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Correlation Effect on the Singlets $\pi\pi^*$ Transition Energies of Polyacenes

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The π correlation effect of the first singlet states of polyacenes has been studied for naphthalene, anthracene, tetracene using a perturbation expansion up to second order. The influence of the extent of configurations has been analysed.

1. Introduction

The π-π^* transition energies of polyacenes are examined from the point of view of the effect of π orbitals in complete configuration interaction by a Rayleigh-Schrödinger perturbation expansion up to second order. A minimal basis set has been used and the π molecular orbitals obey self consistent conditions for the ground state. The study is concerned firstly with troncature effect of the configuration interaction expansion on transition energies, secondly with the variation in term of the cycles number of the transition energies for naphthalene, anthracene, tetracene.

2. The Theoretical Method

The zero order hamiltonian matrix is built with the ground state self-consistent π orbitals. These are given as the result of a Pariser-Parr-Pople calculation [1] using the program written by Bessis-Chalvet [2]. The model hamiltonian is given by:

$$\boldsymbol{H} = \sum_{pq} H_{pq}^{N} \boldsymbol{a}_p^+ \boldsymbol{a}_q + \tfrac{1}{2} \sum_{pq} \gamma_{pq} \boldsymbol{a}_p^+ \boldsymbol{a}_q^+ \boldsymbol{a}_q \boldsymbol{a}_p$$

where $\boldsymbol{a}_p^+$ and $\boldsymbol{a}_p$ are respectively creation and annihilation operators for one electron on the orbital $2pz$. The parameters have been taken to be:

$$Z = 3.25; \quad E = 0.69; \quad W = 11.22; \quad \beta = -2.39\,.$$

The Hartree Fock hamiltonian is:

$$\boldsymbol{H}^0 = \sum_{p} \varepsilon_p \boldsymbol{b}_p^+ \boldsymbol{b}_p$$

b_p^+ being the operator of creation of a self consistent orbital φ_p and the total hamiltonian according to the Moller-Plesset partition is merely given by:

$$\boldsymbol{H} = \boldsymbol{H}^0 + \boldsymbol{V}.$$

The second order approximation on the energy of the ground singlet state S_0 is:

$$e_0^{(2)} = \sum_{I \neq 0} \frac{|\langle 0|V|I\rangle|^2}{E_0^0 - E_I^0}$$

whereas the second order energy of the S_α excited singlet state is given by:

$$e_\alpha^{(2)} = \sum_{J \neq \alpha} \frac{|\langle \alpha|V|J\rangle|^2}{E_\alpha^0 - E_J^0}$$

S_α is assumed to be non degenerate.

In the following expressions for the transition energy:

$$E_{S_\alpha \leftarrow S_0} = E_\alpha^{\mathrm{SCF}} - E_0^{\mathrm{SCF}} + e_\alpha^{(2)} - e_0^{(2)}$$

an important cancellation [3] appears. Let:

$$|\alpha\rangle = \boldsymbol{S}^+ |0\rangle,$$
$$|I\rangle = \boldsymbol{T}^+ |0\rangle,$$
$$|J\rangle = \boldsymbol{T}^+ |\alpha\rangle.$$

All the configurations $|I\rangle$ and $|J\rangle$ coming from the same excitation $\boldsymbol{T}^+$ applied to $|0\rangle$ and $|\alpha\rangle$ respectively, and so that this excitation $\boldsymbol{T}^+$ has no orbital common with $\boldsymbol{S}^+$, disappear.

The Epstein-Nesbet *partition* [4, 5]

In practice, the Möller-Plesset perturbation expansion converges rather slowly. A new partition of $\boldsymbol{H}$ can be obtained by inserting certain groups of terms in the zeroth order hamiltonian:

$$\boldsymbol{H} = \boldsymbol{H}'^0 + \boldsymbol{V}'$$
$$\boldsymbol{H}'^0 = \boldsymbol{H}^0 + \sum_I \langle I|V|I\rangle\, |I\rangle\langle I|.$$

With this choice the diagonal elements of V' are zero. This partition (Epstein-Nesbet) has been used in our calculation.

