1) Z_A \mathbf{r}_{A1} / r_{A1}^3 d\mathbf{r}_1 - Z_A \sum_{B(\neq A)} Z_B \mathbf{R}_{AB} / R_{AB}^3 \quad (1)$$

$$\Delta E(\alpha \rightarrow \beta) = \int \rho_{\alpha\beta}(\mathbf{r}_1) \Delta \mathcal{H}_{ne} d\mathbf{r}_1 + V_{nn} \quad (2)$$

(1) Belfer Graduate School of Science, Yeshiva University, New York, N. Y. 10033.

(2) H. Nakatsuji, *J. Amer. Chem. Soc.*, **96**, 24 (1974).

(3) (a) H. Hellmann, "Einführung in die Quantenchemie," Deuticke, Vienna, 1937, p 285; (b) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

(4) R. G. Parr, *J. Chem. Phys.*, **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); J. I. Musher, *ibid.*, **43**, 2145 (1965).

where the notations are the same as those used in the preceding paper. The first feature is *the electron-cloud incomplete following* which means that some centroid of the local electron cloud near the moving nucleus follows incompletely the movement of the nucleus. It should occur for the changes satisfying the following two conditions: (a) the change is from stable to unstable configuration; (b) throughout the change, the electronic parts (the first terms) of eq 1 and 2 remain larger in magnitude than the nuclear parts (the second terms). The function of the electron-cloud incomplete following is to *resist* the nuclear movement. Note that the change satisfies the condition (b), if it satisfies the following more restrictive condition (b'). Namely, (b') the change accompanies some decrease in nuclear repulsion. The second feature is *the electron-cloud preceding* which

means that some centroid of the local electron cloud near the nucleus precedes the position of the nucleus in the direction of the change. It should occur for the changes satisfying the following two conditions: (a) the change is from unstable to stable configuration; (b) throughout the change, the electronic parts of the theorems 1 and 2 remain larger in magnitude than the nuclear parts. The function is to *accelerate* the movement of the nucleus. Note that the change satisfies the above condition (b) if it satisfies the following more restrictive condition (b'). Namely, (b') the change accompanies some increase in the nuclear repulsion.

In the previous series of papers,⁵ an electrostatic force (ESF) theory has been developed and applied to the shapes of the ground- and excited-state molecules and to the simple reactions. The roles of atomic dipole (AD), exchange (EC), and gross charge (GC) or extended gross charge (EGC) forces have been discussed in detail. Here, we deal again with the shapes of AH_n molecules in order to show the importance of the electron-cloud incomplete following and preceding in the actual problems.

When the above resume of the preceding results² is rewritten as appropriate for the problems of molecular shape, we obtain the following guiding principle. If the electron-cloud preceding occurs when the molecule is bent from the planar shape, the constituent nuclei receive further the forces which accelerate this bending movement. Then, the shape of the molecule is expected to be bent. On the other hand, in the case of the electron-cloud incomplete following, the shape is expected to be planar. We consider here how the electron-cloud incomplete following and preceding appear and work in the actual problems and will confirm the above guiding principle.

In the following sections, we depict the electron-cloud incomplete following and preceding in AH_n molecules from the nonempirical SCF wave functions, taking CH_3^- , CH_3 , and CH_3^+ as typical examples. The roles of the electron-cloud incomplete following and preceding are clarified in the language of the ESF theory. Some of the previous results on molecular shapes^{5a-c} are interpreted through the present concept. Next, the generality of occurrence of the "bent bond" at equilibrium structure is proven as a special case of the electron-cloud preceding. A description of the electron-cloud incomplete following and preceding by means of the localized orbital method⁶ is also presented. Lastly, a connection of the present approach with the second-order Jahn-Teller theory⁷⁻¹⁰ is described.

Electron-Cloud Incomplete Following and Preceding and the Shapes of Molecules

Previously,^{5a,d} some examples of the incomplete following and preceding have been depicted during the

(5) (a) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345 (1973), paper I; (b) *ibid.*, **95**, 354 (1973), paper II; (c) *ibid.*, **95**, 2084 (1973), paper III; (d) H. Nakatsuji, T. Kuwata, and A. Yoshida, *ibid.*, **95**, 6894 (1973).

(6) (a) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963), and the references cited therein; (b) V. Magnasco and A. Perico, *J. Chem. Phys.*, **47**, 971 (1967).

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

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

(9) 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).

(10) (a) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); (b) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, **91**, 5947 (1969).

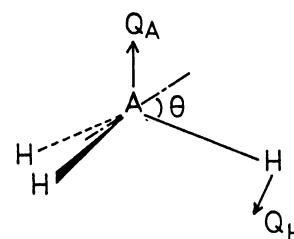


Figure 1. Definition of the out-of-plane bending displacement Q of AH_3 molecules from planar to pyramidal configurations. The arrows Q_A and Q_H represent the bending movements of the central atom A and the protons, respectively. θ is the out-of-plane angle.

internal rotations of H_mABH_n molecules. The importance of their roles in determining the rotational shapes and barriers has been shown with the ESF theory. Here, we give further examples of the electron-cloud incomplete following and preceding and explain their roles in determining the shapes of molecules. Since CH_3^- , CH_3 , and CH_3^+ have been the key molecules in the application of the ESF theory to molecular shapes,^{5a-c} we take these molecules as prototype examples.

First, let us examine the electron-cloud following and preceding in CH_3^- and CH_3^+ during the out-of-plane bending displacement defined in Figure 1. Q_C and Q_H represent the displacements of carbon and proton, respectively, from planar structure, and θ denotes the out-of-plane angle. Figure 2 shows the changes in electron density induced by the nuclear displacements in CH_3^- (Figure 2a) and CH_3^+ (Figure 2b) from planar ($\theta = 0^\circ$) to slightly pyramidal ($\theta = 30^\circ$) configurations. The contour maps are calculated from the nonempirical SCF-MO's based on the minimal set of Slater orbitals.^{11,12} The density obtained at $\theta = 0^\circ$ was subtracted from that obtained at $\theta = 30^\circ$, the coordinates of the C-H₁ bond, written by real line, being taken in common. The C-H distance was held fixed at 1.079 Å (experimental value for methyl radical¹³) for both CH_3^- and CH_3^+ .

