

$\pi \rightarrow \pi^*$ transition energies for the $\pi\pi^*$ states that are well described by a minimal basis set.¹⁹ To obtain good vertical excitation energies to diffuse excited states, such as the V state in ethylene, one must modify the integral approximation to allow more flexible basis sets.

For an approximate integral method to be useful in describing interesting chemical processes, it must provide good results in conjunction with correlated wave functions. Since the available approximations have

(19) W. R. Wadt and W. A. Goddard III, unpublished results.

been based on the HF wave function and are not always reliable, even when used with HF wave functions, the results with correlated wave functions cannot be expected to be very good. This appears to be the case. It is clear that new approximate integral methods must be developed in the context of suitably correlated wave functions. If the initial wave function cannot correctly describe the system, how can the integral approximations be expected to be properly balanced? We are presently developing and analyzing integral approximations with correlated wave functions.

Electrostatic Force Theory for a Molecule and Interacting Molecules. IV. Long-Range Forces between Two Atoms

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Abstract: The electrostatic force (ESF) theory which was shown previously to be useful for *molecular structures* and *chemical reactions* is here applied to *long-range forces*, using the same laboratory fixed coordinate system. In the ESF theory, the basic concepts are common to all of these important phenomena. The origins of the long-range forces between two well-separated atoms are shown to be the atomic dipole (AD) and the extended gross-charge (EGC) forces. For the long-range forces between two neutral S-state atoms, only the AD force is responsible for the leading terms. If one of the interacting atoms is a bare nucleus, the long-range force can be obtained only from the EGC force. In a perturbative treatment, the n th order corrections to the AD and EGC forces are obtained from the n th order and $(n - 1)$ th order corrections to the electron density, respectively. These long-range AD and EGC forces are calculated for two simple systems: the H(1s)–H⁺ and H(1s)–H(2p) systems. Both of the AD and EGC forces are shown to be very important. Excellent agreements are obtained between the energetic and force treatments in the final numerical values. However, the theoretical origins and the interpretations of the long-range forces are quite different from those of the energetic theories. The differences between these standpoints are discussed in some detail. The necessity of the "higher order" wave function for the calculation of the Hellmann–Feynman force does not mean the "complexity" of the results. The results preserve the *conceptual simplicity* of the ESF theory.

Recently, there seems to be some renewed interests on the use of the electrostatic Hellmann–Feynman theorem^{2,3} for many chemically important phenomena.^{4–7} One motive common to these studies lies in the conceptual simplicity of the theorem written in a laboratory fixed coordinate system as

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

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(2) H. Hellmann, "Einführung in die Quantenchemie," Deuticke, Vienna, 1937, p 285.

(3) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939).

(4) B. M. Deb, *Rev. Mod. Phys.*, **45**, 22 (1973), and the references cited therein.

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

(6) A. B. Anderson, N. C. Handy, and R. G. Parr, *J. Chem. Phys.*, **50**, 3634 (1969); A. B. Anderson and R. G. Parr, *ibid.*, **53**, 3375 (1970), and the succeeding papers.

(7) (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, *ibid.*, **95**, 6894 (1973); (c) H. Nakatsuji, *ibid.*, **96**, 24, 30 (1974).

where the notations are the same as those in the previous reports.⁷ Namely, the force acting on a nucleus A of a system is given through the classical electrostatics for the interactions among charged nuclei and the electron cloud, if a reasonably good⁸ electron density is obtained by quantum-mechanical calculations.

For the long-range interactions, Feynman³ stated in his original report a conjecture that the van der Waals forces would be due to the simultaneous inward polarizations of the electron clouds of the interacting atoms, the extent of the polarization being proportional to $1/R^7$. After this report, no calculations had been done for 27 years until Frost⁹ applied this theorem to the long-range interactions of the H(1s)–H⁺ and H(1s)–H(1s) systems. However, his numerical results were unsatisfactory when he used the approximate wave functions for the calculations. It is well known that

(8) (a) A. C. Hurley, *Proc. Roy. Soc., Ser. A*, **226**, 170, 179, 193 (1954); "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 161; (b) L. Salem and E. B. Wilson, Jr., *J. Chem. Phys.*, **36**, 3421 (1962).

(9) A. A. Frost, University of Wisconsin Theoretical Chemistry Report, WIS-TCI-204, Dec 1966.

the calculation of the Hellmann–Feynman force requires more knowledge of the wave function than the energetic theory does,⁸ except for some special cases.¹⁰ Just after the report of Frost, Hirschfelder and Eliason¹¹ obtained a very accurate value of the leading term of the $1/R$ expansion for the long-range interaction of the ground state H_2 . Their results confirmed the validity of Feynman's original conjecture.^{3,12} Moreover, Bader and Chandra¹³ showed that the inward polarization of the electron density, essentially similar to the above one, continued to be the dominant origin of the attractive force between two hydrogen atoms until the separation of 5 au (2.6 Å).

In this paper, we will extend the electrostatic force (ESF) theory,⁷ which was shown previously to be useful for molecular structures and chemical reactions, to the long-range interactions between two atoms. The simplicity of the subject serves to clarify the concept of the ESF theory. First, the origins of the long-range forces are considered in the next section from the viewpoint of the ESF theory. Some perturbation theoretic aspects are also discussed. The conjecture of Feynman³ and the results of Hirschfelder and Eliason¹¹ are shown to correspond to the special simpler case. Then, we apply the results to the long-range forces between a proton and a hydrogen atom and between 1s and 2p hydrogen atoms. Although these systems are much easier to apply than the ground state H_2 , there seems to be no satisfactory applications to the best of our knowledge. The basic wave functions are calculated by the method of Coulson¹⁴ for the H_2^+ system and of Kołos¹⁵ for the excited H_2 system. For both systems, excellent agreements are obtained between the energetic and the present force treatments in the final numerical values, although the theoretical origins and the interpretations of the long-range forces are quite different between these two standpoints. The energetic accounts of these long-range interactions are found in every textbook.¹⁶ Some extensive energetic studies of the H(1s)–H(2p) system were reported, for example, by Linder and Hirschfelder,^{17a} Mulliken,^{17b} and Kołos.¹⁵

Origins of the Long-Range Forces between Two Atoms

In this section, we consider the origins of the long-range forces between two atoms from the viewpoint of the ESF theory. As previously,⁷ we use the laboratory fixed coordinate system throughout this paper.

First, let us divide the force operator in a perturbative

(10) (a) R. Yaris, *J. Chem. Phys.*, **39**, 863 (1963); (b) E. Steiner, *ibid.*, **59**, 2427 (1973).

(11) (a) J. O. Hirschfelder and M. A. Eliason, *J. Chem. Phys.*, **47**, 1164 (1967); (b) J. O. Hirschfelder and W. J. Meath, *Advan. Chem. Phys.*, **12**, 3 (1967).

(12) See also ref 10b.

(13) R. F. W. Bader and A. K. Chandra, *Can. J. Chem.*, **46**, 953 (1968).

(14) (a) C. A. Coulson, *Proc. Roy. Soc. Edinburgh, Sect. A*, **61**, 20 (1941); (b) C. A. Coulson and C. M. Gillam, *ibid.*, **62**, 360 (1948).

