Common Natures of the Electron Cloud of the System Undergoing Change in Nuclear Configuration

Hiroshi Nakatsuji[1]

Contribution from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. Received June 12, 1973

Abstract: Two general features of the electron cloud of the system undergoing the change in nuclear configuration are deduced from the Hellmann–Feynman and integral Hellmann–Feynman theorems. First is the *electron-cloud incomplete following* which means that the centroids of the local electron clouds near the moving nuclei follow incompletely the movements of the nuclei. Its function is to *resist* the nuclear movements. The other is the *electron-cloud preceding* which means that the centroids of the local electron clouds near the moving nuclei precede the positions of the nuclei in the direction of the movement. Its function is to *accelerate* the movements of the nuclei. The former is common to the changes from stable to unstable configurations and the latter is common to the reverse changes. Therefore, the most important application of the former is expected to be found in the fields of molecular vibrations around equilibrium positions and that of the latter in the fields of chemical reactions and long-range dispersion forces. These features of electron cloud reorganization can be expressed separately with the perturbation theory, if the unperturbed nuclear configuration is chosen at the saddle point on the potential surface of the system. For systems composed of homopolar nuclei, these features of the electron clouds are included chiefly in the interference density introduced by Ruedenberg. Moreover, the atomic dipole (AD), exchange (EC), and extended gross charge (EGC) forces presented in the previous paper are interpreted as the intraatomic interference force, interatomic interference force, and quasiclassical force, respectively. Therefore, the electron-cloud incomplete following and preceding manifest themselves chiefly in the forms of the AD and EC forces. This is another reason of the importance of the AD and EC forces.

The conceptual utility of the electrostatic Hellmann–Feynman theorem[2] is well known. The theorem describes the force acting on a nucleus in a molecule as being due to the classical electrostatic interactions of the positively charged nucleus with the negatively charged electron cloud and with the other positively charged nuclei of the molecule. In developing an electrostatic force (ESF) theory in the previous articles,[3] the physical simplicity and visuality of the theorem have been fully utilized. Since the ESF theory deals with the phenomena which are described through the movements of the nuclei of a system, it seems very important as a basis of the theory to grasp the general features of the electron cloud of the system under the change in nuclear configuration. This problem is treated in the present paper on the basis of the Hellmann–Feynman[2] and integral Hellmann–Feynman[4] theorems.

Linnett and Wheatley[5a] were perhaps the first persons who pointed out the possibility of distortions of bond-forming orbitals in the course of molecular vibrations. Many investigations followed to point out the importance of this effect for infrared intensities,[5] temperature dependence of esr hfs constants,[6] etc. Quantum

mechanical calculations were also performed for small hydrides and confirmed the distortions of bond orbitals during molecular vibrations.[7] Bader and his coworkers studied the effect of relaxation of the molecular charge distribution on vibrational force constants of diatomic molecules from the Hellmann–Feynman force picture.[8] They characterized the manner of relaxation as depending on whether the bond is covalent or ionic. Anderson and Parr derived some interesting formulas connecting between the vibrational force constants and the electron density distributions.[9] In our previous papers,[3] the distortion of the bond orbital was depicted during the internal rotation of H_mABH_n molecules.

Feynman[2b] suggested that the van der Waals forces might be due to the simultaneous inward polarizations of the individual atomic densities with the induced atomic dipoles (and then the AD forces) being proportional to $1/R^7$. Hirschfelder and Eliason[10] confirmed this prediction for the van der Waals forces between two hydrogen atoms using a wave function correct to second order in perturbation. Bader and Chandra[11] traced the reorganization of the electron cloud of the two interacting hydrogen atoms along the reaction coordinate, $H + H \rightarrow H_2$, and found that the attractive force due to this kind of inward polarization of atomic density continues

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

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

(3) (a) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345, 354, 2084 (1973), which are referred to in the text as papers I, II, and III; (b) H. Nakatsuji, T. Kuwata, and A. Yoshida, *J. Amer. Chem. Soc.*, **95**, 6894 (1973).

(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).

(5) (a) J. W. Linnett and P. J. Wheatley, *Trans. Faraday Soc.*, **45**, 33, 39 (1949); (b) D. C. McKean and P. N. Schatz, *J. Chem. Phys.*, **24**, 316 (1956); (c) N. V. Cohen and C. A. Coulson, *Trans. Faraday Soc.*, **52**, 1163 (1956); (d) C. A. Coulson and M. J. Stephens, *ibid.*, **53**, 272 (1957); (e) W. D. Jones and W. T. Simpson, *J. Chem. Phys.*, **32**, 1747 (1960).

(6) 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).

(7) (a) T. Itoh, K. Ohno, and M. Kotani, *J. Phys. Soc. Jap.*, **8**, 41 (1953); (b) P. C. H. Jordan and H. C. Longuet-Higgins, *Mol. Phys.*, **5**, 121 (1962); (c) S. Y. Chang, E. R. Davidson, and G. Vincow, *J. Chem. Phys.*, **52**, 5596 (1970).

(8) R. F. W. Bader and A. D. Bandrauk, *J. Chem. Phys.*, **49**, 1666 (1968); R. F. W. Bader and J. L. Ginsburg, *Can. J. Chem.*, **47**, 3061 (1969).

