

Force concept for predicting the geometries of molecules in an external electric field

Yasushi Honda ^a, Hiroshi Nakatsuji ^{a,b,*}

^a Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

^b The Institute for Fundamental Chemistry, 34-4 Takano Nishi-Hiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan

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Abstract

An intuitive Hellmann–Feynman (H–F) force concept is presented for predicting the geometries of molecules in external electric fields of various strengths. The field-induced H–F force consists of internal and external forces and their balance determines the molecular geometry. Our previous model is valid in both strong and weak fields except for non-protic hydrogens. This exception is explained to be due to the local nature of the field-induced density reorganization, i.e. H-to-bond and bond-to-H electron flow. The force concept including this bond effect is applicable to various molecules in electric fields of various strengths. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Variations in molecular properties due to the presence of an external electric field are of interest in many fields of chemistry and physics and particularly in electrochemistry, STM, surface science, biochemistry and related fields. Theoretical investigations of the effects of electric fields on geometry and vibration have been performed by several authors. Pancir and co-workers [1,2] studied ethylene and acetylene in an electric field using a semi-empirical INDO method. We previously proposed an intuitive force concept for predicting the geometries of molecules in an external electric field [3]. Hermanson and Tepper [4–7] discussed the frequency shifts of some diatomic molecules. Andres and co-workers

[8–11] studied the vibrational Stark effects in various molecules.

The force concept based on the Hellmann–Feynman (H–F) electrostatic theorem provides a perspective for the electronic origins of nuclear rearrangement processes on potential-energy hypersurfaces. We have developed a force and density concept for molecular geometries and chemical reactions, the so-called electrostatic force (ESF) or H–F force theory [12–19]. It provides an intuitive and useful chemical concept for predicting the geometries of molecules in ground and excited states. This concept has been extended to studies of the geometries of molecules in an external electric field. The force induced by an external electric field was partitioned into ‘internal’ and ‘external’ forces and the geometry was considered to reflect the balance of these two component forces.

However, a problem with this H–F force approach lay in the calculation of the H–F force itself.

* Corresponding author.

While the H–F theorem is valid for exact and ‘stable’ [20,21] wavefunctions, the theorem breaks down with the use of the LCAO (linear combination of atomic orbitals) approximation and we have to calculate so-called energy gradients. However, when we use energy gradients, the intuitive H–F force concept is not applicable. One solution to this problem is to ‘float’ the basis set away from the nuclear position, but the actual calculation is not realistic for molecules of moderate sizes. Another solution is to improve the basis set by adding the derivative basis set to the original set [22–25], which is called the (r, r') method. Using this method, one can use the H–F force concept to study complex chemical phenomena by means of ab initio molecular orbital calculations.

In this Letter, we establish the ESF or H–F force concept to predict the geometries of molecules in an external electric field. The previous force model [3] is valid for a strong electric field, but some modifications are necessary when the applied field is weaker. We calculated the H–F forces and densities of various molecules in a relatively weak electric field using the (r, r') method. Since the Mulliken population analysis is not valid for this basis set, we use the NAO (natural atomic orbital) analysis proposed by Reed and co-workers [26–28]. The present model corrects some oversimplification in our previous model, which was problematic for weak-field cases, and provides a quantitatively reliable force concept for predicting the geometries of molecules in an external electric field over a wide range of field strengths. This model is applicable to a variety of molecules and we present here some typical and illustrative examples.

