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Complete Configuration Interaction Calculation of Singlet Energy Levels of Benzene in π-Electron Approximation

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Singlet energy levels of benzene molecule were calculated using the complete CI method in π-electron approximation for two sets of semiempirical parameters. The inclusion of triply-, tetra-, and hexa-excited configurations has practically no effect on the values of singlet energy levels as far as parametrizations which are common in semiempirical procedures are employed. On the other hand, using parameters which are very similar to those obtained with theoretically calculated molecular integrals, appreciable changes in the energy spectrum are observed.

Die Singulettenergieniveaus des Benzol-Moleküls wurden mittels der vollständigen CI-Methode im Rahmen der π-Elektronennäherung für zwei Gruppen von halbempirischen Parametern berechnet. Der Einschluß von drei-, vier- und sechsfach angeregten Zuständen hat praktisch keinen Einfluß auf die Singulettenergieniveaus, wenn die Parameterwerte den halbempirischen Verfahren entnommen sind. Demgegenüber kommt bei Benutzung von Parameterwerten, die weitgehend theoretisch berechneten Molekülintegralen entsprechen, eine beträchtliche Änderung des Energiespektrums zustande.

Les énergies des états singulets dans la molécule de benzène ont été calculées par la méthode des interactions de configuration complète dans l'approximation π-électronique pour deux séries de paramètres semiempiriques. La considération des configurations tri-, tetra-, et hexa-excitées n'excerce pratiquement aucune influence sur les énergies des états singulets si l'on emploie les mêmes paramètres que dans les procédés semiempiriques. Si on emploie, par contre, des paramètres très similaires à ceux qui résultent des intégrales moléculaires calculées théoriquement, on constate des changements sensibles dans le spectre d'énergie.

Introduction

In a recently published paper [*3*] the semiempirical CI treatment of benzene molecule in the π-electron approximation considering mono-, doubly-, and triply-excited configurations was presented. It was shown that inclusion of higher excited configurations changes significantly the character of the singlet states energy spectrum and that these changes are dependent on the parametrization used. Therefore, it was interesting to study the influence of further extension of CI up to the complete CI (in terms of π-electron approximation) on the correlation energy, excitation energies and, particularly, on the sequence of lower lying singlet excited states.

Not only the semiempirical methods, but also so called theoretical methods using the π-electron approximation cannot be considered as "*ab initio*" calculations. Therefore, it is not possible to make the "*a priori*" general statement that enlargment of the extent of CI will give better results in respect to the experimental values of excitation energies without the detailed study of the effect of the parametrization used. This is the reason why we study in this paper the qualitative changes in the energy spectrum with the extension of the CI rather than comparing our results with the experimental data.

The Method

The carbon-carbon internuclear distance was assumed to be 1.39 Å. Two sets of parameters were used in our calculations (compare Tab. 1). The first set was essentially due to Pariser and Parr [*6*] except for the value of the resonance integral β, which was estimated from the relationship:

Table 1. *Parameters used (in* eV*)*

	$-\beta$[a]	γ_{00}[b]	γ_{01}[b]	γ_{02}[b]	γ_{03}[b]	K_{01}[c]	K_{02}[c]	K_{03}[c]	A[d]
PP II[e]	2.805	10.530	7.300	5.460	4.900	1.245	0.445	0.325	0.53
M[f]	2.388	10.840	5.298	3.855	3.505	1.463	0.865	0.741	1.45
T[g]	2.734	17.618	8.924	5.574	4.876	2.682	1.333	1.007	2.31

[a] Resonance integral.

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

[c] K_{0j} are defined as in [*2*], eq. (35).

[d] A is defined as in [*1*], eq. (3).

[e] Parameters chosen according to [*2*], β adapted according to eq. (1) of this paper.

[f] Parameters chosen according to [*4*].

[g] Parameters chosen according to [*7*], adapted in a way mentioned in the paper [*1*].

$$\frac{\beta_{\text{benzene}}}{\beta_{\text{ethylene}}} = \frac{S\,(1.39)}{S\,(1.34)}\,, \tag{1}$$

where $S(r)$ is the overlap integral of $2p_z$-atomic orbitals in π-orientation located at a distance r Å with effective nuclear charge 3.02.

