538. *The Lowest Singlet Excited Levels of Naphthalene. Part II.*[1] *Restricted Calculations.*

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Restrictions are introduced in the calculations of the lowest singlet excited levels of naphthalene reported in Part I. The present results indicate that the calculation of accurate excitation energies is still difficult. Nonetheless, the new calculations make possible a much more certain characterisation of the near-ultraviolet spectrum of naphthalene than was possible in Part I. One of our calculations closely follows the semi-empirical theory developed by Moffitt for the spectra of polycyclic hydrocarbons. It is shown that a relation exists between the characterisation of the transitions in the schemes proposed by Moffitt and by Dewar and Longuet-Higgins.

The results given in Part I[1] for the calculations on the near-ultraviolet spectra of naphthalene were inconclusive. Which of the two lowest singlet–singlet transitions ${}^1A_{1g} \longrightarrow {}^1B_{1u}$ or ${}^1A_{1g} \longrightarrow {}^1B_{2u}$ would be the weaker and thus correspond to the lowest transition observed in the spectrum was not evident. In this paper two more restrictions concerning (i) certain molecular integrals and (ii) molecular orbitals will be introduced in an attempt to clarify this point.

(i) The value of the integral

$$\alpha_K = \int \chi_K{}^* H^{\mathrm{SCF}} \chi_K \mathrm{d}\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where K is any carbon centre in the molecule) will be restricted.

Use of the hypotheses proposed by Pariser and Parr[2] gives for α_K (cf. Pople[3]):

$$\alpha_K = W_{2p} + \tfrac{1}{2}[KK|KK] + \sum_{p \neq K} [p|KK] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where W_{2p} is the ionisation potential of an electron in a $2p$-orbital in the valence state of carbon, $[KK|KK]$ is the two-electron coulomb integral, where both electrons are on the same centre, and $[p|KK]$ is the penetration integral between neutral atom p and distribution $|\chi_K|^2$.

There are three different ways of calculating α_K.

(*a*) The penetration integrals are given an approximate value and only the carbon skeleton of the molecule is specifically considered. This was the method adopted[4] in the calculation of the self-consistent field orbitals used in Part I. The value of α_K then depends on K as some of the carbon atoms are linked to three other carbon atoms and the others to two. The self-consistent field orbitals which are computed from these values of α_K are not related by pairs of bonding and antibonding orbitals as in the Hückel theory.[5]

(*b*) If a point-charge approximation is used to estimate the values of the atomic integrals, all penetration integrals vanish; α_K is independent of K. This is the procedure that Pople[3] used. The self-consistent field orbitals calculated from this approximation are necessarily paired, as in the Hückel approximation.

(*c*) The same paired property of self-consistent field orbitals can be obtained without implying the neglect of the penetration integrals. If the hydrogen atoms were specifically included in the calculation of the penetration integrals, the difference in the values of α_K found in (*a*) should be much smaller. It has been tacitly assumed by Pariser and Parr[2] that if penetration integrals with hydrogen atoms are considered the values of α_K should be equal.

In this paper, it will be assumed that the value of α_K is independent of K. We believe that this property follows from (*c*) rather than from (*b*).

(ii) Only molecular orbitals will be used in which the bonding and antibonding orbitals

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[1] Part I, Lefebvre and Moser, *J.*, 1956, 1557. In the last textual line of p. 1559 the first transition should be described as $A_{1g} \longrightarrow B_{1u}$.

[2] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466, 767.

[3] Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

[4] Moser, *J. Chim. phys.*, 1955, **52**, 24.

[5] Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193.

are paired. Of the three sets considered in the first paper, only the Hückel and cyclic orbitals obey this restriction; only calculations based on these two sets will now be considered.

