ON THE ROLE OF CONFIGURATION INTERACTION AND MULTICENTRE CORRECTIONS IN SEMIEMPIRICAL Pi--ELECTRON THEORY*

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The role of configuration interaction and of multicentre corrections in semiempirical pi-electron theory is analyzed on the example of the benzene molecule. It is shown that a correct interpretation of all the bands of the experimental pi-electronic spectrum of benzene is possible only in the case when at least doubly excited configurations are taken into account. The multicentre corrections are more important than the influence of triply excited configurations, however their introduction leads to an improvement of the results only if simultaneously at least doubly excited configurations are taken into account.

1. Introduction

Numerous calculations involving large CI (configuration interaction) bases have shown that inclusion of doubly and triply excited configurations leads to very drastic change in the calculated pi-electron spectrum [1, 2, 3]. An unsatisfactory agreement between results of these calculations and experiment has stimulated attempts to recalibrate the values of empirical parameters in order to improve the results [4, 5, 6, 7]. To that purpose methods of evaluating the empirical parameters from spectral data have been formulated [4, 8]. The results obtained using such methods have led to new conclusions concerning the theoretically possible assignments of electronic levels [4, 5] and the geometry of excited states [6] in benzene.

The question "how much CI is indispensable in the semiempirical methods?" has been posed many times (see *e. g.* [9]) but still remains one of the most important problems to be solved. The overwhelming success of the semiempirical calculations involving very limited CI bases has given rise to a widely spread conviction that the effect of truncation of CI basis can be almost completely compensated by a proper calibration of the values of

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electron interaction integrals. In particular it is believed that the inclusion of singly excited configurations is quite sufficient, at least for a description of the locations of energy levels to be made. The results of this paper show the incorrectness of such a view, proving that it is not possible to compensate the influence of multiexcited configurations by any recalibration of the empirical parameters.

The role of non nearest neighbour core resonance integrals in semiempirical calculations has been investigated by several authors (for a review see [10]). Recently, the importance of non-Coulomb two-electron integrals was shown by de Bruijn [11]. However, no investigations concerning the relative importance of these corrections and the ones resulting from inclusion of multi-excited configurations have been reported.

The aim of this paper is to present the results of an energy levels calculation performed using a variable CI basis and neglecting or including the corrections due to the multicentre integrals. The empirical parameters are optimized in the sense of the previously reported method [4]. All the calculations are performed for the benzene molecule.

2. *Method of calculation*

The integrals treated as empirical parameters, the values of the experimental energies used for their calibration, and the assignment of the electronic levels are the same as in he preceding paper [4]. However eight, instead of seven, experimental values of the excitation energies are now involved in the process of the calibration of empirical parameters.

TABLE I

Number of variational parameters M_N and values of errors D_I and D_{II} *versus* N

N	0	1	2	3	4	~7[a]
M_N	2	7	9	38	61	136
D_I(eV)	1.46	0.89	0.63	0.47	0.20	0.24
D_{II}(eV)	1.83	1.07	0.79	0.40	0.11	0.07

[a] All up to triply excited configurations.

In opposition to [4], the experimental energy of $^1E_{2g}$ state has now also been used in the spectral matching procedure. The values of parameters were optimized separately for every considered stage of approximation of the theory, using the method previously described [4].

The CI basis was varied, starting from the minimal one to that including all configurations up to the triply excited ones. All these configurations for which $|k_0 - k_n| \leqslant N$, where $N = 0, 1, 2, 3, 4$, were successively included (k_0 and k_n denote the coefficients with which the β integral appears in the diagonal matrix elements corresponding respectively to the lowest and the n-th configurations of a particular symmetry representation). Additionally the basis including all up to triply excited configurations was used. This last case corresponds to $N = 7$ approximately. The CI basis including all up to doubly excited configurations corresponds roughly to $N = 4$. For $N = 0$ the basis is the minimal one. The total

number M_N of CI variational parameters, which are not determined by the space or spin symmetry requirements, *versus* N, is given in Table I.

For integrals which appear in the expressions for the CI matrix elements two kinds of approximations were used.

Approximation I. The non nearest neighbour core resonance integrals β_2 and β_3, as well as non-Coulomb two-electron integrals are neglected. This corresponds to the conventional ZDO scheme.