The value of the resonance integral for ethylene molecule (β ethylene $= -3.02$ eV) was obtained by adjusting the theoretical value of excitation energy calculated with electron repulsion integrals according to Ref. [*6*], to the value of the experimental excitation energy of the longest wavelength transition in the absorption spectrum of ethylene (7.6 eV). The increase in the resonance integral compared with the original value used by Pariser and Parr necessitates a decrease of the quantity A which is defined in the paper [*3*]. The value of A — determining the character of the benzene energy spectrum — obtained above is less than the value of A according to Anno and Sado [*1*].

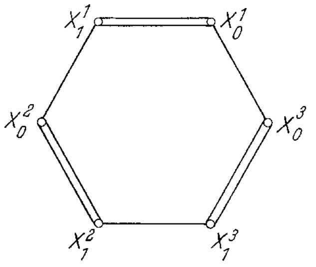

Fig. 1. Benzene molecule as formed from three ethylene molecules

On the other hand, the second set of parameters used corresponding to the usual parametrization due to Mataga and Nishimoto [*4*] is characterized by the large value of A. Therefore, with the two sets of parameters used we can expect to obtain the limiting cases as regards the changes of the character of the energy spectrum due to the extension of CI.

The states corresponding to the irreducible representations A_{1g}, B_{2u} and B_{1u}

of the symmetry group D_{6h} were also calculated using the theoretical parameters determined by the procedure described in the paper [*3*].

For one-electron functions from which the Slater determinants were constructed we took the molecular orbitals of the carbon skeleton of three ethylene molecules from which the benzene molecule may be formed as shown in Fig. 1 (cf. Ref. [*2*]). This procedure enables us to simultaneous calculation of other molecules which contain six conjugated carbon atoms. Therefore, the molecular orbitals, corresponding to "ethylene" σ ($\sigma = 1, 2, 3$), are

$$u^{\sigma}_{\mu} = \frac{1}{\sqrt{2}} (\chi^{\sigma}_{0} + (-1)^{\mu} \chi^{\sigma}_{1}) ; (\mu = 0,1) \; . \tag{2}$$

The Slater determinants constructed from these orbitals are then given by the expression:

$$| \boldsymbol{q}, \boldsymbol{m}, \boldsymbol{p}, \xi \rangle = \frac{1}{\sqrt{6!}} \sum_{P} (-1)^{P} P \prod_{k=1}^{6} u^{\sigma_k}_{\mu_k} (k) \, \eta_{\nu_k} (k) \; , \tag{3}$$

where permutation P permutes coordinates k. Further, the following notation was used:

$\boldsymbol{q} \equiv (q_1, q_2, q_3)$, where q_k is the number of functions $u^{k}_{\mu i}$,
$\boldsymbol{m} \equiv (m_1, m_2, m_3)$, where m_k is the number of functions u^{k}_{1},
$\boldsymbol{p} \equiv (p_1, p_2, p_3)$, where p_k is the number of functions $u^{k}_{\mu i} \alpha$;

η_{ν_k} is a spin function ($\eta_1 = \alpha$, $\eta_2 = \beta$) and ξ distinguishes Slater determinants having the same values of $\boldsymbol{q}$, $\boldsymbol{m}$ and $\boldsymbol{p}$.

The singlet states were constructed from Slater determinants given by (3) having zero eigenvalue of the operator S_z. The rules for the calculation of matrix elements using the approximation of zero differential overlap and GOEPPERT-MAYER and SKLAR potential are presented in the Appendix.

Along the actual calculations only a subgroup of the symmetry group of the model was used, namely the symmetry group C_{2v} and certain part of the calculations were repeatead using the symmetry group C_{3v}.

Matrix diagonalization of the CI-matrices was carried out in the Computing Laboratory of Oxford University unless the order of the matrix was less than 70. The matrices of lower orders were diagonalized in the Computing Center of "Kancelářské stroje".

The Results

The energies of states obtained from the CI including mono-, doubly-, etc. up to the hexa-excited configurations are given in Tab. 2. Classification of configurations was accomplished on the basis of SCF molecular orbitals of benzene.