(15) W. Kołos, *Int. J. Quantum Chem.*, **1**, 169 (1967). In the course of the calculations, we found some numerical errors in the B_{8s} coefficients of his Table IV. The correct values are -388.80 , -654.75 , -740.94 , -763.22 , -767.97 , -769.76 , -770.28 , -770.41 , -770.43 , -770.44 , and -770.44 . Consequently, the values of B_s in Table VI are -14285.8 for 1s2p $^1\Sigma_u^+$, $^3\Sigma_g^+$, -16814.7 for 1s2p $^1\Sigma_g^+$, $^3\Sigma_u^+$, -7472.9 for 1s2p $^1\Pi_g$, $^3\Pi_u$, and -8709.6 for 1s2p $^1\Pi_u$, $^3\Pi_g$. Drs. T. Stephens and A. Dalgarno also found these numerical errors (private communication from Dr. W. Kołos).

(16) For example, H. Margenau and N. Kestner, "Theory of Intermolecular Forces," Pergamon Press, London, 1967.

(17) (a) B. Linder and J. O. Hirschfelder, *J. Chem. Phys.*, **28**, 197 (1958); (b) R. S. Mulliken, *Phys. Rev.*, **120**, 1674 (1960).

sense. Two atoms A and B are well-separated by a distance R . The Hamiltonian of the system appearing in eq 1 may be divided into

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{H}^1 \quad (2a)$$

$$\mathcal{H}^0 = \sum_{\mu} (-1/2\Delta_{\mu} - Z_A/r_{A\mu}) + \sum_{\mu>\mu'} 1/r_{\mu\mu'} + \sum_{\nu} (-1/2\Delta_{\nu} - Z_B/r_{B\nu}) + \sum_{\nu>\nu'} 1/r_{\nu\nu'} \quad (2b)$$

$$\mathcal{H}^1 = - \sum_{\nu} Z_A/r_{A\nu} - \sum_{\mu} Z_B/r_{B\mu} + \sum_{\mu,\nu} 1/r_{\mu\nu} + Z_A Z_B/R \quad (2c)$$

where Z_A is the nuclear charge of the atom A and other notations are self-evident. \mathcal{H}^0 is the sum of the Hamiltonians of the separated atoms and \mathcal{H}^1 the perturbative interaction Hamiltonian. Since at large distances we can neglect the electron exchange, the electrons μ and ν are assigned to the atoms A and B, respectively. Similarly, the force operator associated with the nucleus A may be divided into

$$\mathcal{F}_A = \mathcal{F}_A^0 + \mathcal{F}_A^1 \quad (3a)$$

$$\mathcal{F}_A^0 = -\partial\mathcal{H}^0/\partial R_A = Z_A \sum_{\mu} f_{A\mu}^0 \quad (3b)$$

$$\mathcal{F}_A^1 = -\partial\mathcal{H}^1/\partial R_A = Z_A (\sum_{\nu} f_{A\nu}^1 - Z_B/R^2) \quad (3c)$$

where

$$f_{A\mu}^0 = z_{A\mu}/r_{A\mu}^3 \text{ and } f_{A\nu}^1 = z_{A\nu}/r_{A\nu}^3 \quad (4)$$

In eq 3 and 4 and hereafter, we consider only the z-directional force because of the symmetry of the system (z direction is the coordinate pointing to the other nucleus). The operator \mathcal{F}_A^0 and its one-electron operator $f_{A\mu}^0$ are the zeroth-order force operators, whereas \mathcal{F}_A^1 and $f_{A\nu}^1$ are the interaction (first-order) force operators. This distinction is very useful in the perturbative treatment.

Now, let us rewrite the electrostatic force (ESF) theory⁷ so as to be appropriate for the long-range forces. It may be reasonable to presume that the exact one-electron density function $\rho(\mathbf{r}_1)$ of the system can be expanded by an extended atomic orbital (AO) basis set $\{\chi_r\}$ which is centered at each nucleus as

$$\rho(\mathbf{r}) = \sum_r \sum_s P_{rs} \chi_r(\mathbf{r}) \chi_s(\mathbf{r}) \quad (5)$$

These basic AO's need not be the eigenfunctions of the Hamiltonian of the separated atoms or some approximations to it (e.g., hydrogenic or Hartree–Fock operator). They are, for example, the complete orthonormal set of AO's used by Löwdin and Shull¹⁸ and Hirschfelder and Löwdin,¹⁹ for which we can avoid the treatment of the otherwise rather annoying continuum wave functions. Decomposing the force given by eq 1 with respect to the regions of the density function, we obtain the expressions of the atomic dipole (AD), exchange (EC), and extended gross-charge (EGC) forces first introduced in paper I.⁷

$$F_A = F_A(\text{AD}) + F_A(\text{EC}) + F_A(\text{EGC}) \quad (6a)$$

(18) P.-O. Löwdin and H. Shull, *Phys. Rev.*, **101**, 1730 (1956).

(19) J. O. Hirschfelder and P. O. Löwdin, *Mol. Phys.*, **2**, 229 (1956); **9**, 491 (1966).

$$F_A(\text{AD}) = Z_A \sum_{\tau(\infty)}^A \sum_{\tau(\infty)}^B P_{\tau A_s A} \langle r_A | f_{A1} | s_A \rangle \quad (6b)$$

$$F_A(\text{EC}) = 2Z_A \sum_{\tau}^A \sum_{\tau}^B P_{\tau A_s B} \left\{ \langle r_A | f_{A1} | s_B \rangle - \frac{1}{2} \langle r_A | s_B \rangle \langle s_B | f_{A1} | s_B \rangle \right\} \quad (6c)$$

$$F_A(\text{EGC}) = Z_A \left\{ \sum_{\tau}^A \sum_{\tau}^B P_{\tau A_s B} \langle r_A | s_B \rangle \langle s_B | f_{A1} | s_B \rangle + \sum_{\tau}^B \sum_{\tau}^B P_{\tau B_s B} \langle r_B | f_{A1} | s_B \rangle - Z_B / R^2 \right\} \quad (6d)$$

where $F_A = F_{A_2}$ and $f_{A1} = z_{A1}/r_{A1}$.³ r_A in the integral means $\chi_{\tau A}$, A being the center of the AO.

At large separations, the overlap integrals $\langle r_A | s_B \rangle$ and the two-center exchange integrals $\langle r_A | f_{A1} | s_B \rangle$ vary as $\exp(-2R)$ and become negligible with respect to terms which vary as powers of $1/R$. Therefore, F_A -(EC) and the first term of F_A (EGC) may be neglected at large separations. Moreover, noting that the integrals in the AD and EGC forces include only the AO's of the atoms A and B, respectively, and that the electron exchange can be neglected, we can replace the operators f_{A1} in (6b) and (6d) by f_{A1}^0 and f_{A1}^1 of eq 4, respectively.^{19a} Thus, at large separations, eq 6 reduces to

$$F_A = F_A(\text{AD}) + F_A(\text{EGC}) \quad (7a)$$

$$F_A(\text{AD}) = Z_A \sum_{\tau(\infty)}^A \sum_{\tau(\infty)}^B P_{\tau A_s A} \langle r_A | f_{A1}^0 | s_A \rangle \quad (7b)$$

$$F_A(\text{EGC}) = Z_A \left\{ \sum_{\tau}^B \sum_{\tau}^B P_{\tau B_s B} \langle r_B | f_{A1}^1 | s_B \rangle - Z_B / R^2 \right\} \quad (7c)$$

Equations 7b and 7c can also be written in the following equivalent expressions

$$F_A(\text{AD}) = \langle \Psi | \mathcal{F}_A^0 | \Psi \rangle = Z_A \int \rho_A(\mathbf{r}_1) f_{A1}^0 \, d\mathbf{r}_1 \quad (8a)$$

$$F_A(\text{EGC}) = \langle \Psi | \mathcal{F}_A^1 | \Psi \rangle = Z_A \left\{ \int \rho_B(\mathbf{r}_1) f_{A1}^1 \, d\mathbf{r}_1 - Z_B / R^2 \right\} \quad (8b)$$

where Ψ is the exact wave function of the perturbed system and $\rho_A(\mathbf{r}_1)$ is the electron density associated with the perturbed atom A. The sum of ρ_A and ρ_B satisfies

$$\rho(\mathbf{r}) = \rho_A(\mathbf{r}) + \rho_B(\mathbf{r}) \quad (9)$$

No cross term appears in eq 9 because the overlap between the AO's with different centers can be neglected for this system.

