2864 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 2864—2868 (1981) [Vol. 54, No. 10

Electron Spin-Spin Interaction in Excited Triplet States of Aromatic Hydrocarbons with a Trigonal Symmetry Axis

Jiro Higuchi

Department of Chemistry, Faculty of Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240

(Received December 20, 1980)

Zero-field splitting (ZFS) parameters of benzene, triphenylene, and coronene molecules in their lowest and second excited triplet states are calculated from the electron spin-spin interaction using semi-empirical self-consistent-field π-electron molecular orbitals. The results show that in obtaining a good agreement of the evaluated ZFS parameters with the experimental values the selection of the basis functions in LCAO-MO's with zero-differential overlap is actually important. The ZFS parameters in some distorted structures are also calculated.

Since the detection of electron spin resonance (ESR) signals for the phosphorescent naphthalene molecule by Hutchison and Mangum,[1] many theoretical works on the zero-field splittings (ZFS) of aromatic molecules in their triplet states have been carried out with various degrees of approximations.[2–8] Nevertheless, the progress in such a calculation has essentially been slow in spite of the development in the theory of electronic structures of molecules. For large molecules, *ab initio* studies have scarcely been done except a work of benzene by Langhoff, Davidson, and Kern.[3] On the other hand, semi-empirical calculations have usually been concerned with the explanation of experimental values without careful reexamination of points in question. In most of these works, the electron spin-spin interactions were evaluated by using Slater-type or Gaussian-type atomic orbitals (AO's) as the AO bases and adopting the zero differential overlap (ZDO) approximation. The spin-orbit interactions were ignored in expecting their minor influence.[9]

As the basis functions of semi-empirical LCAO-MO's cannot pertinently be approximated by AO's of the corresponding free atoms, these calculations usually include some adjustable parameters although they are not always explicitly specified. That is, for obtaining a good agreement between the calculated values and the experimental ones, many works employed one of the following modifications: (1) use of partly adjusted values of spin-spin interaction integrals;[4] (2) use of adjusted orbital exponent of Slater-type 2p AO;[6,7] (3) inclusion of unsuitable approximation in exchange-type spin-spin interaction integrals,[8] and so on. In these works, the meanings of modified points were not distinctly explained.

With the recent development of accurate measurements in magnetic resonance experiments, detailed experimental data on the phosphorescent triplet states of aromatic molecules have been accumulated using methods such as conventional ESR and the optically detected magnetic resonance. From the standpoint of theoretical calculation, however, instructive information on ZFS parameters is still insufficient in discussing the values evaluated, except the case of benzene.[3,5] Under these circumstances, it may be desirable to reexamine the semi-empirical calculations of ZFS parameters on the basis of the works of benzene. Besides, there are many interesting experiments on the lowest triplet states of aromatic molecules with trigonal symmetry.[10–16] For these molecules, a relatively simple approximation with only Coulomb-type spin-spin interaction integrals is fairly satisfactory, since the other integrals have minor influence upon the ZFS parameters when the E value is very small.[5] Especially for benzene, the ratios among coefficients of AO's in the π-electron LCAO-MO's are uniquely determined from only the molecular symmetry and the calculated ZFS parameters may not largely be affected by the selection of semi-empirical parameters. In the present work, therefore, ZFS parameters of benzene, triphenylene, and coronene in the lowest and second excited triplet states were evaluated from the electron spin-spin interactions:

$$\begin{aligned}\mathscr{H}_{\mathrm{ss}} &= \frac{\mu_0 g^2\beta^2}{4\pi}\left[\frac{(\boldsymbol{s}_1\cdot\boldsymbol{s}_2)}{r_{12}{}^3}-\frac{3(\boldsymbol{s}_1\cdot\boldsymbol{r}_{12})(\boldsymbol{s}_2\cdot\boldsymbol{r}_{12})}{r_{12}{}^5}\right]\\ &= \frac{\mu_0 g^2\beta^2}{8\pi}\left[s_{\mathrm{x}}{}^2\left(\frac{r_{12}{}^2-3x_{12}{}^2}{r_{12}{}^5}\right)+s_{\mathrm{y}}{}^2\left(\frac{r_{12}{}^2-3y_{12}{}^2}{r_{12}{}^5}\right)\right.\\ &\quad +s_{\mathrm{z}}{}^2\left(\frac{r_{12}{}^2-3z_{12}{}^2}{r_{12}{}^5}\right)-(s_{\mathrm{y}}s_{\mathrm{z}}+s_{\mathrm{z}}s_{\mathrm{y}})\frac{3y_{12}z_{12}}{r_{12}{}^5}\\ &\quad \left.-(s_{\mathrm{z}}s_{\mathrm{x}}+s_{\mathrm{x}}s_{\mathrm{z}})\frac{3z_{12}x_{12}}{r_{12}{}^5}-(s_{\mathrm{x}}s_{\mathrm{y}}+s_{\mathrm{y}}s_{\mathrm{x}})\frac{3x_{12}y_{12}}{r_{12}{}^5}\right] \end{aligned} \quad (1)$$

(μ_0: vacuum permeability; $\boldsymbol{S}=\boldsymbol{s}_1+\boldsymbol{s}_2$: total spin) using a standard and simple approximation with only Coulomb-type integrals.[8,17] In terms of the principal magnetic axes shown in Figs. 1—3, the ZFS parameters can be expressed as

$$D = \frac{3\mu_0 g^2\beta^2}{16\pi hc}\left\langle\frac{r_{12}{}^2-3z_{12}{}^2}{r_{12}{}^5}\right\rangle \quad (2)$$

$$E = \frac{3\mu_0 g^2\beta^2}{16\pi hc}\left\langle\frac{y_{12}{}^2-x_{12}{}^2}{r_{12}{}^5}\right\rangle. \quad (3)$$

Calculation

The wavefunctions (WF's) used were constructed from Pariser-Parr-Pople-type (PPP) LCAO-MO's[18,19] by including configurations arising from all the single excitations relative to the ground state. ZFS parameters were calculated by adopting one of the following three kinds of treatments:

(A) The basis AO used was a double-zeta SCF-AO of carbon atom by Clementi.[20] This treatment corresponds to the conventional standard calculations except the used AO instead of a single Slater-type AO (STAO). A similar work with all the spin-spin interaction integrals evaluated with single STAO's has been carried out for benzene and naphthalene by Godfrey,

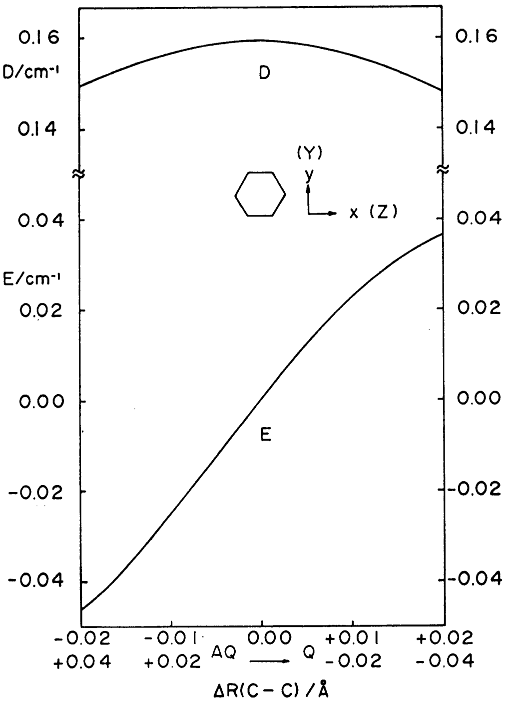

Fig. 1. Variation of the calculated zero-field splitting parameters of benzene with antiquinonoidal (AQ) and quinonoidal (Q) forms. The lower and the upper value in ΔR(C–C) are the change of length in two C–C bonds which are parallel to the x axis and that for the other four C–C bonds, respectively. The axis system for D_{2h} symmetry is indicated in parentheses.