Pople [6] used ground-state self-consistent field orbitals to describe the excited states of naphthalene and showed that it is possible to reproduce Dewar and Longuet-Higgins's [7] empirical theory for the characterisation of the ultraviolet spectrum in a scheme where electron repulsion is introduced in every step of the calculation. It can be shown that exactly the same mathematical development is possible when one uses (i) the approximations described by Pariser and Parr [2] to calculate the molecular integrals, (ii) the restriction of equal values of α_K, and (iii) any set of molecular orbitals in which the bonding and antibonding orbitals are paired. The development does not depend on the use only of self-consistent field molecular orbitals for the ground state.

Application of the Approximations due to Dewar and Longuet-Higgins and to Pople to Different Models of Naphthalene.—The purpose of this paper is to present several calculations made with application of these three conditions. The results of the calculations are summarised in the Tables.

(i) Calculations have been made by using Hückel and cyclic orbitals as in Part I, that is by using experimentally determined bond lengths (Tables 1 and 2). The values for the atomic integrals have been given previously.[4]

TABLE 1. *Effects of introducing equal values of α_K in the calculation made with the Hückel orbitals.*

Level	α_K	Wave-functions	Energies (in ev)	*f*-values
First B_{1u}	Unequal	$0{\cdot}784\ {}^1\Psi'{}_1^{5,7} - 0{\cdot}621\ {}^1\Psi'{}_1^{4,6}$	4·710	0·02
	Equal	$0{\cdot}707\ ({}^1\Psi'{}_1^{5,7} - {}^1\Psi'{}_1^{4,6})$	4·704	0·00
Second B_{1u}	Unequal	$0{\cdot}621\ {}^1\Psi'{}_1^{5,7} + 0{\cdot}784\ {}^1\Psi'{}_1^{4,6}$	6·644	2·47
	Equal	$0{\cdot}707\ ({}^1\Psi'{}_1^{5,7} + {}^1\Psi'{}_1^{4,6})$	6·638	2·50

TABLE 2. *Effects of introducing equal values of α_K in the calculation made with the cyclic real orbitals.*

Level	α_K	Wave-functions	Energies (in ev)	*f*-values
First B_{1u}	Unequal	$0{\cdot}772\ {}^1\Psi'{}_1^{5,7} + 0{\cdot}636\ {}^1\Psi'{}_1^{4,6}$	3·074	0·02
	Equal	$0{\cdot}707\ ({}^1\Psi'{}_1^{5,7} + {}^1\Psi'{}_1^{4,6})$	3·836	0·00
Second B_{1u}	Unequal	$0{\cdot}636\ {}^1\Psi'{}_1^{5,7} - 0{\cdot}772\ {}^1\Psi'{}_1^{4,6}$	5·481	3·43
	Equal	$0{\cdot}707\ ({}^1\Psi'{}_1^{5,7} - {}^1\Psi'{}_1^{4,6})$	6·760	4·27

TABLE 3.

	Before configuration interaction			
	Hückel		Cyclic	
	energy (ev)	*f*	energy (ev)	*f*
${}^1E_1^{5,6}$	4·346	0·53	4·204	0·50
${}^1E_1^{5,7}$ ${}^1E_1^{4,6}$	5·792	1·09	6·026	1·53
${}^1E_1^{4,7}$	7·378	0·64	6·875	0·35

	After configuration interaction			
	Hückel		Cyclic	
	energy (ev)	*f*	energy (ev)	*f*
B_{2u}	4·161	0·30	4·086	0·35
B_{1u}	4·722	0·00	4·586	0·00
B_{2u}	6·762	1·11	6·993	0·59
B_{1u}	7·563	2·54	7·466	3·80

(ii) Two different calculations have been made in which all bond lengths are assumed to be equal. In Table 3 it has been assumed that all values of β_{ij} are equal when i and j are neighbours ($\beta_{ij} = \int \chi_i{}^* H^{\mathrm{SCF}} \chi_j \mathrm{d}\tau$) and β_{ij} values for non-neighbours have been calculated from the formula:

$$\beta_{ij} = \beta_{ij}{}^c - \tfrac{1}{2} P_{ij}[ii|jj] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\beta_{ij}{}^c = \int \chi_i{}^* H^c \chi_j \mathrm{d}\tau$, P_{ij} is the bond order between atoms i and j, and $[ii|jj]$ is the Coulomb attraction integral between i and j. In Table 4 it has been assumed that all

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[6] Pople, *Proc. Phys. Soc.*, 1955, *A*, **68**, 81.