As seen from eq 7 or 8, the *origins* of the long-range forces between two well-separated atoms are the *AD and EGC forces*. The former represents the force due to the *polarization* of the electron cloud of the atom A induced by the long-range interaction with the atom B. The centroid of the polarized electron density attracts the nucleus A in the direction of the polarization.^{7c} The EGC force represents the force due to the electrostatic interactions of the nucleus A with the electron density of the interacting atom B and with the nucleus B.

In a perturbative sense, the AD force is obtained from the operation of the zeroth-order force operator, \mathcal{F}_A^0 and f_{A1}^0 , and the EGC force from that of the interaction (first-order) force operator, \mathcal{F}_A^1 and f_{A1}^1 . This dis-

(19a) NOTE ADDED IN PROOF. The electron 1 denoted by the operator f_{A1}^0 belongs to the electrons μ , but that denoted by f_{A1}^1 belongs to the electrons ν (see eq 4).

tion is very useful in the perturbative treatment of the long-range forces. When the n th-order correction to the long-range force is denoted as $F_A^{(n)}$, it is given by

$$F_A^{(n)} = F_A^{(n)}(\text{AD}) + F_A^{(n)}(\text{EGC}) \quad (10a)$$

$$F_A^{(n)}(\text{AD}) = Z_A \int \rho_A^{(n)}(\mathbf{r}_1) f_{A1}^0 \, d\mathbf{r}_1 \quad (10b)$$

$$F_A^{(n)}(\text{EGC}) = Z_A \left\{ \int \rho_B^{(n-1)}(\mathbf{r}_1) f_{A1}^1 \, d\mathbf{r}_1 - \delta_{n1} Z_B / R^2 \right\} \quad (10c)$$

where $\rho_A^{(n)}(\mathbf{r}_1)$ is the n th-order correction to the density of the atom A. For the calculation of the n th-order correction to the AD force, $F_A^{(n)}(\text{AD})$, we need a wave function correct up to n th order, but for the calculation of $F_A^{(n)}(\text{EGC})$, we need a wave function correct to $(n-1)$ th order.

From eq 10, we can deduce the following two important consequences. First, as shown in Appendix A, if the two atoms A and B are neutral and if each atom belongs to the S state for the angular momentum operation, then the EGC force does not contribute to the leading term of the $1/R$ expansion of the long-range forces. Only the AD force is responsible. Thus, the origins of the *leading terms* of the long-range forces are summarized as

{ for the neutral atoms belonging to the S states; AD force (11a)

{ otherwise; AD force + EGC force (11b)

The conjecture stated by Feynman³ and the long-range interactions of the H(1s)-H(1s) system studied by Hirschfelder and Eliason¹¹ correspond to the simpler case of (11a). The long-range interactions of the H(1s)-H⁺ and H(1s)-H(2p) systems correspond to the case of (11b). As shown in the next section, both of the AD and EGC forces are very important for the latter cases. In Table I, the $1/R$ expansions of the

Table I. $1/R$ Expansions of the Integrals $\langle r_B | f_{A1}^1 | r_B \rangle$ Calculated from Slater-Type AO's (au)^a

r_B	Degeneracy	$\langle r_B f_{A1}^1 r_B \rangle$
$ns\sigma$	1	$\frac{1}{R^2}$
$np\sigma$	1	$\frac{1}{R^2} + \frac{3C_4}{5R^4}$
$np\pi$	2	$\frac{1}{R^2} - \frac{3C_4}{10R^4}$
$nd\sigma$	1	$\frac{1}{R^2} + \frac{3C_4}{7R^4} + \frac{5C_6}{14R^6}$
$nd\pi$	2	$\frac{1}{R^2} + \frac{3C_4}{14R^4} - \frac{5C_6}{21R^6}$
$nd\delta$	2	$\frac{1}{R^2} - \frac{3C_4}{7R^4} + \frac{5C_6}{84R^6}$

^a $C_4 = (n+1)(2n+1)/a^2$, $C_6 = (n+1)(n+2)(2n+1)(2n+3)/a^4$, where n and a denote the principal quantum number and the orbital exponent, respectively.

integrals $\langle r_B | f_{A1}^1 | r_B \rangle$ appearing in the EGC force (eq 7c) are calculated using the Slater type AO's for $\chi_{\tau B}$.^{19b} Evi-

(19b) NOTE ADDED IN PROOF. Only the diagonal integrals are given in Table I. The odd-power terms arise from the off-diagonal integrals, e.g., $\langle ns\sigma_B | f_{A1}^1 | np\sigma_B \rangle = (2n+1)/\sqrt{3a} R^{-3}$.

dently, the relation expressed by (11a) is found even for this basis.

The second consequence obtained from eq 10 is as follows. If one of the interacting atoms, say the atom A, is the bare nucleus, $F_A^{(n)}(\text{AD})$ vanishes identically for all n so long as the no-resonance treatment can be admitted. Therefore, we have only to calculate the EGC force which requires *less* knowledge of the wave function than the usual cases by one order. This is a special case of the result of Yaris^{10a} in which \mathcal{H}^0 does not depend on the nuclear coordinate \mathbf{R}_A . Of course, if we look at the nucleus B, we have to calculate the perturbed density correct to the n th order. This suggests the existence of some simple relation between the $(n - 1)$ th and n th-order densities of this system.

It should be noted again that we have used here, as in the previous papers of this series, the *laboratory fixed coordinate system*. In the treatment of the long-range forces between two atoms, it is also possible to adopt a *relative coordinate system* in which the origin of the coordinate is taken on each nucleus.¹⁰ In Appendix B, we have discussed briefly the merit and the demerit of the relative coordinate system. In the relative coordinate system, the concept of the AD force disappears and another quantity arises instead (Appendix B). It gives the same magnitude of force as the AD force, even though it requires *less* knowledge of the wave function *by one order* (merit). However, this new concept is applicable *only* for the long-range forces (demerit). In this paper, we have used the laboratory fixed coordinate system, since there the concept is *common* to other important fields such as molecular structures, vibrations, and chemical reactions.⁷ One should note that the above order discussion applies *only* to this choice of coordinate system. The treatment of the long-range forces in the relative coordinate system will be given separately.

Applications

In this section, we calculate the leading terms of the long-range AD and EGC forces for the interactions of the H(1s)-H⁺ and H(1s)-H(2p) systems and give different interpretations from the energetic theories. In order to calculate the Hellmann-Feynman force correct to n th order, we need, in general, the wave function correct to the same order (see, however, Appendix B and ref 10). This is a computational deficiency of the Hellmann-Feynman force in comparison with the energetics where the wave function correct to n th order gives the energy correct to order $2n + 1$.²⁰ Then, we calculate the wave function correct up to second order for the former system and to first order for the latter. The Salem's sum rule²¹ guarantees the *numerical* equivalence of the force and the energetic treatments for the latter system. Note that, as shown below, the necessity of the "higher-order" wave function for the calculation of the Hellmann-Feynman force does not mean the "complexity" of the results. *The results preserve the conceptual simplicity of the ESF theory.*

(i) **Long-Range Force between a Proton and a Hydrogen Atom.** In the energetic theory for the interaction of the H(1s)-H⁺ system,¹⁴ the first-order energy

(20) J. O. Hirschfelder, W. B. Brown, and S. T. Epstein, *Advan. Quantum Chem.*, **1**, 256 (1964).