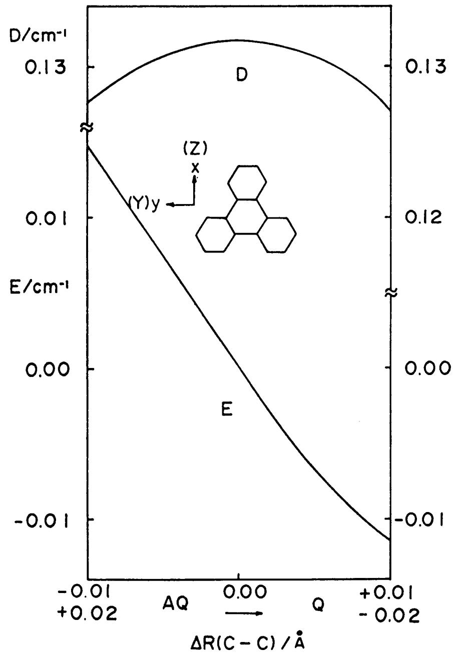

Fig. 2. Variation of the calculated zero-field splitting parameters of triphenylene with antiquinonoidal (AQ) and quinonoidal (Q) forms. The lower and the upper value in ΔR(C–C) are the change of length in C–C bonds which are parallel to the y axis and that for the other C–C bonds, respectively. The axis system for C_{2v} symmetry is indicated in parentheses.

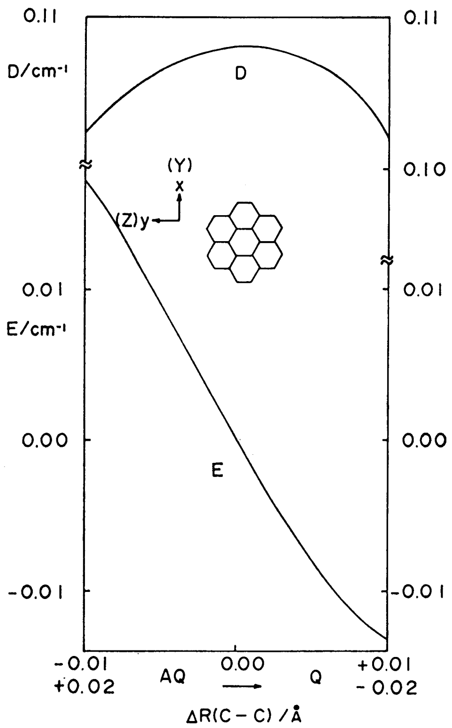

Fig. 3. Variation of the calculated zero-field splitting parameters of coronene with antiquinonoidal (AQ) and quinonoidal (Q) forms. The lower and the upper value in ΔR(C–C) are the change of length in C–C bonds which are parallel to the y axis and that for the other C–C bonds, respectively. The axis system for D_{2h} symmetry is indicated in parentheses.

Kern, and Karplus.[5)]

(B) The basis AO used was an adjusted single STAO, the orbital exponent of which was chosen to give the experimental D value of benzene [D=0.1593 cm^{-1}].[12)] The value of δ=1.5055 thus obtained is considerably different from that of Capello-Pullman's improved AO (δ=1.37)[6)] which was determined from the SCF-AO of carbon atom. In any case, such AO's should not generally be better than the double-zeta AO used in Treatment (A).