[7] Dewar and Longuet-Higgins, *ibid.*, 1954, *A*, 67, 795.

values of β_{ij}^c are equal when atoms i and j are neighbours; all values of β_{ij} have been calculated from eqn. (3).

The values assigned to the atomic integrals and those calculated for molecular integrals for the models of equal bond lengths are given in Table 5.

TABLE 4.

	Before configuration interaction					After configuration interaction			
	Hückel		Cyclic			Hückel		Cyclic	
	energy (ev)	f	energy (ev)	f		energy (ev)	f	energy (ev)	f
$^1E_1^{5,6}$	4·586	0·55	4·586	0·55	B_{2u}	4·289	0·20	4·314	0·20
$^1E_1^{5,7}$	5·373	1·01	5·560	1·41	B_{1u}	4·403	0	4·120	0
$^1E_1^{4,6}$					B_{1u}	6·343	2·36	7·000	3·56
					B_{2u}	6·597	1·05	5·834	0·71
$^1E_1^{4,7}$	6·300	0·54	5·563	0·28	—	—	—	—	—

TABLE 5.

(a) *Values over atomic integrals* (ev) (for numbering used, see Part I).

[11|11]	10·53	[22|33]	7·30	[10, 10|33]	4·90
[11|22]	7·30	[22|44]	5·46	[10, 10|44]	5·46
[11|33]	5·46	[22|55]	4·90	[10, 10|55]	7·30
[11|44]	4·90	[22|66]	3·38	[10, 10|66]	5·46
[11|55]	5·46	[22|77]	2·82	[10, 10|77]	4·90
[11|66]	3·79	[22|88]	2·93	[10, 10|88]	5·46
[11|77]	3·38	[22|99]	3·79	[10, 10|99]	7·30
[11|88]	3·79	[22|10, 10]	5·46		
[11|99]	5·46				
[11|10, 10]	7·30				

$\beta_{ij}^c = -2·39$ ev

(b) *Values over molecular integrals* (ev)

	Hückel orbitals	Cyclic orbitals		Hückel orbitals	Cyclic orbitals
$\gamma_{5,6}$	5·674	5·674	$\zeta_{6,7}^{4,5}$	0·144	0·104
$\delta_{5,6}$	0·790	0·790	$\zeta_{5,6}^{4,7}$	0·314	0·239
$\gamma_{5,7}$	5·520	5·606	$\zeta_{5,7}^{4,6}$	0·557	0·772
$\delta_{5,7}$	0·557	0·772			
$\delta_{4,7}$	0·679	0·513			
$\gamma_{4,7}$	5·944	6·037			

	Hückel orbitals		Cyclic orbitals	
	Table 3	Table 4	Table 3	Table 4
ε_4	$\alpha - 5·982$	$\alpha - 5·443$	$\alpha - 5·943$	$\alpha - 5·287$
ε_5	$\alpha - 4·216$	$\alpha - 4·336$	$\alpha - 4·145$	$\alpha - 4·336$

In Tables 1 and 2 the results for the $^1B_{2u}$ class have not been included, for they are identical with those given in Part I. This is so because the values of α_K do not appear in the quantities $\varepsilon_6 - \varepsilon_5$ and $\varepsilon_7 - \varepsilon_4$ (for a definition of this notation see Part I) even if α_K is dependent on K.

