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The Electronic Structure of Naphthalene

By

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Electronic energy levels of naphthalene were calculated by semi-empirical ASMO-CI method including a part of doubly excited configurations as well as all singly excited configurations. The result obtained seems to indicate that with respect to the amount of the mixing of CI to be invoked it is sufficient to take into account all singly excited configurations only.

The interpretation of spectra was also discussed.

Die Energieniveaus der Elektronen im Naphthalin-Molekül wurden mittels einer halbempirischen ASMO-CI-Methode unter Einschluß einer Reihe von einfach und doppelt angeregten Zuständen berechnet. Dabei zeigt sich, daß es wahrscheinlich genügt, nur einfach angeregte Zustände in die Rechnung einzubeziehen.

Les états énergétiques du naphthalène ont été calculés par une méthode ASMO-CI semiempirique où une partie des configurations diexcitées et toutes les configurations monoexcitées ont été incluses. Le résultat indique qu'il suffit de ne tenir compte que des configurations monoexcitées. Les spectres sont discutés.

1. Introduction

The calculation of the electronic energy levels of naphthalene by semi-empirical ASMO-CI (antisymmetrized molecular orbital configurational interaction) method including all singly excited configurations was shown by PARISER [14] in excellent agreement with experiments within the accuracy of a few tenths eV. Possible electronic wave function of the ground state or singlet excited state, Ψ_a should be expressed in the form

$$\Psi_a = A \psi_0 + \sum_{j \leq m} \sum_{k > m} a_j^k \psi_j^k \quad (1)$$

where

$$\psi_0 = |\varphi_1 \bar{\varphi}_1 \cdots \varphi_j \bar{\varphi}_j \cdots \varphi_m \bar{\varphi}_m| \equiv |1 \bar{1} \cdots j \bar{j} \cdots m \bar{m}| \quad (2)$$

and

$${}^{1,3} \psi_j^k = \frac{1}{\sqrt{2}} (|j \bar{k} m \bar{m}| \pm |k \bar{j} m \bar{m}|) \quad (3)$$

In the expression, $\varphi_1, \varphi_2 \cdots$ are Hückel orbitals of usual LCAO-type, and the upper and lower sign is associated with the singlet and triplet configuration, respectively.

His calculation seems implicitly to suggest that in the approximation of PARISER and PARR [13], doubly excited configurations such as $\Psi_{ii}^{kk}, \Psi_{ii}^{kl}, \Psi_{ij}^{kk}, \Psi_{ij}^{kl}$ are unimportant in the wave functions of the ground state or excited states. If the starting orbitals were self-consistent type, there would in fact be no interactions between Ψ_0 and Ψ_i^k , but interactions between Ψ_0 and each doubly excited configuration such as $\Psi_{ii}^{kk}, \Psi_{ii}^{kl}, \Psi_{ij}^{kk}, \Psi_{ij}^{kl}$ would arise. Therefore, the fact that the

energy depression of the ground state ${}^1A_{1g}^-$ calculated by PARISER was nearly zero shows that the Hückel orbitals of naphthalene are close to SCF-orbitals.

It is needless to say that how much CI should be included depends on the choice of the starting orbitals and the values of atomic integrals adopted. At any rate, it may be necessary to take into account an appropriate number of CI in order to interpret the electronic spectra, as has already been understood. The aim of this paper is to interpret the spectra, allowing for the lowering of the ground state by interactions not only with all singly excited states, but also with doubly excited states starting from Hückel orbitals. The method of calculating two-center atomic integral proposed by one of the authors [3, 4] was used.

The theoretical method is based on the framework of ASMO-CI approximation proposed by PARISER and PARR, including a part of doubly excited configurations as well as all singly excited configurations.

The procedure will be briefly outlined in the appendix. The following approximations are assumed:

- a) only the π -electrons are considered.
- b) differential overlap is formally neglected.
- c) doubly excited configurational wave functions to be considered are limited to those of Ψ_{ii}^{kk} , Ψ_{ij}^{kk} , Ψ_{ii}^{kl} -type (vide infra).
- d) the electronic repulsion integrals over atomic orbitals ($aa | bb$) are determined by the following formula [3, 4]:

$$Z^{-1}(aa | bb) = 0.1227 - 0.005093 \varrho + 0.000070 \varrho^2 \quad (\text{in a. u.}) \quad (4)$$

$\varrho = ZR | a_H$. Here Z is the effective nuclear charge, R the internuclear distance $a-b$, a_H the 1-quantum Bohr radius. Eq. (4) is obtained by extrapolating theoretical values for large internuclear distance R down to $R = 0$ to fit the one-center integral ($aa | aa$), which was determined 10.848 eV through empirical calculations from atomic spectroscopic data.

- e) the resonance integral $\beta = -2.371$ eV is used: this has been empirically obtained by PARISER [14] through fitting the energies of the six lowest electronic states of benzene to the experimental values.

2. General Consideration of Configurations

In the procedure of expanding the various integrals over MO's into integrals over AO's the following procedure may be convenient to simplify the calculation.