Table 2. *Energies of benzene excited states and ground state energy depression (in* eV*)*

	PP II[b]				M[b]			
N[a]	1	2	3	6	1	2	3	6
A_{1g}	0	−0.50	−0.51	−0.52	0	−1.31	−1.33	−1.42
B_{2u}	5.73	4.84	4.70	4.69	4.90	2.85	2.40	2.25
E_{1u}	7.78	7.25	6.97	6.96	6.96	6.03	5.59	5.56
B_{1u}	6.04	5.87	5.81	5.80	6.14	5.69	5.33	5.32
E_{2g}	10.14	8.00	7.78	7.78	8.48	5.44	4.69	4.51

[a] Configuration interaction including up to N-times excited states.
[b] Cf. Tab. 1.

The origin of the energy scale was chosen for each set of parameters to coincide with the ground state energy (A_{1g}) calculated with a one-determinant function constructed on the basis of SCF molecular orbitals. The excitation energies are given in Tab. 3.

Table 3. *Excitation energies of benzene molecule (in* eV*)*

	PP II[b]				M[b]			
N[a]	1	2	3	6	1	2	3	6
A_{1g}	0	0	0	0	0	0	0	0
B_{2u}	5.73	5.34	5.21	5.21	4.90	4.16	3.73	3.68
E_{1u}	7.78	7.75	7.47	7.48	6.96	7.34	6.92	6.98
B_{1u}	6.04	6.37	6.31	6.32	6.14	7.00	6.66	6.75
E_{2g}	10.14	8.50	8.29	8.30	8.48	6.75	6.02	5.93

[a] Cf. Tab. 2.

[b] Cf. Tab. 1.

The energy spectra are compared for different width of CI in Figs. 2 and 3. The correlation energy of the ground state, using the theoretical parameters of T, was -3.261 eV and the energies of the lowest lying B_{2u} and B_{1u} states were 0.256 eV and 5.744 eV, respectively.

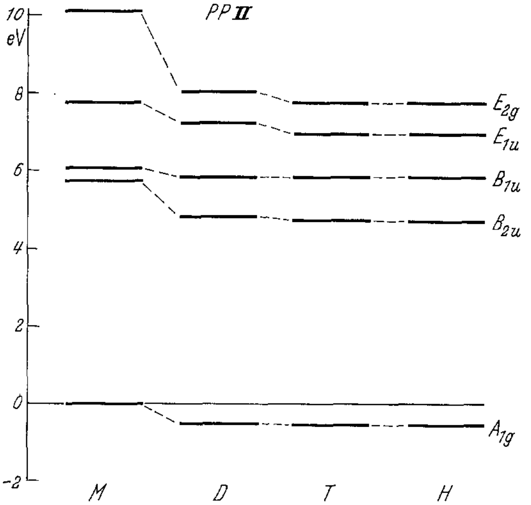

Fig. 2

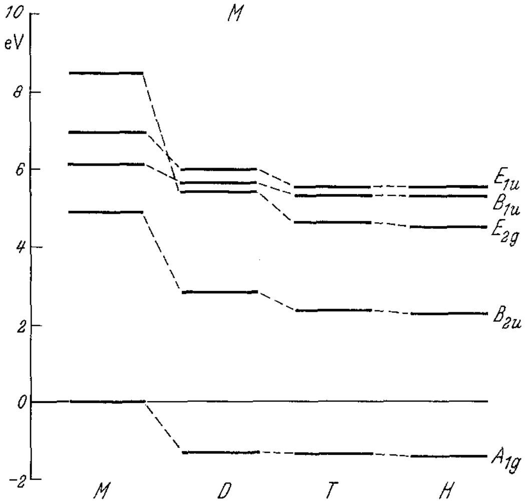

Fig. 3

Fig. 2. The graphical representation of the effect of the extent of CI on the energy levels. Parameters designated by PP II were used. M: CI with mono-excited configurations, D: CI with mono- and doubly-excited configurations, T: CI with mono-, doubly-, and triply-excited configurations, H: complete CI

Fig. 3. The graphical representation of the effect of the extent of CI on the energy levels. Parameters designated by M were used

Discussion

The sequence of levels in the energy spectrum calculated with all configurations included is the same as in the case when only mono-, doubly- and triply-excited configurations were considered. Further, the energy differences which follow from the complete CI treatment are nearly the same as those calculated with mono- and doubly-excited configurations only for both sets of parameters P II and M, in contrast to the situation when values of the energy differences calculated with mono-excited states only and corresponding values calculated with both mono- and doubly-excited configurations are compared.