It will be seen that the assumption that all bond lengths are equal has had a considerable effect on the mixing of the two $^1B_{2u}$ functions. In Table 3 this mixing is nearly negligible, but it is somewhat larger in Table 4.

The most important difference between the calculations reported here and those in Part I is that now the two $^1B_{1u}$ functions are always degenerate; this is essential for the theory of Dewar and Longuet-Higgins to characterise the near ultraviolet spectrum of naphthalene.

The order of levels predicted by these calculations varies rather considerably. From Table 1 the order is: $^1B_{1u}$, $^1B_{2u}$, $^1B_{1u}$, $^1B_{2u}$; from Table 2: $^1B_{1u}$, $^1B_{2u}$, $^1B_{2u}$, $^1B_{1u}$; from Table 3: $^1B_{2u}$, $^1B_{1u}$, $^1B_{2u}$, $^1B_{1u}$; from Table 4 (Hückel): $^1B_{2u}$, $^1B_{1u}$, $^1B_{1u}$, $^1B_{2u}$; from Table 4 (cyclic): $^1B_{1u}$, $^1B_{2u}$, $^1B_{2u}$, $^1B_{1u}$. Relatively small changes in the model used therefore produce large changes in the results of the calculation of excitation energies. This is indeed unfortunate, for it means that the calculation of the order of levels is still difficult. This is particularly important in a semi-empirical procedure, such as we have used, where the value for the atomic integrals is chosen empirically. There are several procedures which can be used to assign values for the atomic integrals. A Referee has suggested that the calculation of the order of levels might be less hazardous if the values of the atomic integrals were taken from experimental measurements. Already the value of the integrals [11|11] and β_{ij}^c are taken from experimental data; it is possible that at least some of the others might also be obtained in this way.

Despite the uncertainty of the order of levels, the characterisation of the near ultraviolet spectrum of naphthalene is possible, because always there is found in these calculations an ${}^1A_{1g} \longrightarrow {}^1B_{1u}$ transition of zero intensity and, consequently, always less intense than that of the ${}^1A_{1g} \longrightarrow {}^1B_{2u}$ transition.

We tend back to Dewar and Longuet-Higgins's original point, which is to try to characterise the various transitions and then make the correspondence with the experimentally observed bands. This is particularly easy in the case of naphthalene since the observed bands possess rather different characteristics. It is just because rather wide choices of molecular orbitals, bond lengths, and atomic integrals all give the essential characterisation suggested by Dewar and Longuet-Higgins that it is possible to be confident in their assignment. Heis plausible that the best choice of orbitals and atomic integrals would fall somewhere within the limits of the values used here and in Pople's calculation.

Moffitt's Theory.[8]—The theories due to Dewar and Longuet-Higgins and to Moffitt both show how the first band system in the ultraviolet spectrum of naphthalene could result from a very weak but nonetheless allowed transition. The results described in the previous section show that the essence of Dewar and Longuet-Higgins's theory is reproduced by using functions built either from Hückel or cyclic real orbitals.

In this section we shall indicate the mathematical development for the wave functions built on complex orbitals. The numerical results will be the same as those computed from cyclic real orbitals because of the identities which exist between the two sets of functions [Part 1; eqn. (10)]. Our purpose now is to introduce electron repulsion by using the many-electron Hamiltonian at every stage in Moffitt's theory, as Pople has done for the theory of Dewar and Longuet-Higgins. Also, the relation between the theories due to Moffitt and to Dewar and Longuet-Higgins will be briefly discussed.

The cyclic complex orbitals have the form:

$$\theta_L = 10^{-\frac{1}{2}} \sum_K \exp\,[2\pi i KL/10]\chi_K \qquad (L = 0, \pm 1, \ldots . \pm 4, 5) \quad . \quad . \quad (4)$$

In the ground state the orbitals up to $L = \pm 2$ are doubly occupied.