(9) A. B. Anderson, N. C. Handy, and R. G. Parr, *J. Chem. Phys.*, **50**, 3635 (1969); A. B. Anderson and R. G. Parr, *ibid.*, **53**, 3375 (1970); **55**, 5490 (1971); A. B. Anderson, *ibid.*, **57**, 4143 (1972); **58**, 381 (1973).

(10) J. O. Hirschfelder and M. A. Eliason, *J. Chem. Phys.*, **47**, 1164 (1967); see also A. A. Frost, University of Wisconsin Theoretical Chemistry Report, WIS-TCI-204, Dec 1966.

(11) R. F. W. Bader and A. K. Chandra, *Can. J. Chem.*, **46**, 953 (1968); see also A. K. Chandra and R. Sundar, *Mol. Phys.*, **22**, 369 (1971).

to be dominant until the separation of 2.6 Å. At separations less than 2.6 Å, the electron density flows rapidly into the region common to both hydrogens. We have reported previously some interesting features of the reorganization of the electron cloud during the dimerization reaction of two methyl radicals.[3b]

The general features of the electron clouds of the systems reported in these articles maybe classified into two types. One is the incomplete following type and the other is the preceding type. The former means that some centroids of the local electron cloud near the moving nucleus follow incompletely the movement of the nucleus. It is found for the nuclear displacements from stable to unstable configurations. For example, Chang, Davidson, and Vincow[7c] depicted that the C–H bond orbitals of the methyl radical incompletely follow the out-of-plane bending movement of protons. Another example was reported in paper III for the internal rotation of ethylene. On the other hand, the preceding type means that some centroid of the local electron cloud near the moving nucleus precedes the position of the nucleus in the direction of the movement. It is found for the movements from unstable to stable nuclear configurations. An example was reported in paper III for the internal rotation of the π–π* excited state of ethylene. Another example is seen in whole stages of the combination reaction of two hydrogen atoms.[10,11] The centroids of the electron clouds in the regions near the protons always precede the positions of protons in the direction of the reaction coordinate. Some interesting preceding behaviors of the electron cloud were also found out previously for the dimerization reaction of two methyl radicals.[12] In the present paper the above two features of the electron cloud of the system under the change in nuclear configuration are referred to as *electron-cloud following* and *electron-cloud preceding*. The orbital following and preceding discussed in paper III are the special cases of the present electron-cloud following and preceding.[13]

In the next section, the generality of the electron-cloud following and preceding in the course of the change in nuclear configuration is considered through the Hellmann–Feynman[2] and integral Hellmann–Feynman[4] theorems. The electron-cloud following and preceding are expressed in some special cases with perturbation theory. A relation between these features of electron cloud and the interference partitioning of density due to Ruedenberg[14] is examined. The physical meaning of the atomic dipole (AD), exchange (EC), and extended gross charge (EGC) forces presented

in paper I is reconsidered in connection with the quasiclassical and interference densities.[14] The importance of the electron-cloud following and preceding will be exemplified in the succeeding paper for molecular shapes.[15]

Generality of the Electron-Cloud Incomplete Following and Preceding

Here we consider the change in nuclear coordinate Q of a system from initial (i) to final (f) states (see Figure 1). We refer to the intermediate nuclear configuration between the points i and f as configuration α and the final one as configuration β. In general, Q is expressed by some appropriate linear combination of the nuclear coordinates of the system.[16] The nucleus A is supposed to be an important element of Q.

Assuming the Born–Oppenheimer approximation,[17] one may derive easily from the Schrödinger equation the following Hellmann–Feynman[2] and integral Hellmann–Feynman[4] theorems. In eq 1, $\mathbf{F}_A{}^\alpha$ is the force

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

$$\Delta E(\alpha \rightarrow \beta) = \int \rho_{\alpha\beta}(\mathbf{r}_1) \Delta \mathcal{H}_{ne}(r_1) d\mathbf{r}_1 + \Delta V_{nn} \quad (2)$$

acting on the nucleus A at the nuclear configuration α. $\rho_\alpha(\mathbf{r}_1)$ is the density of the electron cloud associated with the configuration α. It is defined in three dimensional space by

$$\rho_\alpha(\mathbf{r}_1) = N \int \Psi_\alpha(x_1, x_2, \ldots, x_N) \times$$
$$\Psi_\alpha(x_1, x_2, \ldots, x_N) ds_1 dx_2 \ldots dx_N \quad (3)$$

where Ψ_α is the (correct) wave function of the system at the configuration α. s and x are the spin and spin–space variables, respectively; N is the total number of electrons. Other notations in eq 1 are trivial and the same as those in paper I. In eq 2, $\Delta E(\alpha \rightarrow \beta)$ is the change in total energy for the isoelectronic process $\alpha \rightarrow \beta$. $\rho_{\alpha\beta}$ is the one-electron normalized transition density defined from the wave functions Ψ_α and Ψ_β associated with the nuclear configurations α and β

$$\rho_{\alpha\beta}(\mathbf{r}_1) = \frac{N}{S_{\alpha\beta}} \int \Psi_\alpha(x_1, x_2, \ldots, x_N) \times$$
$$\Psi_\beta(x_1, x_2, \ldots, x_N) ds_1 dx_2 \ldots dx_N \quad (4)$$

where $S_{\alpha\beta}$ is the overlap integral between Ψ_α and Ψ_β. $\Delta \mathcal{H}_{ne}(r_1)$ denotes the change in nuclear–electron attraction operator $\mathcal{H}_{ne}(r_1)$.

$$\Delta \mathcal{H}_{ne}(r_1) = \mathcal{H}_{ne}{}^\beta(r_1) - \mathcal{H}_{ne}{}^\alpha(r_1) \quad (5)$$

ΔV_{nn} is the change in nuclear–nuclear repulsion energy.