The second order energy is now:

$$e_0^{(2)} = \sum_{I \neq 0} \frac{|\langle 0|V|I\rangle|^2}{E_0^{\mathrm{SCF}} - E_I^{\mathrm{SCF}}}.$$

The exact cancellation previously described does not occur because the denominators now differ by coulombian exchange integrals. It can be shown however that these terms contribute only to the third and higher order energy[1].

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[1] This means that, when one neglects the diagrams which previously cancel in Möller-Plesset, then the effect is of third and higher order on the Rayleigh-Schrödinger perturbation using the Epstein-Nesbet partition of the hamiltonian.

In the degenerate case, we have to evaluate non-diagonal elements such as:

$$e^{(2)}_{\alpha\beta} = \sum_{J \neq D} \frac{\langle\alpha|V|J\rangle \langle J|V|\beta\rangle}{E_D^{\mathrm{SCF}} - E_J^{\mathrm{SCF}}}$$

where $|\alpha\rangle$ and $|\beta\rangle$ belong to the degenerate sub space D.

The different perturbation subroutines were written by Levy and Malrieu [6, 7]. One calculates the oscillator strengths $S_0 \rightarrow S_i$ by a double perturbation technique to first order both in V' and $\boldsymbol{d}$, the electric dipole moment. The program has been adapted to PPP approximation and completely automatized.

We expect from such a perturbation expansion the benefit of the inclusion of all interacting configurations; for instance, highly excited states are seen to be described as accurately as lowest ones. In the highly excited states however, frequently occurring quasi degeneracies necessitate a special treatment. Of course, the inconveniences linked to the choice of the basis and to the PPP approximation do not disappear. The third order correction has been completely neglected. The computing time grows roughly as $n^{2.5}$ where n is the number of π electrons.

3. Study of Some Polyacenes

a) The Influence of the CI *Extent*

Two calculations were carried out, the first concerning the α and β naphthalene bands, the second, the p band of antracene. Let

$$\psi_0 = a_0|0\rangle + a_1|1\rangle + a_2|2\rangle + \cdots$$

$$\psi_\alpha = b_0|\alpha\rangle + b_1|1\alpha\rangle + b_2|2\alpha\rangle + \cdots$$

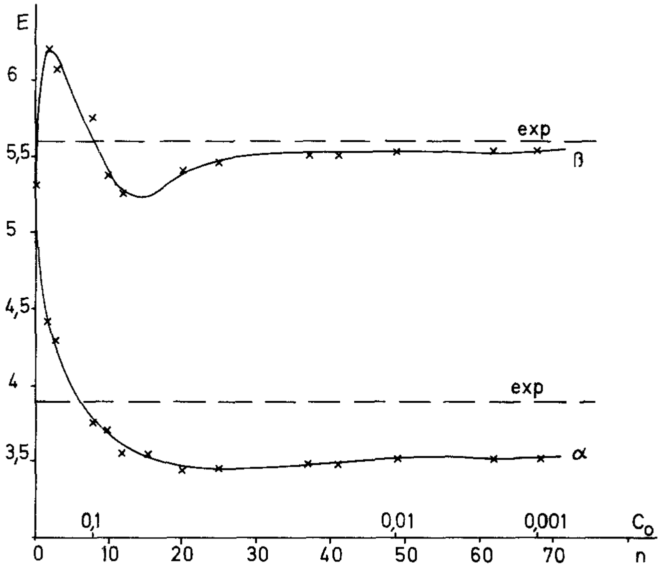

Fig. 1. Naphthalene – α and β bands. Energy in eV in function of n, number of configurations and of C_0, upper limit for the absolute value of the weight of the configuration