As seen in Figure 2a, when CH_3^- is bent from the planar configuration, the electron cloud increases in the region immediately above the carbon nucleus and decreases in the region immediately below the carbon nucleus. This shows the formation of the upward atomic dipole on the carbon atom. The resulting AD force acting on carbon facilitates further the displacement of carbon along Q_C . This formation of atomic dipole is nothing else but the preceding of the one-center electron cloud. The important role of the AD force originating from the lone-pair orbital discussed in paper I is the manifestation of this kind of electron-cloud preceding. In Figure 2a, the electron density in the regions along the C-H axis increases in the downward region and decreases in the upward region. This reorganization of electron cloud induces the EC force on the proton which accelerates the bending movement

(11) The exponents of the Slater AO's are 5.68 for C(1s), 1.71 for C(2s), 1.66 for C(2p), and 1.23 for H(1s), which are referred to from the optimized values for methyl radical reported by Chang, Davidson, and Vincow (*J. Chem. Phys.*, **52**, 5596 (1970)).

(12) The integrals were calculated by expanding the Slater orbital with the three-term Gaussian bases. The expansion coefficients and the Gaussian orbital exponents are due to R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

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

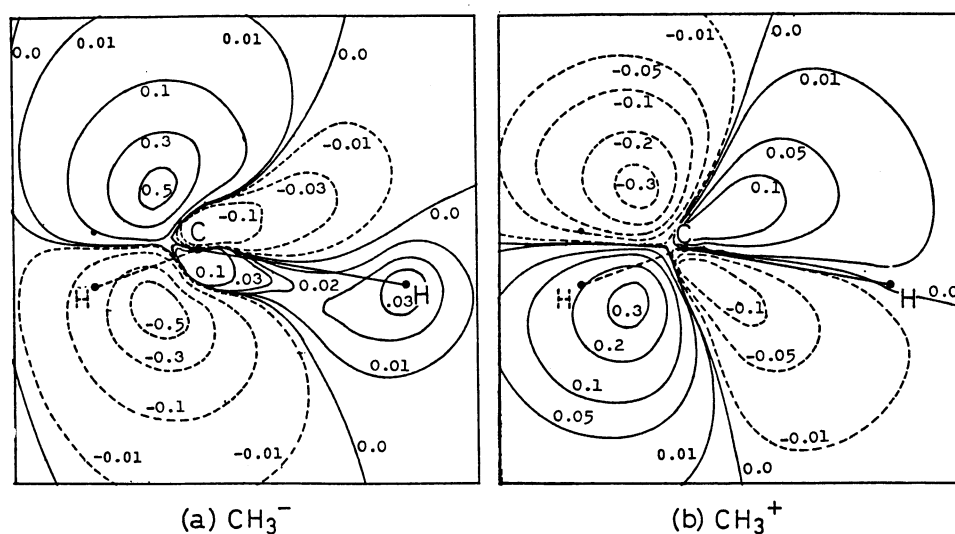


Figure 2. The contour maps showing the changes in the electron densities of CH_3^- and CH_3^+ induced by the out-of-plane bending displacement of $\theta = 30^\circ$. The real and dotted lines show an increase and a decrease in density, respectively. The density obtained at $\theta = 0^\circ$ is subtracted from that obtained at $\theta = 30^\circ$. The calculation is due to the nonempirical SCF-MO method based on the minimal set of Slater orbitals.

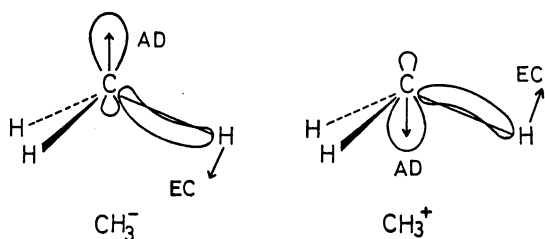


Figure 3. Illustrations of the electron-cloud preceding in CH_3^- and the electron-cloud incomplete following in CH_3^+ during the out-of-plane bending movements. The arrows show the AD and EC forces induced by these electron-cloud preceding and incomplete following.

of the proton along Q_H . This is the preceding of the electron cloud belonging to the C-H bond region. In Figure 3, the general feature of the electron-cloud preceding found for the CH_3^- is illustrated. The arrows show the AD and EC forces induced by these electron-cloud precedings. They operate to make the molecule non-planar in agreement with experiment.¹⁴ Note that during the out-of-plane bending displacement of CH_3^- , the displacement Q_C does not satisfy the condition (b'), although it satisfies the condition (b). The displacement Q_H satisfies both conditions (b) and (b').

Figure 2b is the contour map for CH_3^+ and offers an example of the electron-cloud incomplete following. In comparison with Figure 2a, the change in electron density in the regions above and below the carbon atom is reverse to that found for CH_3^- . Namely, the direction of the atomic dipole generated on the carbon of CH_3^+ is downward. Then, the resultant AD force acting on carbon operates to resist the displacement Q_C . This is the incomplete following of the one-center electron cloud. Likewise, the change in electron density along the C-H bond is also reverse to that found for CH_3^- . The resulting EC force acting on the proton operates to resist the displacement of proton, Q_H . This shows the occurrence of the incomplete following of the C-H bond electron cloud. The feature of the