First, let us consider the generality of the electron-cloud preceding. For the present, we consider the change in nuclear configuration satisfying the following two conditions. (a) It is a monotonous change from unstable to stable configuration. (b′) The change accompanies some increase in nuclear repulsion (the

(12) In the dimerization reaction of two methyl radicals, the following three types of the electron-cloud preceding were found to be cooperative to drive the reaction.[3b] First is the preceding of the electron cloud into the overlap region between the two carbons, which induces the attractive EC force on carbon. Second is the preceding of the C–H bond orbital in the direction of the bending displacement of each methyl radical. Third is the preceding of the electron cloud in the vicinity of the carbon atom, which induces the attractive AD force on carbon. Among these, the last one is remarkable in that it is induced as a result of the bending movement of each methyl radical. This is mostly responsible for the crucial role of the change in molecular geometry in the course of this reaction. See ref 3b.

(13) The term "orbital following" has been used in the previous articles (e.g., ref 6) to refer to the extent of incomplete following of the *bond orbital* during molecular vibrations. However, since the concept dealt with in the present paper cannot be included in this terminology, we dare to call the present concepts as "electron-cloud following and preceding."

(14) K. Ruedenberg, *Rev. Mod. Phys.*, 34, 326 (1962).

(15) H. Nakatsuji, *J. Amer. Chem. Soc.*, 96, 30 (1974).
(16) E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955.
(17) M. Born and J. R. Oppenheimer, *Ann. Phys. (Leipzig)*, 84, 457 (1927).
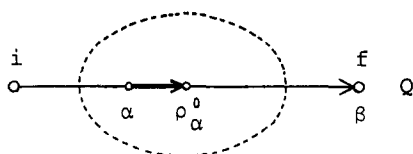
Figure 1. Illustration of the electron-cloud preceding in the Hellmann–Feynman picture. The dotted ellipse means the electron cloud of the system associated with the nuclear configuration α. ρ_α^0 shows the projection of the centroid of the force density on the coordinate Q, and the arrow pointing from α to ρ_α^0 means the electronic part of the driving force acting at the configuration α.

(a)

(b)

Figure 2. Illustrations of the electron-cloud preceding in the integral Hellmann–Feynman picture. (a) The ellipse illustrates the transition density $\rho_{\alpha\beta}(r_1)$ between the wave functions associated with the configurations α and β. The density is higher in the doubly hatched region near β than in the singly hatched region near α. (b) The ellipse corresponds to the wave function associated with the configuration α and is responsible for the electron-cloud preceding. The circle centered on β corresponds to the wave function of the final state. The hatched region shows the high-density region of the transition density $\rho_{\alpha\beta}$. Note that the hatched region is nearer to the position β than to the position α.

second terms of eq 1 and 2).[18] For example, these changes are seen in the following phenomena: (i) molecular structure and molecular vibration, e.g., the changes from unstable linear or planar shapes to stable bent or pyramidal ones of AX_n molecules; (ii) reactions forming stable (ground state) diatomic molecules from two neutral atoms $(A + B \rightarrow A\text{–}B)$; (iii) approaches of two neutral atoms into the regions of dispersion forces.
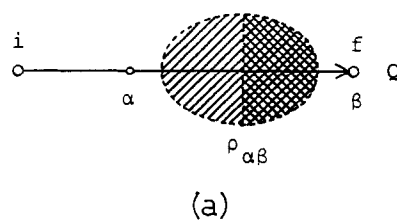
The physical simplicity and visuality of the Hellmann–Feynman and integral Hellmann–Feynman theorems permit us to grasp general features of the electron cloud of the system under the above change in nuclear configuration. In the following paragraphs, we consider the general feature of the electron cloud of the system first through the Hellmann–Feynman theorem and second through the integral Hellmann–Feynman theorem.