TABLE II

Corrections to the matrix elements in the minimal CI basis introduced in Approximation II

Space symmetry	Matrix element	Correction (eV)	
		singlet state	triplet state
B_{2u}	H_{11}	$2\beta_3+0.205$	$2\beta_3-0.036$
B_{1u}	H_{11}	$2\beta_3+0.135$	$2\beta_3+0.145$
E_{1u}	H_{11}	$2\beta_3+0.150$	$2\beta_3+0.054$
E_{2g}	H_{11}	$3\beta_2+0.396$	$3\beta_2+0.322$
	H_{22}	$-3\beta_2-0.019$	$-3\beta_3-0.060$
	H_{12}	0.056	0.066

TABLE III

The optimal values of empirical parameters (in eV)[a] as a function of N

N	Approximation I				Approximation II			
	x	y	z	β	x	y	z	β
0	2.909	1.465	1.317	−2.517	2.923	1.402	1.239	−2.501
1	3.671	1.124	0.458	−2.633	3.834	1.109	0.328	−2.632
2	3.419	1.192	0.616	−2.632	3.561	1.176	0.495	−2.630
3	3.766	1.312	0.350	−2.785	4.120	1.233	−0.012	−2.810
4	3.389	1.545	0.676	−2.653	3.693	1.470	0.350	−2.676
~7[b]	3.204	1.557	0.756	−2.616	3.471	1.471	0.428	−2.626

[a] Parameters x, y, z and β are defined in [4].
[b] All up to triply excited configurations.

Approximation II. For all the integrals neglected in Approximation I, the values calculated by Chong [12] using the orthogonalized Slater-type $2p\pi$ orbitals with the effective nuclear charge 3.18 are taken. With respect to non-Coulomb two-electron integrals only these matrix elements are corrected which correspond to the CI basis determined by $N = 0$ apart from the dimension of the basis actually used. It was shown by de Bruijn that such, a simplification is reasonable [11]. The values of these corrections are given in Table II. The corrections due to the core integrals are introduced to the whole CI matrices. The

TABLE IV

Differences between best fitted theoretical and experimental excitation energies (in 10^{-2} eV) as a function of N, and experimental values of Franck-Condon maxima for transitions from the ground state (E_{exp}) — in eV

N	$^1B_{2u}$	$^1B_{1u}$	$^1E_{1u}$	$^1E_{2g}$	$^3B_{1u}$	$^3E_{1u}$	$^3B_{2u}$	$^3E_{2g}$
Approximation I[a]								
0	−9	−6	0	41^+	36	−18	−76	8^+
1	37	2	−7	8^-	28	2	−30	-21^+
2	33	0	−3	16^-	6	4	−34	-12^+
3	−28	−2	−8	21^-	11	−12	7	10^+
4	−15	1	−2	10^-	17	−1	3	-3^+
~7[b]	−16	0	−2	16^-	14	0	2	-6^+
Approximation II								
0	−1	−8	−6	52	35	−26	−92	14
1	50	2	−4	−1	26	−5	−41	−18
2	46	0	0	6	4	−3	−45	−8
3	−22	−3	−8	15	8	−19	7	11
4	−8	1	−1	0	14	−7	4	−2
~7[b]	−8	0	−1	7	11	−5	3	−6
E_{exp}[c]	4.93	6.21	6.96	7.48	3.95	4.75	5.60	6.75

[a] Superscripts "+" and "−" correspond to the states E_{2g}^+ and E_{2}^- respectively.
[b] All up to triply excited configurations.
[c] For references see Table I in [4].

values of these integrals (calculated in [12]) are: $\beta_2 = +0.066$ eV, $\beta_3 = -0.055$ eV. The same integrals as those in Approximation I are considered as empirical parameters. However they are optimized after the above mentioned corrections were introduced.

3. *Results*

The optimal values of empirical parameters are given in Table III. The differences between calculated (the best fitted) and experimental values of the excitation energies, for the states involved in the spectral matching procedure, are presented in Table IV. The theoretical excitation energies of the two remaining levels, lying below the ionization potential, as well as the depression of the ground state caused by CI are given in Table V.

The experimental energy of the second triplet of E_{2g} species (~8.9 eV [13]) was not used in the spectral matching procedure and was not accounted for in the further discussion of the errors connected with the specific approximations of the theory, because its location seems to be too uncertain. It is however worthwhile noting, that its calculated energy falls well within the limits of experimental uncertainty, at least for $N > 2$.

The uncertainty in determining the experimental energies of Franck-Condon transitions cannot be less than the splitting between consecutive lines of the totally symmetric progres-

TABLE V

Values of excitation energies from the ground state to the states which have not been used in the spectral matching procedure and depression of the ground state caused by CI (in eV), as a function of N

N:	0	1	2	3	4	~7[b]
Approximation I[a]						
$^1E_{2g}$	9.21$^-$	8.68$^+$	8.50$^+$	9.25$^+$	8.77$^+$	8.63$^+$
$^3E_{2g}$	9.21$^-$	8.54$^-$	8.64$^-$	8.93$^-$	8.98$^-$	8.96$^-$
Δ^1A_{1g}[c]	0.00	0.00	0.00	0.00	−0.36	−0.51
Approximation II						
$^1E_{2g}$	9.35	9.07	8.89	9.91	9.40	9.22
$^3E_{2g}$	9.22	8.55	8.65	8.93	8.98	8.96
Δ^1A_{1g}[c]	0.00	0.00	0.00	0.00	−0.35	−0.55

[a] Superscripts "+" and "−" correspond to the states E^+ and E_{2g}^- respectively.
[b] All up to triply excited configurations.
[c] Depression of the ground state caused by CI.