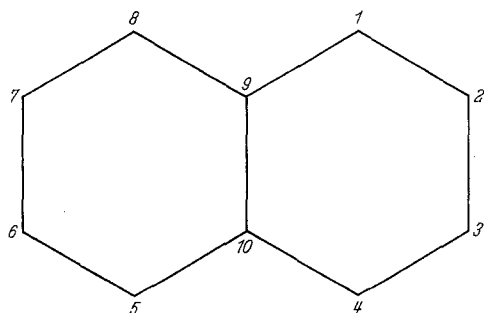


Fig. 1. Geometry of Naphthalene

Let the vectors ($i |$ or $| i$) be defined by the components (C_{1i}^* , C_{2i}^* , \dots , C_{ni}^*), and (C_{1i} , C_{2i} , \dots , C_{ni}). Let the occupied MO's be named by $i, j, k, l \dots$ in order of increasing energy, and unoccupied MO's, by $i', j', k', l' \dots$ in order of decreasing energy. Further, atoms are numbered 1, 2, 3, 4, \dots 10 in the carbon skeleton structure as shown in Fig. 1.

Naphthalene is assumed to be planar, made up of regular hexagon,

with all carbon-carbon distance equal to 1.396 Å. The formulae of PARISER derived through making allowance for alternant hydrocarbon will be reproduced here:

$$\begin{aligned}
 (ij' | &= (i' j | , & (ii | &= (i' i' | , & (ij | &= (i' j' | \\
 2 \sum_f (ii | ff) &= (ii | 1), & & & 2 \sum_f (ij | ff) &= (ij | 1) \\
 \sum_f [(fi | fi) + (fi' | fi')] &= (11 | 11) , & \sum_f [(fi | fj') + (fi' | fj)] &= 0 \\
 \sum_f (fi | fj) + (fi' | fj') &= 0 , & \sum_f (fi | fi') &= 0 \\
 I_{ii} &= - (ii | 1) + \lambda_i \beta - A , & I_{i'i'} &= - (i'i' | 1) - \lambda_i \beta - A \\
 I_{ij} &= - (ij | 1) , & I_{i'j'} &= - (i'j' | 1) \\
 I_{ij'} &= - (ij' | 1) , & I_{i'j} &= - (i'j | 1)
 \end{aligned} \tag{5}$$

where A is the valence state $2p\pi$ electron affinity and λ_i is given by

$$\lambda_i = \sum_{s,t}^{\text{all neighbors}} C_{si}^* C_{it} . \tag{6}$$

In deriving above expressions for I , all penetration integrals were neglected. Using Eq. (16) and the relations

$$\begin{aligned}
 F_{ij'} &= -F_{i'j} , & F_{ij} &= -F_{i'j'} , & F_{ii} + F_{i'i'} &= -2A - (11 | 11) \\
 J_{ij'} &= J_{i'j} , & K_{ij'} &= K_{i'j} ,
 \end{aligned}$$

one easily obtains

$$\begin{aligned}
 \Delta^{1,3} E_i^{j'} &= \Delta^{1,3} E_j^{i'} , & \Delta^1 E_{ii}^{k'k'} &= \Delta^1 E_{kk}^{i'i} , & \Delta^{1,3} E_{ii}^{k'l'} &= \Delta^{1,3} E_{kl}^{i'i'} \\
 \Delta^{1,3} E_{ij}^{k'l'} - \Delta^{1,3} E_{kl}^{i'i'} &= J_{i'i'} - J_{j'k'} + \frac{1}{2} (K_{ij} \mp K_{ij'}) - \frac{1}{2} (K_{k'l} \mp K_{k'l'}) .
 \end{aligned} \tag{7}$$

Thus pairs of the configurational wave functions $\psi_i^{j'}$ and $\psi_j^{i'}$, $\psi_{ii}^{k'k'}$ and $\psi_{kk}^{i'i}$, and $\psi_{ii}^{k'l'}$ and $\psi_{kl}^{i'i'}$ are degenerate, so that the linear combinations*

$$\begin{aligned}
 {}^{1,3}\Psi_1^\pm &= \frac{1}{\sqrt{2}} (\psi_i^{j'} \pm \psi_j^{i'}) , & {}^1\Psi_2^\pm &= \frac{1}{\sqrt{2}} (\psi_{ii}^{k'k'} \mp \psi_{kk}^{i'i'}) , \text{ and} \\
 {}^{1,3}\Psi_3^\pm &= \frac{1}{\sqrt{2}} (\psi_{ii}^{k'l'} \pm \psi_{kl}^{i'i'})
 \end{aligned} \tag{8}$$

enable us to factorize each configurational secular determinant into two determinants which were called $a +$ state and $a -$ state by PARISER. However, the states $\psi_{ij}^{k'l'}$ and $\psi_{kl}^{i'i'}$ are not degenerate and do interact with both the $+$ and $-$ states. It is also found that ψ_0 and $\psi_{ii}^{i'i'}$ behave like the $-$ state, and $\psi_i^{i'}$ the $+$ state.

