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A Localized Molecular Orbital Approach to the Bond Moment Theory

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The bond moment theory was reinvestigated by use of localized molecular orbitals derived from INDO canonical orbitals. Bond moments were defined in terms of localized molecular orbital and, together with their derivatives with respect to a C–H stretching motion, were evaluated for some simple molecules; the bond moments of acetylene and hydrogen cyanide in the C–H bending geometry were also calculated. It is concluded that the first-order approximation for the bond moment theory is inadequate to interpret infrared absorption intensity. In the C–H stretching vibration the change in *trans*-sited bond moment is considerably large.

Some properties of a molecule have been analyzed by relating them to several characteristic values of bonds in the molecule. Furthermore, those values for particular kinds of bonds, *e.g.*, the C–H bond, are expected to be capable of being transfered from one molecule to another. A method of analyzing infrared absorption intensities along this line is well known as the bond moment theory.

Experimental approaches to the bond moment theory have been involved in some difficulties. The most serious one is that the number of intensity parameters needed for the application of the theory usually exceeds the number of pieces of experimental information. In practical treatments, therefore, we have been obliged to approximate the theory by neglecting a large part of parameters. Another difficulty is that the sign of dipole moment derivative with respect to the normal coordinate can not be decided uniquely from the experimental intensity.

There are some reports in which infrared absorption intensities were subjected to molecular orbital calculations.[1,2] In most studies molecular orbital calculations played only a supplemental role in the decision of the sign, which constitutes the second difficulty in experimental approach.[1] Recently, with the advance of electronic computer and with the popularization of molecular orbital calculations, infrared absorption intensities as well as vibrational frequencies have been calculated by the molecular orbital method, and successful results have been obtained.[2] Up to now, however, there are not so many reports on the bond moment theory conducted on the basis of molecular orbital calculations.

In this study, localized molecular orbitals (LMOs) which had been transformed from INDO canonical orbitals[3] by the Edmiston and Ruedenberg method[4] were used to define bond moments. The Edmiston and Ruedenberg method is based on maximization of the sum of intraorbital Coulomb repulsion energies and is called the energy localization method. Three other methods for determining LMOs were proposed by Foster and Boys,[5] von Niessen,[6] and Magnasco and Perico.[7] The agreement among results obtained by these four methods was generally good.[8] Figeys *et al.*[9] compared LMOs from *ab initio* canonical orbitals with those from semiempirical canonical orbitals, pointing out that the choice of canonical orbitals is important to gain a quantitative reliability. In this study, however, INDO canonical orbitals were used, because the main aim of the study lies in a qualitative check of the approximations which have been introduced into the bond moment theory and because INDO method gives fairly good electron distributions as compared with the other semiempirical methods. Bond moment derivatives with respect to a C–H stretching were calculated for several small molecules and also bond moments of acetylene and hydrogen cyanide were calculated with a condition of the C–H bond being bent.

The bond moment theory and the approximations introduced into it are described in the following section.

The Bond Moment Theory

The infrared absorption intensity A_a of the fundamental band for a normal vibration a is expressed, with the assumption of the harmonic oscillator approximation, as follows:[10]

$$A_a = \frac{N\pi}{3c}\sum_m \sum_n \left(\frac{\partial \boldsymbol{\mu}}{\partial R_m}\right)_0 \cdot \left(\frac{\partial \boldsymbol{\mu}}{\partial R_n}\right)_0 L_{ma}L_{na}, \tag{1}$$

where $\boldsymbol{\mu}$ is the molecular total dipole moment, c the velocity of light, N the Avogadro number, L_{ma} the element of the well-known transformation matrix between the internal coordinates $\{R_m\}$ and the normal coordinates $\{Q_a\}$. The starting point of the bond moment theory is that the total dipole moment $\boldsymbol{\mu}$ in Eq. 1 is given as the sum of bond moments, $\boldsymbol{\mu}_k$'s:

$$\boldsymbol{\mu} = \sum_k \boldsymbol{\mu}_k. \tag{2}$$

Introducing this expression, we rewrite Eq. 1 as follows:

$$A_a = \frac{N\pi}{3c}\sum_m \sum_n \sum_k \sum_l \left(\frac{\partial \boldsymbol{\mu}_k}{\partial R_m}\right)_0 \cdot \left(\frac{\partial \boldsymbol{\mu}_l}{\partial R_n}\right)_0 L_{ma}L_{na}. \tag{3}$$

As seen from this equation, the infrared absorption intensity can be interpreted in the terms of $(\partial \boldsymbol{\mu}_k/\partial R_m)_0$'s, bond moment derivatives with respect to the internal coordinates.

