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# The Effect of the Choice of Parameters on the Order of Energy Levels of Benzene Calculated in the $\pi$-Electron Approximation by the Configuration Interaction Method Including Double- and Triple-Excited Configurations

By

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A study is reported of the effect of the choice of parameters on the character of the spectrum of benzene calculated in the $\pi$-electron approximation by the configuration interaction method including double- and triple-excited configurations. Only the integrals which are not neglected in the usual versions of the Pariser, Parr, and Pople method have been taken into account. It is confirmed that the order of levels in the spectrum, in particular for the lowest $E_{2g}$ and $B_{1u}$ levels, depends markedly on the choice of parameters. We find that a simple expression permits an *a priori* prediction, from the parameter set used, of the order of the lowest $E_{2g}$ and $B_{1u}$ energy levels resulting from configuration interaction including higher excited configurations. The effect of the inclusion of triple-excited configurations can be neglected only in the case of the ground state (cf. [*16*]). However, it does not change the over-all character of the spectrum.

Es wird der Einfluß der verschiedenen Wahl der Parameter auf den Charakter des Benzol-Spektrums in der $\pi$-Elektronennäherung unter Einschluß zwei- und dreifach angeregter Konfigurationen studiert. Es werden nur diejenigen Integrale berücksichtigt, die auch in den üblichen Versionen der Methode von Pariser, Parr und Pople nicht vernachlässigt werden. Es wird bestätigt, daß die Reihenfolge der Niveaus, speziell der tiefsten $E_{2g}$- und $B_{1u}$-Terme, stark von der Wahl der Parameter abhängt. Ein einfacher Ausdruck wird angegeben, der, ausgehend vom verwendeten Parametersatz, die *a priori*-Voraussage der Reihenfolge der niedrigsten $E_{2g}$- und $B_{1u}$-Niveaus ermöglicht, unter Berücksichtigung höher angeregter Konfigurationen. Der Einfluß der dreifach angeregten Konfigurationen ist nur für den Grundzustand vernachlässigbar (s. [*16*]); er ändert jedoch nicht den qualitativen Charakter des Spektrums.

Dans le présent travail est étudiée l'influence du choix des paramètres sur le caractère du spectre du benzène dans les calculs utilisant l'approximation $\pi$-électronique et la méthode des interactions de configuration avec les configurations diexcitées et triexcitées. Seulement de telles intégrales sont considérées qui ne sont pas négligées dans les versions habituelles de la méthode de Pariser, Parr et Pople. Il est confirmé que l'ordre des niveaux énergétiques dans un spectre, en particulier entre les $E_{2g}$ et $B_{1u}$ les plus bas, dépend essentiellement du choix des paramètres. Une expression simple est trouvée qui permet de prévoir, étant donné le jeu de paramètres, l'ordre de ces deux niveaux tout en considérant les configurations polyexcitées. Les configurations triexcitées sont négligeables au cas de l'état fondamental seulement [*16*], mais elles ne transforment pas le caractère qualitatif du spectre.

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The success of the semiempirical method of PARISER and PARR makes it desirable to discuss the approximations involved. One of the most important approximations is the restriction of configuration interaction to monoexcited states. In our opinion, the neglect of higher excited configurations cannot be justified by referring to the unrealistically high energy of these configurations. It seems to us that such an argumentation overestimates the physical meaning of monoexcited configurations. For this reason, we have studied the effect of inclusion of all double- and triple-excited configurations on the relative position of the resulting energy levels of benzene. This appears interesting in view of the uncertain assignment of the second absorption band of benzene, the experimental data available being insufficient to determine whether the band is due to a $B_{1u} \leftarrow A_{1g}$ or a $E_{2g} \leftarrow A_{1g}$ transition [*1, 5, 6*].

The aim of this paper is to examine the effect of the choice of semiempirical parameters upon the order of energy levels if higher excited configurations are included. This problem has been dealt with in the paper of BLOOR, LEE and GARTSIDE [*3*]. These authors pointed out that the choice of parameters has considerable influence upon the character of the spectra. However, the values of parameters chosen did not correspond to those usually adopted in the semiempirical methods, and also the extent of configuration interaction was considerably limited (see below). The other papers work with one set of parameters only [*2, 4, 11, 13*].