2. Previous model

First, we will briefly explain the force concept proposed previously [3] for predicting the geometries of molecules in an external electric field. The H–F force acting on the nucleus A of a molecule in an external electric field \mathbf{E} is given by

$$\mathbf{F}_A^E = Z_A \left[\int \rho_E(\mathbf{r}_1) \frac{\mathbf{r}_{A1}}{r_{A1}^3} d\mathbf{r}_1 - \sum_{B \neq A} \frac{Z_B \mathbf{R}_{AB}}{R_{AB}^3} \right] + \mathbf{E}, \quad (1)$$

using standard notations [3]. Note that $\rho_E(\mathbf{r}_1)$ denotes the electron density of a molecule in an external electric field \mathbf{E} . The effect of the external electric field on the force acting on nucleus A is given by

$$\Delta \mathbf{F}_A = \mathbf{F}_A^E - \mathbf{F}_A^0 = Z_A \int \Delta \rho(\mathbf{r}_1) \frac{\mathbf{r}_{A1}}{r_{A1}^3} d\mathbf{r}_1 + Z_A \mathbf{E}, \quad (2)$$

where $\Delta \rho = \rho_E - \rho_0$, i.e. the density reorganization due to the external field. We define the two terms in Eq. (2) as the internal force $\mathbf{F}_A^{\text{int}}$ and the external force $\mathbf{F}_A^{\text{ext}}$, respectively:

$$\mathbf{F}_A^{\text{int}} = Z_A \int \Delta \rho(\mathbf{r}_1) \frac{\mathbf{r}_{A1}}{r_{A1}^3} d\mathbf{r}_1, \quad \mathbf{F}_A^{\text{ext}} = Z_A \mathbf{E}. \quad (3)$$

The internal force represents the force due to the density reorganization and the external force represents the electrostatic interaction between the nucleus A and the external field. Note that this decomposition is exact and independent of the choice of basis sets.

When an external electric field is applied to a molecule, the electron cloud of the molecule flows toward the positive pole of the field, so that $\mathbf{F}_A^{\text{int}}$ should be oriented toward the positive pole, while $\mathbf{F}_A^{\text{ext}}$ is oriented exactly toward the negative pole. The net force ($= \mathbf{F}_A^{\text{int}} + \mathbf{F}_A^{\text{ext}}$) is determined by a balance between these two forces. In the previous model, we postulated that the balance of these forces is dependent on the electron population on the nucleus A [3];

$$\begin{aligned} |\mathbf{F}_A^{\text{int}}| &> |\mathbf{F}_A^{\text{ext}}|, & \text{if } \delta_A < 0, \\ |\mathbf{F}_A^{\text{int}}| &< |\mathbf{F}_A^{\text{ext}}|, & \text{if } \delta_A > 0, \end{aligned} \quad (4)$$

where δ_A denotes the atomic charge on the nucleus A in the electric field. Thus, when the electron population on nucleus A exceeds the nuclear charge, the electronic effects overwhelm the nuclear effects, and vice versa. For molecules in an electric field of 0.1 au ($\sim 5 \times 10^{10}$ V/m), all of the forces follow this rule [3]. However, when the electric field becomes much weaker, this model may fail for forces acting on non-protic hydrogens, as shown below for CH_4 . Of course, the magnitude of the induced forces becomes small as the applied field becomes weak.

3. Computational method

We calculate the H–F forces acting on CO, CO₂, C₂H₂, H₂O, NH₃, CH₄, C₂H₄ and H₂CO in an external electric field of 0.005 au ($\sim 2.5 \times 10^9$ V/m), which is much weaker than the previous field strength 0.1 au [3]. For CH₄, the field strengths of

0.005, 0.01, 0.05 and 0.1 au are applied. Electric field vectors are defined to be in the direction from the positive pole of the field to the negative (the direction was reverse that in the previous case [3]). All of the calculations were performed using the restricted Hartree–Fock method. The basis sets we used are Huzinaga–Dunning's (9s5p/4s)/[4s2p/2s]