In the course of the changes characterized by the condition (a), the constituent nuclei A of the system at the configuration α must receive the driving forces $F_A{}^\alpha$ in the direction of the coordinate of the change, Q. From the condition (b′), the dominant origin of the driving forces $F_A{}^\alpha$ should come from the electronic part of eq 1. In the Hellmann–Feynman picture, this is possible if and only if the centroid of the three dimensional force density defined by $(r_{A1}/r_{A1}{}^3)\rho_\alpha(r_1)$ precedes the position of the nucleus A at α in the direction of the coordinate Q. This situation may be illustrated as Figure 1. The point ρ_α^0 in Figure 1 corresponds to the projection of this centroid on the coordinate Q, and the arrow pointing from α to ρ_α^0 shows the electronic part of the driving force acting at the configuration α. The force due to the nuclear part is reverse to and smaller than this force. Furthermore, this preceding of force density is expected to occur if the centroid of the electron density $\rho_\alpha(r_1)$ within some local region near the nucleus A precedes the position of the nucleus A in the direction of Q. The locality comes from the weight $r_{A1}/r_{A1}{}^3$ which appears in the force density and falls off rapidly with an increase in r_{A1}. This preceding of the local electron cloud is nothing else but the electron-cloud preceding defined in the previous section.[19]
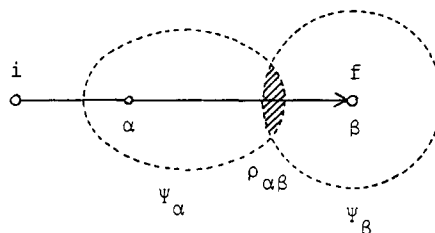
The integral Hellmann–Feynman theorem given by eq 2 provides also interesting information on the transition density $\rho_{\alpha\beta}(r_1)$. For the changes defined by the conditions (a) and (b′), the destabilization energy

coming from the nuclear part ΔV_{nn} must be surpassed effectively by the stabilization energy due to the electronic part, resulting in the total stabilization energy $\Delta E(\alpha \rightarrow \beta)$ for the change. Referring to eq 2 and 5, we see that the nuclear–electron attraction operator associated with the nuclear configuration β contributes to stabilization, while that associated with α contributes to destabilization. Therefore, the effective stabilization due to the electronic part of eq 2 is possible if the transition density $\rho_{\alpha\beta}(r_1)$ defined by eq 4 is more dense in the neighborhood of moving nuclei specified by β rather than those specified by α. In other words, the centroid of the transition density $\rho_{\alpha\beta}(r_1)$ should be closer to the nuclear configuration β than to the configuration α. This situation may be illustrated as Figure 2a, where the density is higher in the doubly hatched region than in the singly hatched region. The situation like Figure 2a is possible if the electron-cloud preceding occurs at the configuration α. An illustration is given in Figure 2b, where the hatched region corresponds to the transition density $\rho_{\alpha\beta}(r_1)$.

Now, a remark is necessary for the condition (b′). As may be clear from the above discussions, the condition (b′) is introduced in order to assure that the electronic part of eq 1 or 2 takes a dominant part of the driving force $F_A{}^\alpha$ or the stabilization energy $\Delta E(\alpha \rightarrow \beta)$ throughout the change. In other words, the electron-cloud preceding may occur even if the condition (b′) is replaced by the following more unrestrictive condition (b). That is, (b) throughout the change, the electronic parts of eq 1 and 2 remain larger in magnitude than the nuclear parts. If a change satisfies the condition (b′), it satisfies automatically the condition (b). Thus, *the electron-cloud preceding is expected to occur during the change in nuclear configuration satisfying the above conditions (a) and (b).* Since the condi-

(18) As shown in later paragraph, the condition (b′) can be replaced by the more loose condition.

(19) The correspondence between the preceding of the force density and that of the electron density is usually pretty good. For homopolar systems, this is due to the fact that the EGC force is small in comparison with the AD and EC forces (see ref 3), since, as shown later, the AD and EC forces represent chiefly the effect of the electron-cloud incomplete following and preceding.

tions (a) and (b) are certainly very unrestrictive, the generality of occurrence of the electron-cloud preceding may be understood.

In the above discussions, the "locality" of the electron-cloud preceding results from the forms of the operator. Namely, the operator r_{A1}/r_{A1}^3 falls off rapidly with an increase in r_{A1}. On the other hand, we have derived from eq 1 the three well-defined and yet pictorial forces such as the AD, EC, and EGC forces.[3] Among these, the importance of the AD and EC forces has been recognized in various applications of the ESF theory hitherto given.[3] Since both of the AD and EC forces are due to the local electron clouds near the nucleus A,[20] the former being due to the polarization of the electron cloud belonging to the AO's of the atom A and the latter being due to the electron cloud belonging to the A–B bond region, the electron-cloud preceding discussed above is expected to manifest itself chiefly in the forms of the AD and EC forces. This is also expected for the electron-cloud incomplete following discussed later. The smallness of the EGC force[3,20] seems to support this expectation and corresponds well to the situations demanded by condition (b). These points are examined again in the later section in connection with the theoretical relation of the AD and EC forces with the interference density introduced by Ruedenberg.[14]

An example of the electron-cloud preceding is seen for the internal rotation of the π–π^* excited state of ethylene. The left-hand side of Figure 3 gives an illustration of the general feature of the C–H bond electron cloud reported in paper III. In this case, Q corresponds to the internal rotation from planar to bisected configurations. α corresponds to the configuration of intermediate rotational angle and β to the bisected configuration (stable configuration of the π–π^* excited state[21]). As have been shown in paper III, the electron clouds associated with the C–H bonds precede the rotational displacement of protons in the direction of Q (orbital preceding). It causes the EC forces acting on protons which accelerate the movement of protons along Q. Moreover, the resulting bent C–H bonds at α can overlap effectively with the final straight C–H bonds at β in the manner similar to that illustrated in Figure 2. It is noteworthy that the present rotational movement Q does not fulfill the condition (b') but satisfies the condition (b).