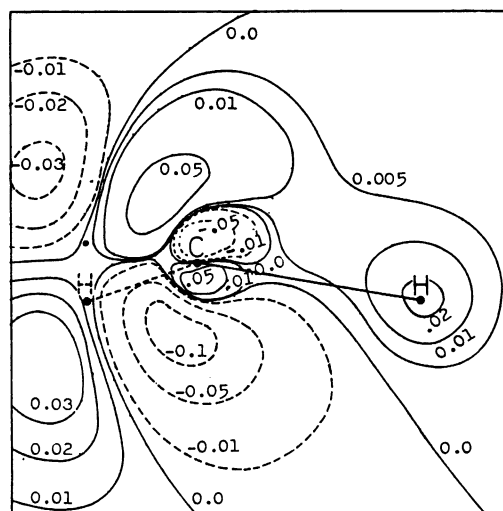


Figure 4. The contour map showing the change in the electron density of methyl radical induced by the out-of-plane bending displacement of $\theta = 30^\circ$. The real and dotted lines show an increase and a decrease in density, respectively.

electron-cloud incomplete following found for CH_3^+ is illustrated in Figure 3. The arrows show that AD and EC forces induced by the electron-cloud incomplete following. They operate to make the molecule planar in agreement with the previous theoretical calculations.¹⁵ Note that for CH_3^+ the displacement Q_H does not satisfy the condition (b'), though it satisfies the condition (b). The displacement Q_C satisfies both conditions (b) and (b').

Next, we examine the reorganization of electron cloud for methyl radical, which is intermediate between CH_3^- and CH_3^+ . Figure 4 is the contour map for methyl radical obtained at $\theta = 30^\circ$. The method of calculation is the same as those used for CH_3^- and CH_3^+ , except that the unrestricted Hartree-Fock method¹⁶ is

(14) C. Bugg, R. Desiderato, and R. L. Sass, *J. Amer. Chem. Soc.*, **86**, 3157 (1964).

(15) (a) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *J. Chem. Phys.*, **45**, 734 (1966); (b) G. V. Bünau, G. Diercksen, and H. Preuss, *Int. J. Quantum Chem.*, **1**, 645 (1967); (c) R. E. Kari and I. G. Csizmadia, *J. Chem. Phys.*, **50**, 1443 (1969).

(16) J. A. Pople and R. K. Nesbet, *ibid.*, **22**, 571 (1954).

used for methyl radical. When CH_3 is bent to $\theta = 30^\circ$, a slight electron-cloud preceding occurs in the regions above and below the carbon atom.¹⁷ In comparison with Figure 2a, the feature of the electron-cloud preceding near the carbon atom is similar to that of CH_3^- , but the extent is *by far* smaller than that found for CH_3^- . On the other hand, the change in electron density near the proton of CH_3 is quite different from that of CH_3^- . Although the electron cloud near the proton of CH_3^- precedes the bending displacement Q_H , that of CH_3 slightly follows incompletely the displacement Q_H .¹⁷ Moreover, the extent of this incomplete following is shown to increase with the increase in the out-of-plane angle θ .¹⁷ It causes the EC force on the proton which resists the movement of the proton along Q_H .

The occurrence of the incomplete following of the C-H bond orbital in methyl radical has been pointed out by many investigators.¹⁸⁻²¹ Itoh, Ohno, and Kotani¹⁸ showed the existence of the incomplete following from valence-bond calculations. Schrader and Karplus²⁰ pointed out the importance of the incomplete following for the esr hyperfine splitting constants and their temperature dependence. Chang, Davidson, and Vincow²¹ studied similar problems from nonempirical calculations and depicted the presence of the incomplete following from the contour maps of the localized C-H bond orbitals at various bending angles, θ . Here, we have considered the role of the incomplete following for the shape of methyl radical.

It is noteworthy that the above differences in the electron-cloud following and preceding among CH_3^- , CH_3^+ , and CH_3 are attributable chiefly to the single molecular orbital (MO), namely the highest occupied (HO) MO of CH_3^- , though all the MO's are different slightly among these molecules. This fact is important in the reasoning of the Walsh rule²² from the force concept.^{5a-c, 9, 23}

In order to confirm the above discussions on the roles of the electron-cloud following and preceding in determining the shapes of CH_3^- , CH_3^+ , and CH_3 , we calculated in Tables I and II the Hellmann-Feynman forces acting on carbons and protons respectively at $\theta = 30$ and 61° (equal to the out-of-plane angle of NH_3). These forces are the elements in the same direction as Q_C and Q_H and are referred to as bending forces. A positive force accelerates the bending movement and a negative force resists it. When $\theta = 0^\circ$ (planar), the

(17) In Figure 4, the small increase and decrease in electron density in the small regions immediately below and above the carbon atom are shown from the examination of data to belong to the exchange density between carbon and hydrogen. This may be understood from a comparison of Figure 4 with Figure 2a. Therefore, it may be said that the electron cloud in the C-H bond region of CH_3 at $\theta = 30^\circ$ follows incompletely near proton but precedes near carbon the displacement of proton. However, when CH_3 is bent to $\theta = 61^\circ$, the extent of the incomplete following increases rapidly in almost all the regions along the C-H bond. These facts may correspond to the small out-of-plane bending force constant of methyl radical (see ref 13 and 15c). The contour map obtained at $\theta = 61^\circ$ is omitted for brevity.

(18) T. Itoh, K. Ohno, and M. Kotani, *J. Phys. Soc. Jap.*, **8**, 41 (1953).

(19) P. C. H. Jordan and H. C. Longuet-Higgins, *Mol. Phys.*, **5**, 121 (1962).

(20) D. M. Schrader and M. Karplus, *J. Chem. Phys.*, **40**, 1593 (1964); D. M. Schrader, *ibid.*, **46**, 3895 (1965); see also R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).

(21) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 5596 (1970).

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

(23) C. A. Coulson and B. M. Deb, *Int. J. Quantum Chem.*, **5**, 411 (1971); B. M. Deb, *Rev. Mod. Phys.*, **45**, 22 (1973).