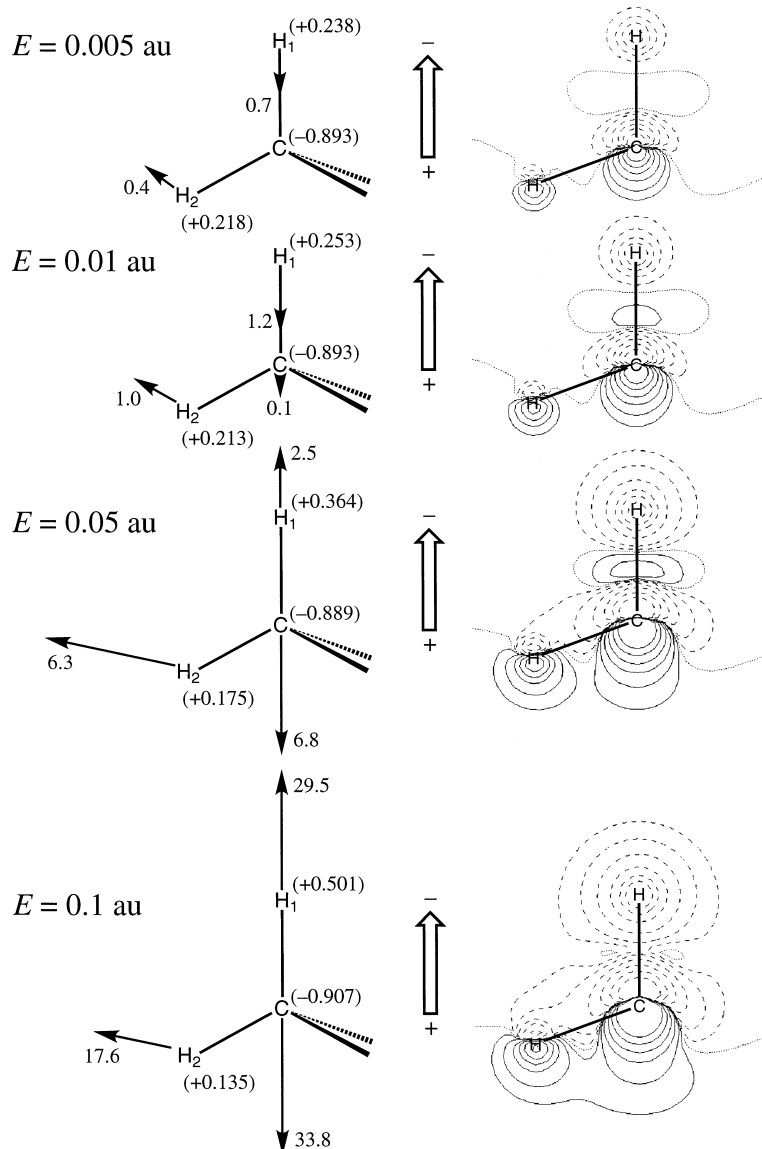


Fig. 1. Hellmann–Feynman forces (in 10^{-3} au) and contour maps of electron density reorganization of CH₄ induced by external electric fields of different strengths. The atomic charges (natural charges) are shown in parentheses. The solid and broken lines in the maps (± 0.001 , ± 0.003 , ± 0.010 , ± 0.030 , ± 0.090 and ± 0.270) represent increased and decreased electron density, respectively.

with standard scaling factors [29] plus their derivative basis sets [22,25]. The H–F forces are dramatically improved in quality by including the derivative terms, so that this method gives quantitatively much better results than those by normal energy gradient methods [22,25]. The population analysis was done using the NAO (natural atomic orbital) analysis [26–28], since the Mulliken population analysis becomes less reliable as the size of the basis set increases [27]. In the NAO analysis, the bond polarity is somewhat overestimated, but the basis-set dependence, etc., are greatly improved over the Mulliken population analysis. All of the calculations except for the NAO analyses were performed using a modification of the HONDO 8.1 program package [30]. NAO analyses were performed using the GAUSSIAN 94 package [31]. In this package, the molecular geometries are optimized such that the H–F forces, rather than the energy gradients, should be equal to zero.

4. Field-strength dependence of the Hellmann–Feynman forces acting in CH₄

First, we examine the dependence of the H–F forces on the strength of the external electric field. Fig. 1 shows the results for CH₄. The molecular geometry is a non-field equilibrium geometry, i.e. the equilibrium geometry in the absence of an external field. The forces are given in 10⁻³ au (hartree/bohr). The values in parentheses denote the atomic charges (natural charges) on the atom. The contour map of the reorganized electron density $\Delta\rho$ is displayed for each field strength.