(C) Since the usual AO's χ_p's do not satisfy the orthogonal relation in the PPP LCAO-MO's, approximate orthogonalized AO's were taken as the basis functions. In reality, the calculation was carried out as described below. As the AO bases of PPP MO's should essentially be different from the usual AO's χ_p's in the valence state of constituent atoms, the following orthogonalized AO's ϕ_p's proposed by Löwdin[21)] may be chosen as one of suitable bases:

$$\boldsymbol{\phi} = \boldsymbol{\chi}(\boldsymbol{1}+\boldsymbol{S})^{-1/2}, \tag{4}$$

where $\boldsymbol{S}$ is a matrix with elements

$$S_{pq} = \int \chi_p{}^* \chi_q d\tau - \delta_{pq}. \tag{5}$$

Since the π-electron MO's of benzene are essentially unique as described above, the PPP MO's taking the orthogonalized AO's ϕ_p's as the bases are exactly identical with those in which the nonorthogonality between the AO's χ_p's is strictly included.[22)] For alternant hydrocarbons, the PPP MO's with basis functions of the orthogonalized AO's ϕ_p's may semiempirically be good approximations of the SCF-MO's with inclusion of all overlap integrals as pointed out by Parr,[22] although this relation should not exactly be valid. In Treatment (C), the ZFS parameters were simply calculated by using LCAO-MO's which the coefficients of AO's χ_p's are in the same ratios as those of the PPP MO's, and by including the nonorthogonality between the nearest neighboring AO's χ_p's, as a first step of approximation with orthogonalized AO's. In this case, the overlap integrals were evaluated by using the aforementioned double-zeta AO's.[20]

In the present work, molecular structures of benzene, triphenylene, and coronene were assumed to be planar with symmetry D_{6h}, D_{3h}, and D_{6h}, respectively.[23–25] Since triphenylene and coronene are deformed in crystals,[24–26] structures with symmetry C_{2v} and D_{2h}, respectively, were taken as typical examples of such conformations. The internuclear distances and bond angles used were obtained by averaging the observed values in each ground state[23–26] for each equivalent bond and angle. A similar study was carried out by assuming hypothetical structures with which all the benzene rings involved are the same size as in the ground state of benzene. As the observed E values are nonzero for these molecules,[10,12–15] the influence of distortion from hexagonal or trigonal symmetry upon the ZFS parameters was also examined for conformations in which the benzene rings of the system are all antiquinonoidal (AQ) or all quinonoidal (Q) forms. Such a calculation was carried out under the following assumptions: (i) the sum of the six nearest C–C bond lengths of each benzene ring and all the bond angles are unchanged from those of the ground state with symmetry D_{6h}, D_{3h}, and D_{6h} for benzene, triphenylene, and coronene, respectively; (ii) the changes of the lengths in a pair of parallel C–C bonds [ΔR(C–C)] are taken to be identical with each other and twice as large as the change in each of the other four C–C bond lengths [$-\Delta R$(C–C)/2]. The coordinate system used for ZFS parameters of each molecule is indicated by small letters in Figs. 1—3.

When the SCF π-electron MO's were calculated for each ground state with the PPP approximation,[18,19] the Coulomb integrals were evaluated by using Ohno-Klopman-type (OK) approximation:[27]

$$J_{pq} = e^2/(k^2a^2+r_{pq}^2)^{1/2}, \tag{6}$$

where $a=e^2/(I_p-A_p)$, $I_p(\mathrm{C})=11.16$ eV, $A_p(\mathrm{C})=0.03$ eV[28] and r_{pq} is an internuclear distance between atoms p and q. The parameter k is chosen as 1.0 and 0.7[29] for electron repulsion and electron-core attraction integrals, respectively. The resonance integrals were evaluated by adopting Wolfsberg-Helmholz-type approximation[30] in which β_{cc} for benzene was assumed to be -2.60 eV[31] and the overlap integrals were calculated by using the double-zeta AO by Clementi.[19]

Results and Discussion

For the lowest triplet state of benzene with symmetry D_{6h}, the D value in Treatment (A) is fairly small [$D=0.1341$ cm^{-1}], while a rather larger value is obtained, if a single STAO with conventional orbital exponent of $\delta=1.59$ (or 1.625) is used [$D=0.1770$ (or 0.1842) cm^{-1} with the present approximation and 0.1671 cm^{-1} with all the spin-spin interaction integrals[5]]. Also, if one use Capello-Pullman's improved STAO with $\delta=1.37$,[6] the D value becomes 0.1295 cm^{-1} still smaller than that obtained in Treatment (A). Further, a fairly good agreement with the observed value cannot be obtained, if only the C–C distances are varied within their permissible limits of the bond lengths. In Treatment (C), however, the evaluated D value [0.1594 cm^{-1}] is very close to the experimental one, in spite of the fact that orthogonalized AO's used were not strictly obtained.