In the first stage of investigation, each bond moment was supposed to be parallel to any one bond in the molecule and its magnitude not to be changed without change in the bond length. Therefore, the bending mode which does not change the bond length will

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cause a variation in the total dipole moment only through a reorientational contribution of the bent bond. Within the restricted supposition, the calculated intensity did not agree with the experimental.[11) Hornig and McKean loosened the supposition,[12) adopting the following three approximations:

(a) When a bond is stretched by an amount dr, a moment $(\partial\mu/\partial r)\mathrm{d}r$ is produced in the direction of the bond.

(b) When a bond is bent through an angle dα, a moment $\mu^e\mathrm{d}\alpha$, where μ^e is the "*effective*" bond moment, is produced in the plane of bending and perpendicular to the direction of the bond.

(c) When any one bond is bent or stretched, no moments are produced in the other bonds.

They investigated experimental infrared intensities of many molecules on the basis of these approximations and concluded that the "*effective*" bond moment of a given bond is not constant, that is, intensities of two different vibrational modes including the bond derive different values of the "*effective*" bond moment. They also concluded that in molecules containing lone pair electrons their effect must be taken into account explicitly. Orville-Thomas and his coworkers studied infrared absorption intensities of several triatomic molecules on the bond moment theory.[13–15) They concluded that the approximations introduced by Hornig and McKean are inadequate to interpret intensities. Therefore, they replaced the approximation (c) given above by a new approximation as follows:

(c′) When a particular bond is bent or stretched, a moment is produced in adjacent bonds.

They called the new set of approximations the "first-order bond moment theory" in contrast with the old one called the "zero-order bond moment theory." The intensity parameters in the new approximations are so many as to make impossible their evaluation from experimental intensities. Then, they had to elaborate some parameters in the form of composite term.[14) They also revealed that in bending modes atomic polarization terms of dipole moment, called rehybridization terms, are significant for interpreting intensities.[15)

Anyway, the investigations described above were founded on the assumption that each bond moment μ_k in Eq. 2 must belong to a certain bond in a molecule. Therefore, the lone pair electrons and the atomic polarization terms had to be treated as if they were new kinds of moments. Some investigations on the bond moment have been carried out by use of some terms of LMOs.[16,17) They will be discussed in comparison with our results.

Methods of Calculation

LMOs $\{\phi_i\}$ were calculated by the Edmiston and Ruedenberg method. The degree of localization was judged in our program as follows: The weight of atom A, w_A, in LMO ϕ_i is calculated by summing the squares of the LCAO coefficients of the atomic orbitals which belong to the atom. When w_A is larger than 0.9, LMO ϕ_i is regarded to be localized on atom A and the degree of localization is given by w_A. When any one w_A does not exceed 0.9 and the sum of w_A and w_B is larger than 0.9, LMO ϕ_i is regarded to be localized at bond A–B and the degree of localization is given by w_A+w_B.

The definition of localized orbital moment for each LMO follows that of Gordan and England[16) as follows:

(1) When LMO ϕ_i is localized at bond A–B, the localized orbital moment is expressed as

$$\mu_i = -2\langle\phi_i|e\boldsymbol{r}|\phi_i\rangle + (\boldsymbol{R}_A+\boldsymbol{R}_B)e. \tag{4}$$

(2) When LMO ϕ_i is localized on atom A as lone pair orbitals or as inner shell orbitals, the localized orbital moment is expressed as

$$\mu_i = -2\langle\phi_i|e\boldsymbol{r}|\phi_i\rangle + 2\boldsymbol{R}_Ae. \tag{5}$$

In the above expressions $\boldsymbol{R}_A$ is the position vector of atom A and $\boldsymbol{r}$ is that of an electron. In the INDO calculation the second type of LMO always corresponds to a lone pair orbital. In this study the bond moment is defined as follows:

(1) The bond moment of bond A–B is the sum of the localized bond moments of the LMOs which are localized at the bond.

(2) If LMO ϕ_i is a lone pair orbital, its localized orbital moment itself is regarded as a kind of bond moment. The definitions, particularly (2), are useful in comparing bond moments and their derivatives between various molecules.