For 0.1 and 0.05 au, all of the forces are consistent with the previous model, i.e. the forces acting on positively charged H atoms are directed toward the negative pole and those acting on the negatively charged C atoms are directed toward the positive pole. However, for 0.01 and 0.005 au, the force acting on the H₁ atom is directed toward the positive pole despite its positive atomic charge. Thus, the previous model is valid for strong electric fields, but it becomes problematic with a weak field. To apply the model to molecules in a weak electric field, some modification is necessary. Although the NAO population analysis tends to overestimate the polarity of the bond in comparison with the Mulliken population

analysis used previously [3], this alone cannot account for this problem. Furthermore, note that the force acting on H₂ has a component vertical to the direction of the field. We also want to account for the origin of this force.

5. Hellmann–Feynman forces for molecules in a weak electric field

Figs. 2–4 show the H–F forces (in 10⁻³ au) acting on several molecules in a weak electric field of 0.005 au. Since all of the geometries are non-field equilibrium geometries, the vectors displayed represent the force induced by the field, ΔF_A defined by Eq. (2). The values in parentheses denote the atomic charges (natural charges) on the atom. The atomic charges for molecules without a field are described in the figure caption.

Fig. 2 shows linear molecules. Fields parallel and anti-parallel to the direction of the polarity yield the forces which would shorten and lengthen the bonds, respectively. A field perpendicular to the bond in a non-polar molecule causes bond bending. The force directions are vertical to the bond, and the bond length remains almost constant. In these molecules, all of the forces clearly follow the rule expressed by Eq. (4). Fig. 3 shows the H–F forces on H₂O and NH₃ molecules. The forces act on the molecule so as to shorten the bonds when the field is parallel to the polarity, whereas the reverse occurs for an anti-parallel field. One also observes the forces which work to increase and decrease the H–O–H and H–N–H angles for $E_z = +0.005$ au and $E_z = -0.005$ au, respectively. Again, the force acting on each nucleus can be predicted by Eq. (4). However, we see that the forces on the H atoms slightly include the components perpendicular to the field. In the case of $E_z = +0.005$ au, the perpendicular components would lengthen the O–H and N–H bonds, whereas they would shorten the bonds for $E_z = -0.005$ au. However, this component is smaller than the parallel component and is secondary in these molecules.

Fig. 4 shows the H–F forces for CH₄, C₂H₄ and H₂CO. The behavior of the C–O bond in H₂CO is similar to those in CO and CO₂ and is consistent with Eq. (4). However, other bonds do not always follow the rule. The external field from C toward H₁

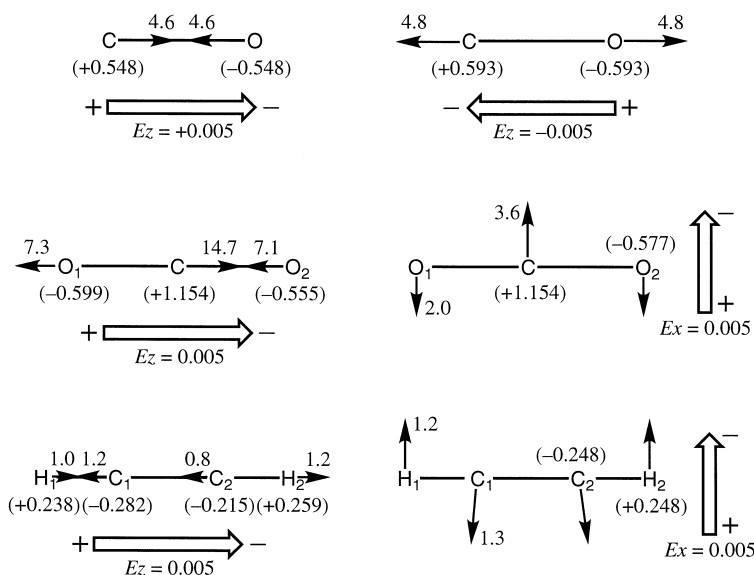


Fig. 2. Hellmann-Feynman forces (in 10^{-3} au) in linear molecules at their non-field equilibrium geometries in the presence of an electric field. Atomic charges (natural charges) on each atom are shown in parentheses. The atomic charges in the absence of the field are: CO: +0.570 for C and -0.570 for O; CO_2 : +1.154 for C and -0.577 for O; C_2H_2 : -0.248 for C and +0.248 for H.

