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Effect of Atomic Dipole in Semi-Empirical Calculation of π-Electron Energy Levels

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The importance of the effect of atomic dipole is emphasized and clarified in semi-empirical calculations for π-electron energy levels of molecules with lone pair electrons. The actual examples taken up here are the excitation energies in CO_2 molecule and NCN radical. The calculation was carried out by improving the treatment used for oxygen molecule by Fumi and Parr [1]. It is shown that the experimental results cannot satisfactorily be explained by disregarding the terms of charge-dipole interaction except in some limited cases.

Die Bedeutung des Effekts von Atomdipolen wird hervorgehoben und in semiempirischen Rechnungen für π-Elektronen Energieniveaus von Molekülen mit einsamen Elektronenpaaren näher erläutert. Als Beispiel werden die Anregungsenergien des CO_2 Moleküls und des NCN Radikals berechnet. Diese Berechnung wurde mit der von Fumi und Parr [1] für das Sauerstoffmolekül benutzten Methode, die verbessert wurde, durchgeführt. Es wird gezeigt, daß die experimentellen Ergebnisse nur in Ausnahmefällen ohne Berücksichtigung der Ladungs-Dipol-Wechselwirkung zufriedenstellend erklärt werden können.

Introduction

On the multipole expansion of charge distribution in molecules, the second important part is the charge (monopole)-dipole interaction. However, in usual semi-empirical calculation of π-electron energy levels such as Pariser-Parr-Pople method [2], such terms are not *explicitly* included. In the present work, the importance of the effect of charge-dipole interaction will be emphasized and clarified by a semi-empirical calculation for π-electron energy levels of some symmetric linear molecules in which such a contribution is predominant. The examples taken up here are ACA-type molecules, which A is an atom with lone pair electrons and C is a central carbon atom bonded to the two A atoms. In this case, the σ bonding electrons of the C atom may simply be assumed as the sp hybridized orbitals:

$$\chi_{\substack{1C\\2C}} = 2^{-1/2}[\chi_{sC} \pm \chi_{\sigma C}] \, . \tag{1}$$

where χ_{sX} and $\chi_{\sigma X}$ are, respectively, the $2s$ and the $2p\sigma$ orbitals of atom X. If the $2s$-character of A atom with N_A valence electrons is taken as n_A, the bonding and the lone pair σ orbitals of A atom may be expressed as

$$\chi_{bA} = (1+\lambda_A^2)^{-1/2}[\chi_{sA} + \lambda_A \chi_{\sigma A}] \tag{2}$$

and

$$\chi_{lA} = (1+\lambda_A^2)^{-1/2}[\lambda_A \chi_{sA} - \chi_{\sigma A}] \, , \tag{3}$$

respectively, where

$$\lambda_A = [(n_A - 1)/(2 - n_A)]^{1/2} \, . \tag{4}$$

Including the effect of atomic dipoles, the Coulomb integrals of atoms C and A are described as follows:

$$\begin{aligned}\alpha_{\mathrm{C}} = {} & W_{\pi\mathrm{C}} - F_{\pi\mathrm{C}} - 2N_{\mathrm{A}}(\mathrm{A}:\pi_{\mathrm{C}}\pi_{\mathrm{C}}) + 2n_{\mathrm{A}}(\pi_{\mathrm{C}}\pi_{\mathrm{C}}:s_{\mathrm{A}}s_{\mathrm{A}}) \\ & + 2(N_{\mathrm{A}}-n_{\mathrm{A}})(\pi_{\mathrm{C}}\pi_{\mathrm{C}}:\sigma_{\mathrm{A}}\sigma_{\mathrm{A}}) - 4\lambda_{\mathrm{A}}(1+\lambda_{\mathrm{A}}^2)^{-1}(\pi_{\mathrm{C}}\pi_{\mathrm{C}}:s_{\mathrm{A}}\sigma_{\mathrm{A}})\end{aligned} \tag{5}$$