As MOFFITT [11] and DEWAR and LONGUET-HIGGINS [2] pointed out, interaction between degenerate configurations (first-order configuration interaction) such as $\psi_i^{i'}$ and $\psi_j^{i'}$, $\psi_{kk}^{i'i}$ and $\psi_{ii}^{k'k'}$, $\psi_{ii}^{k'l'}$ and $\psi_{kl}^{i'i'}$ will give larger effect to the energy levels and their intensities, while interaction with non-degenerate and higher energy configurations (second-order configuration interaction) such as $\psi_{ij}^{k'l'}$ and $\psi_{kl}^{i'i'}$ may surely play the secondary role. LYKOS [8] also concluded that the important configuration interaction to be invoked is those between degenerate configurations. The $\psi_{ij}^{k'l'}$ -type wave functions, therefore, were not considered in order to simplify the calculation.

* Note that $\frac{1}{\sqrt{2}} (\psi_{ii}^{k'k'} - \psi_{kk}^{i'i'})$ belongs to the $+$ state, and $\frac{1}{\sqrt{2}} (\psi_{ii}^{k'k'} + \psi_{kk}^{i'i'})$ the $-$ state.

The selection rule in this restriction is found to be allowed only between + and - states, and the π -electron density at each carbon atom in the ground state after including doubly excited configurations is shown to be unity, that is the same as in the case of taking account of all singly excited configurations only [14].

3. Results and Discussion

The results are shown in Tab. 1-4. Experimental values of singlet states in Tab. 2 are taken from the absorption maxima given by KLEVENS and PLATT

Table 1. *Atomic repulsion integral*

center	distance	(aa bb)	eV
1,1	0	(11 11)	10.848
1,2	1.396	(11 22)	7.436
1,3	2.418	(11 33)	5.526
1,4	2.792	(11 44)	4.951
1,10	2.418	(11 10,10)	5.526
1,5	3.694	(11 55)	3.819
1,6	4.188	(11 66)	3.360
1,7	3.694	(11 77)	3.819
1,8	2.418	(11 88)	5.526
1,9	1.396	(11 99)	7.436
2,3	1.396	(22 33)	7.436
2,6	5.034	(22 66)	2.847
2,7	4.836	(22 77)	2.935
2,9	2.418	(22 99)	5.526
2,10	2.792	(22 10,10)	4.951
9,10	1.396	(99 10,10)	7.436

[6], and those of triplet states are taken from the work by KASHA and NAUMAN [7]. The low-lying energy levels, that is, long axis polarized state (${}^1B_{3u}^-$) and short axis polarized state (${}^1B_{2u}^+$) are in good agreement with the experimental results of KASHA and NAUMAN, McCLURE and SCHNEPP [10], and CRAIG, LYONS and WALSH [1].

The ${}^1B_{3u}^+$ state calculated to be 6.144 eV is assigned by KLEVENS and PLATT to the very strong band having a peak at 5.6 eV. The deviation is rather large (about 0.51 eV), but the present calculation seems to give a reasonable value if we consider that this band spreads

over to 6.14 eV in their data. 1C_b transition band of KLEVENS and PLATT (6.51 eV) is assigned to ${}^1B_{2u}^+$ state in this paper, but this assignment is not conclusive. Our calculation of triplet states shows only a bit improved results in comparison with those of PARISER.

The energy depression of the ground state due to singly excited configuration interactions is only -0.0299 eV. This is little different from -0.0246 eV obtained by PARISER. The fact that the energy depression due to interactions of the ground state with all singly excited states is very small shows that the Hückel orbital of naphthalene is fairly close to SCF-orbital. The lowering of the ground state by further mixing of doubly excited configurations amounts to -0.24972 eV, and this may suggest the importance of the latter effect. However, the amount of the lowering of each lowest excited state with different symmetry is found to be about the same magnitude as that of the ground state. Thus the values of transition energies finally obtained are not very different from those calculated with all singly excited configurations only (see Tab. 2).

Inclusion of doubly excited configurations does not play significant roles even in the calculation of oscillator strength (Tab. 2), bond order, and bond distance (Tab. 3). It would therefore be sufficient to take into account only singly excited configurations, when one would like to calculate the low-lying energy levels.

The possibility of an important further application of this paper should be cited. As it has been shown [3] that the mixing of doubly excited states of a hydro-