For triphenylene and coronene, the D and E values by Treatment (C) are surprisingly close to those by Treatment (B) and in fair agreement with the experimental values as compared with the case of Treatment (A). These results are listed in Table 1. For the cases where the structures for the lowest triplet states were changed

TABLE 1. CALCULATED LOWEST EXCITED TRIPLET STATE ENERGIES AND ZERO-FIELD SPLITTING PARAMETERS[a]

	E_T/eV	Treatment (A)		Treatment (B)		Treatment (C)		Experimental		
		D/cm^{-1}	E/cm^{-1}	D/cm^{-1}	E/cm^{-1}	D/cm^{-1}	E/cm^{-1}	E_T/eV	D/cm^{-1}	E/cm^{-1}
Benzene										
(D_{6h})	3.872	0.1341	0.0000	0.1593	0.0000	0.1594	0.0000	3.65[c]	0.1593[d]	0.0091[d]
	[2.672]	[0.1358]	[0.0000]	[0.1593]	[0.0000]	—	—		0.1593[d]	0.0115[d]
Triphenylene										
(D_{3h})	3.194	0.1125	0.0000	0.1337	0.0000	0.1318	0.0000	2.86[e]	0.1367[e]	0.0026[e]
	[2.210]	[0.1164]	[0.0000]	[0.1367]	[0.0000]	—	—			
(C_{2v})	3.185	0.1117	0.0034	0.1328	0.0037	0.1309	0.0041			
(Benz)[b]	3.155	0.1110	0.0000	0.1319	0.0000	0.1305	0.0000			
Coronene										
(D_{6h})	2.585	0.0920	0.0000	0.1094	0.0000	0.1081	0.0000	2.40[f]	0.0967[f]	0.0030[f]
	[1.754]	[0.0963]	[0.0000]	[0.1131]	[0.0000]	—	—			
(D_{2h})	2.737	0.0930	−0.0046	0.1108	−0.0050	0.1096	−0.0057			
(Benz)[b]	2.581	0.0897	0.0000	0.1066	0.0000	0.1062	0.0000			

a) Values in brackets were calculated with NM approximation. b) (Benz) means a structure with which all the benzene rings are the same size as in the ground state of benzene. c) Paper cited in Ref. 29. d) Ref. 12. e) Ref. 14. f) Ref. 15.

from hexagonal and/or trigonal symmetry, therefore, only the ZFS parameters obtained in Treatment (C) are shown in Figs. 1-3.

In general, the D-type spin-spin interaction integrals except the Coulomb-type ones are relatively small compared with those of the E-type ones.[5] Since such integrals were disregarded here, the *D* values obtained may possibly be more reliable than the *E* values. Comparing with the observed *E* value, the calculated *E* value of benzene shown in Fig. 1 is relatively large at a distorted structure where the change of bond lengths from the equilibrium ones are nearly the same as those obtained by the SCF-MO-CI calculation.[4,32] This result is quite similar with those of the previous works.[4,5] Under the present circumstances, therefore, the quantitative estimation of the distorted structures in crystals is actually difficult from the calculated ZFS parameters, even if all the spin-spin interaction integrals were included.[3,5]

As can be seen in Figs. 2 and 3, the change of the ZFS parameters of triphenylene and coronene with the molecular distortion have a similar trend with that of benzene, although the influence on the *E* value is fairly small compared with the case of benzene. The calculated *E* value of triphenylene assuming the aforementioned C_{2v} structure in a crystal is not much different from the observed value. On the other hand, the experimental *E* value of coronene changes slightly according to the host crystal,[15,16] as is seen in benzene.[12,13] This makes it very difficult to infer whether the intramolecular pseudo-Jahn-Teller instability significantly affects the *E* value or not.