(21) L. Salem, *Phys. Rev.*, **125**, 1788 (1962).

$E^{(1)}$ vanishes identically and the second-order energy $E^{(2)}$ gives the leading term. In the force treatment given here, the leading term is calculated in three different ways. Two of these are the no-resonance treatments calculating the force either on the hydrogen atom A or on the proton B. The third is the resonance treatment. All of these calculations give identical results, although only the resonance treatment is acceptable for the intermediate- and short-range interactions. The first- and second-order wave functions are obtained in analytical form by modifying the method of Coulson.¹⁴

First, we give the no-resonance treatment calculating the force acting on the hydrogen atom A. The perturbation Hamiltonian of the system is expressed as

$$\mathcal{H}^1 = -1/r_{B1} + 1/R = \sum_{k=2}^{\infty} V_k/R^k \quad (12)$$

where

$$V_k = -r_{A1}^{k-1} P_{k-1}(\cos \theta) \quad (13)$$

$P_k(\cos \theta)$ is the Legendre polynomial and θ is the angle between \mathbf{r}_{A1} and \mathbf{R}_{AB} . The zeroth-order wave function is written in this treatment as

$$|0\rangle = 1s(A1) \quad (14)$$

Suppose that the exact wave function and energy are expanded in a power series of $1/R$ and that these expansion formulas are substituted into the Schrödinger equation. The analytical form of the exact wave function can be determined by equating the coefficients of the various powers of $1/R$. The resultant wave functions,¹⁴ however, involve the corrections of various orders with respect to the perturbation. The first- and second-order wave functions, $|1\rangle$ and $|2\rangle$, only which are necessary in the present study, can be picked up from them by considering the R dependence and the angular dependence of the first- and second-order wave functions. The resultant expressions are

$$\left\{ \begin{aligned} |1\rangle &= \frac{1}{R^2} \varphi_2^{(1)} + \frac{1}{R^3} \varphi_3^{(1)} + \frac{1}{R^4} \varphi_4^{(1)} + \\ &\quad \frac{1}{R^5} \varphi_5^{(1)} + \cdots \quad (15a) \\ |2\rangle &= \frac{1}{R^4} \varphi_4^{(2)} + \frac{1}{R^5} \varphi_5^{(2)} + \cdots \quad (15b) \end{aligned} \right.$$

where

$$\left\{ \begin{aligned} \varphi_2^{(1)} &= \frac{1}{\sqrt{\pi}} e^{-r} \left(\frac{1}{2} r^2 + r \right) P_1(\cos \theta) \\ \varphi_3^{(1)} &= \frac{1}{\sqrt{\pi}} e^{-r} \left(\frac{1}{3} r^3 + \frac{1}{2} r^2 \right) P_2(\cos \theta) \\ \varphi_4^{(1)} &= \frac{1}{\sqrt{\pi}} e^{-r} \left(\frac{1}{4} r^4 + \frac{1}{3} r^3 \right) P_3(\cos \theta) \\ \varphi_5^{(1)} &= \frac{1}{\sqrt{\pi}} e^{-r} \left(\frac{1}{5} r^5 + \frac{1}{4} r^4 \right) P_4(\cos \theta) \end{aligned} \right. \quad (16a)$$

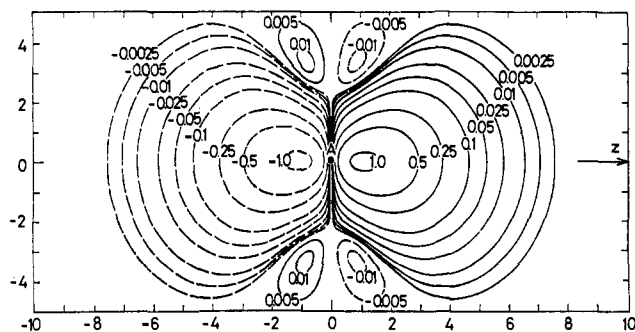


Figure 1. Profile of the perturbed polarized density $\rho_{A,5}^{(2)}$ of the hydrogen atom A in the no-resonance state of the $H_A(1s)-H_B^+$ system (au). The solid and broken lines mean an increase and a decrease in the electron density, respectively. The bare proton B is located at the right-hand side of the hydrogen atom A.

$$\left\{ \begin{aligned} \varphi_4^{(2)} &= \frac{1}{\sqrt{\pi}} e^{-r} \left\{ \left(\frac{1}{12} r^4 + \frac{5}{12} r^3 + \frac{5}{8} r^2 \right) P_2(\cos \theta) + \left(\frac{1}{24} r^4 + \frac{1}{4} r^3 + \frac{3}{4} r^2 \right) P_0(\cos \theta) \right\} \\ \varphi_5^{(2)} &= \frac{1}{\sqrt{\pi}} e^{-r} \left\{ \left(\frac{1}{10} r^5 + \frac{9}{20} r^4 + \frac{3}{5} r^3 \right) P_3(\cos \theta) + \left(\frac{1}{15} r^5 + \frac{23}{60} r^4 + \frac{23}{20} r^3 + \frac{23}{8} r^2 + \frac{23}{4} r \right) P_1(\cos \theta) \right\} \end{aligned} \right. \quad (16b)$$

From (14) ~ (16), we can calculate the leading terms of the long-range AD and EGC forces. The first-order correction is given as

$$F_A^{(1)}(\text{AD}) = \langle 0 | \mathcal{F}_A^0 | 1 \rangle + \langle 1 | \mathcal{F}_A^0 | 0 \rangle = \frac{1}{R^2} \quad (17a)$$

$$F_A^{(1)}(\text{EGC}) = \langle 0 | \mathcal{F}_A^1 | 0 \rangle = -\frac{1}{R^2} \quad (17b)$$

where \mathcal{F}_A^0 and \mathcal{F}_A^1 are the force operators defined in eq 3. Namely, the first-order force vanishes identically in agreement with the energetic theory, $E^{(1)} = 0$. The leading term of the second-order force is calculated as

$$\left\{ \begin{aligned} F_A^{(2)}(\text{AD}) &= \langle 1 | \mathcal{F}_A^0 | 1 \rangle + \{ \langle 0 | \mathcal{F}_A^0 | 2 \rangle + \langle 2 | \mathcal{F}_A^0 | 0 \rangle \} = \frac{9}{R^5} + O\left(\frac{1}{R^7}\right) \end{aligned} \right. \quad (18a)$$

$$F_A^{(2)}(\text{EGC}) = \langle 0 | \mathcal{F}_A^1 | 1 \rangle + \langle 1 | \mathcal{F}_A^1 | 0 \rangle = 0 \quad (18b)$$

Then, the leading term of the long-range force correct up to the second order is $9/R^5$, which just agrees with the energetic theory, $E^{(2)} = -9/4R^4$. Note that $9/2$ is just the electric polarizability α of the hydrogen atom.²²

In (18a), the contribution of the first term is only $1/R^5$. The dominant contribution, $8/R^5$, comes from the *second-order* wave function. This situation is very similar to that found by Hirschfelder and Eliason¹¹ for the long-range interaction between two ground state hydrogen atoms. Moreover, it is remarkable that the second-order energetic correction $E^{(2)}$ comes utterly from the first-order wave function $\varphi_2^{(1)}$ in eq 16a, while

(22) H. R. Hassé, *Proc. Cambridge Phil. Soc.*, **26**, 542 (1930).

the first term of (18a), $\langle 1 | \mathcal{F}_A^0 | 1 \rangle$, contributes only $1/9$ of the second-order force and comes from the cross term between $\varphi_2^{(1)}$ and $\varphi_3^{(1)}$ of eq 16a. This shows clearly the differences in the theoretical origins of the long-range forces between the energetic and the present force standpoints.