Bond moment derivatives with respect to a C–H stretching were calculated from bond moments for the C–H bond displaced +0.1 Å from the equilibrium length.

Results and Discussion

The Cartesian coordinate system used to calculate

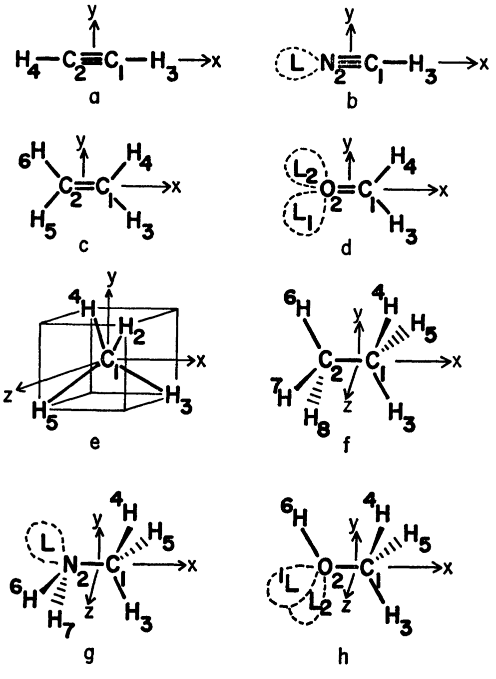

Fig. 1. Numbering of atoms and coordinate system. a: Acetylene. b: Hydrogen cyanide. c: Ethylene. d: Formaldehyde. e: Methane. f: Ethane. g: Methylamine. h: Methanol.

TABLE 1. CALCULATED BOND MOMENTS AND THEIR COMPONENTS AT EQUILIBRIUM MOLECULAR GEOMETRY
(1 D=3.33564×10^{-30} C m)

Bond[a]	$\lvert\mu\rvert$ / D	μ_x / D	μ_y / D	μ_z / D	θ[b] / °	s-Character[c] / %
Acetylene						
C_1-H_3	2.000	−2.000	0.0	0.0	0.0	45.7
Hydrogen cyanide						
C_1-H_3	2.049	−2.049	0.0	0.0	0.0	50.5
C_1-N_2	1.182	1.182	0.0	0.0	0.0	
L	3.319	3.319	0.0	0.0		
Ethylene						
C_1-H_3	1.959	−1.044	1.658	0.0	0.854	32.3
Formaldehyde						
C_1-H_3	2.278	−1.225	1.921	0.0	1.514	39.9
C_1-O_2	2.056	2.056	0.0	0.0	0.0	
L_1	2.740	1.146	2.489	0.0		
Methane						
C_1-H_2	2.037	−1.176	−1.176	−1.176	0.0	27.3
Ethane						
C_1-H_3	1.956	−0.646	1.846	0.0	0.303	26.3
Methylamine						
C_1-H_3	2.152	−0.738	2.022	0.0	0.590	28.0
C_1-H_4	2.067	−0.638	−0.978	−1.706	1.470	28.7
C_1-N_2	0.676	0.657	0.158	0.0	13.62	
N_2-H_6	1.221	0.315	0.662	−0.977	7.862	22.8
L	3.338	0.982	−3.190	0.0		
Methanol						
C_1-H_3	2.099	−0.600	2.011	0.0	2.933	30.4
C_1-H_4	2.173	−0.690	−1.032	−1.783	1.087	29.6
C_1-O_2	1.237	1.234	−0.089	0.0	3.995	
L_1	2.875	0.804	1.215	−2.478		
O_2-H_6	0.626	0.058	−0.623	0.0	13.80	18.5

a) The numbering of atoms, designation of lone pair orbitals, and coordinate systems are shown in Fig. 1. b) The angle between the bond and the corresponding bond moment. c) The weight of the 2s-orbital per the overall weight of atom X in the X-H localized orbital.

dipole moment values is shown in Fig. 1. The numbering of atoms and the designation of lone pair orbitals in each molecule are also shown.