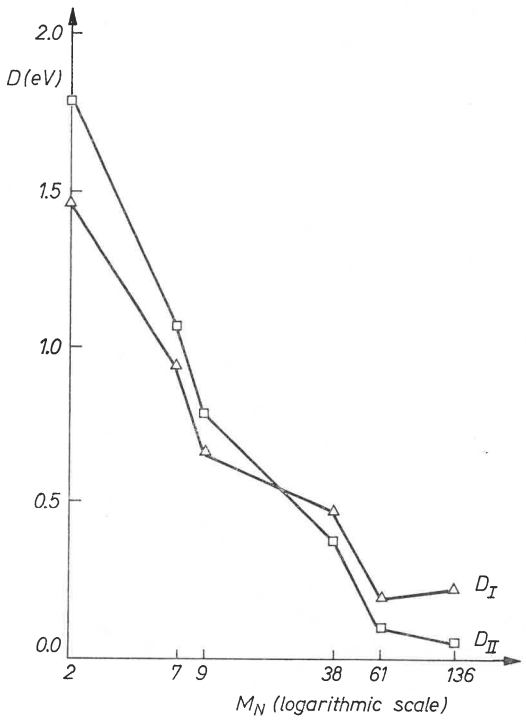

Fig. 1. D_I and D_{II} plotted *versus* M_N

sion in the vibrational spectrum. For benzene the frequency of a_{1g} vibrations is 900 cm^{-1} – 1000 cm^{-1} (0.12 eV–0.13 eV)[1]. Therefore the error in estimated Franck-Condon excitation energies is assumed to be ± 0.06 eV for the levels observed in electron impact experiments (six levels of *ungerade* type) and ± 0.1 eV for the two ones known from optical experiments only ($^1E_{2g}$ and $^3E_{2g}$ levels). The sums of the absolute values of deviations of calculated energies over these ranges of the error, extended over the eight energy levels under consideration, are denoted D_{I} and D_{II} (indices I and II refer to Approximations I and II respectively). The values of D_{I} and D_{II} are calculated separately for every N and are used here as a measure of correctness of the specific approximation. Their values are given in Table I and are plotted, *versus* M_N, in Figure 1.

4. *Discussion*

The Approximation I with the minimal CI basis ($N = 0$), and with inclusion of all singly excited configurations ($M_N = 4$) was discussed earlier by other authors [14]. In these cases it was possible to reproduce the experimental locations of $^1B_{2u}$, $^1B_{1u}$, $^1E_{1u}$ and $^3B_{1u}$ levels of benzene. Until 1965 only these four excited levels of benzene were experimentally detected. However up till now transitions to nine levels have already been reported (for references see [4]). The results presented in Table IV shown that a proper interpretation of the whole spectrum is disputable using such a limited CI. The main sources of the error are connected with the accidental degeneration of $^1B_{2u}$ and $^3B_{2u}$ levels, as well as with the reversed order of $^1E_{2g}^+$ and $^1E_{2g}^-$ levels when compared to that in large CI bases. The $^1B_{2u}-{}^3B_{2u}$ degeneration occurs exactly for $N < 3$ in Approximation I but it is removed in Approximation II when multicentre corrections are introduced. However the introduction of these corrections causes that the $^3B_{2u}$ level becomes lower than the $^1B_{2u}$ one, contrary to the experiment. The locations of $^1B_{2u}$ and $^3B_{2u}$ levels which qualitatively agree with the experimental ones can be obtained only in the case of relatively large CI basis ($N \geqslant 3$). This results from the fact that the configurations of B_{2u} species which can interact with the ground configuration of this symmetry may be formed only for $N \geqslant 3$. For this reason inclusion of multicentre corrections is not effective for $N < 3$ (compare Figure 1). Inclusion of some doubly excited configurations is also necessary in order to obtain the proper sequence of the levels of E_{2g} species.