Table 2. Energy levels and intensities for naphthalene excited states

states	D & S	f	S	f	exptl.	states	D & S	f	S	f	exptl.
$^1A_{1g}^-$	0.000	Ref.	0.000	Ref.		$^3A_{1g}^-$	6.157	0.157	5.940	0.069	
	5.695	0	5.983	0			8.107	0.535	7.892	0.533	
	6.636	0	7.851	0			11.120		11.263		
	7.928	0	11.240	0			13.324				
	10.174	0									
	11.300	0									
	11.524	0									
	12.367	0									
	13.300	0									
	14.866	0									
17.083	0										
$^1A_{1g}^+$	7.038	0	7.375	0		$^3A_{1g}^+$	4.830	0	4.558	0	
	7.605	0	7.752	0			6.860	0	6.792	0	
	9.843	0	10.446	0			9.892	0	9.687	0	
	10.659	0					13.167	0			
	11.832	0									
	13.306	0									
	14.839	0									
16.742	0										
$^1B_{1g}^+$	5.750	0	5.606	0		$^3B_{1g}^+$	3.882	0	3.767	0	
	6.998	0	6.948	0			5.703	0	5.749	0	
	8.862	0	12.539	0			8.532	0	11.263	0	
	10.803	0					10.125	0			
	12.804	0					11.314	0			
$^1B_{1g}^-$	13.364	0				12.478	0				
	14.011	0				12.928	0				
	5.745	0	6.333	0		$^3B_{1g}^-$	6.187	0.605	6.333	0.580	
	7.040	0	8.668	0			7.931	0.007	8.668	0.002	
	9.099	0	13.910	0			8.913		13.211		
	11.733	0					11.332				
	11.566	0					11.767				
	13.176	0					12.771				
13.966	0				13.683						
4.249	0.138	4.188	0.158	4.29 0.18	$^3B_{2u}^+$		2.483	Ref	2.321	Ref.	2.64
6.006	0.207	6.155	0.266	6.51 0.20		4.619	0	4.493	0		
7.286	1.260	7.310	1.364	7.41 0.6		6.512	0	6.540	0		
9.003		8.858				7.385	0	7.102	0		
10.124		11.038				9.347	0	11.344	0		
11.107		13.910				10.866	0				
12.779						11.689	0				
13.834						12.267	0				
14.068						13.409	0				
15.303						14.367	0				
$^1B_{2u}^-$	9.167	0	9.777	0		$^3B_{3u}^-$	9.256	0	9.777	0	
	9.644	0					9.937	0			
	12.030	0					11.256	0			
	12.593	0					12.663	0			
	14.185	0					13.263	0			

D & S: means energy levels obtained by solving secular equations which consist of doubly excited CI as well as all singly excited CI.

S: is limited to all singly excited CI.

Table 2 (continued)

states	D & S	f	S	f	exptl.	states	D & S	f	S	f	exptl.
${}^1B_{3u}^+$	6.144	2.140	6.300	2.325	5.63 1.70	${}^3B_{3u}^+$	3.953	0	3.878	0	3.71
	7.778	0.570	8.372	0.411			6.648	0	6.866	0	
	9.022	0.565	9.867	0.133			7.151	0	10.617	0	
	12.377						7.401	0			
	13.568						10.910	0			
	15.173						11.296	0			
16.800					12.238	0					
${}^1B_{3u}^-$	4.188	0	4.137	0	3.97 0.002	${}^3B_{3u}^-$	4.195	0	4.137	0	
	6.855	0	8.515	0			7.024	0	8.515	0	
	9.133	0	9.625	0			9.264	0	9.625	0	
	10.334	0					9.658	0			
	12.004	0					11.162	0			
	13.572	0					11.361	0			
	14.923	0					11.972	0			

Table 3. Bond order and bond distance

	P_{12} (r_{12})	P_{23} (r_{23})	P_{14} (r_{14})	$P_{9,10}$ ($r_{9,10}$)
Hückel	0.757 (1.385)	0.603 (1.408)	0.555 (1.417)	0.518 (1.424)
S	0.757 (1.380)	0.627 (1.403)	0.574 (1.413)	0.518 (1.419)
D & S	0.815 (1.370)	0.668 (1.396)	0.656 (1.398)	0.627 (1.403)
obs.	(1.365)	(1.404)	(1.425)	(1.393)

Table 4. Configuration wave functions for low-lying energy levels

	${}^1\Psi_{DS}$	${}^1\Psi_S$	${}^3\Psi_{DS}$	${}^3\Psi_S$
${}^{1,3}A_{1g}^-$ ψ_0	-0.98912	0.99773		
$\frac{1}{\sqrt{2}}(\psi_4^{3'} - \psi_3^{4'})$	0.05479	-0.06658	-0.83309	0.83407
$\frac{1}{\sqrt{2}}(\psi_5^{3'} - \psi_2^{5'})$	0.00128	0.00469	0.54800	-0.54650
$\psi_{55}^{5'5'}$	0.09081			
$\frac{1}{\sqrt{2}}(\psi_{55}^{4'4'} + \psi_{44}^{5'5'})$	0.06073			
$\frac{1}{\sqrt{2}}(\psi_3^{1'} - \psi_1^{3'})$	-0.00978	0.00940	0.07301	-0.07524
$\psi_{44}^{4'4'}$	0.05961			
$\frac{1}{\sqrt{2}}(\psi_{55}^{3'3'} + \psi_{33}^{5'5'})$	0.03476			
$\frac{1}{\sqrt{2}}(\psi_{14}^{5'5'} - \psi_{55}^{1'4'})$	0.00616		0.01829	
$\frac{1}{\sqrt{2}}(\psi_{44}^{3'3'} + \psi_{33}^{4'4'})$	0.03100			

Table 4 (continued)