and

$$\begin{aligned}\alpha_{\mathrm{A}} = {} & W_{\pi\mathrm{A}} - F_{\pi\mathrm{A}} - 4(\mathrm{C}:\pi_{\mathrm{A}}\pi_{\mathrm{A}}) + (\pi_{\mathrm{A}}\pi_{\mathrm{A}}:s_{\mathrm{C}}s_{\mathrm{C}}) + (\pi_{\mathrm{A}}\pi_{\mathrm{A}}:\sigma_{\mathrm{C}}\sigma_{\mathrm{C}}) \\ & - N_{\mathrm{A}}(\mathrm{A}':\pi_{\mathrm{A}}\pi_{\mathrm{A}}) + n_{\mathrm{A}}(\pi_{\mathrm{A}}\pi_{\mathrm{A}}:s_{\mathrm{A}'}s_{\mathrm{A}'}) + (N_{\mathrm{A}}-n_{\mathrm{A}})(\pi_{\mathrm{A}}\pi_{\mathrm{A}}:\sigma_{\mathrm{A}'}\sigma_{\mathrm{A}'}) \\ & - 2\lambda_{\mathrm{A}}(1+\lambda_{\mathrm{A}}^2)^{-1}(\pi_{\mathrm{A}}\pi_{\mathrm{A}}:s_{\mathrm{A}'}\sigma_{\mathrm{A}'}),\end{aligned} \tag{6}$$

where $W_{\pi\mathrm{X}}$ is average π-electron energy of the corresponding valence state of the X atom, $F_{\pi\mathrm{X}}$ is an average interaction energy of the π-electron in question with the other π-electrons in the same atom,

$$(\mathrm{X}:pq) = \int \chi_p^*(1)\,(1/r_{\mathrm{X}1})\,\chi_q(1)\,d\tau_1 \tag{7}$$

and

$$(pq:rs) = \iint \chi_p^*(1)\,\chi_r^*(2)\,(1/r_{12})\,\chi_q(1)\,\chi_s(2)\,d\tau_1\,d\tau_2\,. \tag{8}$$

The last term of Eqs. (5) and (6) is evidently due to the charge-dipole interaction. The other procedures adopted are similar with those of oxygen molecule by Fumi and Parr [1] in which the assumption of zero overlap and zero differential overlap was made except that in a same atom. The $W_{\pi\mathrm{A}}$'s for various values of n_{A} are linearly interpolated as a function of n_{A} from the ionization energy of the corresponding valence state with $s^2p^{N_{\mathrm{A}}-2}$ configuration and that with $sp^{N_{\mathrm{A}}-1}$ configuration. The $F_{\pi\mathrm{A}}$'s and the other one-center integrals were estimated from the experimental data [3] using the method of least-squares. The two-center integrals of CO_2 molecule are taken from the paper by Mulligan [4], and those of NCN and HCCCH radicals are obtained by using the simple Slater orbitals with orbital exponent of $\delta_{\mathrm{C}} = 1.625$ and $\delta_{\mathrm{N}} = 1.950$. The internuclear distances are taken as $R_{\mathrm{CO}} = 1.162\,A$, $R_{\mathrm{CN}} = 1.232\,A$ and $R_{\mathrm{CC}} = 1.277\,A^1$ and $1.3084\,A^2$. The LCAO-MO's used are the solutions of the restricted Hartree-Fock equations.

CO_2 Molecule

In the CO_2 molecule, the three lowest excited states observed [7] are due to the excitation of one of the π-electrons from the ground state ${}^1\Sigma_g^+$ into the other π-orbitals. They are the ${}^1B_2$, ${}^1A_1$, and ${}^1B_1$ states with symmetry of C_{2v} corresponding to the ${}^1\Delta_u$, ${}^1\Delta_g$, and ${}^1\Sigma_g^-$ states with symmetry $D_{\infty h}$, respectively. This may show the fact that the CO_2 molecule is a fairly suitable example for knowing the contribution of the charge-dipole interaction, although the definite values of the vertical excitation energies may be rather difficult to estimate because of lack of the experimental data. In the present work, these energies from the ground state ${}^1\Sigma_g^+$ to the lower electronic states were calculated by varying the ratio of $2s-2p$ hybridization of the oxygen orbitals, (2) and (3), and also the value of resonance integral $\beta_{\mathrm{CO}}(CO_2)$ between the π-orbitals of carbon and oxygen. The ${}^1\Delta_g$ state obtained is always close to locate the ${}^1\Sigma_g^-$ state in good agreement with the experiment [7].