Table 1. *Values of Integrals (*eV*) and Derived Quantities*

| | PP$^a$ | P$^a$ | AS$^a$ | BLG$^a$ | M$^a$ | T$^a$ |
|---|---|---|---|---|---|---|
| $-\beta^b$ | 2.390 | 2.371 | 2.722 | 2.300 | 2.388 | 2.734 |
| $\gamma^c_{00}$ | 10.530 | 10.959 | | | 10.840 | 17.618 |
| $\gamma^c_{01}$ | 7.300 | 6.895 | | | 5.298 | 8.924 |
| $\gamma^c_{02}$ | 5.460 | 5.682 | | | 3.855 | 5.574 |
| $\gamma^c_{03}$ | 4.900 | 4.978 | | | 3.505 | 4.876 |
| $K^d_{01}$ | 1.245 | 1.199 | 1.348 | 1.800 | 1.463 | 2.682 |
| $K^d_{02}$ | 0.445 | 0.560 | 0.498 | 1.000 | 0.865 | 1.333 |
| $K^d_{03}$ | 0.325 | 0.592 | 0.365 | 0.800 | 0.741 | 1.007 |
| $A^e$ | 0.69 | 1.03 | 0.64 | 1.92 | 1.45 | 2.31 |

a) Parameters chosen according to [*15*] – (PP), [*12*] – (P), [*2*] – (AS), [*3*] – (BLG), [*8*] – (M) and [*13*] – (T), obtained [*9*] by transformation into integrals over orthonormal orbitals [*7*], the other parameters being neglected).

b) Resonance integral.

c) $$\gamma_{\mu\nu} = \iint r_{\mu\nu}^{-1} \, [a_\mu(1)]^2 \, [a_\nu(2)]^2 \, dV_1 \, dV_2 ,$$
where $a_\mu(i)$ is a localized orbital at the $\mu$th carbon atom.

d) $K_{0j}$ are defined as in [*14*], eq. 35.

e) $A$ is defined by eq. (3) cf. eqs. (4), (5).

Further, it seems interesting to investigate the possibilities of an *a priori* estimate of the order of these energy levels without time-consuming numerical calculation.

We used the sets of parameters presented in Tab. 1. These sets have been used in semiempirical calculations previously [*2, 8, 12, 15*] with the exception of the BLG [*3*] and theoretical ones [*7, 9, 13*]. The theoretical set has been included in our calculations in order to make possible a comparison with theoretical methods.

Table 2. *Energies of Excited States and Ground State Depressions* (eV)

| Symmetry | N[a] | PP[b] | P[b] | AS[b] | BLG[b] | M[b] | T[b] |
|---|---|---|---|---|---|---|---|
| $A_{1g}$ | 1 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| | 2 | −0.57 | −0.77 | −0.60 | −1.81 | −1.31 | −2.84 |
| | 3 | −0.58 | −0.78 | −0.61 | −1.85 | −1.33 | −2.92 |
| $B_{2u}$ | 1 | 4.90 | 4.71 | 5.58 | 4.80 | 4.90 | 5.79 |
| | 2 | 3.90 | 3.50 | 4.50 | 2.08 | 2.85 | 1.70 |
| | 3 | 3.75 | 3.27 | 4.34 | 1.43 | 2.40 | 0.65 |
| $E_{1u}$ | 1 | 6.95 | 6.55 | 7.77 | 7.40 | 6.96 | 9.83 |
| | 2 | 6.34 | 5.94 | 7.14 | 6.07 | 6.03 | 7.62 |
| | 3 | 6.04 | 5.65 | 6.83 | 5.54 | 5.59 | 6.75 |
| $B_{1u}$ | 1 | 5.20 | 5.96 | 5.93 | 5.99 | 6.14 | 7.04 |
| | 2 | 5.01 | 5.65 | 5.73 | 5.44 | 5.69 | 6.32 |
| | 3 | 4.94 | 5.43 | 5.65 | 5.01 | 5.33 | 5.75 |
| $E_{2g}$ | 1 | 8.89 | 8.36 | 10.00 | 8.70 | 8.48 | 11.23 |
| | 2 | 6.59 | 6.09 | 7.56 | 4.63 | 5.44 | 4.79 |
| | 3 | 6.31 | 5.62 | 7.31 | 3.59 | 4.69 | 3.19 |
| $E_{2g}$ | 1 | 8.18 | 8.20 | 9.29 | 9.10 | 9.02 | 11.19 |
| | 2 | 7.76 | 7.77 | 8.86 | 8.30 | 8.42 | 9.93 |
| | 3 | 7.55 | 7.51 | 8.82 | 7.59 | 7.89 | 8.87 |

a) Configuration interaction including up to $N$-times excited states.
b) cf. Tab. 1.

No attempt was made to find a set of parameters which would give numerical agreement with experiment. We do not consider this essential at present.