As a preliminary step, the ZFS parameters of these molecules were also calculated by using Nishimoto-Mataga-type (NM) two-center integrals:[33]

$$J_{pq} = e^2/(ka+r_{pq}). \tag{7}$$

In this case, Treatments (A) and (B) were adopted by using the traditional parameters: $I_p(C)=11.22$ eV, $A_p(C)=0.62$ eV,[34] and $\beta_{cc}(\text{Benzene})=-2.39$ eV.[18] As given in Table 1,[35] the OK approximation does not always give a better result for the ZFS parameters than the NM one, while the former formula may yield better electronic energies for the triplet state rather than the latter one.[31] Actually, the present results with the use of OK approximation are in general satisfactory compared with the previous works on these molecules used various different treatments.[36]

For the second excited triplet state of these molecules, the ZFS parameters were similarly calculated as is given in Table 2. These values may have some theoretical interest, although the experimental values have not yet been available. The *E* value of benzene might apparently be zero because of its D_{6h} symmetry and can be obtained to be zero using complex WF's of $\Psi(^3E_{1u\pm})=2^{-1/2}[\Psi(^3B_{1u})\pm i\Psi(^3B_{2u})]$.[37] However, if the real WF's of $\Psi(^3B_{1u})$ and $\Psi(^3B_{2u})$ were separately used as the limit forms of D_{2h} symmetery, the *E* values so obtained are negative and positive, respectively, as given in Table 2 and both the ZFS levels obtained are still degenerate. This might appear the fact that each of such real WF's does not seemingly satisfy the condition of symmetry D_{6h}. For D_{2h} structures which are slightly deformed from D_{6h}, the influence of the off-diagonal element of $\langle\Psi(^3B_{1u})|-2x_{12}y_{12}/r_{12}^5|\Psi(^3B_{2u})\rangle$ upon *E* values should be considerable if the separation between the $^3B_{1u}$ and $^3B_{2u}$ states is the same order as their *E* values. Similar results were obtained by using real WF's of $\Psi(^3B_2)$ and $\Psi(^3A_1)$ for triphenylene[38] and those of $\Psi(^3B_{2u})$ and $\Psi(^3B_{1u})$ for coronene[39] (see Table 2). With the OK approximation, the $^3E_{1u}$ state of coronene is calculated to be located slightly lower than the $^3B_{2u}$ state. Because of the perturbation from this state, the *D* value becomes fairly small as compared with that obtained with the NM approximation where the $^3B_{2u}$ state is not much close to the $^3E_{1u}$ state. This is a rather different type of interaction than the abovementioned slightly deformed case. To examine these points, further studies are necessary from the viewpoint of both theory and experiment. In near future, it is hoped to observe fine structures of the second excited triplet state using some new refined technique.

In previous studies, ZFS parameters were evaluated by using various treatments which do not always give

TABLE 2. CALCULATED SECOND EXCITED TRIPLET STATE ENERGIES AND ZERO-FIELD SPLITTING PARAMETERS[a)]

