

Commentationes

Study of the Electronic Structure of Radicals by the CI Method

2. Ground State of the Benzyl Radical

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Received December 20, 1968/ August 20, 1969

Results are presented which were obtained in the π -electronic approximation for the ground state properties of the benzyl radical (total energy, distribution of the electronic and spin density) by the CI method on closed and open shell SCF orbitals taking into account all singly and some doubly excited configurations. Some of the singly excited configurations which in the first order perturbation theory do not interact with the ground state configuration contribute to the ground state more than some of those which interact with the latter. Certain doubly excited configurations contribute more than some singly ones. The consideration of all singly excited configurations leads to a lower ground state energy if the closed shell orbitals are used compared with the open shell ones. The former bring about the non-uniform electron density distribution becoming more smooth as the set of the basis configurations becomes larger. The spin density distribution strongly depends on the number of the configurations as well as on the orbitals used for their construction. The computation of the benzyl radical done by Hinchliffe by the CI method on open shell orbitals is believed to be wrong.

Rechnungen im Rahmen der π -Elektronen-Näherung für den Grundzustand des Benzyl-Radikals (Gesamtenergie, Verteilung von Elektronen- und Spin-Dichte) mittels des SCF-CI-Verfahrens für geschlossene und offene Schalen unter Einschluß aller einfach und einiger zweifach angeregten Konfigurationen werden mitgeteilt. Dabei zeigt sich, daß einfach angeregte Konfigurationen, die in der Störungsrechnung erster Ordnung nicht mit der Grundfiguration kombinieren, zum Grundzustand mehr als solche, die kombinieren, beitragen.

Die Berücksichtigung aller einfach angeregten Konfigurationen führt zu einer niedrigeren Grundzustandsenergie, wenn die Einteilchenfunktionen, die sich für geschlossene Schalen ergeben, an Stelle derer für offene Schalen verwendet werden. Erstere führen zu ungleichförmiger Verteilung der Elektronendichte, die um so mehr geglättet ist, je größer die Anzahl der Konfigurationen wird. Die Verteilung der Spin-Dichte hängt stark von der Anzahl der Konfigurationen wie auch von den benutzten Orbitalen ab. Die Berechnung des Benzyl-Radikals von Hinchliffe mittels des CI-Verfahrens für offene Schalen wird als unrichtig angesehen.

Propriétés de l'état fondamental du radical benzyle (énergie totale, distribution des densités électroniques et de spin) dans l'approximation π par la méthode d'I.C. sur les orbitales SCF des couches complètes et incomplètes avec introduction de toutes les configurations monoexcitées et de certaines configurations diexcitées. Certaines configurations monoexcitées qui n'interagissent pas avec la configuration fondamentale au premier ordre de la théorie des perturbations apportent à l'état fondamental une contribution plus élevée que certains de ceux qui interagissent à ce stade là. Certaines configurations diexcitées ont une contribution plus forte que certaines monoexcitées. Si l'on tient compte de toutes les configurations monoexcitées, on obtient une énergie plus basse en utilisant les orbitales des couches complètes et non celles des couches ouvertes. On obtient ainsi une distribution électronique dont la non uniformité va en s'affaiblissant lorsque la base de configurations s'élargit. La distribution de densité de spin dépend fortement du nombre de configurations employé ainsi que des orbitales utilisées. Le calcul d'I.C. d'Hinchliffe sur le radical benzyle à l'aide des orbitales des couches ouvertes semble faux.

1. Introduction

In the theory of neutral conjugated radicals the benzyl radical plays the same role as benzene does in the theory of conjugated molecules. Being one of the simplest conjugated radicals the benzyl radical is the most convenient system for the first applications of new methods to compute the electronic structure. On the other side being stable enough the benzyl radical is well studied experimentally which permits to check theoretical results thoroughly.

We too shall use the benzyl radical as the first test for the application of the previously described [1, 2] configuration interaction (CI) method in the second quantization representation. The basis configurations have been constructed on the SCF closed and open shell orbitals (CICS¹ and CIOS methods, respectively).