The interpretation of the above result is very simple. The second-order electron density of the hydrogen atom A, $\rho_A^{(2)}$, is written as

$$\rho_A^{(2)} = \frac{1}{R^4} \rho_{A,4}^{(2)} + \frac{1}{R^5} \rho_{A,5}^{(2)} + \dots \quad (19a)$$

$$\left\{ \begin{aligned} \rho_{A,4}^{(2)} &= \varphi_2^{(1)*} \varphi_2^{(1)} + \{ \varphi_0^{(0)*} \varphi_4^{(2)} + \varphi_4^{(2)*} \varphi_0^{(0)} \} \\ \rho_{A,5}^{(2)} &= \{ \varphi_2^{(1)*} \varphi_3^{(1)} + \varphi_3^{(1)*} \varphi_2^{(1)} \} + \{ \varphi_0^{(0)*} \varphi_5^{(2)} + \varphi_5^{(2)*} \varphi_0^{(0)} \} \end{aligned} \right. \quad (19b, 19c)$$

where $\varphi_0^{(0)} = |0\rangle$ and $\varphi_2^{(1)}$, etc., are defined in eq 15 and 16. Since $\rho_{A,4}^{(2)}$ is symmetric with respect to the nucleus A, $\rho_{A,5}^{(2)}$ is the origin of the AD force given by eq 18a. In Figure 1, the profile of $\rho_{A,5}^{(2)}$ is given. It shows an *inward* polarization of the electron cloud of the atom A, which is induced by the long-range interaction with the proton. The centroid of this atomic dipole attracts the nucleus A in the inward (attractive) direction. The magnitude of this induced ("permanent" not "instantaneous") atomic dipole varies as $1/R^5$, as shown in eq 19a.

Next, we give the second no-resonance treatment. If we *look at* the proton B, it has no electron density in its vicinity to induce the AD force. Nevertheless, the proton B must also receive the same amount of attractive force as the above AD force the hydrogen atom A receives. It can be shown generally or using the wave functions given in eq 14–16 that the role of the AD and EGC forces are interchanged in this case. Namely, the first-order force vanishes and the second-order force becomes

$$\left\{ \begin{aligned} F_B^{(2)}(\text{AD}) &= \langle 1 | \mathcal{F}_B^0 | 1 \rangle + \{ \langle 0 | \mathcal{F}_B^0 | 2 \rangle + \langle 2 | \mathcal{F}_B^0 | 0 \rangle \} = 0 \end{aligned} \right. \quad (20a)$$

$$\left\{ \begin{aligned} F_B^{(2)}(\text{EGC}) &= \langle 0 | \mathcal{F}_B^1 | 1 \rangle + \langle 1 | \mathcal{F}_B^1 | 0 \rangle = \frac{9}{R^5} + O\left(\frac{1}{R^7}\right) \end{aligned} \right. \quad (20b)$$

The sum of the AD and EGC forces is, of course, identical with the previous result. Equation 20a results, as the previous eq 17b and 18b, from the fact that the electron density of the system is associated only with the nucleus A. Thus, we need in this case only the *first-order* wave function of the system. This is an example of the second general consequence of eq 10 given in the previous section and was also used by Frost.⁹ Although the system has a positive net charge, the EGC force is attractive. This is due to the interaction of the proton B with the distorted first-order density of the hydrogen atom A. An interpretation of the similar situation to this will be given in the next section.

Third, this system can also be treated considering the effect of the resonance. The zeroth-order wave function is chosen in this case as

$$|0\rangle = 2^{-1/2} \{ 1s(A1) + 1s(B1) \} \quad (21)$$

The first-order force vanishes as previously.

$$\begin{cases} F_A^{(1)}(\text{AD}) = 1/2R^2 \\ F_A^{(1)}(\text{EGC}) = -1/2R^2 \end{cases} \quad (22)$$

The leading term of the second-order force is given by

$$\begin{cases} F_A^{(2)}(\text{AD}) = (9/2R^5) + O(1/R^7) \\ F_A^{(2)}(\text{EGC}) = (9/2R^5) + O(1/R^7) \end{cases} \quad (23)$$

Because the wave function represents the superposition of the two states, *i.e.*, $H(\text{A})-H^+(\text{B})$ and $H^+(\text{A})-H(\text{B})$, the second-order EGC force does not vanish. However, the sum of the second-order AD and EGC forces is, as expected, identical with the previous results of no resonance.

(ii) **Long-Range Resonance Force between 1s and 2p Hydrogen Atoms.** Since the electron exchange can be neglected at large separations,²³ the zeroth-order wave function of this system is written in the resonance form as

$$|0\rangle = 2^{-1/2}\{1s(\text{A})12p\sigma(\text{B}) \pm 2p\sigma(\text{A})1s(\text{B})\} \quad (24)$$

for 1s2p σ states (the plus sign corresponds to the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states and the minus sign to the $^1\Sigma_u^+$ and $^3\Sigma_g^+$ states) and

$$|0\rangle = 2^{-1/2}\{1s(\text{A})12p\pi(\text{B}) \pm 2p\pi(\text{A})1s(\text{B})\} \quad (25)$$

for 1s2p π states (the plus sign corresponds to the $^1\Pi_u$ and $^3\Pi_g$ states and the minus sign to the $^1\Pi_g$ and $^3\Pi_u$ states). Energetically, the leading term of the long-range interaction comes from the first-order energy $E^{(1)}$ as

$$E^{(1)} = \pm(2^{16}/3^{10})(1/R^3) = \pm 1.1098579/R^3 \quad (26)$$

for the wave functions given by eq 24 and

$$E^{(1)} = \pm(2^{15}/3^{10})(1/R^3) = \pm 0.5549290/R^3 \quad (27)$$

for the wave functions given by eq 25.

The first-order wave function (and also the exact wave function) of the system may be expanded as

$$|1\rangle = \sum_{i,j} b_{ij}\{\chi_i(\text{A})\chi_j(\text{B}) \pm \chi_j(\text{A})\chi_i(\text{B})\} \quad (28)$$

where $\chi_i(\text{A})$ is a *complete* orthonormal set of AO's centered at the nucleus A, the explicit form of which were given by Hirschfelder and Löwdin.¹⁹ A set of the first-order coefficients b_{ij} were calculated here by the method of Kołos¹⁵ using 220 terms in the expansion (eq 28). As shown below, the results were well converged with this basis. (Kołos did not give the coefficients b_{ij} in his paper.¹⁵)

As seen from eq 10c, the first-order correction to the EGC force is calculated from the zeroth-order wave function. It is immediately obtained from Table I using the fact that the 1s and 2p AO's of the present system are identical with the Slater AO's. The results are shown in Table II.

As to the long-range AD force, the first-order wave function is required. The first-order wave function calculated by the method of Kołos is composed of four independent parts corresponding to eq 39 of his paper.¹⁵ For the 1s2p σ states, their contributions to the long-range AD force are as follows.