	E_T/eV	Treatment (A)		Treatment (B)		Treatment (C)		Experimental		
		D/cm^{-1}	*E*/cm^{-1} [b)]	*D*/cm^{-1}	*E*/cm^{-1} [b)]	*D*/cm^{-1}	*E*/cm^{-1} [b)]	E_T/eV	*D*/cm^{-1}	*E*/cm^{-1}
Benzene										
(D_{6h})	4.896	0.0625	0.0000(±0.0742)	0.0685	0.0000(±0.0793)	0.0696	0.0000(±0.0826)	4.58[d)]	—	—
	[4.063]	[0.0625]	[0.0000(±0.0741)]	[0.0680]	[0.0000(±0.0785)]	—	—			
Triphenylene										
(D_{3h})	3.835	0.0965	0.0000(∓0.0076)	0.1128	0.0000(∓0.0083)	0.1159	0.0000(∓0.0115)			
	[2.846]	[0.1151]	[0.0000(∓0.0160)]	[0.1340]	[0.0000(∓0.0171)]	—	—			
(C_{2h})	3.887	0.0998	−0.0074	0.1168	−0.0081	0.1206	−0.0111	3.38[e)]	—	—
	3.780	0.0952	0.0131	0.1112	0.0143	0.1138	0.0178			
(Benz)[c)]	3.804	0.0951	0.0000(∓0.0125)	0.1111	0.0000(∓0.0136)	0.1146	0.0000(∓0.0172)			
Coronene										
(D_{6h})	3.299	0.0375	0.0000(∓0.0383)	0.0419	0.0000(∓0.0410)	0.0429	0.0000(∓0.0440)			
	[2.529]	[0.0957]	[0.0000(∓0.0404)]	[0.1110]	[0.0000(∓0.0430)]	—	—			
(D_{2h})	3.433	0.0388	−0.0360	0.0431	−0.0385	0.0439	−0.0404	—	—	—
	3.442	0.0373	0.0445	0.0416	0.0476	0.0424	0.0517			
(Benz)[c)]	3.284	0.0389	0.0000(∓0.0383)	0.0435	0.0000(∓0.0410)	0.0450	0.0000(∓0.0445)			

a) Values in brackets were calculated with NM approximation. b) Values in parentheses calculated by using the real WF's in stead of the corresponding complexWF's. c) (Benz) means a structure with which all the benzene rings are the same size as in the ground state of benzene. d) Paper cited in Ref. 29. e) Ref. 14.

a satisfactory D value for benzene without some modifications. Concerning this point, however, no detailed explanation was made in such publications, except a paper in which the effect of overlap integrals was nonempirically pointed out.[3] In the present work, such a difficulty is partly reduced by using the approximate orthogonalized AO's which are given by a linear combination of SCF-AO's. Although the present work includes various points to be improved such as spin-spin interaction integrals, orthogonalized AO's, configuration interactions, and so on, the general trend for the calculated D value should not significantly be changed. In view of these facts, the present results may show the fact that for evaluating physical constants such as ZFS parameters using semi-empirical LCAO-MO's with ZDO approximation their basis functions should carefully be chosen without use of the usual AO's.

This work was undertaken in collaborating with Professor M. Kinoshita, The University of Tokyo, in connection with the work on the triplet state of triphenylene.[14] At several stages, the author is indebted to him for his suggestion and discussions. The author also wished to thank Professor Y. Gondo, Kyushu University, for informing the error in a formula of spin-spin interaction integrals appeared in Ref. 17, and Dr. S. Iwata, The Institute of Physical and Chemical Research, for his helpful suggestion. The numerical calculations were carried out on HITAC 8700/8800 at Computer Centre, The University of Tokyo.

References

1) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **34**, 908 (1961).

2) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1969), p. 329; S. R. Langhoff and C. W. Kern, "Applications of Electronic Structure Theory," ed by H. F. Schaefer, III, Plenum Press, New York (1977), p. 381.

3) S. R. Langhoff, E. R. Davidson, and C. W. Kern, *J. Chem. Phys.*, **63**, 4800 (1975).

4) M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963); J. H. van der Waals and G. ter Maten, *ibid.*, **8**, 301 (1964).

5) M. Godfrey, C. W. Kern, and M. Karplus, *J. Chem. Phys.*, **44**, 4459, (1966).

6) D. Capello and A. Pullman, *Theor. Chim. Acta*, **8**, 383 (1967).

7) J. Zuclich, *J. Chem. Phys.*, **52**, 3592 (1970).

8) Y. Gondo and A. H. Maki, *J. Chem. Phys.*, **50**, 3270, 3638 (1969); Y. Gondo and Y. Kanda, *Bull. Chem. Soc. Jpn.*, **43**, 3943 (1970).

9) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952); M. Mizushima and S. Koide, *ibid.*, **20**, 765 (1952).