The generality of the occurrence of the electron-cloud incomplete following is derived similarly from the Hellmann–Feynman and integral Hellmann–Feynman theorems for the reverse changes in nuclear configuration to the above cases. Namely, *the electron-cloud incomplete following is expected to occur during the change in nuclear configuration satisfying the following two conditions.* (a) It is a monotonous change from stable to unstable configuration. (b) Throughout the change, the electronic parts of eq 1 and 2 remain larger in magnitude than the nuclear parts. Condition (b) is satisfied automatically if the following condition (b') is fulfilled by the change. Namely, (b') the change accompanies some decrease in nuclear repulsion.

As an example of the electron-cloud incomplete fol-
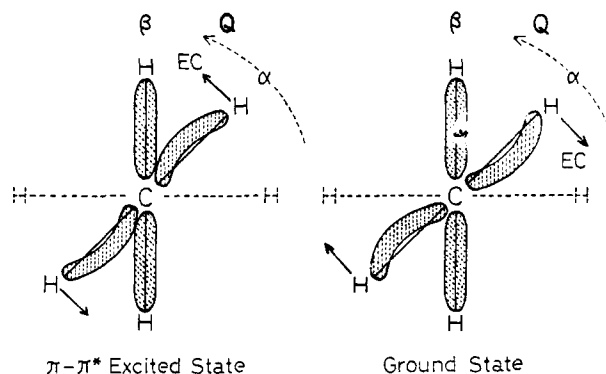

π–π^* Excited State   Ground State

Figure 3. Newman diagram type illustrations of the general features of the C–H bond electron clouds during the internal rotation of the ground and π–π^* excited states of ethylene. The dotted C–H bond belongs to the back-side methylene group. Q is the coordinate of the internal rotation from planar to bisected configurations. α corresponds to the configuration of the intermediate rotational angle and β to the bisected configuration. The arrows starting from protons at α show the EC forces acting on protons due to the preceding (π–π^* excited state) and the incomplete following (ground state) of the C–H bond electron clouds.

lowing, we give in the right-hand side of Figure 3 an illustration of the general feature of the C–H bond electron clouds of the ground state of ethylene, which has been reported in paper III. The definitions of Q, α, and β are the same as those given in the previous paragraph. In this case, the electron clouds associated with the C–H bonds follow incompletely the rotational movement of protons (orbital following). It induces the EC forces on protons which resist the movement of protons along Q. Moreover, the overlap between the resulting bent C–H bonds at α and the straight C–H bonds at β is smaller than the overlap which would be expected if the C–H bond orbitals followed *completely* the rotational movement Q, resulting in straight C–H bonds at α. This is the reason of unstabilization caused from the rotational movement Q in the integral Hellmann–Feynman picture.

Perturbational Description

The electron-cloud incomplete following and preceding discussed in the previous section have some connection with the second-order Jahn–Teller theory due originally to Bader[22] and extended by Bartell,[23] Pearson,[24] and Salem.[25] Taking a small change in nuclear configuration of a system as a perturbation, Bader[22] obtained an expression of the electron density correct to first order in perturbation as

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

$$(E_k - E_0)]\rho_{0k}(\mathbf{r},Q_0) \quad (6)$$

where $\rho(\mathbf{r},Q)$ is the electron density of the system at the nuclear configuration $Q = Q_0 + \delta Q$ with δQ very small. E_0 and E_k denote the energies of the ground and excited states of the system at the nuclear configuration Q_0. $\rho_{0k}(\mathbf{r},Q_0)$ is the transition density be-

(20) The EGC force represents the interaction of the nucleus A with the electron cloud belonging to the other nuclei B.

(21) R. G. Wilkinson and R. S. Mulliken, *J. Chem. Phys.*, 23, 1895 (1955); R. McDiarmid and E. Charney, *ibid.*, 47, 1517 (1967).

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

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

(24) R. G. Pearson, *J. Amer. Chem. Soc.*, 91, 1252, 4947 (1969); *J. Chem. Phys.*, 52, 2167 (1970); 53, 2968 (1970); *Chem. Phys. Lett.*, 10, 31 (1971).

(25) (a) L. Salem, *Chem. Phys. Lett.*, 3, 99 (1969); (b) L. Salem and J. S. Wright, *J. Amer. Chem. Soc.*, 91, 5948 (1969).

tween these states. $\mathbf{f}(\mathbf{r}, Q_0)$ is the force operator defined at the nuclear configuration Q_0

$$\mathbf{f}(\mathbf{r}, Q_0) = -(\partial \mathcal{K}/\partial Q)_{Q_0} \tag{7}$$

In eq 6, the first term represents the unperturbed density associated with the nuclear configuration Q_0 and the second term (called hereafter $\Delta\rho$) is responsible for the reorganization of the unperturbed density due to the small nuclear displacement δQ. Its integration over all space is equal to zero.