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[1] The internuclear distance of C_3 radical [5].

[2] The internuclear distance of allene molecule [6].

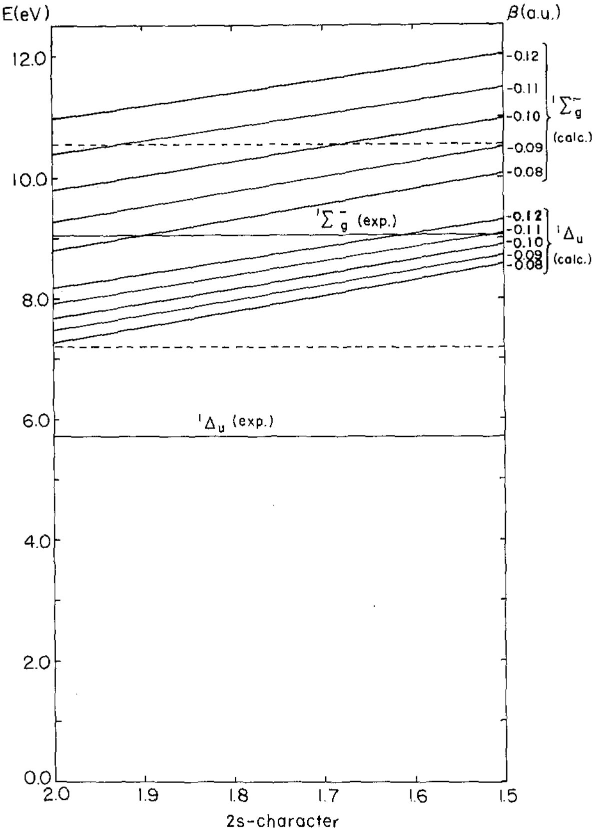

Fig. 1. Vertical π-electron excitation energies without charge-dipole interaction in CO_2 molecule as a function of 2*s*-character of oxygen and of resonance integral between π-orbitals of carbon and oxygen (β). The horizontal full lines are the experimental excitation energies to the $^1B_2(^1\Delta_u)$ and the $^1B_1(^1\Sigma_g^-)$ states with equilibrium structure, while the dotted lines are the roughly estimated ones to these states with linear structure, i.e. 1.5 eV above the experimental values

The vertical excitation energies from the ground state $^1\Sigma_g^+$ to the $^1\Delta_u$ and the $^1\Sigma_g^-$ states calculated for various conditions are shown in Figs. 1 and 2 corresponding to the cases without and with the terms of charge-dipole interaction, respectively. In these cases, the restricted configuration interaction (CI) was included among $(1\pi_u)^4(1\pi_g)^4$, $(1\pi_u)^4(1\pi_g)^2(2\pi_u)^2$, $(1\pi_u)^3(1\pi_g)^4(2\pi_u)$ and $(1\pi_u)^4(1\pi_g)^3(2\pi_u)$. Because of lack of experimental data, the vertical excitation energies to these states may roughly be estimated to be 1.5 ± 0.3 eV above the values between the most stable structures of the states concerned. It should be noted here that the results without CI and those without charge-dipole interaction are completely unsatisfactory in elucidating both the excitation energies, even if the change of the molecular structure in the excited states is taken into consideration. As can be seen in Fig. 2, however, the results with such interactions are fairly good under some restricted conditions: for example, $n_O = 1.90 \sim 1.96$ for $\beta_{CO}(CO_2) = -0.13$ a.u., and $n_O = 1.80 \sim 1.83$ for $\beta_{CO}(CO_2) = -0.14$ a.u. Evidently, this does show the