An additional reason which caused an increased interest to the benzyl radical is connected with a deviation between its experimental ESR spectra and the spin density distribution computed theoretically (see e.g. [5]). In contrast to the experiment the π -spin density on the para-atom C₄ is calculated, as a rule, to be less than on the ortho-atom C₂. The seriousness of this disagreement is realized now by many theorists. Numerous attempts to achieve an agreement with the experiment have failed². In the present communication we shall not discuss this problem in details³ for the disagreement might be caused not only by the insufficient accuracy of the calculated π -electronic spin density but also by an insufficiently correct transition from the π -spin density to the proton splittings.

Numerical results obtained by the CI method on the open shell orbitals are already present in the literature [7–9]. The authors of [7–9] were mostly interested in the agreement on different experimental data and did not compare their results with those which may be obtained on the closed shell SCF orbitals of a radical. It is appropriate to carry out this comparison depending on the number and the type of the basis configurations as well as to clear up which orbitals in the CI method (closed or open shell) lead to better results in the sense of the variational principle.

2. Details of Computations

Our computations were performed in the zero differential π -electronic approximation without taking account of the penetration integrals.

Bond angles have been put equal to 120° and bond lengths to 1.4 Å. The integrals $\gamma_{\mu\nu}$ were computed by the Mataga-Nishimoto (MN) formula [10–12] and by the Ohno formula [12, 13]. The integral β was supposed to be equal to -2.274 eV according to the exponential R -dependence usually used by us [12]. For the non-neighbouring atoms β was put equal to zero. The valence ionization

¹ See also [3, 4].

² But see [6] where the authors considered different C–C bond lengths calculated from the consistent bond orders by the simple Hückel method. The spin density distribution computed by the McLachlan method was in agreement with the experiment. The primitiveness of this approach does not permit to close the problem.

³ We only note that a recently finished *ab initio* computation of the benzyl radical by the unrestricted SCF method on a gaussian basis done by H. Preuss, R. Janoschek, and one of us (Yu.K.) led to hopeful results.

potential I_C was taken as 11.16 eV and the electron affinity A_C as 0.03 eV [14]. Thus, the integral $\gamma_{\mu\mu}$ was equal to 11.13 eV. The standard numbering of atoms in the benzyl radical was used which corresponds to an addition of the methylenic group CH_2 to the atom C_1 .

The closed shells of the ground state of the radical which correspond to the cation $(\text{benzyl})^+$ were taken as the vacuum state for the CICS and CIOS methods. It was computed by the standard PPP procedure [15, 3] for the former method, but for the latter one the vacuum state was built on the ground state orbitals of the radical computed by the SCF open shell theory [16, 3].

The SCF computations were performed by the programs PPP-1 and PPP-2, and the CI computations by the program CI-2 which are described in details and are listed in ALGOL 60 in Ref. [3]⁴. The program CI-2 [3] initially devised for the CICS computations was slightly changed according to the logical scheme for the CIOS computations described in [1].

Now we shall describe the configurational sets using the terminology and designations from our previous communications [1, 2]. The closed shell orbitals of the radical will be designated by letters k and l . The number of the upper doubly filled MO's of the ground configuration will be n_F with the total number of the π -electrons in the radical equal to $2n_F + 1$. All other MO's will be designated by letters m and n . The number of them is equal to $N - n_F$ if N is the number of atoms with π -electrons in the radical. Computing the ground and excited states of the radical we considered the interaction of the configurations built by creation of holes and particles against the vacuum state; the total number of them does not exceed 3, and the number of the particles is always larger than the number of the holes by one. All such configurations correspond to the following three types: $(-, m)$, (k, mm) , and (k, mn) where the indices before the comma numerate the hole orbitals, and after comma the particle orbitals.

In the present communication we shall discuss the properties of the ground state only. Its symmetry is 2B_2 . Therefore we shall take into account only those configurations which have symmetry 2B_2 . The number of the one-configurational basis vectors corresponding to each type of the configurations is $Q(-, m) = 3$, $Q(k, mm) = 8$, $Q(k, mn) = 18$. There are 29 basis vectors at all. Here we have taken into account that each configuration of the type (k, mn) generates two basis vectors.