The force acting on the constituent nucleus at the displaced coordinate Q is obtained from eq 6 as

$$\mathbf{F}(Q) = \int \rho(\mathbf{r}, Q_0)\, \mathbf{f}(\mathbf{r}, Q_0)\mathrm{d}\mathbf{r} + \delta Q \int \rho(\mathbf{r}, Q_0) \times$$

$$\left[\frac{\partial \mathbf{f}(\mathbf{r}, Q)}{\partial Q}\right]_{Q_0} \mathrm{d}\mathbf{r} + 2\delta Q \sum_k{}' \left[\int \rho_{0k}(\mathbf{r}, Q_0)\mathbf{f}(\mathbf{r}, Q_0)\mathrm{d}\mathbf{r}\right]^2 \Big/$$

$$(E_k - E_0) \tag{8}$$

where we have used the following first-order relation.

$$\mathbf{f}(\mathbf{r}, Q) = \mathbf{f}(\mathbf{r}, Q_0) + \left[\frac{\partial \mathbf{f}(\mathbf{r}, Q)}{\partial Q}\right]_{Q_0} \delta Q$$

In eq 8, the first and second terms represent the forces originating from the unperturbed density. They also include the nuclear repulsive force. The third term represents the force coming from the reorganized density $\Delta\rho$. Since the element of summation in the third term is positive, the force due to $\Delta\rho$ is always in the same direction as Q. Namely, it always facilitates the nuclear displacement of the system along Q. On the other hand, the force due to the second term resists this displacement, since the term represents the force acting on the *displaced* nuclei due to the *unperturbed* electron cloud $\rho(\mathbf{r}, Q_0)$. If we choose the coordinate Q_0 at the saddle point of the potential surface of the system, the force due to the first term vanishes.[26]

Therefore, in the special cases where Q_0 is the *saddle point* of the potential surface,[26] the first and second terms of eq 6 correspond to the electron-cloud incomplete following and preceding, respectively. The first term represents the *rigid* electron cloud which is unchanged by the nuclear displacement. The second term represents that part of the electron cloud which always precedes the small displacement of nuclei, δQ. As the sum of these two terms, the total electron cloud $\rho(\mathbf{r}, Q)$ may follow incompletely in some cases or may precede in other cases the movement of the nuclei. Note, however, that if we choose the point Q_0 at the intermediate point between the saddle points, the unperturbed electron cloud $\rho(\mathbf{r}, Q_0)$ itself has already some characteristics of the electron-cloud preceding, when the change Q is from unstable to stable configurations.

Connection with the Interference Partitioning of Density and the Meaning of the AD, EC, and EGC Forces

In this section, a relation is described between the electron-cloud incomplete following and preceding and the interference partitioning of density introduced by Ruedenberg.[14] Then, the physical meaning of the AD, EC, and EGC forces given in paper I is reconsidered in

connection with the quasiclassical and interference densities.[14]

Ruedenberg partitioned the electron density of a system into the quasiclassical and interference densities (interference partitioning).[14,27] Although his partitioning was made with respect to atomic and interatomic regions, it seems more convenient to modify it slightly to the partitioning into atomic orbital (AO) and interatomic orbital regions.[28]

The electron density of a system defined by eq 3 may be expanded by a suitable (extended) AO basis set $\{\chi_r\}$ as

$$\rho(\mathbf{r}) = \sum_{r,s} P_{rs} \chi_r(\mathbf{r})\chi_s(\mathbf{r}) \tag{9}$$

where P_{rs} is the density matrix element between AO's χ_r and χ_s and the suffixes α and 1 are omitted for brevity. Following the formulation given by Ruedenberg,[14] one may partition the electron density of a system into the quasiclassical density $\rho^{\mathrm{CL}}(\mathbf{r})$ and the interference density $\rho^{\mathrm{I}}(\mathbf{r})$ as

$$\rho(\mathbf{r}) = \rho^{\mathrm{CL}}(\mathbf{r}) + \rho^{\mathrm{I}}(\mathbf{r}) \tag{10}$$

$$\rho^{\mathrm{CL}}(\mathbf{r}) = \sum_r N_r \chi_r(\mathbf{r})\chi_r(\mathbf{r}) = \sum_A \sum_r{}^A N_{rA}\chi_{rA}(\mathbf{r})\chi_{rA}(\mathbf{r}) \tag{11}$$

$$\rho^{\mathrm{I}}(\mathbf{r}) = \sum_{r(\neq)s}\sum P_{rs}\left\{\chi_r(\mathbf{r})\chi_s(\mathbf{r}) - \frac{S_{rs}}{2}[\chi_r(\mathbf{r})\chi_r(\mathbf{r}) + \chi_s(\mathbf{r})\chi_s(\mathbf{r})]\right\} \tag{12}$$

where N_r is the atomic orbital population defined by Mulliken[29] as

$$N_r = \sum_s P_{rs} S_{rs} \tag{13}$$

The quasiclassical density is composed of the *simple superposition* of the AO density having the electron population N_r. Its integration over all space leads to the total number of electrons, N, of the system.

$$\int \rho^{\mathrm{CL}}(\mathbf{r})\mathrm{d}\mathbf{r} = N \tag{14}$$

The interference density is responsible for the reorganization of the quasiclassical density due to the interference effects[14] and then its integration over all space vanishes.

$$\int \rho^{\mathrm{I}}(\mathbf{r})\mathrm{d}\mathbf{r} = 0 \tag{15}$$

As seen from eq 11, the quasiclassical density $\rho^{\mathrm{CL}}(\mathbf{r})$ is *locally symmetric* about the respective nuclei, since the element $\chi_{rA}(\mathbf{r})\chi_{rA}(\mathbf{r})$ is symmetric with respect to the nucleus A. On the other hand, the interference density is not at all locally symmetric with respect to the position of the nucleus; if both of the AO's χ_r and χ_s belong to the same atom, it gives rise to the atomic dipole, and if χ_r and χ_s belong to different atoms, it is responsible for the accumulation

(26) The nuclear configuration corresponding to the maximum symmetry capable for a system is a frequent example of the saddle point on the potential surface.