Values of bond moments and their components and of angles between bond moments and corresponding bonds were calculated for the equilibrium geometries. The results are listed in Table 1, except those which are clear from the geometrical properties. The values of angles for the C–H bonds are not so large and are in the same order as those reported by Gordon and England.[16] Bruns *et al.*[18] calculated the dipole moment derivatives of ammonia with respect to the symmetry coordinates. In their report the angles between the bond moment and the corresponding N–H bond is 2.15°. On the other hand in our results, the values for the N–H and C–N bonds in methylamine and for the O–H and C–O bonds in methanol are somewhat large. From these results it may be said that the bond moment direction of an X–Y bond, where X and/or Y have lone pair orbitals, largely deviates from the bond and that hydrogen cyanide, formaldehyde, and ammonia fall in special cases where highly symmetrical geometries are possessed.

Since the Edmiston and Ruedenberg method for calculating LMOs has no guarantee for giving full localization, the degree of localization was tested for molecules in equilibrium geometry. It was greater than 0.99 for the bond localized orbital, while for the lone pair orbital it was less than 0.99 with a minimum of 0.969 for hydrogen cyanide. Gordon and England[16] calculated the degree of localization for many hydrocarbons and concluded that the overflow of electrons due to a very small delocalization, which they called tail, was not negligible for some properties of molecules. Therefore, each bond moment of hydrogen cyanide and formaldehyde which reveal the large delocalization was divided into two contribution parts, *i.e.*, the *intra*-LMO part and the *extra*-LMO part. The calculated results are listed in Table 2. It is seen from the table that the contribution of the *extra*-LMO part is at most 5%.

It is found from the first column of Table 1 that the absolute values of the C–H bond moments are varied in the range from 1.96 to 2.28 D (1 D=3.33564×10^{-30} C m). Their average and standard deviations are 2.077 and 0.096 D, respectively. The deviation is somewhat large as compared with the results of Kapuy and Kozmutza,[17] who investigated properties of LMOs by the *ab initio* molecular orbital calculation. If the LMO of C–H bond is fully localized, the bond moment is a function of the C–H distance vector, the bond polarization of the electron distribution in the LMO, and the s-character of the hybrid orbital in the carbon atom. When the bond polarization does not appear, it is a function of only the s-character and the values of the bond moments are 2.258, 2.128, and 1.955 D for the sp-, sp^2-, and sp^3-hybrid orbitals, respectively; that is, the bond moment changes with the increase in s-character. The s-character of atom X in the X–H bond is shown in the last column of Table 1. It is shown that the order of magnitude for the calculated C–H bond moments does not agree with that of the s-character. Thus it is concluded that the C–H bond moment is determined by not only the s-character but also the bond polarization. The latter factor is dominantly affected by the environment of the C–H bond, so that the

TABLE 2. INTRA-ORBITAL AND EXTRA-ORBITAL CONTRIBUTION TO BOND MOMENTS

Bond[a)]	*Intra*		*Extra*	
	μ_x/D	μ_y/D	μ_x/D	μ_y/D
Hydrogen cyanide				
C_1-H_3	−2.078		0.029	
C_1-N_2	1.184		−0.002	
L	3.287		0.033	
Formaldehyde				
C_1-H_3	−1.221	1.940	−0.004	−0.020
C_1-H_4	−1.221	−1.940	−0.004	0.020
C_1-O_2	2.058	0.0	−0.002	0.0
L_1	1.187	2.573	−0.041	−0.084
L_2	1.187	−2.573	−0.041	0.084

a) See footnote a) in Table 1.