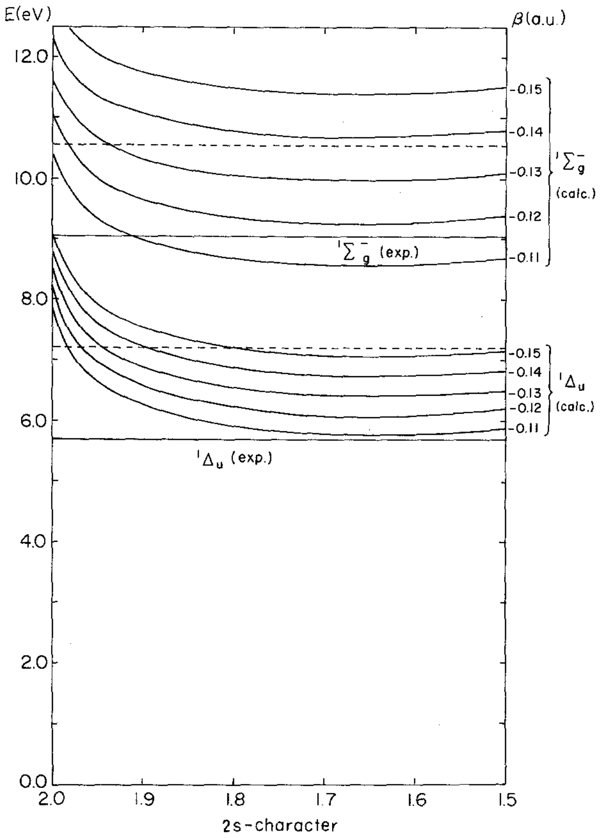

Fig. 2. Vertical π-electron excitation energies with charge-dipole interaction in CO_2 molecule as a function of 2*s*-character of oxygen and of resonance integral between π-orbitals of carbon and oxygen (β). The horizontal full lines are the experimental excitation energies to the $^1B_2(^1\Delta_u)$ and the $^1B_1(^1\Sigma_g^-)$ states with equilibrium structure, while the dotted lines are the roughly estimated ones to these states with linear structure, i.e. 1.5 eV above the experimental values

importance of inclusion of the electron-atomic dipole interaction. Table 1 gives the two examples for the calculated vertical excitation energies of the lower electronic states with $n_O = 1.90$ and $\beta_{CO}(CO_2) = -0.13$ a.u. and those with $n_O = 1.80$ and $\beta_{CO}(CO_2) = -0.14$ a.u. Although these results should not be final, the probable values of the 2*s*-character of oxygen n_O do not essentially contradict to the σ-electron populations of $(2s)^{1.84}(2p\sigma)^{1.16}$ obtained from the SCF-LCAO-MO's by Mulligan [4].

NCN Radical

Although the electronic structure of the NCN radical is rather similar to that of the oxygen molecule, the observed lower electronic states due to the $\pi_u - \pi_g$ type excitation have hardly been known, except for the $^3\Sigma_u^-$ state [8]. Therefore, the estimation of excitation energies from the ground state $^3\Sigma_g^-$ to

Table 1. Vertical π-electron excitation energies in CO_2 molecule (eV)

State	$n_O = 1.90$ $\beta = -0.130$ a.u.				$n_O = 1.80$ $\beta = -0.140$ a.u.			
	With charge-dipole interaction		Without charge-dipole interaction		With charge-dipole interaction		Without charge-dipole interaction	
	With CI	Without CI	With CI	Without CI	With CI	Without CI	With CI	Without CI
$^1\Sigma_g^-$	10.36	11.60	11.81	12.58	10.79	12.21	12.63	13.37
$^3\Sigma_g^-$	10.26	11.54	11.74	15.85	10.66	11.19	12.56	16.76
$^1\Delta_g$	10.19	11.73	11.67	12.63	10.60	12.36	12.49	13.44
$^3\Delta_g$	9.96	10.92	11.37	11.97	10.34	11.51	12.18	12.75
$^3\Sigma_g^+$	9.67	10.24	10.97	11.36	10.17	10.80	11.77	12.13
$^1\Sigma_g^+$	8.47	9.62	9.70	10.84	8.96	10.07	10.44	11.54
$^1\Delta_u$	6.90	6.27	8.65	8.36	6.88	6.13	9.13	8.85
$^1\Sigma_u^-$	6.75	6.11	8.61	8.33	6.67	5.92	9.08	8.81
$^3\Sigma_u^-$	6.75	6.11	8.61	8.33	6.67	5.92	9.08	8.81
$^3\Delta_u$	6.22	5.58	8.16	7.87	6.11	5.36	8.62	8.34
$^3\Sigma_u^+$	5.70	5.05	7.70	7.42	5.55	4.80	8.15	7.88
$^1\Sigma_g^+$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

these states is of interest from both the experimental and the theoretical viewpoints.