10) M. S. de Groot, I. A. M. Hesselmann, and J. H. van der Waals, *Mol. Phys.*, **13**, 583 (1967); **16**, 45 (1969).

11) J. H. van der Waals, A. M. D. Berghuis, and M. S. de Groot, *Mol. Phys.*, **13**, 301 (1967); **21**, 497 (1971).

12) Ph. J. Vergragt and J. H. van der Waals, *Chem. Phys. Lett.*, **36**, 283 (1975); **42**, 193 (1976).

13) Ph. J. Vergragt and J. H. van der Waals, *Mol. Phys.*, **33**, 1507 (1977).

14) N. Nishi, K. Matsui, M. Kinoshita, and J. Higuchi, *Mol. Phys.*, **38**, 1 (1979).

15) K. Ohno, N. Nishi, M. Kinoshita, and H. Inokuchi, *Chem. Phys. Lett.*, **33**, 293 (1975).

16) A. M. Merle, M. Lamotte, S. Risemberg, C. Hauw, J. Gaultier, and J. Ph. Grivet, *Chem. Phys.*, **22**, 207 (1977).

17) S. A. Boorstein and M. Gouterman, *J. Chem. Phys.*, **41**, 2776 (1964).

18) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

19) J. A. Pople, *Trans, Faraday Soc.*, **49**, 1375 (1953).

20) E. Clementi, "Tables of Atomic Functions" [supplement to *IBM J. Res. Develop.*, **9**, 2 (1965)] Table 45-01.

21) P.-O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

22) R. G. Parr, *J. Chem. Phys*, **33**, 1184 (1960).

23) A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34**, 350 (1956).

24) F. R. Ahmed and J. Trotter, *Acta Crystallogr.*, **16**, 503 (1963).

25) J. M. Robertson and J. G. White, *J. Chem. Soc.*, **1945** 607.

26) J. K. Fawcett and J. Trotter, *Proc. R. Soc. London, Ser. A*, **289**, 366 (1966).

27) K. Ohno, *Theor. Chim. Acta*, **2**, 219 (1964); G. Klopman, *J. Am. Chem. Soc.*, **86**, 4550 (1964); **87**, 3300 (1965).

28) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

29) It may be noted that with $k=0.7$ for the electron-core attraction integrals the calculated lowest three triplet states of naphthalene are located to be the same ordering as its experiment [J. B. Birks, L. G. Christophorous, and R. H. Huebner, *Nature*, **217**, 809 (1968)]. For benzene, no appreciable change in the calculated values is found when the core-attraction integrals with $k=1.0$ are used instead of those with $k=0.7$.

30) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

31) K. Schulten, I. Ohmine, and M. Karplus, *J. Chem. Phys.*, **64**, 4422 (1976).

32) Y. Fujimura, H. Yamaguchi, and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **45**, 384 (1972).

33) K. Nishimoto and N. Mataga, *Z. Phys. Chem. (Frankfurt am Main)*, **12**, 335 (1957).

34) G. Pilcher and H. A. Skinner, *J. Inorg. Chem.*, **24**, 937 (1962).

35) With the NM approximation, the value of δ determined in Treatment (B) is 1.4955.

36) S. A. Boorstein and M. Gouterman, *J. Chem. Phys.*, **39**, 2443 (1963); Y.-N. Chiu, *ibid.*, **39**, 2736 (1963); J. H. van der Waals and G. ter Maten, *Mol. Phys.*, **8**, 301 (1964); Y. Gondo and Y. Kanda, *Bull. Chem. Soc. Jpn.*, **43**, 3943 (1970).

37) For the states indicated in real WF's, the axis system is chosen for D_{2h} symmetry as shown in parentheses in Fig. 1.

38) For the states indicated in real WF's, the axis system is chosen for C_{2v} symmetry as shown in parentheses in Fig. 2.

39) For the states indicated in real WF's, the axis system is chosen for D_{2h} symmetry as shown in parentheses in Fig. 3.