From the 29 basis vectors available we took 25 giving up those 4 vectors which correspond to presumable highly lying configurations (2,77), (1,77), and (1,67) where the digits numerate the orbitals with increasing electronic energies. This set of configurations which includes all singly and a part of the doubly excited configurations will be denoted by the number IV.

The set III will include all singly excited configurations of the symmetry 2B_2 . The number of them is equal to $Q(-, m) = 3$, $Q(k, mm) = 2$, and $Q(k, mn) = 10$. There are 15 configurations at all.

According to [2], if the SCF open shell orbitals are used, the ground state configuration $(-, m_0)$ does not directly interact with the basis vectors of the

⁴ The computer M-220A of the Institute of Cybernetics of the Ukrainian Academy of Sciences (Kiev) was used. Its average speed is about 20,000 operations/second. All computations of one radical taking in account 25 configurations need 5 min.

configurations $(-, m)$ with $m \neq m_0$, $(k, m_0 m_0)$, and with $|\Psi_4\rangle$ (see [2]) of $(k, m_0 n)$. Thus, there remain 6 basis vectors interacting directly with $(-, m_0)$. This will be the set II.

Finally, the trivial set I consists of only one vector $(-, m_0)$.

The spin density of the benzyl radical was already calculated with the set II by the CI method on the open shell orbitals [8]. We repeated the computations of Hinchliffe [8] with his parameters [7]. They are different from our ones in the following: integral $\gamma_{\mu\mu} = 11.4$ eV, two-center integrals $\gamma_{\mu\nu}$ were computed in [7] by the Pariser-Parr formula [15], integral $\beta = -2.395$ eV. Our results obtained with these parameters will be denoted by PP. The value of I_C was also put equal to 11.16 eV for both computations with the γ 's by MN and Ohno. We decided to repeat Hinchliffe's computation [8] for two reasons: 1) he did not publish a computation scheme of the CI method on the open shell orbitals despite it is different of the standard CI method, and 2) the spin density was calculated in [8] by the first order perturbation theory. We shall give exact values of the spin density computed with the set II as well as other results obtained with the parameters from [7, 8].

3. Results of Computation and Discussion

In Table 1 we give the expansion coefficients of the ground state wave function of the benzyl radical with regard to the basis vectors computed with different configurational sets and parameters. It was previously noted that among the basis vectors for the singly excited configurations there are such vectors which do not interact directly with the ground state configuration if the open shell orbitals are used. Nevertheless, as it is seen from Table 1, some of them contribute to the ground state more than those vectors which do interact. Many of the doubly excited configurations also contribute more than some of the singly excited ones.

The wave functions computed with the γ 's by Ohno and PP are only slightly different between each other and, as it will be seen later, lead to practically equal results.

The ground state energy of the benzyl radical computed in different approximations is given in Table 2. The lower value of the ground state energy computed with the set I on the open shell orbitals in comparison with the use of the closed shell orbitals reflects the obvious fact that the open shell orbitals are the self-consistent orbitals in the one-configurational approximation. Table 2 shows also that the addition of those singly excited configurations which do not interact directly with the ground state configuration (set II) does not change the mutual arrangement of calculated energies.

It seems that an extension of the basis configurations will lead to a further uniform lowering of the energy computed on the closed as well as on the open shell orbitals without changing their mutual arrangement. Nevertheless, as one sees from Table 2, as soon as all basis vectors corresponding to the singly excited configurations (set III) are taken the use of the open shell orbitals leads to a less lowering of the energy than in the case of the closed shell orbitals. Further extension of the basis by doubly excited configurations (set IV) redoubles the effect only. Moreover, the CI with the smaller set III on the closed shell orbitals leads to a

Table 1. Expansion coefficients of the ground state wave function of the benzyl radical with regard to the basis vectors computed in different approximations