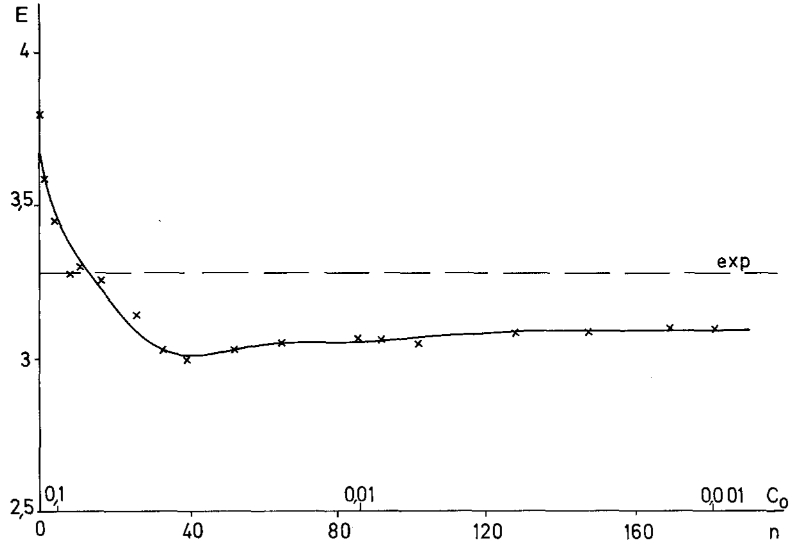

Fig. 2. Anthracene – *p* band. Energy in eV in function of *n* number of configurations and of C_0 weight of the configuration

with

$$a_I = \frac{\langle 0|V|I\rangle}{E_0^{\mathrm{SCF}} - E_I^{\mathrm{SCF}}}; \quad b_J = \frac{\langle \alpha|V|J\rangle}{E_\alpha^{\mathrm{SCF}} - E_J^{\mathrm{SCF}}}.$$

In the first step, only the configurations which have a weight greater than a given C_0 have been taken into account

$$|a_I|, \quad |b_J| \geqq C_0$$

then C_0 is varied from 0 (all configurations) to 0.3 or 0.5 (1 configuration). The results are reproduced in Figs. 1 and 2. Oscillations are important when the number of configurations occurring is small because their amplitude is about $\frac{|\langle V\rangle|^2}{\Delta E}$.

Table 1. Most active configurations in the value of the transition energy in anthracene *p*-band

Excitation with respect to ground state		$C_0 = 0.06$
		7–7→8–8 6–7→9–8
with respect to 7–8	mono exc.	4→ 8 7→11 5→ 9 6→10
	doubly exc.	7–8→10–9 6–5→ 7–8 3–8→12–7 6–8→ 9–7

The curves show that stabilization is obtained at about 40 configurations in the case of α and β naphthalene bands, 90 in the case of the antracene p-band; in both cases, the value of C_0 can then be estimated around 0.01.

For instance in Fig. 2 the 90 configurations comprise 10 monoexcited B_{2u}, 40 doubly excited B_{2u} with respect to 7–8 and 40 doubly excited with respect to the ground state A_g; no monoexcited configuration with respect to the ground state can intervene due to Brillouin's theorem. *Furthermore, all configurations giving equal contribution in both S_0 and S_α have disappeared.* By these methods, the configurations which most influence the value of the transition energy are selected; for instance Table 1 reproduces the 10 configurations having the highest weight in the case of the anthracene p-band.

b) Calculation of the Singlet-Singlet Transition Strengths and Transition Energies of Naphthalene, Anthracene, Tetracene

Many theoretical studies were undertaken since Pariser [8] published his important and exhaustive "theory of electronic spectra and structure of the polyacenes", which includes a configuration interaction very limited, on a LCAO MO basis. Nishimoto [9] calculates these transition energies with a variable β-modification of the Pariser-Parr-Pople method.