Table I. Bending Force Acting on Carbon^a (au)

Molecule	Out-of-plane angle (θ), deg	AD force	EC(C-H) force ^b	EGC force	Total force
CH_3^-	30	1.516	-0.920	0.044	0.640
	61	2.913	-1.868	0.088	1.134
CH_3^+	30	-0.208	-0.261	0.290	-0.178
	61	-0.538	-0.632	0.729	-0.442
CH_3	30	0.631	-0.687	0.165	0.108
	61	1.026	-1.307	0.403	0.122

^a The force is parallel with the out-of-plane bending displacement of carbon, Q_C . ^b Vector sum of the three EC forces associated with the three C-H bonds.

bending force is equal to zero from symmetry. The densities used for the force calculations are the same as those used in drawing Figures 2 and 4. Since the Hellmann-Feynman force is very sensitive to the small inaccuracies included in the density used,²⁴⁻²⁶ these forces may be regarded as semiquantitative ones to this level of nonempirical wave functions.²⁷

In Table I, the preceding and the incomplete following of the electron clouds near carbon atoms manifest themselves in the values of the AD forces acting on the carbon atoms. The preceding in CH_3^- (Figure 2a) gives rise to the positive accelerating AD force, while the incomplete following in CH_3^+ (Figure 2b) causes the negative resisting AD force. The methyl radical is the median of CH_3^- and CH_3^+ and the small extent of preceding (Figure 4) gives correspondingly small positive AD force. The EC(C-H) force shown in Table I is the vector sum of the three EC forces associated with the three C-H bonds. As shown in paper I, the function of the EC(C-H) force is always to resist the out-of-plane displacement of carbon, Q_C . Since we neglected the differences in the C-H distances among CH_3^- , CH_3^+ , and CH_3 and among the configurations $\theta = 0$, 30 , and 61° , the values of the EC(C-H) forces shown in Table I have only a qualitative importance.²⁸ The meaning of the EGC force is approximately parallel with that of the GC force defined in paper I. Thus, the value increases with increasing positive charge of the molecule. As seen from the value of total force, CH_3^- is expected to be nonplanar in agreement with experiment.¹⁴ The dominant origin is the AD force which is a manifestation of the electron-cloud preceding. On the other hand, the shape of CH_3^+ is expected to be planar. This agrees also with the previous theoretical results.¹⁵ The AD and EC (C-H) forces are cooperative to make the molecule planar. The former is due to the electron-cloud incomplete following. However, for CH_3 , the value

(24) (a) L. Salem and E. B. Wilson, Jr., *J. Chem. Phys.*, **36**, 3421 (1962); (b) L. Salem and M. Alexander, *ibid.*, **39**, 2994 (1963); (c) J. Goodisman, *ibid.*, **45**, 4689 (1966); **47**, 334 (1967).

(25) A. C. Hurley, *Proc. Roy. Soc., Ser. A*, **226**, 170, 179, 193 (1954); **235**, 224 (1956); "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 161.

(26) (a) C. W. Kern and M. Karplus, *J. Chem. Phys.*, **40**, 1374 (1964); (b) R. F. W. Bader and A. D. Bandrauk, *ibid.*, **49**, 1666 (1968).

(27) The present nonempirical wave function based on the minimal set of Slater orbitals does not satisfy the Hellmann-Feynman theorem (see ref 25). The most important defects would be the neglect of polarization of electron cloud near proton, resulting zero AD force acting on proton (see ref 24), and the inholdness of translational invariance pointed out by Kern and Karplus (see ref 26).

(28) Due to the reason stated in the text, the value of the EC(C-H) force may include the stretching force which operates to lengthen or to shorten the C-H bond length.

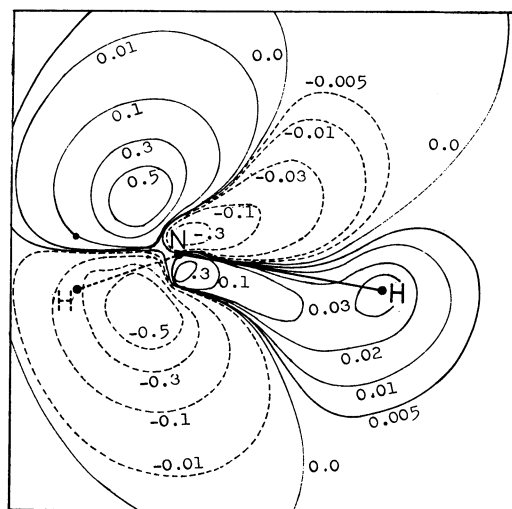
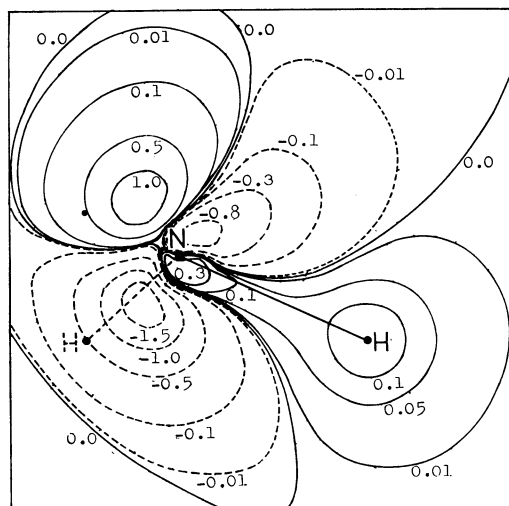
(a) $\theta = 30^\circ$ (Intermediate)(b) $\theta = 61^\circ$ (Equilibrium)

Figure 5. The contour maps showing the changes in the electron density of NH_3 induced by the out-of-plane bending displacements of $\theta = 30$ and 61° . The real and dotted lines show an increase and a decrease in density, respectively. The configuration at $\theta = 61^\circ$ corresponds to the equilibrium structure.

of total force gives incorrect prediction, since the experimental shape is planar.¹³ The reason seems to lie mainly in the incorrectness of the $\text{EC}(\text{C}-\text{H})$ force.