Conf. ^a	CIOS			MN			Ohno			PP					
	MN	Ohno	PP	MN	Ohno	PP	MN	Ohno	PP	MN	Ohno	PP			
(-4)	0.958	0.945	0.944	0.973	0.956	0.955	0.973	0.958	0.957	0.984	0.960	0.957	0.988	0.977	0.975
(3,45)	-0.170	-0.143	-0.127	-0.124	-0.108	-0.095	-0.125	-0.108	-0.096	-0.101	-0.126	-0.116	-0.077	-0.088	-0.078
2,46)	-0.198	-0.173	-0.165	0.169	0.149	0.140	0.169	0.147	0.139	0.127	0.188	0.188	0.114	0.150	0.148
(2,47)	-0.017	-0.006	-0.001	-0.023	-0.015	-0.010	-0.020	-0.013	-0.008	-0.030	-0.040	-0.042	-0.027	-0.030	-0.031
(1,46)	0.054	0.064	0.065	-0.058	-0.066	-0.066	-0.056	-0.063	-0.062	0.030	0.040	0.042	0.027	0.030	0.031
(1,47)	-0.103	-0.087	-0.082	-0.073	-0.061	-0.057	-0.071	-0.060	-0.057	-0.065	-0.086	-0.083	-0.051	-0.062	-0.059
(3,45) ^{''}	-0.058	-0.063	-0.063	-0.043	-0.043	-0.047	-0.072	-0.075	-0.075	0.000	0.000	0.002	-0.000	-0.002	-0.000
(2,46) ^{''}	0.025	0.023	0.023	-0.103	-0.098	-0.098	-0.077	-0.073	-0.073	0.000	0.000	0.000	0.000	0.000	0.001
(2,47) ^{''}	-0.021	-0.020	-0.020	-0.024	-0.024	-0.024	-0.022	-0.021	-0.021	-0.002	-0.002	-0.002	-0.002	-0.002	0.002
(1,46) ^{''}	-0.011	-0.013	-0.013	0.047	0.046	0.046	0.030	0.030	0.030	-0.002	-0.003	-0.003	-0.002	-0.002	0.002
(1,47) ^{''}	-0.002	-0.003	-0.003	0.026	0.025	0.025	0.007	0.007	0.007	-0.000	-0.000	-0.000	-0.000	-0.000	0.000
(-6)	0.035	0.025	0.025	-0.038	-0.035	-0.035	-0.037	-0.034	-0.034	-0.087	-0.102	-0.102	-0.068	-0.082	0.080
(-7)	-0.008	-0.003	-0.003	-0.009	-0.007	-0.007	-0.010	-0.008	-0.008	0.033	0.036	0.036	0.022	0.021	0.022
(2,44)	-0.176	-0.180	-0.180	-0.143	-0.148	-0.148	-0.146	-0.151	-0.151	-0.087	-0.087	-0.087	-0.068	-0.067	0.066
(1,44)	0.092	0.093	0.093	0.075	0.076	0.076	0.072	0.072	0.072	-0.033	-0.033	-0.033	-0.022	-0.022	-0.021
(2,55)	0.014	0.014	0.014	0.017	0.017	0.017	0.015	0.015	0.015	-0.008	-0.008	-0.008	-0.012	-0.012	0.011
(2,66)	0.036	0.036	0.036	0.022	0.022	0.022	0.025	0.025	0.025	-0.018	-0.018	-0.018	-0.019	-0.019	0.019
(1,55)	-0.035	-0.035	-0.035	-0.024	-0.024	-0.024	-0.024	-0.024	-0.024	-0.024	-0.024	-0.024	-0.015	-0.015	-0.017
(1,66)	0.010	0.010	0.010	0.004	0.004	0.004	0.006	0.006	0.006	0.016	0.016	0.016	0.010	0.010	0.012
(3,56)	0.002	0.002	0.002	0.027	0.027	0.027	0.019	0.019	0.019	0.001	0.001	0.001	-0.015	-0.015	0.013
(3,57)	-0.035	-0.035	-0.035	-0.025	-0.025	-0.025	-0.025	-0.025	-0.025	-0.030	-0.030	-0.030	-0.021	-0.021	-0.021
(2,67)	0.027	0.027	0.027	-0.024	-0.024	-0.024	-0.022	-0.022	-0.022	-0.018	-0.018	-0.018	-0.014	-0.014	-0.013
(3,56) ^{''}	0.056	0.056	0.056	-0.068	-0.068	-0.068	-0.060	-0.060	-0.060	0.034	0.034	0.034	0.046	0.046	-0.043
(3,57) ^{''}	-0.011	-0.011	-0.011	0.002	0.002	0.002	-0.003	-0.003	-0.003	-0.015	-0.015	-0.015	-0.011	-0.011	-0.014
(2,67) ^{''}	-0.001	-0.001	-0.001	0.010	0.010	0.010	0.003	0.003	0.003	0.002	0.002	0.002	0.011	0.011	0.006