TABLE 3. BOND MOMENT DERIVATIVES WITH RESPECT TO A C–H STRETCHING

Bond[a,b)]	μ'_x / D Å^{-1}	μ'_y / D Å^{-1}	μ'_z / D Å^{-1}	$\lvert\mu'\rvert$ / D Å^{-1}
Acetylene(C_1-H_3)				
C_1-H_3	0.294			0.294
C_1-C_2	−0.096			0.096
C_2-H_4	−0.144			0.144
Total	0.054			0.054
Hydrogen cyanide(C_1-H_3)				
C_1-H_3	0.365			0.365
C_1-N_2	0.118			0.118
L	−0.562			0.562
Total	−0.079			0.079
Ethylene(C_1-H_3)				
C_1-H_3	0.127	0.093		0.157
C_1-H_4	−0.431	0.146		0.455
C_1-C_2	0.149	0.403		0.430
C_2-H_5	−0.057	−0.046		0.073
C_2-H_6	−0.278	0.143		0.313
Total	−0.490	0.739		0.887
Formaldehyde(C_1-H_3)				
C_1-H_3	0.008	0.237		0.237
C_1-H_4	−0.377	0.371		0.529
C_1-O_2	0.342	0.400		0.526
L_1	0.113	−0.062		0.129
L_2	−0.732	0.246		0.772
Total	−0.646	1.192		1.356
Ethane(C_1-H_3)				
C_1-H_3	0.085	0.122	0.0	0.149
C_1-H_4	−0.214	0.177	−0.183	0.278
C_1-H_5	−0.214	0.177	0.183	0.278
C_1-C_2	0.170	0.301	0.0	0.346
C_2-H_6	−0.186	0.109	0.0	0.216
C_2-H_7	−0.013	−0.015	0.026	0.033
C_2-H_8	−0.013	−0.015	−0.026	0.033
Total	−0.385	0.856	0.0	0.939
Methylamine(C_1-H_3)				
C_1-H_3	−0.005	0.307	0.0	0.307
C_1-H_4	−0.196	0.214	−0.180	0.341
C_1-H_5	−0.196	0.214	0.180	0.341
C_1-N_2	0.184	0.291	0.0	0.344
L	−0.479	0.156	0.0	0.560
N_2-H_6	−0.007	−0.035	0.024	0.043
N_2-H_7	−0.007	−0.035	−0.024	0.043
Total	−0.706	1.112	0.0	1.317
Methanol(C_1-H_3)				
C_1-H_3	0.062	0.114	0.0	0.130
C_1-H_4	−0.172	0.209	−0.185	0.328
C_1-H_5	−0.172	0.209	0.185	0.328
C_1-O_2	0.109	0.201	0.0	0.229
O_2-H_6	−0.183	0.107	0.0	0.212
L_1	0.002	−0.003	0.003	0.005
L_2	0.002	−0.003	−0.003	0.005
Total	−0.352	0.834	0.0	0.905
Methylamine(C_1-H_4)				
C_1-H_3	−0.197	0.055	−0.273	0.341
C_1-H_4	0.048	−0.091	−0.149	0.181
C_1-H_5	−0.189	−0.251	−0.075	0.323
C_1-N_2	0.135	−0.128	−0.204	0.276
L	−0.014	0.009	−0.009	0.019
N_2-H_6	−0.016	−0.011	0.024	0.031
N_2-H_7	−0.191	−0.058	−0.094	0.221
Total	−0.424	−0.475	−0.780	1.007
Methanol(C_1-H_4)				
C_1-H_3	−0.175	0.047	−0.280	0.334
C_1-H_4	0.009	−0.116	−0.202	0.233
C_1-H_5	−0.173	−0.267	−0.103	0.334
C_1-O_2	0.156	−0.111	−0.201	0.278
O_2-H_6	−0.006	0.025	0.007	0.027
L_1	0.030	0.008	−0.011	0.033
L_2	−0.359	−0.026	−0.121	0.380
Total	−0.518	−0.440	−0.911	1.137

a) See footnote a) in Table 1. b) The stretching C–H bond is referred to in the parentheses.

transferability of bond moment is permitted only in rather limited congeners.

Bond moment derivatives with respect to the change in C–H bond length were calculated and are listed in Table 3. In most of the molecules the values of many off-diagonal terms are larger than that of the diagonal term. In the cases of acetylene and hydrogen cyanide the derivative of the neighbouring bond moment is small in comparison with that of the non-neighbouring bond moment. Furthermore, the direction of the vector for the non-neighbouring bond moment derivative is opposite to that of the diagonal term so that a large part of derivatives may be cancelled. In ethylene and formaldehyde the derivatives of the neighbouring and the *trans*-sited bond moments are larger than the diagonal term. A similar situation is also found in the results of ethane, methylamine, and methanol. The values of the diagonal terms are in the range of 0.130 to 0.367 D/Å with a standard deviation of 33.5%. Due to their large deviation, the expectation for the transferability between them must be abandoned. In Fig. 2 are illustrated the vectors of the bond moment derivatives for the planar molecules and the projections of the vectors on the plane of symmetry which includes the stretching C–H bond for the nonplanar molecules. The derivatives of the total dipole moments are also shown in the figure. It is found from the figure that the direction of each bond moment derivative is neither along the bond itself nor along the stretching bond, but that the derivative of the total dipole moment has a direction nearly along the stretching bond. It is noteworthy that the overall configuration of bond moment derivatives in a molecule resembles that in another one. It is concluded from the results that if the bond moment theory is developed with LMOs, the first-order approximation is inadequate to explain the change in dipole moment.