in CH_4 shrinks the C– H_1 bond while a field with a reverse direction elongates this bond. The C–H bonds of C_2H_4 in the field along the y -axis also exhibit

similar behavior and are different from those expected from Eq. (4). Furthermore, when the field is applied along the direction almost perpendicular to

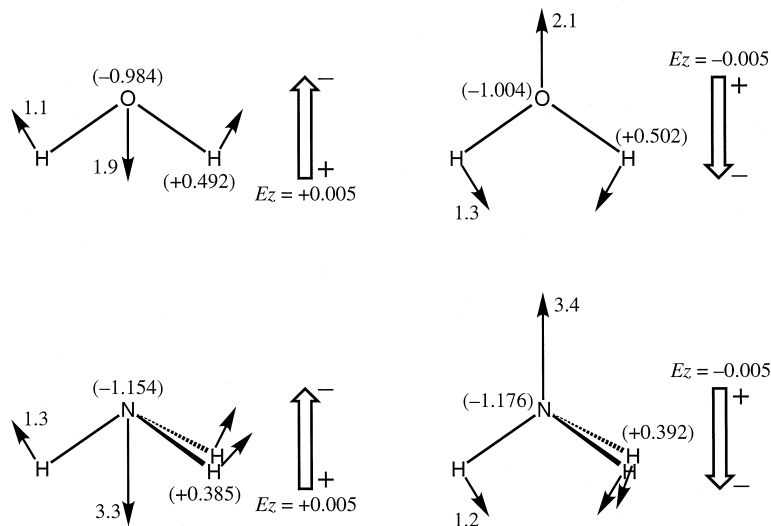


Fig. 3. Hellmann-Feynman forces (in 10^{-3} au) in H_2O and NH_3 at their non-field equilibrium geometries in the presence of an electric field. Atomic charges (natural charges) in the absence of the field are: H_2O : -0.994 for O and +0.497 for H; NH_3 : -1.165 for N and +0.388 for H.

the C–H bond (e.g. $E_z(C_{2v})$ for CH_4 , E_z for C_2H_4 and H_2CO), the behaviors of the C–H bonds strongly resemble each other, while for H atoms the component perpendicular to the field seems to be more essential than the parallel component. These perpen-

dicular components suggest the existence of another effect on H–F forces besides the effect due to the atomic charge.

In summary, although we found that CO , CO_2 , C_2H_2 , H_2O and NH_3 followed the previous model