Table II shows the bending forces acting on protons. The $\text{EC}(\text{H}-\text{C})$ force is due to the electron cloud associated with the $\text{C}-\text{H}$ bond. It reflects the extent of the incomplete following and preceding of the $\text{C}-\text{H}$ bond electron cloud.²⁹ The preceding in CH_3^- (Figure 2a) gives rise to the positive accelerating $\text{EC}(\text{H}-\text{C})$ force, while the incomplete following in CH_3^+ (Figure 2b) causes the negative resisting $\text{EC}(\text{H}-\text{C})$ force. The methyl radical is the median of CH_3^- and CH_3^+ . When it is bent to $\theta = 61^\circ$, an appreciable resisting force due to the incomplete following arises. The vanishing $\text{EC}(\text{H}-\text{C})$ force at $\theta = 30^\circ$ is the result of cancellation.¹⁷ The $\text{EC}(\text{other})$ force denotes the EC force due to the interproton density. Its function is always to resist the bending movement (repulsive) and is similar to the re-

(29) If the electron cloud of the $\text{C}-\text{H}$ bond follows *completely* the movement of the $\text{C}-\text{H}$ axis, the resultant $\text{EC}(\text{H}-\text{C})$ force becomes equal to zero.

Table II. Bending Force Acting on Proton^{a,b} (au)

Molecule	Out-of-plane angle (θ), deg	$\text{EC}(\text{H}-\text{C})$ force	$\text{EC}(\text{other})$ force	EGC force	Total force
CH_3^-	30	0.0091	-0.0024	-0.0143	-0.0076
	61	0.0035	-0.0080	-0.0173	-0.0219
CH_3^+	30	-0.0148	-0.0013	-0.0056	-0.0217
	61	-0.0389	-0.0048	-0.0137	-0.0575
CH_3	30	0.0000	-0.0018	-0.0042	-0.0060
	61	-0.0181	-0.0061	-0.0020	-0.0263

^a The force is parallel with the out-of-plane bending displacement of the proton, Q_{H} . ^b The AD force is neglected for the proton in the present minimal Slater basis calculations.

pulsive interaction between two closed-shell atoms (*e.g.*, helium).^{5d,30} The EGC force also functions to resist the movement Q_{H} . An important remark on Table II is that the AD force acting on the proton is neglected in the present calculation. This is equivalent to the neglect of polarization of the electron cloud near the proton.²⁷ Since the incomplete following and preceding of the electron cloud near the proton manifest themselves not only through the $\text{EC}(\text{H}-\text{C})$ force but also through the AD force, the present neglect of the AD force may result in an underestimate of the effect of the electron-cloud following and preceding. The last column of Table II gives the sum of the $\text{EC}(\text{H}-\text{C})$, $\text{EC}(\text{other})$, and EGC forces. For CH_3^- , the sign of the total force contradicts with the experimental nonplanar shape.¹⁴ A reason may lie in the neglect of the AD force discussed above. For CH_3^+ , the total force predicts the correct planar shape.¹⁵ The $\text{EC}(\text{H}-\text{C})$ force coming from the electron-cloud incomplete following is the most important origin. For methyl radical, the total force gives also the correct prediction of planar shape.¹³ At $\theta = 61^\circ$, the $\text{EC}(\text{H}-\text{C})$ force due to the incomplete following is the most important origin.¹⁷

From the above discussions, the importance of the electron-cloud following and preceding in determining the shapes of AH_n molecules may be clear. In the out-of-plane bending movement defined in Figure 1, the occurrence of the electron-cloud incomplete following and preceding are the important origins of the planar and bent shapes, respectively. The formation of the atomic dipole on atom A in bending the molecule from planar shape is nothing else but the preceding or the incomplete following of the electron cloud near the central atom A. It causes the AD force on atom A which functions respectively to accelerate or to resist the out-of-plane displacement of atom A. The electron clouds belonging to the $\text{A}-\text{H}$ bonds exert the EC forces on atom A which always resist the out-of-plane displacement of the atom A (see paper I). The electron clouds near protons and in the $\text{A}-\text{H}$ bond regions also precede or follow incompletely the bending displacement of protons, depending on whether the molecule is stable in the pyramidal or planar shapes, respectively. This preceding or following causes the EC forces on protons which accelerate or resist the bending movement of protons, respectively. The formation of atomic dipoles on protons which causes the AD force is also expected to be important, though it is disregarded in the present calculations.

(30) L. Salem, *Proc. Roy. Soc., Ser. A*, **264**, 379 (1961).

Connection with Bent Bond in Equilibrium Structure

In this section, we consider the generality of the so-called "bent bond"^{19,31,32} in connection with the electron-cloud preceding discussed in the previous section. In order to clarify the discussion, let us take the NH_3 molecule as an example. Figure 5 shows the contour maps of the change in electron density obtained at $\theta = 30^\circ$ (intermediate) and 61° (equilibrium). They were calculated from the nonempirical SCF-MO's based on the minimal set of Slater orbitals.³³ The N-H length was held fixed at the experimental value (1.014 Å)³⁴ for both planar and pyramidal configurations.