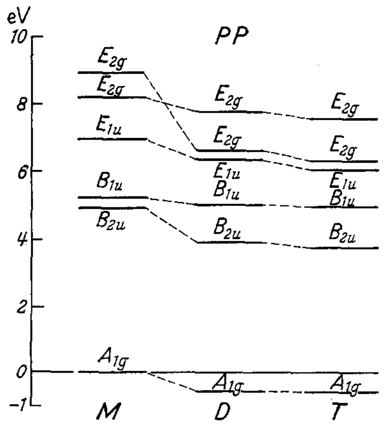

Fig. 1. The graphical representation of the effect of extent of *CI* on energetical levels. Parameters after [*15*]. *M*- up to mono-excited, *B*- up to double-excited *T*- up to triple-excited configurations, respectively

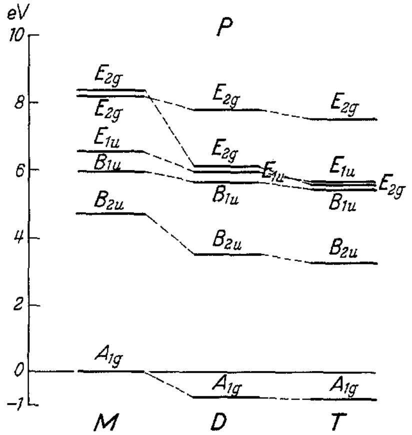

Fig. 2. The graphical representation of the effect of extent of *CI* on energetical levels. Parameters after [*12*]

Tab. 2 shows the energies of the lowest excited states belonging to each of the representations $B_{2u}$, $B_{1u}$, $E_{1u}$ and two lowest excited states of the representation

$E_{2g}$. Ground state depressions are given, too. Fig. 1–6 show the changes in energy levels arising on gradual inclusion of the higher excited configurations.

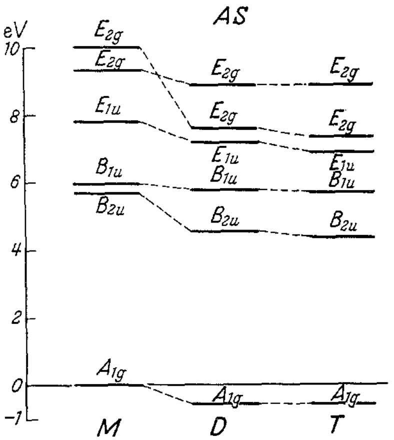

Fig. 3. The graphical representation of the effect of extent of *CI* on energetical levels. Parameters after [2]

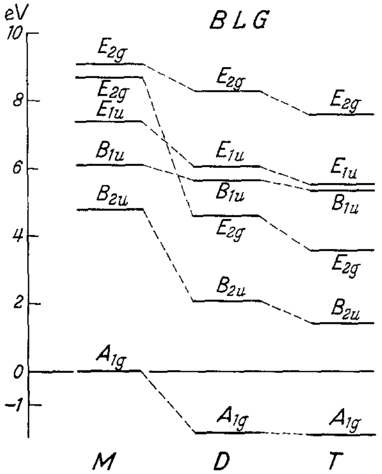

Fig. 4. The graphical representation of the effect of extent of *CI* on energetical levels. Parameters after [3]

Tab. 3 demonstrates the effect of extension of configuration interaction with double-excited states on the position of the energy level of the state

$$\psi^1_{E_{2g}} = a\,\varphi^1_{E_{2g}} + \sum_{\substack{j,k,l,\\ m,b}} c^{l,m}_{j,k}(b)\, x^{l,m}_{j,k}(b) \; . \qquad (1)$$

The notation used is that of MURRELL and McEWEN [11]. $\varphi^1_{E_{2g}}$ is defined as follows:

$$\varphi^1_{E_{2g}} = \frac{1}{\sqrt{2}}(x^2_0 - x^3_1) \; . \qquad (2)$$

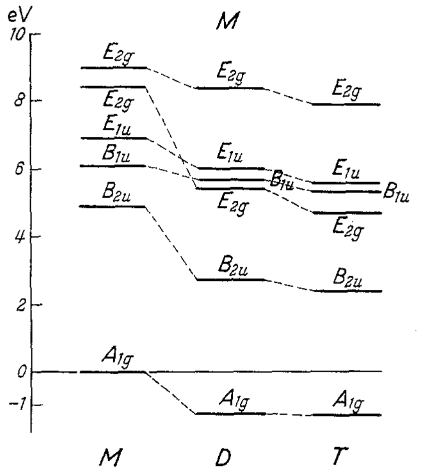

Fig. 5. The graphical representation of the effect of extent of *CI* on energetical levels. Parameters after [8]