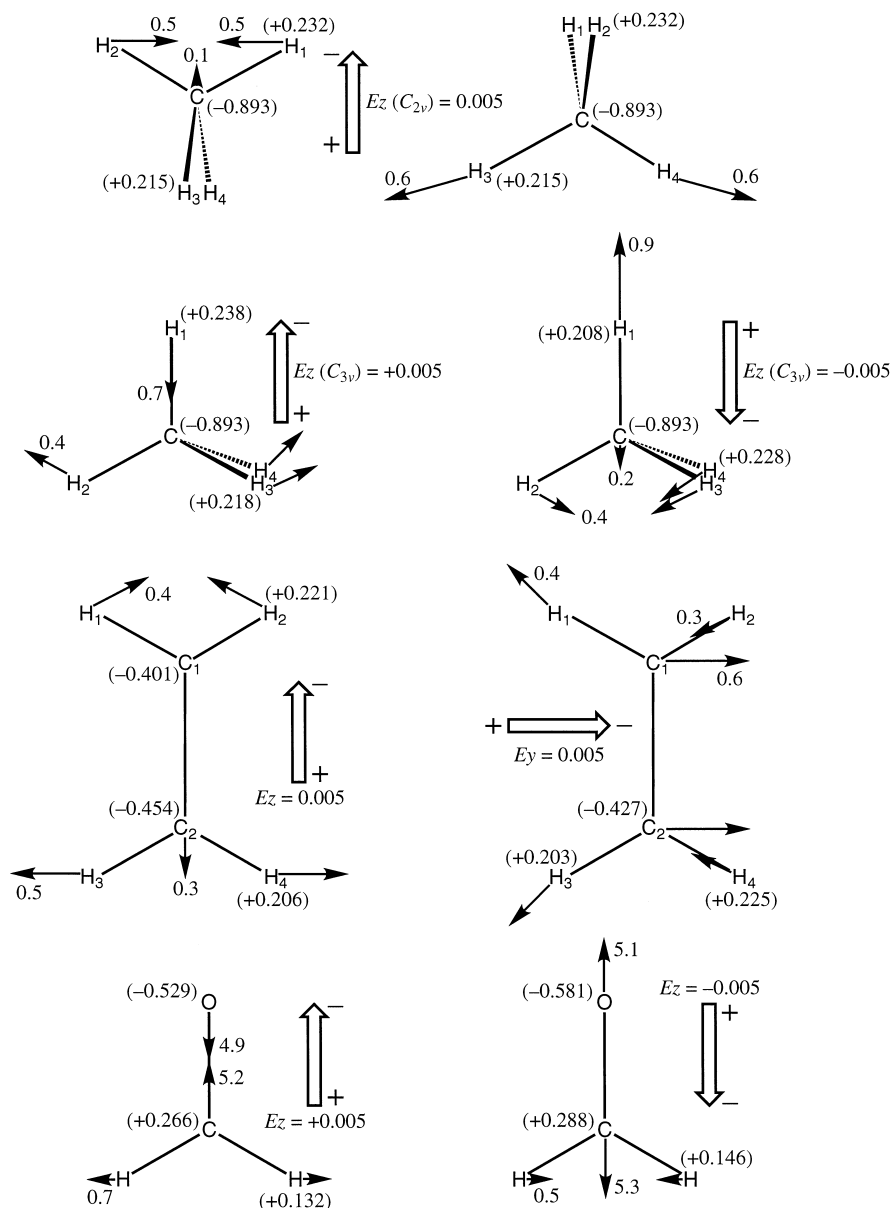


Fig. 4. Hellmann-Feynman forces (in 10^{-3} au) in CH_4 , C_2H_4 and H_2CO at their non-field equilibrium geometries in the presence of an electric field. Atomic charges (natural charges) in the absence of the field are: CH_4 : -0.893 for C and $+0.223$ for H; C_2H_4 : -0.427 for C and $+0.214$ for H; H_2CO : $+0.277$ for C, -0.555 for O and $+0.139$ for H.

without exception, the forces on CH_4 , C_2H_4 and H_2CO did not always follow the previous model. In particular, the previous model does not seem to be adequate for non-protic H atoms in hydrocarbons. Thus, the rule given by Eq. (4) should be re-examined for non-protic H atoms in a weak electric field.

6. Modification of the intuitive model by introducing a bond effect

Since the H–F force induced by the field is related to the electron density reorganization, $\Delta\rho(r_1)$, as shown by Eq. (2), its contour map may provide some insight into the problem encountered above. Such contour maps are shown in Fig. 5 for C_2H_4 in E_z (left) and E_y (right) fields. Similar maps are also given in Fig. 1 for CH_4 . The geometries are non-field equilibrium geometries.