(23) However, see a remark noted by Mulliken (ref 17b).

$$\begin{cases} F_{13} = 0 & \text{for all states} \\ F_{11} = \begin{cases} -20.219718/R^4 & \text{for } ^1\Sigma_g^+ \text{ and } ^3\Sigma_u^+ \text{ states} \\ -15.780284/R^4 & \text{for } ^1\Sigma_u^+ \text{ and } ^3\Sigma_g^+ \text{ states} \end{cases} \\ F_{22} = 0 & \text{for all states} \\ F_{20} = \begin{cases} -1.109850/R^4 & \text{for } ^1\Sigma_g^+ \text{ and } ^3\Sigma_u^+ \text{ states} \\ +1.109850/R^4 & \text{for } ^1\Sigma_u^+ \text{ and } ^3\Sigma_g^+ \text{ states} \end{cases} \end{cases} \quad (29)$$

For the 1s2p π states, the results are obtained simply by multiplying the constant factors to the above values (-0.5 to F_{11} and 0.5 to F_{20}). The final results are summarized in Table II.

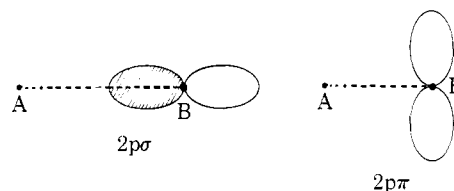
Table II. Leading Terms of the Resonance Forces between H(1s) and H(2p)^a

Force	1s2p σ		1s2p π	
	$^1\Sigma_g^+, ^3\Sigma_u^+$	$^1\Sigma_u^+, ^3\Sigma_g^+$	$^1\Pi_u, ^3\Pi_g$	$^1\Pi_g, ^3\Pi_u$
$F_A^{(1)}(\text{EGC})$	+18.0	+18.0	-9.0	-9.0
$F_A^{(1)}(\text{AD})$	-21.329568	-14.670434	+7.335217	+10.664784
$F_A^{(1)}(\text{total})$	-3.329568	+3.329566	-1.664783	+1.664784
$\partial E^{(1)}/\partial R$	-3.329574	+3.329574	-1.664787	+1.664787

^a Coefficients of the $1/R^4$ terms are given in au. The positive and negative signs mean attraction and repulsion, respectively.

As is shown in Table II, both of the contributions of the AD and EGC forces are quite large. For the 1s2p σ states, the EGC force is always attractive and the AD force is always repulsive. For the 1s2p π states, the relation is just converse. The total forces are the results of cancellations of these two large values. This is different from the result of Hirschfelder and Eliason for the two *ground state* hydrogen atoms in which only the AD force was the origin (the simpler case, eq 11a). As is seen from the last two rows of Table II, the results of the present force treatment agree quite well with those of the energetic treatment (eq 26 and 27). In reference with the Salem's sum rule,²¹ this agreement shows an essential completeness of the 220 basic AO's used in the present calculations.

Despite the fact that the system is neutral, the EGC force is attractive for the 1s2p σ states and repulsive for the 1s2p π states. Referring to Table I, we find that this comes from the existence of the $1/R^4$ terms in the integrals involving 2p σ and 2p π AO's. The appearance of these $1/R^4$ terms is easily understood from the following illustration.



In the 1s2p σ states, the electrons in the shaded area attract nucleus A more than nucleus B repels, because the electrostatic interaction is proportional to $1/r^2$. In the 1s2p π states, the electrons in the 2p π lobe cannot shield nucleus B well from the repulsive force along the A-B axis.

As is shown in Table II, the AD force is always repulsive for the 1s2p σ states and attractive for the 1s2p π states. The first-order change in the electron density

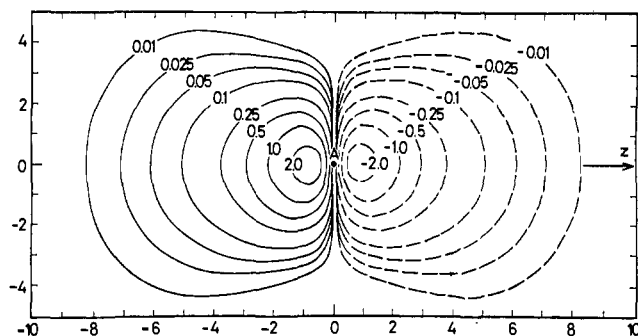


Figure 2. Profile of the perturbed density $\rho_{A,4}^{(1)}$ of the $1\Sigma_g^+$ and $3\Sigma_u^+$ states of the H(1s)-H(2p σ) system (au). The solid and broken lines mean an increase and a decrease in the electron density, respectively. The other nucleus B is located at the right-hand side of nucleus A.

of atom A is written as

$$\rho_A^{(1)} = \frac{1}{R^3} \rho_{A,3}^{(1)} + \frac{1}{R^4} \rho_{A,4}^{(1)} + \dots \quad (30)$$

Since $\rho_{A,3}^{(1)}$ is symmetric with respect to the nucleus A, $\rho_{A,4}^{(1)}$ is responsible for the AD force. In Figures 2 and 3, the profiles of the perturbed densities $\rho_{A,4}^{(1)}$ are shown for the 1s2p σ states. Figure 2 corresponds to the $1\Sigma_g^+$ and $3\Sigma_u^+$ states and Figure 3 to the $1\Sigma_u^+$ and $3\Sigma_g^+$ states. Nucleus B is located at the right-hand side. In both figures, the polarization of the electron cloud occurs in the *outward* direction. The centroid of the polarized electron density, which is at the left-hand side of nucleus A, attracts nucleus A in the outward (repulsive) direction. The extent of polarization is proportional to $1/R^4$ as seen from eq 30. Namely, these formations of the *outward atomic dipoles* depicted in Figures 2 and 3 are the origins of the *repulsive AD forces* of the 1s2p σ states. For the 1s2p π states, the atomic dipoles induced by the perturbation are in the *inward* direction and give rise to the *attractive AD forces* shown in Table II.

Concluding Remarks

In this paper, we have applied the ESF theory to the long-range forces between two atoms. The laboratory fixed coordinate system is used throughout (see Appendix B). The origins of the long-range forces are shown to be the AD and EGC forces. The former is due to the formation of the atomic dipole on atom A and the latter is due to the electrostatic interaction between nucleus A and perturbed atom B. For the interactions of two neutral S state atoms, only the AD force is responsible for the leading term of the long-range forces. In a perturbative sense, the AD force is obtained from the operation of the zeroth-order force operator and the EGC force from that of the interaction force operator. Therefore, the n th-order corrections to the AD and EGC forces are obtained from the n th and $(n-1)$ th-order corrections to the density, respectively. If one of the interacting atoms is bare nucleus, the long-range force can be obtained only from the EGC force so long as the no-resonance treatment is admitted. Therefore, we need less knowledge of the wave function than the usual case by one order.

These long-range AD and EGC forces are calculated for the two simple systems: the long-range interactions

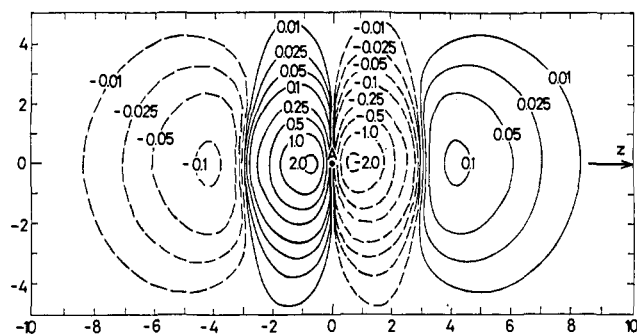


Figure 3. Profile of the perturbed density $\rho_{A,4}^{(1)}$ of the $1\Sigma_u^+$ and $3\Sigma_g^+$ states of the H(1s)-H(2p σ) system (au). The solid and broken lines mean an increase and a decrease in the electron density, respectively. The other nucleus B is located at the right-hand side of nucleus A.

of the H(1s)-H⁺ and H(1s)-H(2p) systems. For both systems, excellent agreements are obtained between the energetic and the present force treatments in the final numerical values, although the theoretical origins and the interpretations of the long-range forces are quite different between these two standpoints. Both of the AD and EGC forces are shown very important for these two systems. This is different from the conjecture of Feynman³ and from the result of Hirschfelder and Eliason¹¹ for the interaction of the two ground state hydrogen atoms (the simpler case, eq 11a).