		${}^1\Psi_{DS}$	${}^1\Psi_S$	${}^3\Psi_{DS}$	${}^3\Psi_S$	
${}^{1,3}B_{1g}^+$	$\frac{1}{\sqrt{2}}(\psi_{55}^{2'2'} + \psi_{22}^{5'5'})$	0.02904				
	$\frac{1}{\sqrt{2}}(\psi_5^{3'} + \psi_3^{5'})$	-0.99144	-0.99598	0.97513	-0.98610	
	$\frac{1}{\sqrt{2}}(\psi_4^{2'} + \psi_2^{4'})$	0.04945	0.04480	0.02993	0.00588	
	$\frac{1}{\sqrt{2}}(\psi_{45}^{5'5'} + \psi_{55}^{4'5'})$	0.02109		-0.12993		
	$\frac{1}{\sqrt{2}}(\psi_{45}^{4'4'} + \psi_{44}^{4'5'})$	-0.00498		0.00383		
	$\frac{1}{\sqrt{2}}(\psi_1^{2'} + \psi_2^{1'})$	-0.06418	-0.07758	0.17006	-0.16608	
	$\frac{1}{\sqrt{2}}(\psi_{45}^{3'3'} + \psi_{33}^{4'5'})$	-0.00454		0.02765		
	$\frac{1}{\sqrt{2}}(\psi_{55}^{1'5'} + \psi_{15}^{5'5'})$	-0.09994		-0.38800		
	${}^{1,3}B_{1g}^-$	$\frac{1}{\sqrt{2}}(\psi_5^{3'} - \psi_3^{5'})$	-0.83236	-0.99204	0.85508	-0.99204
		$\frac{1}{\sqrt{2}}(\psi_{45}^{5'5'} - \psi_{55}^{4'5'})$	-0.52246		-0.39474	
$\frac{1}{\sqrt{2}}(\psi_4^{2'} - \psi_2^{4'})$		0.11321	-0.09261	0.17722	-0.09261	
$\frac{1}{\sqrt{2}}(\psi_{45}^{4'4'} - \psi_{44}^{4'5'})$		-0.09890		0.07410		
$\frac{1}{\sqrt{2}}(\psi_{55}^{1'5'} - \psi_{15}^{5'5'})$		-0.05746		-0.09044		
$\frac{1}{\sqrt{2}}(\psi_{45}^{3'3'} - \psi_{33}^{4'5'})$		0.08732		0.07914		
${}^{1,3}B_{2u}^+$		$\frac{1}{\sqrt{2}}(\psi_2^{1'} - \psi_1^{2'})$	-0.02644	-0.08532	0.09734	-0.08532
		$\psi_5^{5'}$	0.89397	0.88401	-0.90364	0.90009
		$\psi_4^{4'}$	0.39887	0.43222	-0.17603	0.18715
		$\psi_3^{3'}$	0.04810	0.10469	-0.33006	0.32555
	$\frac{1}{\sqrt{2}}(\psi_4^{1'} + \psi_1^{4'})$	-0.06112	-0.07560	-0.03062	0.07484	
	$\psi_2^{2'}$	0.08861	0.11261	-0.15185	0.17899	
	$\frac{1}{\sqrt{2}}(\psi_{55}^{3'4'} + \psi_{34}^{5'5'})$	-0.12923		-0.05196		
	$\frac{1}{\sqrt{2}}(\psi_{55}^{2'5'} + \psi_{25}^{5'5'})$	0.09484		-0.09127		
	$\frac{1}{\sqrt{2}}(\psi_{44}^{3'4'} + \psi_{34}^{4'4'})$	-0.00824		-0.00274		
	$\psi_1^{1'}$	0.03990	0.04857	-0.09151	0.10577	
${}^{1,3}B_{3u}^+$	$\frac{1}{\sqrt{2}}(\psi_{44}^{2'5'} + \psi_{25}^{4'4'})$	-0.02180		0.01043		
	$\frac{1}{\sqrt{2}}(\psi_5^{4'} + \psi_4^{5'})$	0.94053	-0.98293	0.96257	0.97266	

Table 4 (continued)

	${}^1\Psi_{DS}$	${}^1\Psi_S$	${}^3\Psi_{DS}$	${}^3\Psi_S$
$\frac{1}{\sqrt{2}}(\psi_5^{1'} + \psi_1^{5'})$	-0.00865	0.08368	-0.03136	0.03371
$\frac{1}{\sqrt{2}}(\psi_3^{2'} + \psi_2^{3'})$	0.25203	-0.16385	0.22626	0.22977
$\frac{1}{\sqrt{2}}(\psi_{55}^{3'5'} + \psi_{35}^{5'5'})$	-0.06892		-0.05216	
$\frac{1}{\sqrt{2}}(\psi_{35}^{4'4'} + \psi_{44}^{3'5'})$	-0.11332		0.11630	
$\frac{1}{\sqrt{2}}(\psi_{24}^{5'5'} + \psi_{55}^{2'4'})$	-0.16478		0.07078	
$\frac{1}{\sqrt{2}}(\psi_{35}^{3'3'} + \psi_{33}^{3'5'})$	-0.08406		0.00466	
${}^{1,3}B_{3u}^- \frac{1}{\sqrt{2}}(\psi_5^{4'} - \psi_3^{5'})$	-0.97228	0.97335	-0.96162	0.97735
$\frac{1}{\sqrt{2}}(\psi_5^{1'} - \psi_1^{5'})$	0.09667	-0.12373	0.12261	-0.12373
$\frac{1}{\sqrt{2}}(\psi_{55}^{3'5'} - \psi_{35}^{5'5'})$	-0.01135		0.02221	
$\frac{1}{\sqrt{2}}(\psi_3^{2'} - \psi_2^{3'})$	-0.16695	0.19309	-0.09156	0.19309
$\frac{1}{\sqrt{2}}(\psi_{35}^{3'3'} - \psi_{33}^{3'5'})$	0.01952		0.00339	
$\frac{1}{\sqrt{2}}(\psi_{35}^{4'4'} - \psi_{44}^{3'5'})$	0.07371		-0.11837	
$\frac{1}{\sqrt{2}}(\psi_{55}^{2'4'} - \psi_{24}^{5'5'})$	0.10729		-0.09156	