As expected from the preceding discussions, the electron-cloud preceding is found in Figure 5a ($\theta = 30^\circ$) in the regions near nitrogen and along the N-H bond. The roles of these electron-cloud preceding are the same as those explained for CH_3^- (Figure 2a). Cohen and Coulson^{31b} suggested that this kind of distortion of the N-H bond orbital plays an important role for the intensity of the infrared spectrum. It is remarkable that the contour map of NH_3 (Figure 5a) is very similar to that of CH_3^- (Figure 2a). Since NH_3 and CH_3^- are isoelectronic, the similarity corresponds well to the previous reasoning of the Walsh rule²² from the ESF theory.^{5a-c}

On the other hand, when NH_3 is bent to its equilibrium shape ($\theta = 61^\circ$), the electron density in the region along the N-H axis becomes quite different from that obtained at $\theta = 30^\circ$ (compare Figures 5a and 5b). That is, the electron density near the proton becomes almost symmetric with respect to the N-H axis, as seen in Figure 5b. This is reasonable since the bending force acting on the proton must vanish at the equilibrium structure. However, a close examination of Figure 5b shows that the electron density in the region along the N-H axis is slightly distorted inwardly from the N-H axis. Namely, a small extent of the orbital preceding remains even in the equilibrium structure. This is nothing else than the bent bond sometimes pointed out previously.^{19,31,32}

The occurrence of the bent bond is naturally understood from the present standpoint. Since the force acting on protons should vanish at the equilibrium geometry, the interproton nuclear repulsive force acting in the reverse direction to Q_H (Figure 1) must be canceled out exactly by the force of electronic origin. From the similar consideration to that given in the preceding paper,² this is achieved effectively if the electron cloud near the proton and/or in the A-H bond region is distorted inwardly from the A-H axis.³⁵ This is

(31) See, for example, (a) F. O. Ellison and H. Shull, *J. Chem. Phys.*, **23**, 2348 (1955); (b) N. V. Cohen and C. A. Coulson, *Trans. Faraday Soc.*, **52**, 1163 (1956); (c) A. B. F. Duncan, *J. Chem. Phys.*, **27**, 423 (1957); (d) C. Edmiston and K. Ruedenberg, "Quantum Theory of Atoms, Molecules, and the Solid State," P.-O. Löwdin, Ed., Academic Press, New York, N. Y., 1966; (e) U. Kaldor, *J. Chem. Phys.*, **46**, 1981 (1967); (f) S. Rothenberg, *ibid.*, **51**, 3389 (1969); *J. Amer. Chem. Soc.*, **93**, 68 (1971); (g) M. D. Newton, E. Switkes, and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970).

(32) R. F. W. Bader and G. A. Jones, *Can. J. Chem.*, **41**, 586 (1963); *J. Chem. Phys.*, **38**, 2791 (1963).

(33) The exponents of Slater AO's are 7.5 for N(1s), 1.95 for N(2s) and N(2p), and 1.2 for H(1s), which are the same as those used by Kaldor and Shavitt, *J. Chem. Phys.*, **45**, 888 (1966).

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

(35) Bader and Jones (ref 32) calculated the electronic structures of H_2O and NH_3 from the criterion that the forces acting on the nuclei should vanish in the equilibrium structure. They concluded (especially

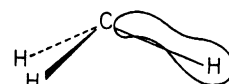
nothing else but the bent bond. The situation is very similar to that found for the orbital preceding discussed in the previous section. Therefore, the bent bond may be considered as a special example of the electron-cloud preceding in the bond region at equilibrium structure.

Recently, Kaldor,^{31e} Rothenberg,^{31f} and Newton, *et al.*,^{31g} have shown from nonempirical calculations of localized orbitals^{6a} that the bent bonds are seen even for the C-H bonds in ethane and ethylene. Although no direct connection in formulas seems to exist between the localized orbitals⁶ and the electron-cloud following and preceding, some intuitive connections do exist between them. In the next section, we deal with this problem.

Description by Means of the Localized Orbital Method

The concept of the "localized" orbital⁶ is intrinsically based on the chemical idea that the electron cloud of a molecule can be partitioned into approximately independent and transferable units such as bonds, lone pairs, cores, etc.³⁶ As shown in the previous² and present papers, the electron-cloud incomplete following and preceding are expressed chiefly through the behaviors of the "local" electron clouds associated with bonds, atoms, etc., during the changes in nuclear configurations. Connecting these two ideas, one may naturally expect that the characteristics of the electron-cloud incomplete following and preceding should be included in the localized orbitals obtained at the nuclear configurations apart from the equilibrium structure. Here, we show from some examples the correctness of this expectation.

Chang, Davidson, and Vincow²¹ calculated from nonempirical wave functions the localized C-H bond orbitals of the methyl radical at various out-of-plane angles. The general feature of the localized C-H bond orbitals obtained by them at the pyramidal configuration may be illustrated as



which shows clearly the characteristic of the incomplete following depicted from the contour map shown in Figure 4.

On the other hand, Kaldor reported an interesting feature of the localized orbitals of NH_3 .^{31e} He reported that the localized N-H bond orbital obtained at the planar structure does *not* lie on the N-H axis, but its bonding hybrid on nitrogen points 18° away from the N-H axis. At the equilibrium structure, the bonding hybrid points only 5.5° inwardly from the N-H axis (bent bond). In Figure 6, we show the density contour

for H_2O that to achieve electrostatic equilibrium, the angle between the bonding orbitals is necessarily less than the structural bond angle (bent bond).

(36) The meaning of the energy localized orbital is, due to Edmiston and Ruedenberg,^{6a} that they approach most closely the behavior postulated for the Hartree orbitals in the Hartree-Fock space. Since the Hartree orbitals do not satisfy the Pauli principle, the electrons in the Hartree orbitals are distinguishable (or countable) from each other. Therefore, the electron pairs in the localized orbitals may be interpreted to be most distinguishable from other electron pairs in the molecule in the sense that they receive minimum average nonclassical interaction. Note that the localization of orbitals is a device of interpretative purpose. It takes advantage of the freedom of unitary transformation among Hartree-Fock orbitals and does not change the total wave function of the system. (See, for example, K. Hirao and H. Nakatsuji, *J. Chem. Phys.*, **59**, 1457 (1973); K. Hirao, *ibid.*, in press.)