The ESF theory of the long-range force is *quite different* from the traditional energetic theories in both theoretical and interpretative views. The first-order wave function of the H(1s)-H(2p) system, for example, was used in the Kołos's paper¹⁵ to calculate the dipole-quadrupole interaction energy (B_3). This shows an essential difference in the theoretical origin. The atomic dipole depicted in Figures 2 and 3 comes from the higher order wave functions than the energetic theory necessitates. However, the necessity of the "higher order" wave function does not necessarily mean the "complexity" of the results. The meanings and the roles of the atomic dipoles depicted in Figures 1-3 are, we believe, as simple as or simpler than the energetic interpretations of the long-range interactions. As reported previously,^{7c} this simplicity can be used to predict approximately the behaviors of the electron clouds of the molecules and reacting systems undergoing changes in nuclear configurations. Moreover, as shown in the previous sections, we have *two and only two* origins, the AD and EGC forces, for the long-range forces of any atomic pair and to any desired accuracy, so long as the electron exchange can be neglected and we use the Hellmann-Feynman theorem in the laboratory fixed coordinate system. We *do not use* the words, in this picture, such as the dipole-dipole, dipole-quadrupole interactions, etc.,²⁴ not only because they make a picture much more complicated, but also because they are applicable *only* to the long-range interactions in comparison with the general applicabilities of the AD and EGC (and EC) forces to molecular structures,²⁵ vibrations, and chemical reactions.⁷

(24) See, for example, H. Margenau, *Rev. Mod. Phys.*, 11, 1 (1939).

(25) After this manuscript was completed, the paper of B. M. Deb, *J. Amer. Chem. Soc.*, 96, 2030 (1974), has appeared. He gave there (ref 76) some "remarks" on our earlier papers of this series.^{7a} It might be appropriate to answer here his remarks. First of all, he wrote as if we "split the atomic plus nuclear repulsion force into the AD and GC

In the *ESF* theory, the basic concepts are common to all of these important phenomena.

Note lastly that the atomic dipoles depicted in Figures 1–3 (the origin of the AD force) are “permanent,” so long as the two atoms interact, in comparison with the so-called “instantaneous” dipole–dipole interaction, the energetic origin of the $1/R^6$ term. This distinction is important in the interpretative sense, because these two dipoles may easily be confused.

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Appendix A

Here, we prove the relation in eq 11a; when the two atoms A and B are neutral and when they belong to the S states for the angular momentum operation, then the EGC force does not contribute to the leading term of the $1/R$ expansion of the long-range force.

First, we show that if the electron density of atom B, ρ_B , is *spherical*, the following integral appearing in the EGC force reduces at large separation to

$$\int \rho_B(\mathbf{r}_1) z_{A1}/r_{A1}^3 d\mathbf{r}_1 = N_B/R^2 \quad (\text{A1})$$

where N_B denotes the number of electrons of atom B. No other power series of $1/R$ appears.

The integral in (A1) can be obtained using the method of Bader²⁷ by expanding the force integral, z_{A1}/r_{A1}^3 , about the center B. Instead, noting that this integral represents the electric intensity at position A due to the *spherical* charge cloud ρ_B , it is more easily derived using the well-known theorem of electrostatics.²⁸ The elec-

forces,” but this is incorrect (see paper I and ref 35 of ref 7c). The transverse force was studied in the later papers (ref 7c). As to the four remarks, we give the answers in his order. (1) The shape of CH_3 radical is a rather delicate problem in that it is a result of a rather critical balance of the AD and EC forces (p 356 of paper II). Therefore, in order to predict its shape, we have to *calculate actually* the forces acting on the nuclei. Figure 1 of paper II is a result of such calculations and *predicts* planar shape. However, some problem might still remain on the reliability of the wave function used. At present, there is no fully reliable *force* calculation of this radical. Then, in a *strict ab initio* sense, the shape of the CH_3 radical might be said, *at present*, to be “accepted” from other theoretical and experimental works. Our theoretical framework has a *verifiableness*, as clearly shown in this paper and ref 7b and 7c, so that we will be able to examine this problem when we have a very reliable wave function in the future. (The relation between the shapes of CH_3 and NH_3^+ , etc., is known from the discussions given in paper I.) The HOMO postulate of Deb “predicted” CH_3 and NH_3^+ to be pyramidal, which seems to contradict with the other theoretical and experimental works which indicate that they are planar, or almost planar, in that the potential barrier is very shallow (see, e.g., ref 30 and ref 32 of paper I). (2) The Mulliken approximation is not necessarily a good approximation, if it is applied inappropriately.²⁶ In all of our force calculations,^{7a–c} we have *never* used this approximation, introducing the EGC force instead of the GC force (see ref 21 of paper I). This approximation was used in paper I in order to derive the simplified concept, the GC force, for the integrals $\langle \chi_{rB} | \mathbf{r}_A/r_{A1}^3 | \chi_{rC} \rangle$ ($B, C \neq A, r \neq s$). The contributions of these integrals are much smaller, in the problems of molecular structures, than the AD and EC forces. In defining the AD, EC, and EGC forces, we have set *no* approximations in the integrals. (3) This gives a trivial statement and might arise from the misreading (see the discussions starting below Figure 6 of paper I). (4) This opinion is very interesting, but more examinations might be necessary. We refer to our later works, especially ref 7b.

(26) B. J. Nicholson, *Advan. Chem. Phys.*, **18**, 249 (1970).

(27) R. F. W. Bader, *Can. J. Chem.*, **40**, 2140 (1962).

(28) See, e.g., J. H. Jeans, “The Mathematical Theory of Electricity and Magnetism,” Cambridge University Press, 1927. The authors are indebted to the referee for this view.

trostatic potential at a point A apart by a distance R from the origin B of a spherical shell of charge of radius r is

$$(1/R)4\pi r^2 \rho_B(r) dr \quad \text{if } r \leq R$$

i.e., at a point outside the shell, the potential acts as if the charge were all concentrated at the origin B, and

$$4\pi r \rho_B(r) dr \quad \text{if } r \geq R$$

i.e., the potential inside the shell is a constant and is the same as the potential just on the surface of the shell. The total potential at R is thus

$$V = \frac{1}{R} \int_0^R 4\pi r^2 \rho_B(r) dr + \int_R^\infty 4\pi r \rho_B(r) dr$$

The force on a unit charge at R in the radial direction is

$$\begin{aligned} F &= \int \rho_B(\mathbf{r}_1) z_{A1}/r_{A1}^3 d\mathbf{r}_1 \\ &= -\frac{\partial V}{\partial R} = \frac{1}{R^2} \int_0^R 4\pi r^2 \rho_B(r) dr = \\ &\quad \frac{\text{charge inside } r \leq R}{R^2} \quad (\text{A2}) \end{aligned}$$

At a large separation, this reduces to eq A1.