carbon and energy transfer states due to transfer of electrons between a substituent and the hydrocarbon plays an important role in some substituted hydrocarbons, the energy levels obtained in this paper seem to be useful for discussing the effects of perturbation which is caused by the introduction of substituents to naphthalene.

Appendix

Singly or doubly excited configurational wave functions are represented as follows:

- ${}^{1,3}\psi_i^j = \frac{1}{\sqrt{2}}(|\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{i}\bar{j}| \pm |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{j}\bar{i}|)$
- ${}^1\psi_{ii}^{kk} = |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{k}\bar{k}|$
- ${}^{1,3}\psi_{ij}^{kk} = \frac{1}{\sqrt{2}}(|\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{i}\bar{j} \cdots \bar{k}\bar{k}| \pm |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{j}\bar{i} \cdots \bar{k}\bar{k}|)$
- ${}^{1,3}\psi_{ii}^{kl} = \frac{1}{\sqrt{2}}(|\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{k}\bar{l}| \pm |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{l}\bar{k}|)$
- ${}^{1,3}\psi_{ij}^{kl} = \frac{1}{2}(\pm |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{i}\bar{j} \cdots \bar{k}\bar{l}| + |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{i}\bar{j} \cdots \bar{l}\bar{k}| \mp |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{i}\bar{j} \cdots \bar{k}\bar{l}| - |\bar{1}\bar{1}\bar{2}\bar{2} \cdots \bar{i}\bar{j} \cdots \bar{l}\bar{k}|)$

(A-1)

If a given wave function is expanded in terms of these determinantal wave functions, the coefficients of the function are determined by the familiar equations:

$$|H_{mn} - \delta_{mn} E| = 0 \quad (\text{A-2})$$

and

$$\sum_m A_m (H_{mn} - \delta_{mn} E) = 0 \quad (\text{A-3})$$

where

$$H_{mn} = \langle \psi_m | \mathcal{H} | \psi_n \rangle \mathcal{H} = \Sigma H_{\text{core}} + \frac{1}{2} \sum'_{pq} \frac{e^2}{r_{pq}}. \quad (\text{A-4})$$

The following matrix elements over molecular orbitals are obtained [12, 15]; diagonal elements (symbol ΔE indicates excitation energy relative to the ground state):

1. $\Delta^{1,3} E_i^j = I_{jj} - I_{ii} + J_{ij} - J_{ii} \pm K_{ij} - \sum'_{f \neq i}^{\text{OCC}} (2J_{fi} - 2J_{ff} - K_{fi} - K_{ff})$
 $= F_{jj} - F_{ii} - (J_{ij} - K_{ij}) \pm K_{ij}$
2. $\Delta^1 E_{ii}^{kk} = 2\Delta^1 E_i^k - 2J_{ik} + J_{ii} + J_{kk} - 2K_{ik}$
3. $\Delta^{1,3} E_{ii}^{kl} = \Delta^{1,3} E_i^k + \Delta^{1,3} E_i^l - J_{ik} - J_{il} + J_{ii} + J_{kl} \mp K_{ik} \mp K_{il} \pm K_{kl}$
4. $\Delta^{1,3} E_{ij}^{kk} = \Delta^{1,3} E_i^k + \Delta^{1,3} E_j^l - J_{ik} - J_{jk} + J_{kk} + J_{ij} \mp K_{ik} \mp K_{jk} \pm K_{ij}$
5. $\Delta^{1,3} E_{ij}^{kl} = \Delta^{1,3} E_i^k + \Delta^{1,3} E_j^l - J_{jk} - J_{jl} + J_{ij} + J_{kl} - \frac{1}{2}(K_{ik} + K_{jl}) \mp (K_{ik} + K_{jl}) +$
 $+ \frac{1}{2}(K_{il} + K_{jk}) + \frac{1}{2}(K_{ij} \pm K_{ij}) \pm K_k$

(A-5)

Non-diagonal elements:

1. ${}^1\langle \psi_0 | \mathcal{H} | \psi_{ij}^j \rangle = \sqrt{2} F_{ij}$
2. ${}^1\langle \psi_0 | \mathcal{H} | \psi_{ii}^{kk} \rangle = K_{ik}$
3. ${}^1\langle \psi_0 | \mathcal{H} | \psi_{ij}^{kk} \rangle = -\sqrt{2} (ik | kj)$
4. ${}^1\langle \psi_0 | \mathcal{H} | \psi_{ii}^{kl} \rangle = \sqrt{2} (ik | il)$
5. ${}^1\langle \psi_0 | \mathcal{H} | \psi_{ij}^{kl} \rangle = - (ik | jl) - (il | jk)$
6. ${}^{1,3}\langle \psi_i^j | \mathcal{H} | \psi_i^l \rangle = \delta_{ic} F_{jl} - \delta_{jl} F_{jk} + (ij | kl) \pm (ij | kl) - (ik | jl)$
7. ${}^{1,3}\langle \psi_r^s | \mathcal{H} | \psi_{ij}^{kl} \rangle = \mp \delta_{sk} \delta_{jr} [F_{ik} - (ik | jr) \mp (ir | jk) + (ik | ks)] + \delta_{sk} [(ir | js) \pm (is | jr)] +$
 $+ \delta_{sk} \delta_{ir} [-F_{js} - (jk | ks) + (ir | jk) \pm (ik | jr)] - \delta_{ir} (jk | sk) \mp \delta_{jr} (ik | sk)$
8. ${}^{1,3}\langle \psi_r^s | \mathcal{H} | \psi_{ii}^{kl} \rangle = \pm \delta_{sk} \delta_{ir} [F_{il} + (il | ks) \pm (ik | ls) - (ir | il)] + \delta_{ir} [(il | ks) \pm (ik | ls)] +$
 $+ \delta_{sl} \delta_{ir} [F_{ik} - (ik | ir) \pm (ik | ls) + (il | ks)] \mp \delta_{sk} (ir | il)$
9. ${}^{1,3}\langle \psi_{ii}^{kl} | \mathcal{H} | \psi_{rs}^{kl} \rangle = \delta_{kl} \delta_{ir} [(ij | ks) \pm (ij | ks) - (is | jk)] + \delta_{sk} \delta_{jr} [(ij | kt) \pm (ij | kt) - (ik | jt)] +$
 $+ \delta_{kt} \delta_{jr} [(ij | ks) \pm (ij | ks) \mp (jk | js)] + \delta_{sk} \delta_{ir} [(ij | ks) \pm (ij | ks) \pm (is | jk)]$
10. ${}^{1,3}\langle \psi_{ii}^{kl} | \mathcal{H} | \psi_{rr}^{lu} \rangle = \delta_{kt} \delta_{lu} K_{ir} + \delta_{ir} [(kt | lu) \pm (lt | ku)]$
11. ${}^{1,3}\langle \psi_{ij}^{kl} | \mathcal{H} | \psi_{rs}^{kl} \rangle = \delta_{ir} \delta_{js} K_{kl} + \delta_{kl} [(ir | js) + (is | jr)]$
12. ${}^1\langle \psi_{ii}^{kl} | \mathcal{H} | \psi_{rs}^{kl} \rangle = \delta_{is} \delta_{kl} \sqrt{2} [F_{ir} + 2(ir | kk) - (ik | kr) - (ir | rr)]$
13. ${}^1\langle \psi_{ii}^{kl} | \mathcal{H} | \psi_{rr}^{kl} \rangle = \delta_{ir} \delta_{sk} \sqrt{2} [F_{kt} - 2(ii | kt) + (ik | it) + (kk | kt)]$
14. ${}^{1,3}\langle \psi_r^s | \psi_{ij}^{kl} \rangle = -\frac{1}{\sqrt{2}} \delta_{sk} \delta_{jr} [F_{ii} - (ir | jl) - (il | jr) + (il | sk) \pm (ik | sl)] -$
 $-\frac{1}{\sqrt{2}} \delta_{sk} \delta_{ir} [F_{jt} - (ir | jl) - (il | jr) + (jl | sk) \pm (jk | sl)] \mp$
 $\mp \frac{1}{\sqrt{2}} \delta_{sl} \delta_{jr} [F_{ik} - (ik | jr) - (ij | kr) + (ik | sl) \pm (il | sk)] \mp$
 $\mp \frac{1}{\sqrt{2}} \delta_{sl} \delta_{ir} [F_{jk} - (ir | jk) - (ik | jr) + (jk | sl) \pm (jl | sk)] -$

$$\begin{aligned}
& -\frac{1}{\sqrt{2}} \delta_{ir} [(il | sk) \pm (jk | sl)] - \frac{1}{\sqrt{2}} \delta_{jr} [(il | sk) \pm (ik | sl)] \pm \\
& \pm \frac{1}{\sqrt{2}} \delta_{sr} [(ir | jk) \pm (ik | jr)] + \frac{1}{\sqrt{2}} \delta_{sk} [2 (ij | lr) - (ir | jr)]
\end{aligned} \tag{A-6}$$

where

$$\begin{aligned}
I_{ij} &= \langle \varphi_i(1) | H_{\text{core}}(1) | \varphi_j(1) \rangle \\
(ij | kl) &= \langle \varphi_i(1) \varphi_k(2) | \frac{e^2}{r_{12}} | \varphi_j(1) \varphi_l(2) \rangle, \quad J_{ij} = (ii | jj), \quad K_{ij} = (ij | ij),
\end{aligned}$$

δ being Kroneker symbol.