In order to determine the value of resonance integral $\beta_{CN}(NCN)$ between the π-orbitals of carbon and nitrogen for the NCN radical, the values of $\beta_{CN}(HCN)$ of the HCN molecule corresponding to the various values of n_N (2s-character of nitrogen) were chosen so as the calculated excitation energy of $^1\Sigma^+(^1A'') \leftarrow {}^1\Sigma^+$ to give the experimental value of 7.434 eV. The procedure used here is quite the same as in the previous CO_2 molecule. Then, the values of $\beta_{CN}(NCN)$ were determined adopting the relation of

$$[\beta_{CN}(NCN)/\beta_{CN}(HCN)] \cong [S_{CN}(NCN)/S_{CN}(HCN)]\,, \tag{9}$$

where the S_{CN} is the overlap integral between π-orbitals of carbon and nitrogen. Using the $\beta_{CN}(NCN)$ so obtained, the restricted SCF-LCAO-MO's were determined and the $\pi - \pi$ excitation energies were calculated for various values of n_N. In these calculations, the vertical excitation energy of the HCN molecule was estimated from the experimental data [9] by assuming that the vibrations of the HC and the CN fragments are harmonic and that the potential energy curve of the HCN bending vibration is quartic parabolic. The electronic configurations included in the restricted CI calculations are as follows: $(1\pi)^4$, $(1\pi)^3(2\pi)$ and $(1\pi)^2(2\pi)^2$ for the HCN molecule, and $(1\pi_u)^4(1\pi_g)^2$, $(1\pi_u)^2(1\pi_g)^4$, $(1\pi_u)^4(2\pi_u)^2$, $(1\pi_u)^3(1\pi_g)^2(2\pi_u)$, $(1\pi_u)^3(1\pi_g)^3$, and $(1\pi_u)^4(1\pi_g)(2\pi_u)$ for the NCN radical. The calculated excitation energies of the NCN radical from the ground state $^3\Sigma_g^-$ are shown as a function of n_N in Figs. 3 and 4, corresponding to the cases without and with charge-dipole interaction, respectively.

Comparing these two figures, the excitation energies to the $^1\Sigma_u^-$, $^3\Delta_u$, and $^3\Sigma_u^+$ states are significantly different near $n_N = 1.98$. This is apparently due to the fact that in the case with charge-dipole interaction the electron configuration with

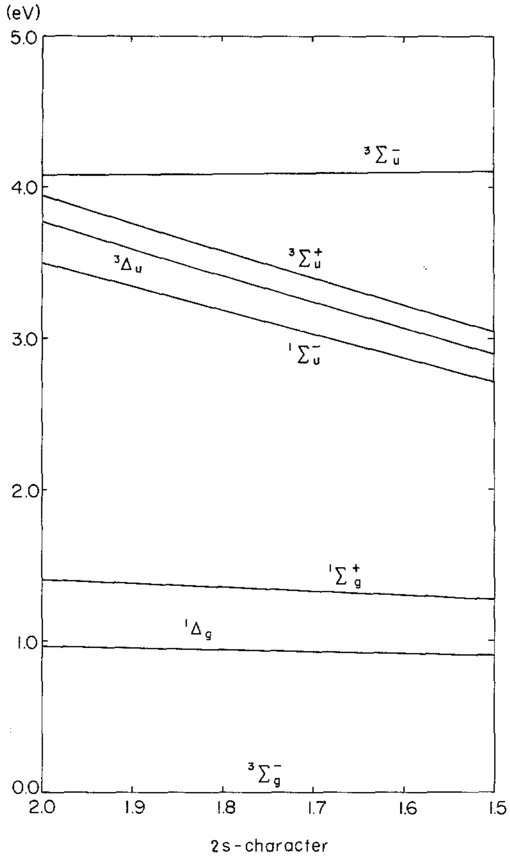

Fig. 3. Vertical π-electron excitation energies without charge-dipole interaction in NCN radical as a function of 2s-character of nitrogen

the greatest contribution changes from $(1\pi_u)^3(1\pi_g)^3$ to $(1\pi_u)^4(1\pi_g)(2\pi_u)$ at this proximity when the n_N decreases, while the main configuration does not change in the case without such an interaction.