For the neutral atoms belonging to the S states in their free states, $N_B = Z_B$ and the zeroth-order density $\rho_B^{(0)}(\mathbf{r}_1)$ is spherical around nucleus B. Thus, we get $F_A^{(1)}(\text{EGC}) = 0$ from (A1) and (10c). Moreover, for this system, we can show that $\rho_A^{(1)}(\mathbf{r}_1) = \rho_B^{(1)}(\mathbf{r}_1) = 0$, because the angular dependence of the first-order wave function is the same as that of the perturbation Hamiltonian which does not include, for the neutral atoms, the spherical components in the multipole expansion formula.¹⁶ Then, $F_A^{(1)}(\text{AD}) = 0$ from (10b). For the second-order corrections, $F_A^{(2)}(\text{EGC})$ vanishes identically since $\rho_B^{(1)}(\mathbf{r}_1) = 0$, whereas $F_A^{(2)}(\text{AD})$ does not vanish in general, giving the leading term of the long-range interactions. Therefore, we reach the conclusion given at the beginning of Appendix A. Note that when the atoms do not belong to the S states, the zeroth-order density cannot be taken to be spherical around the nucleus because of the symmetry of the system (e.g., see eq 24 and 25).

Appendix B

Here, we briefly discuss some features of the *relative coordinate system*,¹⁰ in which the electrons μ are described by the coordinate centered on nucleus A and the electrons ν by that centered on nucleus B. This can be done unambiguously only when the electron exchange can be neglected, *i.e.*, *only* for the long-range interactions between two atoms. The force operator of the relative coordinate system (R) is connected with that of the laboratory fixed coordinate system (L) by

$$-\left(\frac{\partial \mathcal{H}}{\partial \mathbf{R}_A}\right)_R = -\left(\frac{\partial \mathcal{H}}{\partial \mathbf{R}_A}\right)_L - \sum_{\mu} \left(\frac{\partial \mathcal{H}}{\partial \mathbf{r}_{\mu}}\right)_L \quad (\text{B1})$$

The implication of the Hellmann–Feynman theorem depends on the choice of the coordinate system.^{8a,11b,29} The first term of the right-hand side represents the force

(29) C. A. Coulson and A. C. Hurley, *J. Chem. Phys.*, **37**, 448 (1962); P. Philipson, *ibid.*, **39**, 3010 (1963); M. L. Benston and B. Kirtman, *ibid.*, **44**, 119 (1966); M. L. Benston, *ibid.*, **44**, 1300 (1966); S. T. Epstein, *ibid.*, **42**, 3813 (1965); **46**, 571 (1967).

acting on *nucleus* A and the second term may be said to represent the force acting on the *electrons* μ of atom A. Thus, the force operator in the *R* coordinate may be considered to represent the force acting on *atom* A.^{10b} A remarkable merit is that

$$-(\partial\mathcal{J}^0/\partial\mathbf{R}_A)_R = 0 \quad (\text{B2})$$

which means that we can save the required accuracy of the wave function by one order.^{10,30} Equation B2 means also that the concept of the AD force disappears in the *R* coordinate. The operator of the AD force,

(30) Yaris (ref 10a) has discussed further the conditions under which the wave function correct to *n*th order gives the Hellmann-Feynman force to order $2n + 1$.

$-(\partial\mathcal{J}^0/\partial\mathbf{R}_A)_L$, which is an *internal* force in the *R*-coordinate representation, is exactly canceled by the force the electrons μ receive, $-\sum_{\mu}(\partial\mathcal{J}^0/\partial\mathbf{r}_{\mu})_L$. Instead, we have a new operator, $-\sum_{\mu}(\partial\mathcal{J}^1/\partial\mathbf{r}_{\mu})_L$, which satisfies

$$\langle\Psi|-\sum_{\mu}\left(\frac{\partial\mathcal{J}^1}{\partial\mathbf{r}_{\mu}}\right)_L|\Psi\rangle=\langle\Psi|-\left(\frac{\partial\mathcal{J}^0}{\partial\mathbf{R}_A}\right)_L|\Psi\rangle \quad (\text{B3})$$

for the exact wave function Ψ . Namely, the AD force is substituted in the *R*-coordinate representation by the force the electrons μ receive through the long-range interaction with atom B. This correspondence is possible only for the atom-atom long-range interactions. The concept of the long-range forces in the relative coordinate system will be discussed more fully elsewhere.

Mechanistic Studies of the Reduction of *Rhus vernicifera* Laccase by Hydroquinone

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Abstract: Anaerobic stopped flow kinetic studies of the reaction of hydroquinone with *Rhus vernicifera* laccase have been performed with the objective of elucidating the mechanisms by which the three enzymatic copper sites are reduced. The "blue" and esr nondetectable copper sites are reduced in parallel at comparable rates over a wide range of conditions. Second-order rate constants characterizing the hydroquinone reduction of the laccase type 1 and type 3 sites at 25.6°, pH 7.0, and μ 0.1 (phosphate) are 3.25×10^2 and $4.57 \times 10^2 M^{-1} \text{sec}^{-1}$, respectively. Terms proportional to $[\text{H}^+]^{-1}$ are dominant in the rate laws for reduction of both optically observable copper sites, suggesting participation of the phenolate anion HQ^- in the slow steps governing electron transfer. Fluoride and azide inhibition results at pH 6 strongly suggest that inner-sphere complexes between HQ^- and type 2 Cu(II) are intermediates in the closely related electron-transfer pathways to the type 1 and type 3 copper sites in the native enzyme. It is proposed that the disposition of these intermediates involves (1) reduction of the type 2 copper atom followed by intramolecular electron transfer to the type 3 site and (2) initiation of a protein conformational change permitting conduction of an electron from the coordinated substrate to the type 1 copper atom. Displacement of anion from type 2 coordination in the slow step is proposed to account for saturation in observed 614- and 330-nm rate constants for reduction of the type 2 Cu(II)- F^- laccase complex to the respective values 1.13×10^{-1} and $9.8 \times 10^{-2} \text{sec}^{-1}$ (25.1°, pH 6.0, μ 0.2). Displacement of azide ion from type 2 coordination is not a prerequisite for reduction of the "blue" copper site, however, as decay in the 405-nm absorption peak of the azide derivative (N_3^- to type 2 Cu²⁺ charge transfer) is much slower than loss of blue color. A type 1 Cu(I) to type 2 Cu(II) electron-transfer step catalyzed by a bridging azide ion is postulated to account for the first-order $[\text{N}_3^-]$ dependence of observed rate constants for type 2 copper reduction in the laccase-azide complex at pH 6.0 ($k_{\text{obsd}}(405) = 0.106[\text{N}_3^-] \text{sec}^{-1}$; 25.1°, μ 0.2).

Laccases are copper-containing enzymes which catalyze the oxidation of ortho- and para-aryl diamines and diphenols by oxygen, producing the corresponding quinones and water.¹ Two laccases, those from the fungus *Polyporus versicolor* and the lacquer tree *Rhus vernicifera*, have been the subject of much recent study. Both proteins possess four tightly bound copper atoms distributed in three distinct sites.²⁻⁶

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Laccase rapidly reduces oxygen to water only when all of its electron-accepting sites are reduced (four electron equivalents total),⁷ and partial removal of enzymatic copper causes destruction of polyphenol oxidase activity.⁸

Rhus laccase is a glycoprotein containing only about 55% protein by weight and having a molecular weight of 110,000.⁹ Amino acid analysis of the enzyme shows an excess of 38 basic amino acid residues over acidic residues (arginine + histidine + lysine = 56; glutamic acid + aspartic acid - NH_3 = 18), explaining its high isoelectric point of 8.55.⁹ The type 1 (or "blue") copper atom is responsible for the intense blue color of

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