The density maps given in Fig. 5 provide visual information about \mathbf{F}^{int} on each nucleus. The density around each atom mainly flows toward the positive pole of the field and therefore, \mathbf{F}^{int} on each atom is expected to be directed toward the positive pole. On

the other hand, \mathbf{F}^{ext} is directed exactly toward the negative pole and therefore, the resulting net force is expected to be roughly parallel to the field. However, the actual forces calculated for the Hs of C_2H_4 (Fig. 4) are quite different from the above expectation: the forces on the Hs have large components vertical to the electric field. Note that the density flow in the molecule occurs rather locally. It does not go over the entire molecule toward the positive pole. Rather, the flow seems to occur roughly by bond units. In the E_z case, we see an increase below the upper C_1 of the upper C–H units and below the lower two Hs (H_3 and H_4) of the lower C–H units. Note further that the density reorganization around C atoms is rather local, whereas that around H atoms is widespread and ranges over the C–H bond. This is because the electron on the hydrogen is rather weakly bound and widespread (the exponent of about 1.2 is the smallest among the atomic Slater exponents) and gives a hint as to why the forces on H atoms are different from other forces.

Now let us examine in more detail the density map of C_2H_4 in the E_z field. Focusing on the C–H bond region, we notice an increase in the density in the middle of the upper C–H bonds ($\text{C}_1\text{--H}_1$ and

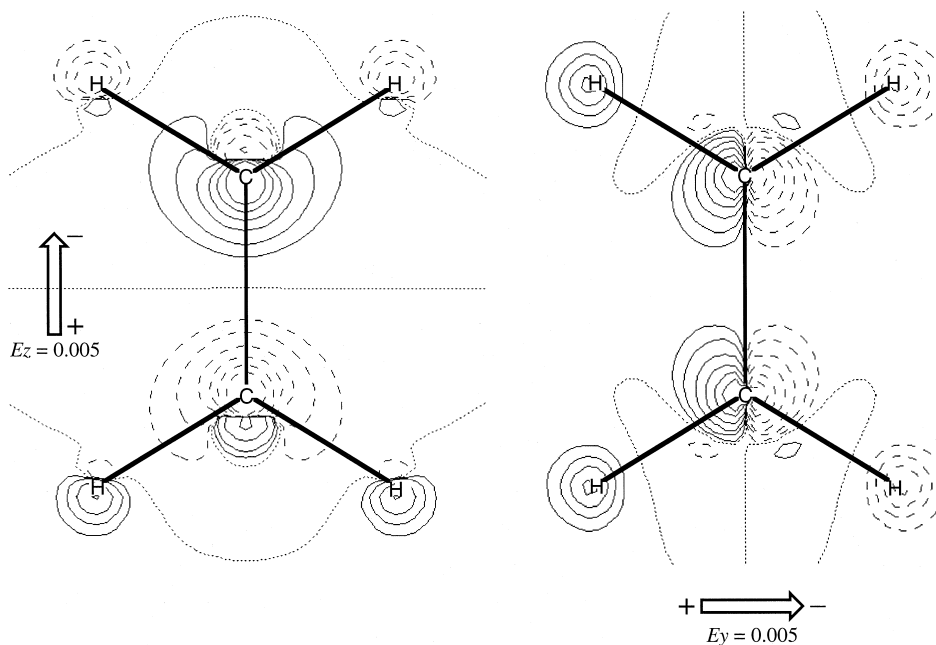


Fig. 5. Contour maps of the electron density reorganization of C_2H_4 due to an external electric field. The solid and broken lines (± 0.001 , ± 0.003 , ± 0.010 , ± 0.030 , ± 0.090 and ± 0.270) represent increased and decreased electron density, respectively.