Table 2. Naphthalene

Etat	Perturbation				Pariser [8]		Exper.	
	Principal excitation	Trans.[b] energ.	Oscil. strength	Pol.	Trans.[b] energ.	Oscil. strength	Trans.[b] energ.	Oscil. strength
$^1B_{2u}^+$	5–6 (p)	4.27	0.049	y	4.49	0.256	4.29[a]	0.18?
	4–7	5.48	0.608	y	6.31	0.699	6.51?[a]	0.21
	3–8	7.07	0.618	y	8.18	0.851	7.40[a]	0.6??
	4–10, 1–7	9.47	0.023	y	8.77			
$^1B_{2u}^-$	$4 \rightarrow 10, 1 \rightarrow 7$	8.09	0		9.20	0		0
$^1B_{3u}^+$	5–7, 4–6 (β)	5.54	1.37	x	5.94	2.115	5.62[a]	1.70
	5–10, 1–6	8.05	0.769	x	7.96	0.043		
$^1B_{3u}^-$	5–7, 4–6 (α)	3.52	0		4.02	0	3.97[a]	0.002
	5–10, 1–6	7.37	0		8.01	0		
$^1A_g^+$	4–8, 3–7	6.61	0		7.09			
	5–9, 2–6	6.69	0		7.42			
	3–10, 1–8	9.47	0		10.21			
$^1A_g^-$	4–8, 3–7	5.29	0		5.72			
	5–9, 2–6	6.09	0		7.36			
	3–10, 1–8	9.43	0		10.74			
$^1B_{1g}^+$	3–6, 5–8	5.47	0		5.50			
	4–9, 2–7	7.73	0		7.56			
$^1B_{1g}^-$	3–6, 5–8	5.07	0		5.98			
	4–9, 2–7	7.39	0		8.22			

[a] Platt [11].

[b] Energy in eV.

Mestechkin [10] who performs a semi-empirical variant of a random-phase approximation, gives a review of all these works to which the reader is brought back.

The experimental data concerning the absorption spectra of aromatic hydrocarbons studied here are mainly those of Klevens and Platt [11, 12] and we refer to their assignments except for a few ones, according to the indications, relating the polarisation given by Zimmermann and Joop [13].

The singlet-singlet transition energies (in eV) and the corresponding oscillator strengths for the *u*-bands of the naphthalene, anthracene and tetracene molecules are reproduced in Tables 2–4. In the first column the symmetry labels of various energy levels are indicated; in columns 2 to 5, our results are grouped under the heading "perturbation". We have named principal excitation this monoexcited configuration which represent at zero order the singlet state S_α. Fig. 3 shows values calculated and observed for the energies of the p, α and β bands.

The experimental and theoretical results are seen to agree very well for the β band and to be slightly too small for the α band. Generally, our result are smaller than experimental values, on the contrary of Pariser's one which were greater.

Table 3. Anthracene

Etat	Perturbation				Pariser [8]		Exper.	
	Principal excitation	Trans. energ.	Oscil. strength	Pol.	Trans. energ.	Oscil. strength	Trans. energ.	Oscil. strength
$^1B_{2u}^+$	7–8 (p)	3.08	0.099	y	3.65	0.386	3.27[a]	0.10
	7–12, 3–8	5.35	0.324	y	5.25	0.091	5.61[b]	0.28
	6–9	5.63	0.139	y	6.58	0.644		
	5–10	5.80	1.16	y	7.84		6.66[a]	0.65
$^1B_{2u}^-$	7–12, 3–8	4.86	0		5.69	0		
$^1B_{3u}^+$	7–9, 6–8 (β)	4.89	2.016	x	5.50	3.23	4.83[a]	2.28
	4–10, 5–11	7.15	0.10	x	7.22	0.091		
$^1B_{3u}^-$	7–9, 6–8 (α)	3.09	0		3.71	0	3.47[c]	
	4–10, 5–11	6.47	0		6.24	0		
$^1A_g^+$	4–8, 7–11	5.86			6.74	0		
	6–10, 5–9	6.49			7.03	0		
	1–8, 7–14	7.59			7.68	0		
	2–10, 5–13	8.49			9.51	0		
$^1A_g^-$	4–8, 7–11	5.04			5.00	0		
	6–10, 5–9	5.06			6.81	0		
	1–8, 7–14	7.15			7.75	0		
	2–10, 5–13	7.82			9.17	0		
$^1B_{1g}^+$	5–8, 7–10	4.42			4.61	0		
	4–9, 6–11	7.32			7.19	0		
$^1B_{1g}^-$	5–8, 7–10	3.73			4.94	0		
	4–9, 6–11	6.70			8.68	0		

[a] Platt [11].