(27) See also C. W. Wilson, Jr., and W. A. Goddard III, *Chem. Phys. Lett.*, **5**, 45 (1970); *Theor. Chim. Acta*, **26**, 195, 211 (1972).

(28) If we follow the original Ruedenberg's partitioning, the AD force is included in the quasiclassical part. Then, the van der Waals force between hydrogen atoms is expressed as being due to the quasiclassical effect (see ref 10). However, it seems more reasonable from the common sense of quantum chemistry to express the van der Waals force between hydrogen atoms as being due to the interference effect between two atoms.

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

or the decrease of electron density in the interatomic region, depending on the sign of P_{rs}. Therefore, *for the homopolar systems, the occurrence of the electron-cloud incomplete following and preceding is chiefly attributable to the interference density $\rho^1(\mathbf{r})$.* As shown in the previous[3b] and succeeding papers,[15] the formation of atomic dipole and the accumulation of electron density in the interatomic region are the typical examples of the electron-cloud preceding. However, there are some cases where the quasiclassical density $\rho^{CL}(\mathbf{r})$ also shares an important part of the electron-cloud following and preceding. A typical example is a transfer of an electron from the electropositive atom to the electronegative one in the ionic atomic pair, which is an example of the electron-cloud preceding in the course of the ionic bond formation.

The interference partitioning of density discussed above leads naturally to the interference partitioning of force into "quasiclassical force" ($\mathbf{F}_A{}^{CL}$) and "interference force" ($\mathbf{F}_A{}^I$). For simplicity, we consider first an interacting system composed of two atoms A and B. Substituting eq 10-12 into eq 1, we obtain the expressions of the quasiclassical and interference forces as

$$\mathbf{F}_A = \mathbf{F}_A{}^{CL} + \mathbf{F}_A{}^I \qquad (16)$$

$$\mathbf{F}_A{}^{CL} = Z_A \left\{ \sum_r{}^B N_{rB} \langle \chi_{rB} | \mathbf{r}_A/r_A{}^3 | \chi_{rB} \rangle - Z_B \mathbf{R}_{AB}/R_{AB}{}^3 \right\} \qquad (17)$$

$$\mathbf{F}_A{}^I = Z_A \left\{ \sum_{r(\neq)s}{}^A \sum_s{}^A P_{rAsA} \langle \chi_{rA} | \mathbf{r}_A/r_A{}^3 | \chi_{sA} \rangle + 2 \sum_r{}^A \sum_s{}^B P_{rAsB} \langle \chi_{rA} | (\mathbf{r}_A/r_A{}^3)_0 | \chi_{sB} \rangle \right\} \qquad (18)$$

where the net-exchange force integral is tentatively defined as[30]

$$\langle \chi_{rA} | (\mathbf{r}_A/r_A{}^3)_0 | \chi_{sB} \rangle \equiv \langle \chi_{rA} | \mathbf{r}_A/r_A{}^3 | \chi_{sB} \rangle - \tfrac{1}{2} S_{rAsB} \langle \chi_{sB} | \mathbf{r}_A/r_A{}^3 | \chi_{sB} \rangle \qquad (19)$$

In eq 19, we have used the fact that the one-center coulombic integrals of the types $\langle \chi_{rA} | \mathbf{r}_A/r_A{}^3 | \chi_{rA} \rangle$ vanish by symmetry for the usual s, p, d, ... basis AO's. With reference to paper I, one may notice that the first and second terms of eq 18 are nothing else but the AD and EC forces, respectively. The difference in the expression of the net-exchange force integral is due to the invariance property and is not essential.[30] Therefore, we can identify the AD, EC, and EGC forces as

quasiclassical force = EGC force

intraatomic interference force = AD force (20)

interatomic interference force = EC force

Expression 20 gives other physical meanings of the AD, EC, and EGC forces. Namely, the EGC force is considered to represent the quasiclassical force which might be expected to act on the nucleus A *if* the atom B, having the electron population N_{rB} in its respective AO's

χ_{rB}, was placed at the distance R_{AB} *without perturbing* the electron cloud of the system. In this hypothetical situation, the electron clouds belonging to the atoms A and B, which are locally symmetric with respect to the nuclei A and B, may "contact" but do not interfere with each other. On the other hand, the AD and EC forces are responsible for the effects of reorganization of the quasiclassical density due to the interference effect.[14] Therefore, *when the interaction between atoms A and B is not ionic, the AD and EC forces represent chiefly the effect of the electron-cloud following and preceding.* This is another reason for the importance of the AD and EC forces. Actually, as shown in the previous papers,[3,11] the EC force is the most important driving force in the formation of covalent chemical binding. The AD force is shown to be important in the initial stage of the reaction.[3b,11] In the case of the destructive interference,[14] the EC force is responsible for the exchange repulsion[31] and the so-called steric repulsion and steric hindrance. However, in the case of ionic pair, the EGC force is also expected to be appreciable,[32] since in this case the EGC force represents also an important part of the electron-cloud incomplete following and preceding. When the interatomic distance R_{AB} becomes very large, the EC force decreases exponentially and becomes negligible at large separation. Therefore, the AD and EGC force is responsible for the origin of the long-range forces.[33]