^a The basis vectors $|^2\Psi_3\rangle$ and $|^2\Psi_4\rangle$ (see [2]) for the configuration (k, mn) are marked by different amount of primes.

Table 2. *The lowering of the ground state energy of the benzyl radical relative to its energy computed on the closed shell orbitals, in eV^a*

Method	Set of conf.	Parameters		
		MN	Ohno	PP
CICS	I	0	0	0
	II	-0.5314	-0.3739	-0.3749
	III	-0.7278	-0.6004	-0.5840
	IV	-0.8110	-0.6905	-0.6591
CIOS	I	-0.4534	-0.3728	-0.3545
	II	-0.6019	-0.5071	-0.4921
	III	-0.6646	-0.5425	-0.5275
	IV	-0.7106	-0.5925	-0.5732

^a The following values of the ground state energy of the benzyl radical computed on the closed shell orbitals were taken as zeros: -175.0471 (MN), -210.4543 (Ohno), and -211.7460 (PP). The energy of the vacuum state for the CICS method is -166.5348 (MN), -201.6686 (Ohno), and -202.9242 (PP), and for the CIOS method is -165.3545 (MN), -200.7304 (Ohno), and -202.0280 (PP). The former may be used to calculate the ionization potential of the benzyl radical. In order to calculate its electron affinity one needs the values of the ground state energy of the benzyl anion (benzyl)⁻. They are -177.7248 (MN), -212.8586 (Ohno), and -213.8442 (PP).

Table 3. *The electron density distribution in the ground state of the benzyl radical computed by the CI method in different approximations*

Method	Set of conf.	μ					
		1	2	3	4	7	
CICS	MN	I	1.021	1.007	0.959	0.962	1.086
		II	1.021	1.007	0.960	0.964	1.082
		III	1.001	0.992	1.005	0.996	1.009
		IV	1.000	0.993	1.010	1.003	0.991
	Ohno	I	1.130	0.971	1.005	0.910	1.009
		II	1.126	0.972	1.004	0.912	1.009
		III	0.997	0.980	1.017	0.996	1.013
		IV	1.001	0.978	1.014	0.995	1.000
	PP	I	1.081	1.011	0.967	0.934	1.030
		II	1.079	1.011	0.967	0.937	1.029
		III	0.993	0.989	1.008	1.003	1.010
		IV	0.996	0.987	1.014	1.003	0.999
CIOS	MN	I, II, III	1.000	1.000	1.000	1.000	1.000
		IV	1.002	1.002	1.003	1.002	0.986
	Ohno	I, II, III	1.000	1.000	1.000	1.000	1.000
		IV	1.004	1.002	1.001	1.003	0.986
	PP	I, II, III	1.000	1.000	1.000	1.000	1.000
		IV	1.003	1.002	1.001	1.003	0.987

Table 4. *The spin density distribution in the ground state of the benzyl radical computed by the CI method in different approximations*