The following four functions can be formed from the four lowest singlet mono-excited wave-functions of the truly cyclic molecule (exciting an electron from $L = \pm 2$ to $L = \pm 3$) which satisfy the symmetry requirements for naphthalene:

$$\Theta_X = ({}^1\Psi_1{}^{-2,-3} + {}^1\Psi_1{}^{2,3})/\sqrt{2} \qquad \Theta_U = ({}^1\Psi_1{}^{-2,3} + {}^1\Psi_1{}^{2,-3})/\sqrt{2}$$
$$\Theta_Y = ({}^1\Psi_1{}^{-2,-3} - {}^1\Psi_1{}^{2,3})/i\sqrt{2} \qquad \Theta_V = ({}^1\Psi_1{}^{-2,3} - {}^1\Psi_1{}^{2,-3})/i\sqrt{2} \quad . \quad (5)$$

Θ_X and Θ_U transform as B_{2u}, and Θ_Y and Θ_V as B_{1u}. Moffitt has proposed that the energies associated with these functions should be located empirically. The mixing of the functions that belong to the same symmetry class is brought about by a perturbation operator which is a sum of undefined one-electron operators P_i.

(a) *Introduction of explicit operators.* The many-electron Hamiltonian will be used to form the secular equation. The diagonal elements are:

$$\int \Theta_W{}^* H \Theta_W \,d\tau = {}^1E_1{}^{2,3} \mp (\zeta_{3,3}{}^{2,2} - 2\zeta_{2,3}{}^{2,3})$$
$$\int \Theta_Z{}^* H \Theta_Z \,d\tau = {}^1E_1{}^{2,-3} \mp (\zeta_{-3,-3}{}^{2,2} - 2\zeta_{2,-3}{}^{2,-3}) \quad . \quad . \quad (6)$$

with $W = X$ (— sign) or Y (+ sign) and $Z = U$ (— sign) or V (+ sign); ${}^1E_1{}^{i,j}$ and $\zeta_{pq}{}^{mn}$ have been defined in Part I.

For benzene similar formulæ reproduce the lowest singlet excited levels in the Goeppert-Mayer and Sklar[9] approximation, except that here there is additional splitting

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[8] Moffitt, *J. Chem. Phys.*, 1954, **22**, 320.

[9] Goeppert-Mayer and Sklar, *ibid.*, 1938, **6**, 645.

due to some of the integrals ζ_{pq}^{mn} which are zero for the cyclic molecule and other than zero for naphthalene.

Because of the lower symmetry of naphthalene compared with that of the hypothetical cyclic molecule, there are the following off-diagonal elements in the energy matrix :

$$\int \Theta_S^* \, H \, \Theta_T \, \mathrm{d}\tau = \varepsilon_{-3,3}^{c} + \sum_{a=0}^{a=\pm 2} [(2\zeta_{3,3}^{a,-a} - \zeta_{-a,3}^{a,3}) - \zeta_{3,3}^{2,-2} + 2\zeta_{-2,3}^{2,3}]$$

$$\mp [\varepsilon_{2,-2}^{c} + \sum_{a=0}^{a=\pm 2} (2\zeta_{2,2}^{a,a} - \zeta_{a,2}^{a,2}) + \zeta_{2,2}^{3,-3} - 2\zeta_{2,-3}^{2,3}] \quad . \quad (7)$$

For B_{2u} symmetry, $S = X$ and $T = U$; for B_{1u} symmetry, $S = Y$ and $T = V$. The minus sign before the second bracket holds for B_{2u} symmetry, the plus sign for B_{1u} symmetry.