Since the calculated excitation energy of the observed state $^3\Sigma_u^-(\Delta E_{\mathrm{obs.}} \cong 4.1\ \mathrm{eV})$ is relatively insensitive to the n_N, it may be difficult to determine the most preferable value of n_N from only the present results, although the n_N of NCN may slightly be smaller than the n_O of CO_2. As an example, the calculated vertical excitation energies of the NCN radical from the ground state $^3\Sigma_g^-$ to the lower electronic states at $n_N = 1.80$ are given in Table 2. It may be noted here that the change of these excitation energies with charge-dipole interaction is not large in the range of $1.80 \geqq n_N \geqq 1.50$ as compared with the case without such terms. The reason why the values of β_{CN}(NCN) are slightly different according to the cases with and without CI is due to the fact that these values used in the calculations with and without CI were determined from the excitation energy of $^1\Sigma^+(^1A'') \leftarrow {}^1\Sigma^+$ in the calculation of HCN with and without CI, respectively. Of course,

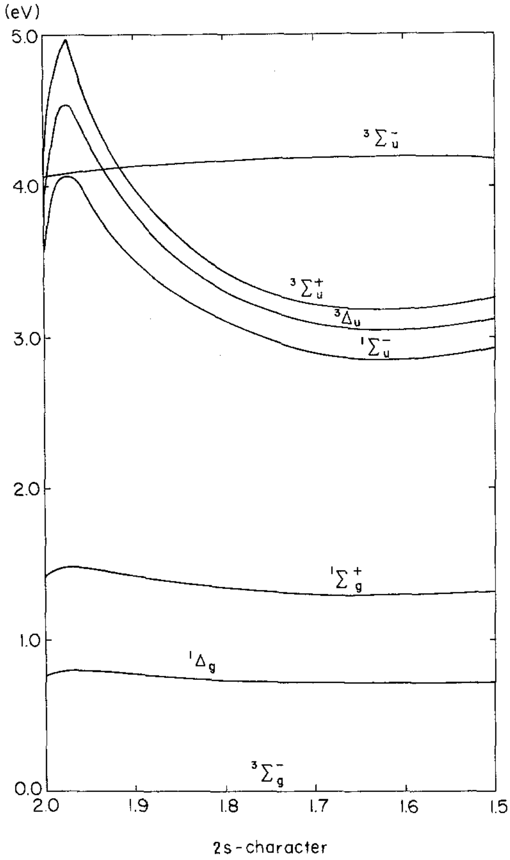

Fig. 4. Vertical π-electron excitation energies with charge-dipole interaction in NCN radical as a function of 2s-character of nitrogen

Table 2. Vertical π-electron excitation energies in NCN radical (eV) [$n_N = 1.80$]

State	With charge-dipole interaction		Without charge-dipole interaction	
	With CI	Without CI	With CI	Without CI
$^1\Delta_u$	5.37	6.54	5.28	6.50
$^3\Sigma_u^-$	4.17	5.56	4.08	5.54
$^3\Sigma_u^+$	3.45	2.49	3.57	2.55
$^3\Delta_u$	3.30	2.38	3.41	2.43
$^1\Sigma_u^-$	3.09	2.27	3.19	2.32
$^1\Sigma_g^+$	1.34	1.41	1.37	1.41
$^1\Delta_g$	0.73	0.70	0.75	0.70
$^3\Sigma_g^-$	0.00	0.00	0.00	0.00
β_{CN}(NCN) (a. u.)	−0.10503	−0.10661	−0.10308	−0.10346

the results with charge-dipole and configuration interactions in Table 2 should not be conclusive but possibly may fairly be useful in estimating the π-electron excitation energies to the unobserved states.