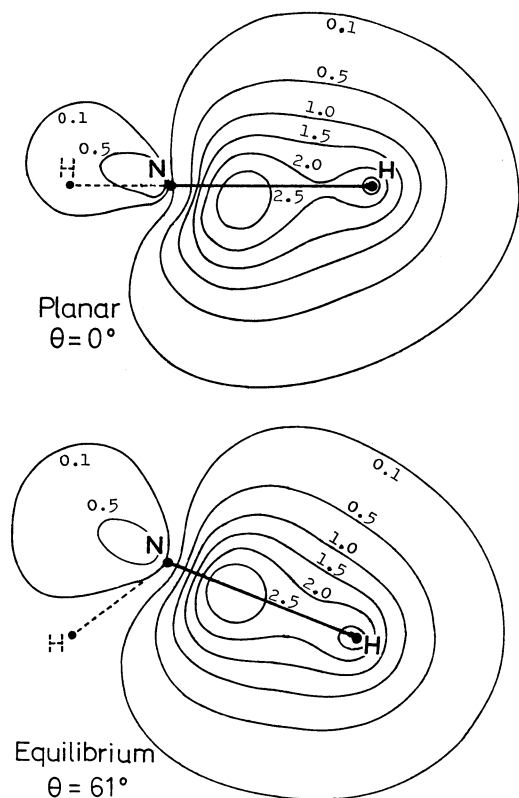


Figure 6. The density contour maps of the localized N-H bond orbitals of NH_3 , obtained at the planar and equilibrium pyramidal configurations. The basic orbitals are due to Kaldor (ref 31e).

maps of the localized N-H bond orbitals of NH_3 . They are calculated from the localized orbitals reported by Kaldor.^{31e} Notwithstanding that the total electron density associated with planar structure is symmetric with respect to the NH_3 plane, the localized N-H bond orbital of planar NH_3 is distorted away from the N-H axis.³⁷ This makes us conceive the bond-orbital preceding which would occur if the molecule was bent from planar configuration (see Figure 5a). On the other hand, the localized N-H bond orbital at equilibrium structure is almost symmetric with respect to the N-H axis. In closer examination, a small bent bond character may be found.

Figure 7 is the density contour maps of the localized lone-pair orbitals of NH_3 , which were calculated also from the orbitals reported by Kaldor.^{31e} The orbital associated with the planar NH_3 is also distorted away from the pure p-type orbital³³ which is symmetric with respect to the NH_3 plane. This is also enough to make us conceive the preceding of the one-center electron cloud which would occur if NH_3 was bent from the planar configuration (compare with Figure 5). The right-hand side of Figure 7 corresponds to the lone-pair orbital at equilibrium structure.

The above results of the localized orbitals of the planar NH_3 shown in Figures 6 and 7 mean that the electron pairs in the planar NH_3 are most amenable to intuitive (semiclassical) chemical interpretation of "bond" and "lone pair" in the distorted forms rather than in the undistorted symmetrical forms.³⁶

(37) Due to C. Trindle and O. Sinanoğlu, *J. Chem. Phys.*, **49**, 65 (1968), this kind of distortion of localized orbital arises from the fact that the electron repulsion integrals are dependent not only on the principal quantum numbers of basic AO's but also on the azimuthal quantum numbers of AO's (s, p, d, etc.).

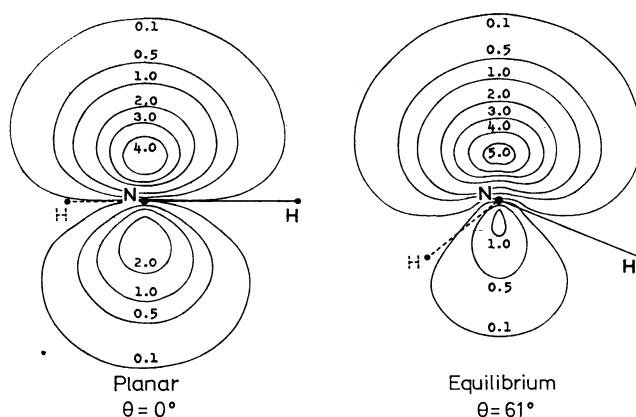


Figure 7. The density contour maps of the localized lone-pair orbitals of NH_3 , obtained at the planar and equilibrium pyramidal configurations. The basic orbitals are due to Kaldor (ref 31e).

These examples show that the localized orbital method is also a useful tool to describe the electron-cloud following and preceding. However, it should be noted that the force calculated from a single localized orbital bears no physical reality.³⁶ The force acting on a nucleus must be calculated from the total electron density of the system. The electron-cloud following and preceding are the behaviors of the total electron density of the system under the change in nuclear configuration.

Connection with the Second-Order Jahn-Teller Theory

In the preceding paper,² it was shown that the electron-cloud incomplete following and preceding could be expressed separately by the perturbation theory, if the unperturbed nuclear configuration was chosen at the saddle point of the potential surface of the system. Namely, in the expression of the electron density correct to first order in small nuclear displacement δQ

$$\rho(\mathbf{r}, Q) = \rho(\mathbf{r}, Q_0) + 2\delta Q \sum_k' \left[\int \rho_{0k}(\mathbf{r}, Q_0) \mathbf{f}(\mathbf{r}, Q_0) d\mathbf{r} / (E_k - E_0) \right] \rho_{0k}(\mathbf{r}, Q_0) \quad (3)$$

the first and second terms are responsible for the electron-cloud incomplete following and preceding, respectively, if Q_0 is chosen at the saddle point of the potential surface. The notations in eq 3 are the same as those used in the preceding paper.