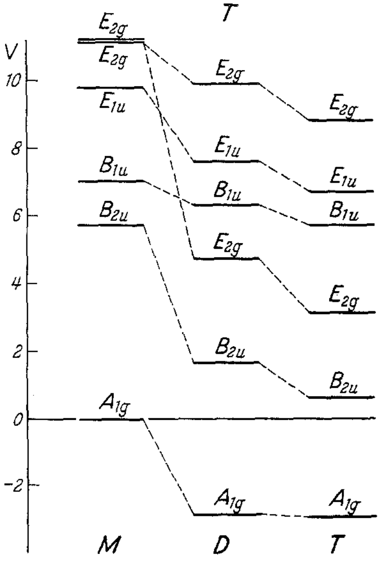

Fig. 6. The graphical representation of the effect of extent of *CI* on energetical levels. Parameters after [7, 9, 13]

Tab. 3 makes it clear that the interaction between $\varphi^1_{E_{2g}}$ and the configuration $x^{22}_{11}$ provides a major contribution to the lowering of the energy of the $\varphi^1_{E_{2g}}$ function.

Accordingly, a convenient measure of the depression of the energy of the $\psi^1_{E_{2g}}$ state obtained on including the double-excited configurations is provided by the parameter

$$A = \frac{B}{C} \,. \tag{3}$$

The term

$$B = \frac{4\,K^2_{01}}{[-\beta + K_{02} - K_{03}]} \tag{4}$$

is the perturbation approximation to the depression of the $\varphi^1_{E_{2g}}$ function due to interaction with the $x^{11}_{22}$ configuration. The term

$$C = -\beta + 2\,K_{01} - 4\,K_{03} \tag{5}$$

is the difference between the energy of the $\varphi^1_{E_{2g}}$ function and that of the linear combination of configurations

$$\varphi^1_{B_{1u}} = \frac{1}{\sqrt{2}}\,(x^2_{-1} + x^{-2}_{1}) \tag{6}$$

which belongs to the $B_{1u}$ representation.

$\varphi^1_{B_{1u}}$ is in weak interaction with $x^3_0$. There are no other monoexcited configurations belonging to the $B_{1u}$ representation. The energy of the $\varphi^1_{B_{1u}}$ function is thus a good approximation to the lowest energy of a $B_{1u}$ type function resulting from interaction with monoexcited configurations only. $\beta$ is the resonance integral and $K_{0j}$ is defined in [*14*].

Since the interaction is strong the perturbation calculation overestimates the depression. It is possible that in this case, to a certain extent, this makes up for the neglect of the depression produced by interaction with other configurations. Changes in the position of the lowest $B_{1u}$ level brought about by *CI* are considerably smaller than those in the position of the lowest $E_{2g}$ level. According to our results, the lowest $E_{2g}$ state lies below the $B_{1u}$ if $A$ is large, while the reverse is true if $A$ is small. The critical value of $A$ is about one (cf. Tab. 1). $A$ thus seems to provide a suitable criterion for energy depression of the $\varphi^1_{E_{2g}}$ wave function even though depression due to interaction with other configurations than $x^{22}_{11}$ is quite important, of course.

Table 3. *Effect of the Extent of Configuration Interaction on the Depression of the Energy of* $\varphi^1_{E_{2g}}$

| *CI* with | PP[b] | P[b] | AS[b] | BLG[b] | M[b] | T[b] |
|---|---|---|---|---|---|---|
| $x^{22}_{11}$ | 0.66 | 0.66 | 0.66 | 0.63 | 0.63 | 0.63 |
| $x^{22}_{11};\ I\,\frac{1}{\sqrt{2}}\left(x^{2-2}_{-1-1} - x^{-2-2}_{1-1}\right)$ | 0.81 | 0.79 | 0.81 | 0.75 | 0.76 | 0.75 |
| all double-excited states | 1 | 1 | 1 | 1 | 1 | 1 |

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a) Relative to the depression resulting from interaction with all double-excited states.
b) cf. Tab. 1.

BLOOR, LEE and GARTSIDE [3] consider only *CI* of $\varphi^1_{E_{2g}}$ with $x^{22}_{11}$ as can be seen on analysis of their numerical values.

In his calculations on benzene, DONATH [4] took into account all single- and double-excited configurations. He used the same values of $\gamma$ as PARISER and PARR [15] and took $\beta$ equal to $-2.48$ eV. The character of the spectrum calculated by him is in agreement with the value $A = 0.65$ resulting from his parameters.

It was impossible to include data of ref. [10] in the comparison with theoretical methods, as the requisite values of integrals were not given in this reference. Moreover, there are no calculations on the $E_{2g}$ state.

It is worth noting that the procedure labelled as $T$, $N = 2$, in Tab. 2 yields results which differ only slightly from those given in ref. [13].

Additional data on matrix elements, energy levels and the corresponding wave functions will be published in Collection Czech. Chem. Commun.

The conclusions are given in the summary above.

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