If we call H^{SCF} the operator

$$H^{\mathrm{SCF}} = H^{c} + \sum_{a=0}^{a=\pm 2} (2J_a - K_a) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

then eqn. (7) can be rewritten as :

$$\int \Theta_S^* \, H \, \Theta_T \, \mathrm{d}\tau = H_{-3,3}^{\mathrm{SCF}} \mp H_{2,-2}^{\mathrm{SCF}} + \Lambda_{S,T} \quad . \; . \; . \; . \quad (9)$$

with

$$\Lambda_{S,T} = -\zeta_{3,3}^{2,-2} + 2\zeta_{-2,3}^{2,3} \mp \zeta_{3,-3}^{2,2} \pm \zeta_{2,-3}^{2,3} \quad . \; . \; . \quad (10)$$

The upper sign in eqns. (9) and (10) refers to B_{2u} symmetry and the lower sign to B_{1u} symmetry.

Between the four orbitals θ_2, θ_{-2}, θ_3, θ_{-3} and the four real orbitals ϕ_4, ϕ_5, ϕ_6, and ϕ_7 (where ϕ_4 and ϕ_5 are the two highest bonding orbitals, ϕ_6 and ϕ_7 the two lowest antibonding) there exist the relations :

$$\phi_4 = (\theta_2 + \theta_{-2})/\sqrt{2} \qquad \phi_6 = (\theta_3 - \theta_{-3})/i\sqrt{2}$$

$$\phi_5 = (\theta_2 - \theta_{-2})/i\sqrt{2} \qquad \phi_7 = (\theta_3 + \theta_{-3})/\sqrt{2} \quad . \; . \; . \; . \quad (11)$$

By using these relations, $\Lambda_{S,T}$ (eqn. 10) can be rewritten in terms of integrals over real orbitals :

$$\Lambda \text{ (for } B_{1u}) = [J_{4,6} - 2K_{4,6} - J_{5,7} + 2K_{5,7}]/2 \quad . \; . \; . \quad (12)$$

$$\Lambda \text{ (for } B_{2u}) = [J_{5,6} - 2K_{5,6} - J_{4,7} + 2K_{4,7}]/2$$

It can be shown (cf. Pople [6]) that under the conditions of this calculation $J_{4,6} = J_{5,7}$ and $K_{4,6} = K_{5,7}$. Thus Λ (for B_{1u}) = 0. In eqn. (10) for the B_{1u} class only the first two terms on the right remain.

Except for the term $\Lambda_{X,U}$ there is a parallel with the formulæ that Moffitt has obtained. The H^{SCF} operator here plays the same rôle as the operator P in Moffitt's formulation. It is interesting to recall that the explicit introduction of electron repulsion in the simple LCAO-MO theory also corresponds to a replacement of an undefined one-electron operator by the SCF operator.

Because of the restrictions used here, only the quantities $\int \chi_K^* H^{\mathrm{SCF}} \chi_L \mathrm{d}\tau (K \neq L)$ appear in the off-diagonal elements of the H^{SCF} operator. Eqn. (9) for the B_{1u} class can be written (cf. Moffitt's quantity μ) :

$$H_{-3,3}^{\mathrm{SCF}} + H_{2,-2}^{\mathrm{SCF}} = (5)^{-1} \sum_{K} \sum_{L>K}' 2 \exp [6\pi i(K + L)/10] \int \chi_K^* H^{\mathrm{SCF}} \chi_L \mathrm{d}\tau \, . \quad (13)$$

where the double summation is taken only over the pairs of atoms for which $(K + L)$ is even. In this case the atoms K and L are either both starred or both unstarred so that $\int \chi_K^* H^{\mathrm{SCF}} \chi_L \mathrm{d}\tau = 0$. Thus eqn. (13) is zero. The functions Θ_Y and Θ_V do not mix. The empirical procedure and the procedure in which electron repulsion has been explicitly introduced give the same results for the B_{1u} class of functions. Eqn. (9) for the B_{2u} class can be written (cf. Moffitt's quantity λ) :

$$\int \Theta_X^* H \Theta_U \, d\tau = (5)^{-1} \sum_K \sum_{L>K}{}' 2 \exp [6\pi i(K + L)/10] \int \chi_K^* H^{\mathrm{SCF}} \chi_L \, d\tau + \Lambda_{X,U} . \quad (14)$$

The summation is taken only over the pairs of atoms for which $(K + L)$ is odd. Eqn. (14) could be simplified by assuming that only values of β_{ij} for nearest neighbours are other than zero and in that case equal. [These restrictions are much more severe than have been used in the calculations but they are analogous to those used by Moffitt.] As a result there would remain in eqn. (14) only the terms due to the cross-bond and the term Λ (for B_{2u}).