Some Remarks

Although the present CI calculations included only the first and the second lowest excited configurations, the results obtained are of some importance and cannot essentially be changed by performing any semi-empirical improvement. It may be of special interest to see that there is a significant difference between the calculated excitation energy with the charge-dipole interaction and that without such terms. Actually, the influence of the atomic dipole is absolutely necessary for elucidating some electronic energy levels as has been shown in a result of the CO_2 molecule. Also, the π-electron density of nitrogen atom in the NCN radical generally decreases with decreasing the 2s-character n_N (except near $n_N = 1.50$) if the charge-dipole interaction is included, while this relation is not satisfied if such terms are disregarded. These facts show the importance of the inclusion of the charge-dipole interaction.

On the other hand, semi-empirical calculations of aromatic molecules have not usually been carried out by including the effect of atomic dipole in formulation, but the obtained values are generally in good agreement with experiment. The reason of this may partly due to the fact that the integrals of charge-dipole interaction are semi-empirically not very easy to estimate separately but such terms can implicitly be included in the Coulomb integrals α_X's in the form of some empirical adjustments. Furthermore, the effect of atomic dipole is almost perfectly cancelled out for π-electrons of aromatic hydrocarbons and also not very large in usual nitrogen-containing heterocyclic aromatic molecules, since the direction of the lone pair orbital makes an angle of about 120° from that of the bonding orbitals directed to the neighboring atoms. As a result, this influence is not as great as in the linear molecules with lone pair electrons discussed here. On the other hand, some calculation of a homonuclear diatomic molecule showed that the results obtained are not sensitive to the hybridization parameter [10]. This may possibly due to the fact that the change of Coulomb integrals α_X's are the same in both atoms and may approximately regard as only an additive constant. These facts may sometimes make possible to treat lightly the influence of dependence on the $s-p$ hybridization in semi-empirical calculations.

For references, a similar calculation with the present work was carried out for the HCCCH linear radical which is isoelectronic with the NCN radical but has no lone pair electron. The C–C internuclear distance has not yet been determined experimentally and was assumed to be that of the C_3 radical [5] and that of the allene molecule [6]. In advance, the resonance integral of acetylene molecule β_{CC}(HCCH) was chosen so as the calculated excitation energy of ${}^1\Sigma_u^+({}^1A_u) \leftarrow {}^1\Sigma_g^+$ to give the value of 6.85 eV which is estimated from the experimental data [11] by assuming that the vibrations of the HC and the CC fragments are harmonic and the potential energy curve of the HCC bending vibration is quartic parabolic. Then, the β_{CC}(HCCCH) was determined assuming the proportionality of β_{XY} to S_{XY} as in Eq. (9). In spite of no lone pair electrons

Table 3. Vertical π-electron excitation energies in HCCCH radical (eV)

State	$R = 1.277$ Å		$R = 1.3084$ Å	
	With CI	Without CI	With CI	Without CI
$^1\Delta_u$	5.20	6.22	5.02	6.12
$^3\Sigma_u^+$	4.11	3.46	4.03	3.33
$^3\Sigma_u^-$	4.03	5.31	3.87	5.24
$^3\Delta_u$	3.91	3.32	3.83	3.19
$^1\Sigma_u^-$	3.62	3.18	3.52	3.06
$^1\Sigma_g^+$	1.39	1.37	1.40	1.36
$^1\Delta_g$	0.75	0.68	0.76	0.68
$^3\Sigma_g^-$	0.00	0.00	0.00	0.00
β_{CC}(HCCCH) (a. u.)	-0.10730	-0.10836	-0.10200	-0.10300

in the HCCCH radical, the form of SCF-LCAO-MO's obtained is rather close to that of the NCN radical with charge-dipole interaction than that without such terms. The vertical excitation energies calculated are summarized in Table 3, while the corresponding observed values have scarcely been known [12].

In an improvement of the present work, it may be possible to use a different hybridization parameter for each excited state from that of the ground state. However, this may correspond to increase the number of adjustable parameters to the experiment in a sense of semi-empirical calculation and is essentially outside the present discussion. At any rate, it should be emphasized that the inclusion of terms with charge-dipole interaction in Coulomb integrals α_X's is desirable for calculations of π-electron energy levels of molecules with lone pair electrons even in a semi-empirical form.

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