[b] Platt [11], however this band is given as an A_g^+ band by Platt and a B_{2u}^+ band by Mestechkin [10].

[c] Zimmermann and Joop.

Table 4. Tetracene

Etat	Perturbation				Pariser [8]		Exper.	
	Principal excitation	Trans. energ.	Oscil. strength	Pol.	Trans. energ.	Oscil. strength	Trans. energ.	Oscil. strength
B_{2u}^{+}	9–10 (*p*)	2.56	0.11	*y*	3.11	0.44	2.62[a]	0.08
	8–11	4.83	0.141	*y*	4.68	0.16	4.23[b]	
	6–10, 9–13	4.87	0.998	*y*	6.54	0.001	5.40[a]	0.28
	7–12	5.81	3.29	*y*	6.94	1.20	5.87[a]	0.45
B_{2u}^{-}	6–10, 9–13	4.16	0		5.14	0		
B_{3u}^{+}	9–12, 7–10 (β)	4.45	2.71	*x*	5.09	3.78	4.55[a]	1.85
	7–13, 6–12	6.96		*x*	7.19	0.086	6.89[a]	0.68
							6.62[a]	0.27
B_{3u}^{-}	9–12, 7–10 (α)	2.85	0		3.56	0	3.22[c]	
	7–13, 6–12	5.42	0		5.78	0		
A_{g}^{+}	7–11, 8–12	5.84	0		4.51	0		
A_{g}^{-}	7–11, 8–12	4.38	0		6.33	0		
B_{1g}^{+}	8–10, 9–11	3.66	0		3.90	0		
	8–13, 6–11	6.04	0		5.09	0		
	5–12, 7–14	7.27	0		7.02	0		
B_{1g}^{-}	8–10, 9–11	2.98	0		4.26	0		
	8–13, 6–11	5.95	0		5.56	0		
	5–12, 7–14	6.33	0		8.12	0		

[a] Platt [11].
[b] Meyer [14].
[c] Zimmermann and Joop [13].

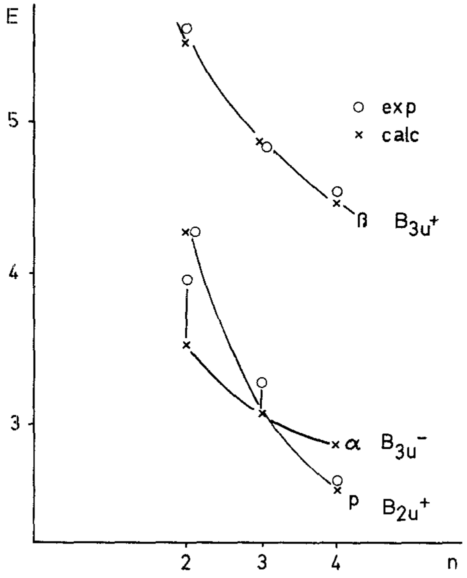

Fig. 3. α, β, p bands of naphthalene, anthracene and tetracene. Energy in eV in function of n, number of cycles

The parametrization should eventually be better adapted for this perturbation type of calculation which includes all configurations.

In conclusion, this work firstly gives energy values which are independent of any artificial truncature of the configurations and depends only of the order of the perturbation and the numerical results show that the second order agree well with experiment; secondly shows that the evolution of the energy is stabilized around $C_0 = 0.01$ and that the number of most interacting configurations is in general greater than usually considered in classical interactions of configurations (the difference being partly implicitely included in the semi-empirical parameters).

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