Method	Set of conf.	I	μ				
			1	2	3	4	7
CICS	MN	I	0.008	0.154	0.001	0.161	0.522
		II	-0.107	0.249	-0.101	0.262	0.549
		III	-0.099	0.189	-0.084	0.166	0.722
		IV	-0.098	0.183	-0.072	0.157	0.719
	Ohno	I	0.005	0.154	0.001	0.162	0.523
		II	-0.096	0.226	-0.081	0.248	0.558
		III	-0.089	0.179	-0.068	0.165	0.702
		IV	-0.085	0.172	-0.057	0.153	0.702
	PP	I	0.005	0.154	0.001	0.157	0.529
		II	-0.096	0.225	-0.080	0.244	0.563
		III	-0.087	0.178	-0.067	0.160	0.706
		IV	-0.084	0.172	-0.058	0.148	0.708
CIOS	MN	I	0	0.059	0	0.033	0.850
		II	-0.093	0.140	-0.060	0.103	0.831
		III	-0.112	0.197	-0.076	0.172	0.698
		IV	-0.110	0.195	-0.073	0.177	0.689
	Ohno	I	0	0.076	0	0.043	0.805
		II	-0.083	0.138	-0.049	0.103	0.802
		III	-0.094	0.174	-0.058	0.156	0.706
		IV	-0.093	0.172	-0.054	0.159	0.699
	PP	I	0	0.077	0	0.043	0.803
		II	-0.083	0.140	-0.049	0.102	0.799
		III	-0.094	0.175	-0.058	0.154	0.706
		IV	-0.093	0.173	-0.055	0.158	0.698

larger lowering of the ground state energy than the CI with the larger set IV on the open shell orbitals.

Table 3 contains the electronic density distribution computed in different approximations. The computations on the closed shell orbitals lead to a non-uniform distribution which, nevertheless, has a tendency to smooth out as the CI basis becomes larger. The appearance of a small positive charge on atom C_7 , when the open shell orbitals of set IV are used, is presumably explained by considering only a small number of doubly excited configurations in our computations.

Table 4 gives the π -spin density distribution computed in different approximations. The computations on the closed shell orbitals with the sets I and II lead to a larger spin density on para-atom C_4 in comparison with the ortho-atom C_2 . This is in agreement with the experimental splittings [5] if the simple McConnell equation is used. This agreement must be considered as to be accidental for a more precise definition of the wave function by an extension of the CI basis as well as the use of the open shell orbitals leads to an opposite relation between the spin densities on para- and ortho-atoms.

The high value of ρ_7 obtained by Hinchliffe [8] is not caused by the choice of the parameters. Therefore his result is not confirmed. An appropriate value of ρ_7 is always obtained if one extends enough the basis for the CI.

Table 5. The elements of the CI matrix computed on the closed (upper values) and open shell (lower values) orbitals with the configurational set II and parameters PP from [7, 8]^a

Conf.	(-,4)	(3,45)'	(2,46)'	(2,47)'	(1,46)'	(1,47)'
(-,4)	2.3382	0.5573	1.3464	0.0150	0.5202	0.5517
	1.0876	0.2803	- 0.6987	- 0.2992	0.2992	0.3530
(3,45)'		7.3650	0.2190	- 0.6448	0.0497	- 1.1742
		5.5975	0.2869	- 0.2020	0.2020	- 1.1298
(2,46)'			10.8453	1.1838	0.8227	1.2586
			7.6189	0.4522	- 0.4522	1.3717
(2,47)'				12.4912	1.2586	0.1239
				10.4442	1.3717	- 0.0336
(1,46)'					12.6381	0.2274
					10.4442	0.0336
(1,47)'						14.3796
						12.8287

^a Computing the values of $H_{\mu\mu}^{\text{core}}$ the potential I_{μ} was put equal to zero.

We must note that our results on the spin density obtained with the PP parameters taken from Hinchliffe's paper [8] are seriously different from those in [8]. The deviation on atom C₃ reaches more than 30%. This cannot be explained by the use of the first order perturbation theory for the spin density calculations in [8]. As the reason of the deviation is still uncertain, in Table 5 we give the elements of the CI matrix computed on the closed and open shell orbitals with the configurational set II and the PP parameters from [7, 8].

Concluding, we note that the orbitals which are the best in the one-configurational approximation might be the worst in the sense of the variational principle when using them in the multi-configurational wave function. Thus, it is appropriate to put the question how to find the orbitals which are the best for the multi-configurational approximation. One can judge about the quality of the multi-configurational wave function built on the fixed orbitals by the degree in which computed properties depend on the orbitals used. In this respect, as we see from the results for the spin density, the configurational set IV is much better than set III. Thus, our computations show in contrast to the widespread opinion [5, 17-19] that the extension of the CI basis by at least doubly excited configurations might considerably affect the spin density distribution.

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