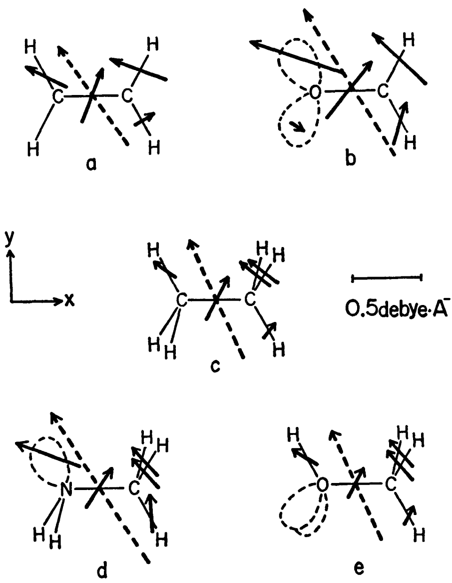

Fig. 2. Projection in xy-plane of bond moment derivatives with respect to a C_1–H_3 stretching.
A C_1–H_3 bond is illustrated in Fig. 1. a: Ethylene. b: Formaldehyde. c: Ethane. d: Methylamine. e: Methanol. ——→: Bond moment derivative; ---→: total dipole moment derivative.

Some investigators have claimed that the hybridization term of dipole moment is significant to interpret the infrared absorption intensity, especially for bending modes. In our calculations, each bond moment can be divided into the (bond) polarization and hybridization terms. Change in bond moment for a C–H bending motion was studied for acetylene and hydrogen cyanide. The results are listed in Table 4. In the table $\Delta\mu=\mu_{10}-\mu_{eq}$, where μ_{10} is the bond moment when a C–H bond is bent 10° and μ_{eq} is that for the equilibrium geometry. It is concluded from the table that the x-components are caused to change slightly and that a main contribution to the change in the y-component arises from the hybridization terms; in the y-component of the diagonal term, *i.e.*, the bond moment change in the bent bond, the hybridization term is opposite in sign to the polarization term. This conclusion seems similar to the conclusion reported by Galabov and Orville-Thomas.[19] But these two conclusions cannot be regarded as the same since in Ref. 19 the rehybridization term is calculated as the atomic polarization for the central atom of bending, whereas in our results the corresponding atomic polarization is divided into the hybridization terms of two bond moments relating to the central atom. Anyway, it is concluded that the hybridization term is important to interpret the bond moment. It is noticeable that the polarization terms for the y-components of the off-diagonal terms are very small but not to be taken as zero. If the LMOs are fully localized at the bonds, the polarization terms do not change.

TABLE 4. CHANGES IN BOND MOMENTS WITH RESPECT TO A C–H BENDING[a)]

Bond[b)]	$\Delta\mu_x$[c)]/D		$\Delta\mu_y$[c)]/D	
	pol.[d)]	hyd.[d)]	pol.[d)]	hyd.[d)]
Acetylene				
C_1-H_3	0.002	0.009	0.050	−0.219
C_1-C_2	−0.008	−0.021	−0.000	0.218
C_2-H_4	0.003	−0.001	−0.002	0.045
Total	−0.003	−0.013	0.048	0.044
Hydrogen cyanide				
C_1-H_3	−0.000	0.011	0.051	−0.242
C_1-N_2	−0.010	−0.019	−0.000	0.160
L	0.005	−0.004	−0.007	0.192
Total	−0.004	−0.011	0.044	0.109

a) The molecular geometries for the C–H bending are shown in Fig. 3. b) See footnote a) in Table 1. c) See text. d) Abbreviations pol. and hyd. refer to the bond polarization term and the hybridization term, respectively.

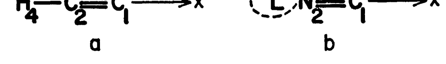

Fig. 3. Molecular geometry at a C–H bending.
a: Acetylene. b: Hydrogen cyanide.

Therefore, their nonzero values are due to the delocalization to the bent bond.

Although localized molecular orbitals are useful to investigate bond moments and their derivatives with respect to an appropriate coordinate, the transferability of intensity parameters in the bond moment theory should carefully and extensively be examined. If the intensity parameters need to be discussed with quantitative accuracy, it is important to use good canonical orbitals.

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