In these equations, i, j, k , and l refer to molecular orbitals, and F_{ij} is the matrix element of the Hartree-Fock operator

$$F_{ij} = I_{ij} + \sum_I^n [2 (ij | nn) - (in | jn)]. \tag{A-7}$$

The transition moment between Ψ_a and Ψ_b is defined by

$$\mathfrak{M}_{ab} = \langle \Psi_a | \mathfrak{M} | \Psi_b \rangle \tag{A-8}$$

where

$$\mathfrak{M} = e \sum_u r_u + \sum_s e_s r_s \tag{A-9}$$

the summation u being over all π -electrons and s over all core nuclei. The oscillator strength f is calculated by the following MULLIKEN and RIEKE's formula:

$$f = 1.085 \cdot 10^{11} \nu \mathfrak{M}_{ab}^2 \tag{A-10}$$

where ν is the frequency of the transition $\Psi_a \rightarrow \Psi_b$ in cm^{-1} .

The matrix elements for x -component of transition moment are as follows:

1. ${}^1\langle \psi_0 | M^x | \psi_0 \rangle = 2e \sum_f m_{ff}^x + \sum_s e_s x_s$
2. ${}^{1,3}\langle \psi_i^j | M^x | \psi_i^j \rangle = 2e \sum_f m_{ff}^x - em_{ii}^x + em_{jj}^x + \sum_s e_s x_s$
3. ${}^1\langle \psi_{ii}^{kk} | M^x | \psi_{ii}^{kk} \rangle = 2e \sum_f m_{ff}^x - 2em_{ii}^x + 2em_{kk}^x + \sum_s e_s x_s$
4. ${}^{1,3}\langle \psi_{ii}^{kl} | M^x | \psi_{ii}^{kl} \rangle = 2e \sum_f m_{ff}^x - 2em_{ii}^x + em_{kk}^x + em_{ll}^x + \sum_s e_s x_s$
5. ${}^{1,3}\langle \psi_{ij}^{kk} | M^x | \psi_{ij}^{kk} \rangle = 2e \sum_f m_{ff}^x - em_{ii}^x - em_{jj}^x + 2em_{kk}^x + \sum_s e_s x_s$
6. ${}^{1,3}\langle \psi_{ij}^{kl} | M^x | \psi_{ij}^{kl} \rangle = 2e \sum_f m_{ff}^x - em_{ii}^x - em_{jj}^x + em_{kk}^x + em_{ll}^x + \sum_f e_s x_s$
7. ${}^1\langle \psi_0 | M^x | \psi_i^j \rangle = \sqrt{2} em_{ij}^x$
8. ${}^1\langle \psi_0 | M^x | \psi_{ii}^{kk} \rangle = 0$
9. ${}^1\langle \psi_0 | M^x | \psi_{ij}^{kk} \rangle = 0$
10. ${}^1\langle \psi_0 | M^x | \psi_{ii}^{kl} \rangle = 0$
11. ${}^1\langle \psi_0 | M^x | \psi_{ij}^{kl} \rangle = 0$
12. ${}^{1,3}\langle \psi_i^j | M^x | \psi_k^l \rangle = e (\delta_{ik} m_{jl}^x - \delta_{il} m_{jk}^x)$
13. ${}^1\langle \psi_r^s | M^x | \psi_{ii}^{kk} \rangle = \delta_{ir} \delta_{sk} \sqrt{2} em_{ik}^x$
14. ${}^{1,3}\langle \psi_r^s | M^x | \psi_{ij}^{kk} \rangle = \mp \delta_{sk} \delta_{jr} em_{ik}^x - \delta_{ir} \delta_{sk} em_{js}^x$
15. ${}^{1,3}\langle \psi_r^s | M^x | \psi_{ii}^{kl} \rangle = \pm \delta_{sk} \delta_{ir} em_{il}^x + \delta_{ir} \delta_{sr} em_{ik}^x$
16. ${}^1\langle \psi_{ii}^{kk} | M^x | \psi_{rs}^{tt} \rangle = \delta_{is} \delta_{kt} \sqrt{2} em_{it}^x$
17. ${}^1\langle \psi_{ii}^{kk} | M^x | \psi_{rr}^{st} \rangle = \delta_{ir} \delta_{sk} \sqrt{2} em_{kt}^x$
18. ${}^{1,3}\langle \psi_{ii}^{kl} | M^x | \psi_{rs}^{tt} \rangle = 0$

$$\begin{aligned}
 19. \quad & {}^1\langle\psi_{ii}^{kk} | M^x | \psi_{ii}^{mm}\rangle = 0 \\
 20. \quad & {}^{1,3}\langle\psi_{ij}^{kk} | M^x | \psi_{rs}^{tt}\rangle = 0 \\
 21. \quad & {}^{1,3}\langle\psi_{ii}^{kl} | M^x | \psi_{rr}^{tu}\rangle = 0
 \end{aligned} \tag{A-11}$$

where

$$m_{ij}^x = \langle\varphi_i(1) | x(1) | \varphi_j(1)\rangle = m_{i'j'}^x, \quad m_{ij}^x = m_{ij'}^x.$$

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