C₁–H₂ in Fig. 3) and a decrease in the lower C–H bonds (C₂–H₃ and C₂–H₄). These changes are expected to be the result of the density flows from the H atom to the bond (upper) and from the bond to the H atom (lower) and should shorten the upper C–H bonds and elongate the lower C–H bonds. We call the effect due to these H-to-bond and bond-to-H local electron flows a bond effect. Considering this effect, we can correctly predict the directions of the forces on the H atoms in C₂H₄ in the E_z field. For H₁ and H₂, since the atoms are positively charged, the forces are directed toward the negative pole, as expected by the original model and, at the same time, are attracted by the density increase in the C–H bond region (bond effect). The resulting net force is their vector sum and the H atoms receive forces to make the H–C–H angle smaller and the C–H distance shorter, as shown in Fig. 5. On the other hand, for the lower H₃ and H₄ the C–H bond density decreases and therefore, they receive forces to elongate the C–H bond (bond effect), in addition to the forces toward the negative pole as the original model suggests. Thus, the lower H–C–H angle would increase and the C–H distance would be elongated by the field.

The forces on C₂H₄ in the E_y field are also accounted for in a similar manner. H-to-bond flow would occur on the right and bond-to-H flow would occur on the left. This bond effect results in a decrease and an increase in the density in the middle of the left and right C–H bonds, respectively, and causes elongation and shortening of the left and right bonds, respectively. Thus, this bond effect accounts for the vertical forces mentioned above. This explanation for C₂H₄ also applies to the forces acting on the H atoms of CH₄ and H₂CO.

The bond effect certainly applies in a weak electric field. Referring to Fig. 1 for CH₄, we see an increase in the electron density in the bond region of the C–H₁ bond for field strengths of 0.005, 0.01 and 0.05 au, while at 0.1 au, the electron flows up to the terminal atoms toward the positive pole. At $E = 0.05$ au, the bond effect gives a force toward the positive pole, but the charge of H₁ is +0.364, so that the external force toward the negative pole overwhelms the force due to the bond effect. Thus, the bond effect is seen only when the field is weak.

On the other hand, the H atoms in H₂O, NH₃ and

C₂H₂ are protic and their gross charges are larger than those of the non-protic H atoms in the hydrocarbons. Therefore, as expected from the previous model, F_A^{ext} is relatively large compared with F_A^{int} . Therefore, although an effect due to density flow to the X–H bond certainly exists (which causes the perpendicular components of the forces acting on the H atoms in H₂O and NH₃), the influence on the net force is small, so that the previous model is valid for these cases. In the NAO analyses, the boundary between protic and non-protic H atoms is an atomic charge of +0.23, though this value depends on the method of population analysis. Note that this bond effect is observed when the field has a component along the bond direction. For example, when the field is applied to C₂H₄ in a direction perpendicular to the molecular plane, the bond effect is small and the forces on H atoms are directed toward the negative pole, as the original model implies, despite their non-protic nature. We also calculated CH₂CN; the result was just a median between C₂H₂ and H₂CO.

Now, we summarize the bond effect. It results from the local nature of the electron reorganization due to the applied electric field. When the electric field is not very strong, the electron flow does not reach the furthest atoms toward the positive pole, but rather remains in the bond region. Since the electrons on the H atoms are very mobile, this effect is important for forces acting on H atoms. When the H atom of the C–H bond, for example, is closer to the negative pole, H-to-bond electron flow occurs, whereas bond-to-H electron flow would occur when it is closer to the positive pole. An increase (decrease) in electron density in the bond region causes a force towards (away from) the bond center and results in shortening (elongation) of the bond. This bond effect is important for the non-protic hydrogens of hydrocarbons. For more positive hydrogens, F_A^{ext} is larger than F_A^{int} , so that the bond effect is not apparent.

7. Conclusion

The purpose of this study is to establish the ESF or H–F force concept for predicting the geometries of molecules in strong to relatively weak external electric fields. Since we found that our previous

model was insufficient when the field is relatively weak, we calculated the forces and the density reorganization for various molecules using relatively weak electric fields. Our previous model is valid for molecules in relatively strong electric fields. The previous model also explains the results for weaker electric fields, except for non-protic H atoms and their counter atoms. For non-protic H atoms, the previous model is valid when it is corrected by the bond effect, which originates from the local nature of the electron density reorganization. The bond effect reflects the density flow to/from the bond region. The present model thus corrects the oversimplification in the previous model and is applicable to a wider range of field strengths.

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