Now, let us consider the shape of the AH_3 molecule from eq 3. The saddle point on the potential surface of the AH_3 molecule may be chosen at the planar configuration and δQ is here a small out-of-plane bending displacement which has A_2'' symmetry (see Figure 1). The molecular orbitals of the planar AH_3 molecule may be written in the order of energy increase as

$$\begin{aligned} \varphi_1(a_1') &= s + (h_1 + h_2 + h_3) \\ \varphi_2(e_x') &= p_x + (2h_1 - h_2 - h_3) \\ \varphi_2(e_y') &= p_y + (h_2 - h_3) \\ \varphi_3(a_2'') &= p_z \\ \varphi_4(a_1') &= s - (h_1 + h_2 + h_3) \\ \varphi_5(e_x') &= p_x - (2h_1 - h_2 - h_3) \\ \varphi_5(e_y') &= p_y - (h_2 - h_3) \end{aligned} \quad (4)$$

where we considered only the valence AO's and omitted the coefficients. The x - y axis lies on the AH_3 plane and s , p_x , p_y , and p_z AO's are associated with the central atom A and h is the $1s$ AO of hydrogen. The MO pairs φ_2 , φ_2' and φ_5 , φ_5' are degenerate and belong to the e' symmetry. Since the operator $f(\mathbf{r}, Q_0)$ in eq 3 has the same symmetry as δQ , it belongs to A_2'' symmetry. As Bader,⁷ Bartell,⁸ and Pearson⁹ did, we presume that only the lowest transition from highest occupied (HO) MO to lowest unoccupied (LU) MO contributes to the second term of eq 3.

For the six-valence-electron molecules, the symmetry of the lowest transition is $(e')(a_2'') = E''$, which is different from the symmetry of $f(\mathbf{r}, Q_0)$. Then, the second term of eq 3 vanishes in this approximation. This means that the electron cloud follows incompletely the nuclear displacement δQ . The nuclei at the displaced configuration $Q = Q_0 + \delta Q$ receive the restoring forces to planar structure. Therefore, the shapes of the AH_3 molecules having six-valence electrons (e.g., BH_3 , CH_3^+) are expected to be planar, which accords with experiments.^{13,34} On the other hand, for the molecules having eight valence electrons, the symmetry of the lowest transition is $(a_2'')(a_1') = A_2''$, which coincides with the symmetry of $f(\mathbf{r}, Q_0)$. Then, the magnitude of the second term of eq 3 is expected to become appreciable. Therefore, the electron cloud of the eight-valence-electron molecule may precede the out-of-plane bending displacement δQ . The nuclei at the displaced configuration $Q = Q_0 + \delta Q$ receive the forces that accelerate the bending displacement. Thus, the shapes of the AH_3 molecules having eight-valence electrons (e.g., NH_3 , CH_3^-) are expected to be pyramidal, which accords with experiments.^{13,34} It is noteworthy that the transition density between the HO-MO and LU-MO has the characteristic of the electron cloud preceding depicted in Figures 2a and 5a. In the illustrations given in Figure 8, the left-hand-side two figures show sketches of the HO-MO (φ_3) and LU-MO (φ_4) given in eq 4. The plus and minus signs denote the nodal character. The product of these MO's gives rise to the transition density $\rho_{34} = \varphi_3\varphi_4$. The right-hand-side figure shows a sketch of the contour map of the transition density ρ_{34} . The plus and minus signs show an increase and a decrease in density, respectively, and the arrows show the direction of δQ . Namely, the increase and decrease in the regions above and below the central atom show a formation of atomic dipole in the direction of δQ_A . The change in electron density in the regions above and below the A-H bonds shows a distortion of the A-H bond electron clouds in the direction of δQ_H . These are nothing else than the electron-cloud preceding (compare with Figures 2a and 5a). For other molecules having the valence electron number different from six and eight, the discussions are similar to the above ones. When the valence electron number is odd, the situation becomes rather diffi-

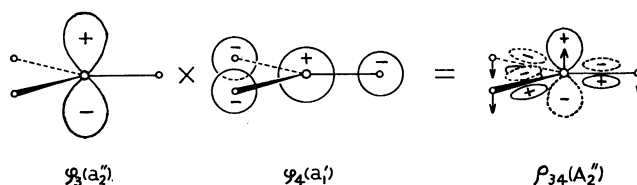


Figure 8. Illustration of the transition density ρ_{34} which is obtained as a product of the HO-MO φ_3 and the LU-MO φ_4 of the eight-valence-electron AH_3 molecule. In the left-hand-side two figures, the plus and minus signs denote the nodal character of the MO's φ_3 and φ_4 . The right-hand-side figure shows a sketch of the contour map of the transition density ρ_{34} . The plus and minus signs show an increase and a decrease in density, respectively, and the arrows show the direction of the small displacement δQ .

cult in this perturbational approach. Salem and Wright^{10b} applied similar considerations to the above ones to the accounts of unimolecular reaction paths.

As may be noticed, the above discussions give the density aspect of the second-order Jahn-Teller theory due originally to Bader⁷ and extended by Bartell,⁸ Pearson,⁹ and Salem.¹⁰ They used the energy criterion, while we have used here the knowledge of the roles of the electron-cloud incomplete following and preceding through force concept. Of course, these two approaches are essentially identical and lead to the same results.

Summary

In the present paper, we have shown the importance of the electron-cloud following and preceding in determining the shapes of molecules through force concept. They appear in the out-of-plane bending displacements of AH_n molecules as a formation of atomic dipole on atom A and as a distortion of the A-H bond electron cloud away from the A-H axis. The AD and EC forces are shown very important as manifestations of the electron-cloud following and preceding. Some results are also obtained which support the previous reasoning of the Walsh rule from the force concept.

The generality of the bent bond in equilibrium structure is shown as a special example of the electron-cloud preceding in the bond region. The characteristics of the electron-cloud incomplete following and preceding are shown to be included in the localized orbitals obtained at the configurations apart from the equilibrium structure. However, it should be noted that the force calculated from a single localized orbital bears no physical reality. Lastly, the perturbational description of the electron-cloud incomplete following and preceding is applied to the shapes of AH_3 molecules. The treatment corresponds to the density approach of the second-order Jahn-Teller theory.

Acknowledgment. The author thanks very much Messrs. S. Kato and S. Yamabe for calculating the non-empirical SCF-MO's with their program. He acknowledges Professors T. Yonezawa and H. Kato for their encouraging interests on the present work.