The effect of higher excited configurations is more significant the larger parameter A. One can say that for the values of A encountered with semiempirical methods the effect of higher than triply-excited configurations is negligible. However, for the set of parameters denoted T the value of A is so large that the effect of higher excited configurations is not negligible: The ground state A_{1g} depression with doubly-excited configurations amounts to -2.84 eV whereas the complete CI gives correlation energy -3.26 eV. The energy of the lowest lying B_{2u} state decreases by 0.39 eV and the energy of the lowest lying B_{1u} state by 0.01 eV in going from the CI with triply-excited states only to the complete CI. The results for the set denoted T with complete CI are in a good qualitative agreement with the theoretical calculations by Moskowitz and Barnett [*6*]. The authors just mentioned obtained for the ground state A_{1g} depression with doubly-excited states the value -2.72 eV and for the correlation energy the value -3.08 eV.

The results presented allow us to draw the conclusion that for parametrizations used in semiempirical methods higher than doubly- or eventually triply-excited configurations are not essential.

The parameter A was shown to be determining the sequence of the lowest lying energy states of symmetry species B_{1u} and E_{2g} when considering the doubly excited configurations.

At first sight it might seem strange why the value of A is able to describe the character of the energy spectrum in general. The apparent explanation is that linear combinations of integrals, which determine the value of matrix elements of the hamiltonian in the basis of configurations, have larger values the faster parameters γ decrease with increasing internuclear separation. In the case of benzene molecule are the linear combinations of integrals mentioned above denoted as K_{0j}. The value of A depends on K_{0j} in such a way, that the faster γ decreases with r, the larger is the value of A. Therefore, the large value of A indicates in general a strong interaction with higher excited configurations.

Appendix

Supposing the validity of Goeppert-Mayer and Sklar potential, e.g. in our notation:

$$\alpha_k^\sigma = \langle \chi_k^\sigma \mid h_{\text{core}} \mid \chi_k^\sigma \rangle = \alpha - \sum_{i=0}^{1} \sum_{\varrho=1}^{3} \gamma_{ki}^{\sigma\varrho} + \gamma_{kk}^{\sigma\sigma} \,, \tag{A 1}$$

and of zero differential overlap approximation the following formulas are obtained for matrix elements of the hamiltonian H:

a) Diagonal elements:

$$\langle \boldsymbol{q}, \boldsymbol{m}, \boldsymbol{p}, \xi \mid H \mid \boldsymbol{q}, \boldsymbol{m}, \boldsymbol{p}, \xi \rangle - \langle \boldsymbol{q}_0, \boldsymbol{m}_0, \boldsymbol{p}_0 \mid H \mid \boldsymbol{q}_0, \boldsymbol{m}_0, \boldsymbol{p}_0 \rangle \tag{A 2}$$
$$= -2\,P\,\beta_{01}^{11} - M B_{11} + \tfrac{1}{2} \sum_{\sigma=1}^{3} \sum_{\varrho=1}^{3} (q_\sigma - 2)\,(q_\varrho - 2)\, B^{\sigma\varrho} \,,$$

where

$$P = \sum_{i=1}^{3} m_i, \quad M = \tfrac{1}{2} \sum_{i=1}^{3} [p_i (p_i - 1) + (q_i - p_i)(q_i - p_i - 1)] \tag{A 3}$$

and

$$\boldsymbol{q}_0 \equiv (2, 2, 2), \boldsymbol{m}_0 \equiv (0, 0, 0), \boldsymbol{p}_0 \equiv (1, 1, 1) \ . \tag{A 4}$$

b) Matrix elements between functions:

$$\begin{aligned} | \boldsymbol{q}_1, \boldsymbol{m}_1, \boldsymbol{p}_1, \xi_1 \rangle &= | u_\varkappa^\varrho \eta_{\nu 1}, u_{\mu_2}^{\alpha_2} \eta_{\nu 2} \ldots\ldots | \\ | \boldsymbol{q}_2, \boldsymbol{m}_2, \boldsymbol{p}_2, \xi_2 \rangle &= | u_\lambda^\sigma \eta_{\nu 1}, u_{\mu_2}^{\alpha_2} \eta_{\nu 2} \ldots\ldots | \ , \end{aligned} \tag{A 5}$$

which differ in one spin orbital:

$$\begin{aligned} &\langle \boldsymbol{q}_1, \boldsymbol{m}_1, \boldsymbol{p}_1, \xi_1 | H | \boldsymbol{q}_2, \boldsymbol{m}_2, \boldsymbol{p}_2, \xi_2 \rangle \\ &= \delta_{\sigma\varrho} \sum_{\substack{\varrho=1 \\ \varrho \neq \sigma}}^{3} B_\sigma^\varrho (q_\varrho - 2) + \\ &+ (1 - \delta_{\sigma\varrho}) [F_{\sigma\varrho} \delta_{0\lambda} \delta_{0\varkappa} + F_\sigma^\varrho \delta_{0\lambda} \delta_{1\varkappa} + F_\varrho^\sigma \delta_{1\lambda} \delta_{0\varkappa} + F^{\sigma\varrho} \delta_{1\lambda} \delta_{1\varkappa}] \ . \end{aligned} \tag{A 6}$$

c) Matrix elements between functions:

$$\begin{aligned} | \boldsymbol{q}_1, \boldsymbol{m}_1, \boldsymbol{p}_1, \xi_1 \rangle &= | u_\varkappa^\varrho \eta_{\nu 1}, u_\lambda^\sigma \eta_{\nu 2}, u_{\mu_3}^{\alpha_3} \eta_{\nu 3} \ldots | \\ | \boldsymbol{q}_2, \boldsymbol{m}_2, \boldsymbol{p}_2, \xi_2 \rangle &= | u_\nu^\tau \eta_{\nu 1}, u_\pi^\omega \eta_{\nu 2}, u_{\mu_3}^{\alpha_3} \eta_{\nu 3} \ldots | \ , \end{aligned} \tag{A 7}$$

which differ in two spin orbitals:

$$\langle \boldsymbol{q}_1, \boldsymbol{m}_1, \boldsymbol{p}_1, \xi_1 | H | \boldsymbol{q}_2, \boldsymbol{m}_2, \boldsymbol{p}_2, \xi_2 \rangle = (\delta_{\varrho\tau} \delta_{\sigma\omega} - \delta_{\nu 1\, \nu 2} \delta_{\varrho\omega} \delta_{\tau\sigma}) B_{\varrho\sigma} \ . \tag{A 8}$$

The above used symbols are defined as follows:

$$\begin{aligned} B^{ij} &= \tfrac{1}{4} \sum_{\mu, \nu=0}^{1} \gamma_{\mu\nu}^{ij}, \ B_{ij} = \tfrac{1}{4} \sum_{\mu, \nu=0}^{1} (-1)^{\mu+\nu} \gamma_{\mu\nu}^{ij} \ , \\ B_j^i &= \tfrac{1}{4} \sum_{\mu, \nu=0}^{1} (-1)^\nu \gamma_{\mu\nu}^{ij} \ , \end{aligned} \tag{A 9}$$

$$\begin{aligned} F^{ij} &= \tfrac{1}{2} \sum_{\mu, \nu=0}^{1} (-1)^{\mu+\nu} \beta_{\mu\nu}^{ij}, \ F_{ij} = \tfrac{1}{2} \sum_{\mu, \nu=0}^{1} \beta_{\mu\nu}^{ij} \ , \\ F_j^i &= \tfrac{1}{2} \sum_{\mu, \nu=0}^{1} (-1)^\nu \beta_{\mu\nu}^{ij} \end{aligned} \tag{A 10}$$

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