In order to find a limit for the dimension of the indispensable CI basis, let us consider the behaviour of D_{I} and D_{II} as a function of N. As results from Figure 1 and Table I, the effect induced by passing from N to $N+1$ is large for $N < 4$. On the other hand, when N changes from 4 to ~ 7, the number of CI variational parameters rises from 61 to 136, while D_{I} and D_{II} remain almost unchanged (D_{I} even slightly increases). On this ground we can conclude that it is needless to extend the CI basis over one corresponding to $N = 4$, because the importance of other neglected factors become then comparable to CI. However, a commonly used limitation of CI to the singly excited configurations only (*i. e.* to 4 variational parameters in the case of benzene) is rather inadequate for a proper

[1] The author is indebted to the referee for his comment concerning this point.

interpretation of the whole lectronic spectrum to be made (see Table IV). The correlation errors resulting from such a reduction of the CI basis cannot be compensated by a recalibration of the empirical parameters. On the other hand, extension of CI reduces the error of fitting the calculated to observed spectra by almost ten times.

The multicentre corrections proved to be of secondary importance when compared to CI. In particular the improvement of the theory by their inclusion leads to worse results when $N < 3$ (see Figure 1). Therefore an inclusion of these corrections in the case of limited CI seems to be useless. On the contrary, in the case of a large CI basis the relative role of multicentre corrections becomes important. For $N = 4$ their introduction reduces the error from $D_{\mathrm{I}} = 0.20$ eV to $D_{\mathrm{II}} = 0.11$ eV, *i. e.* by 45%. In the case when all triply excited configurations are included these corrections are still more important ($D_{\mathrm{I}} = 0.24$ eV while $D_{\mathrm{II}} = 0.07$ eV). In particular, the role of triply excited configurations is negligible, when compared to multicentre corrections[2].

The remaining inadequacy of the theory, resulting in 0.07 eV inaccuracy in fitting the theoretical values of the excitation energies to the experimental ones should probably be attributed to causes lying outside the pi-electron approximation. It seems that the limit value of $D_{\mathrm{II}} = 0.07$ eV can be reduced only slightly by a more careful determination of the values of β_2 and β_3 integrals and the multicenter corrections as well as by further extension of the CI basis. Of course, errors in the estimated values of Franck-Condon excitation energies may also influence the values of D_{I} and D_{II}. Especially for the states of E_{2g} species these errors can be relatively large. However, also for the lowest triplet state the value 4.05 eV has been recently proposed [6]. The differences between calculated and estimated values of the vertical transitions would be further reduced if such a value were used instead of 3.95 eV resulting from electron impact experiments (see Table IV).

It should be noted that, in principle, all these conclusions are valid only for benzene. The question, to what extent are they general is to be answered. However, some results may be considered as quite general ones, because the benzene molecule acts here as a counterexample. In particular it has been shown that:

1. Inclusion of at least doubly excited configurations is necessary if one wants to reach a good agreement between theory and experiment for the whole pi-electron spectrum.

2. Inclusion of the multicentre corrections is justified only in the case of a rather large CI basis.

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REFERENCES

[1] J. E. Bloor, J. Lee, S. Gartside, *Proc. Chem. Soc.*, 413 (1960).
[2] J. Koutecký, K. Hlavatý, P. Hochmann, *Theor. Chim. Acta*, **3**, 341 (1965).
[3] J. W. Moskowitz, P. M. Barnett, *J. Chem. Phys.*, **39**, 1557 (1963).

[2] For larger molecules the multicentre corrections are less important [11].

[4] J. Karwowski, *Acta Phys. Polon.* **A42**, 243 (1972).
[5] J. Karwowski, *Bull. Acad. Polon. Sci., Ser. Sci. Math. Astron. Phys.*, **14**, 319 (1966); **15**, 521 (1967).
[6] S. de Bruijn, *Thesis*, Amsterdam 1969.
[7] P. B. Visscher, L. M. Falicov, *J. Chem. Phys.*, **52**, 4217 (1970).
[8] J. Karwowski, *Acta Phys. Polon.*, **A37**, 417 (1970).
[9] R. G. Parr, *Modern Quantum Chemistry*, Ed. O. Sinanoglu, Academic Press, New York, London 1965, Vol. 1, p. 107.
[10] K. Jug, *Theor. Chim. Acta*, **14**, 91 (1969).
[11] S. de Bruijn, *Theor. Chim. Acta*, **17**, 293 (1970).
[12] D. P. Chong, *Molecular Phys.*, **10**, 67 (1966).
[13] T. S. Godfrey, G. Porter, *Trans. Faraday Soc.*, **62**, 7 (1966).
[14] R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956); K. Ruedenberg, E. M. Layton, *J. Chem. Phys.*, **34**, 1897 (1961); P. G. Lykos, *J. Chem. Phys.*, **35**, 1249 (1961); H. E. Simmons, *J. Chem. Phys.*, **40**, 3554 (1964).