It is not easy *a priori* to say whether the value of eqn. (14) is likely to be large or small. The mixing depends on the specific values assigned to the integrals. From the calculations reported in Part I and in this paper we find the following results :

0·29 ev (experimental bond lengths, from Part I) ;

1·34 ev (this paper, Table 3) ; 0·49 ev (this paper, Table 4).

It will perhaps be well to recall that small mixing of functions built on complex orbitals is equivalent to large mixing of functions built on real orbitals.

(b) *Relation with Dewar and Longuet-Higgins's theory.* Between the functions $\Theta_{S,T}$ and the singlet mono-excited functions built on real orbitals there are the relations :

$$\begin{aligned} \Theta_X &= ({}^1\Psi'^{4,7}_1 + {}^1\Psi'^{5,6}_1)/\sqrt{2} \qquad & \Theta_U &= ({}^1\Psi'^{4,7}_1 - {}^1\Psi'^{5,6}_1)/\sqrt{2} \\ \Theta_Y &= ({}^1\Psi'^{5,7}_1 + {}^1\Psi'^{4,6}_1)/\sqrt{2} \qquad & \Theta_V &= ({}^1\Psi'^{5,7}_1 - {}^1\Psi'^{4,6}_1)/\sqrt{2} \quad . \quad (15) \end{aligned}$$

From eqn. (15) there is another formulation of the off-diagonal matrix elements :

$$\int \Theta_X^* H \, \Theta_U \, d\tau = [{}^1E_1^{4,7} - {}^1E_1^{5,6}]/2 \qquad \int \Theta_Y^* H \, \Theta_V \, d\tau = [{}^1E_1^{5,7} - {}^1E_1^{4,6}]/2 \quad (16)$$

This is entirely equivalent to the previous formulation. It shows that the non-mixing of the functions Θ_Y and Θ_V can be understood from a different viewpoint. The two levels ${}^1E_1^{5,7}$ and ${}^1E_1^{4,6}$ are degenerate. The non-mixing of the two functions, that Moffitt has constructed for the ${}^1B_{1u}$ class, is a consequence of the degeneracy of the ${}^1B_{1u}$ functions considered in Dewar and Longuet-Higgins's theory.

Three points need to be briefly discussed.

(i) The non-mixing of the B_{1u} functions, which is necessary for the characterisation of the ultraviolet spectrum that Moffitt has made, is possible with a variety of values for the atomic integrals, the complex cyclic orbitals always, of course, being used. It is not necessary to make use of the rather severe restrictions that Moffitt introduced to arrive at this result. β_{KL} can be considered as a function of bond length and included even for non-neighbouring atoms. Dewar and Longuet-Higgins's theory is even more flexible than Moffitt's for the characterisation of the spectrum is possible with a variety of both molecular orbitals and atomic integrals.

(ii) In the explicit treatment of both empirical theories it is not possible to predict with any great accuracy whether the mixing of the B_{2u} functions will be small or large. The amount of mixing depends on specific values assigned to the molecular integrals.

(iii) While the cyclic real orbitals ϕ_4 and ϕ_5 correspond to the two highest bonding Hückel orbitals for the case of naphthalene, this would not necessarily be so for all polyacenes. It is possible that for a large polyacene with many cross bonds the two highest bonding cyclic real orbitals would not correspond to the two highest bonding Hückel orbitals. For such a molecule the characterisation of the spectrum by the two empirical theories would not be precisely the same.

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