For the cases in which more than two atoms are included in the system, the first relation of eq 20 does not exactly hold, since the following three-center net-exchange force integrals appear in expression 18. In our

$$\langle \chi_{rB} | (\mathbf{r}_A/r_A{}^3)_0 | \chi_{sC} \rangle = \langle \chi_{rB} | \mathbf{r}_A/r_A{}^3 | \chi_{sC} \rangle - \tfrac{1}{2} S_{rBsC} \{ \langle \chi_{rB} | \mathbf{r}_A/r_A{}^3 | \chi_{rB} \rangle + \langle \chi_{sC} | \mathbf{r}_A/r_A{}^3 | \chi_{sC} \rangle \} \qquad (21)$$

partitioning of force, these three-center terms are included in the EGC force. However, these integrals are expected to be very small, since for these integrals the Mulliken approximation is expected to hold in good approximation.[34] Therefore, the physical meaning of the EGC force given above will suffer little change even in the general cases.

Bader and his coworkers partitioned also the electronic part of the Hellmann–Feynman force into atomic, overlap, and screening forces.[8,32] These forces are different from the present AD, EC, and EGC forces.[35] Therefore, the above connection of the AD, EC, and EGC forces with the interference and quasiclassical forces does not apply to their partitioning of force. It is noteworthy that the reason that we have been able to obtain the relation shown in eq 20 lies in the introduction of the net-exchange force integral given by eq

(30) The second term of eq 19 destroys the invariance of the net-exchange force integral to the rotation of local coordinate axes. Then, in paper I, the second term of eq 19, $\tfrac{1}{2} S_{rAsB} \langle \chi_{sB} | \mathbf{r}_A/r_A{}^3 | \chi_{sB} \rangle$ was replaced by the term $\tfrac{1}{2} S_{rAsB} \langle s_B | \mathbf{r}_A/r_A{}^3 | s_B \rangle$, where s_B is the s type AO belonging to the same shell as χ_{sB}. The magnitudes of these two terms are almost the same in usual cases. Then, it may well be approved to use the expressions 17–19 for the interpretative purpose.

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

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

(33) For the interactions of the two neutral S-state atoms (*e.g.*, hydrogen), the EGC force vanishes and only the AD force is responsible for the dispersion forces.

(34) When the Mulliken approximation holds, the integral given by eq 21 vanishes.

(35) Although the atomic force due to Bader, *et al.*, has a quite similar physical meaning to the present AD force, except for a factor of $1/R_{AB}{}^2$ (R_{AB} is the interatomic distance), the overlap and screening forces are different from the present EC and EGC forces. They defined the overlap force in diatomic molecules using the simple exchange force integral (not using the net-exchange force integral) and the screening force using the screening force integral (two-center coulombic integral). See ref 32.

19. The physical meaning of the net-exchange force integral has been stated in paper I.[36]

Conclusions

In the present paper, the two common features of the electron clouds of the systems under the movements in nuclear configuration are discussed on the basis of the Hellmann–Feynman and integral Hellmann–Feynman theorems. The electron-cloud incomplete following is expected to occur during the change in nuclear configuration from stable to unstable configurations. Its function is to resist this movement. The most frequent examples of such a nuclear movement are found in molecular vibrations around equilibrium positions. On the other hand, the electron-cloud preceding will occur during the change in nuclear configuration from unstable to stable ones. Its function is to accelerate this nuclear movement. The most important applications will be found in the fields of chemical reactions and long-range dispersion forces. The *orbital* following and preceding discussed in paper III are the special case of

(36) See ref 18 of paper I.

the present *electron-cloud* following and preceding, respectively. In the former terminology, the "orbital" denotes the electron cloud associated with a bond.

These features of the electron cloud reorganization can be expressed separately by the perturbation theory if the unperturbed nuclear configuration is chosen at the saddle point on the potential surface of the system. For systems composed of homopolar nuclei, the occurrence of the electron-cloud incomplete following and preceding is chiefly attributable to the interference density introduced by Ruedenberg. Moreover, the atomic dipole (AD), exchange (EC), and extended gross charge (EGC) forces presented in paper I are interpreted as the intraatomic interference force, interatomic interference force, and quasiclassical force, respectively. Therefore, the electron-cloud incomplete following and preceding manifest themselves chiefly in the forms of the AD and EC forces. This is another reason for the importance of the AD and EC forces.

Electron-Cloud Following and Preceding and the Shapes of Molecules

Hiroshi Nakatsuji[1]

*Contribution from the Department of Hydrocarbon Chemistry,
Faculty of Engineering, Kyoto University, Kyoto, Japan. Received June 12, 1973*

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–Feynman[3] and integral Hellmann–Feynman[4] theorems

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

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

(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