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Ab-initio Valence Bond Calculations. VIII. Benzene: an extended basis set treatment

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SEZIONE II
(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Ab-initio Valence Bond Calculations.* VIII. *Benzene: an extended basis set treatment.* Nota di GIAN FRANCO TANTARDINI e MASSIMO SIMONETTA, presentata (*) dal Corrisp. M. SIMONETTA.

RIASSUNTO. — Vengono presentati i risultati di un calcolo VB ab-initio per la molecola del benzene utilizzando la base estesa 6–31 G. La funzione d'onda dello stato fondamentale viene analizzata in termini di strutture per determinare la validità delle teorie VB del legame chimico in sistemi con elettroni delocalizzati. Gli spettri di singoletto, di tripletto e fotoelettronico vengono confrontati con i dati sperimentali e con altri risultati teorici.

1. INTRODUCTION

In a recent paper [1], we reported the results obtained performing ab-initio Valence Bond (VB) calculations on the benzene molecule. The purpose of that study was to investigate to what extent the conclusions drawn in the paper by Norbeck and Gallup [2] concerning the relative importance of the covalent and ionic structures were dependent on the choice of the basis set. The results we obtained using two different minimum basis sets (Slater type orbitals: STO; Gaussian type orbitals: GTO) showed substantial overall agreement with those of Ref. [2] (Gaussian lobes). In the present work we report the results of VB calculations on benzene in which an extended basis set was used, namely the double-zeta (DZ) 6–31 G basis set of Ref. [3].

2. METHOD OF CALCULATION

The geometry reported in Ref. [4] was used: $r_{CC} = 2.6323$ bohr, $r_{CH} = 2.0409$ bohr, $C\hat{C}C = H\hat{C}C = 120^0$ (regular hexagon).

A set of 156 GTO contracted to the 66 functions of the 6–31 G basis set of Ref. [3] was used with the standard scale factors there reported. The 42 electrons of benzene were separated into 36 σ electrons confined to the 'core' of the lowest 18 σ-type SCF molecular orbitals and 6 π electrons explicitly included in the VB treatment (for details see Ref. [1]). The basis set used in VB calculations was the DZ set of the 3 G- and 1 G-type valence p_π atomic orbitals on Carbons [3].

To preserve the interpretative capacity of the method, the VB problem was always reduced to a minimum basis set treatment (six π atomic orbitals)

(*) Nella seduta del 18 novembre 1977.

by contracting the DZ valence set to single-zeta (SZ):

$$p_r = \mathrm{N}\,(p'_r + \lambda p''_r)$$

where p'_r and p''_r indicate the 3 G- and 1 G-type π orbitals on Carbon $r\,(r = 1\,,2\cdots 6)$, N is the normalization constant and λ is the contraction coefficient.

Three different series of VB calculations were performed. In the first (A), the contraction coefficient λ was obtained minimizing the VB total energy corresponding to the full calculation (22 $^1A_{1g}$ symmetry structures).

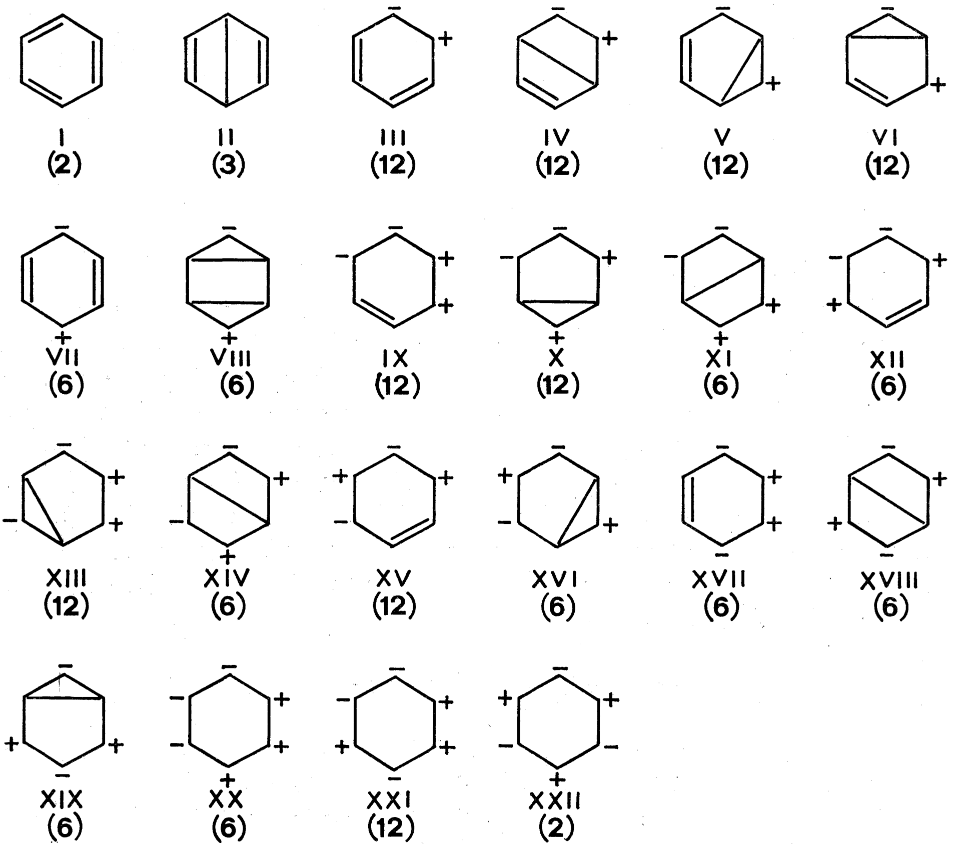

Fig. 1. – Canonical Rumer Diagrams and Number of Equivalent Individual Structures for the $^1A_{1g}$ Symmetry Structures.

To introduce a somewhat higher degree of freedom into the minimum basis set, two other series (B, C) of calculations were performed in the framework of the orbital ' split ' technique [5], that is using two different contraction coefficients for the π orbital p_r depending on whether it appears in a covalent (λ_c) or an ionic (λ_i) bond, respectively. Owing to the fact that the dimension of the secular equation is unchanged but the calculation of the matrix elements between Slater determinants gets more time consuming and

:aking into account the rapid convergence of the VB expansion [1], the largest calculations were limited to the inclusion of the 8 most significant $^1A_{1g}$ symmetry structures which present at least one covalent bond and no charges of the same sign on adjacent Carbon atoms (fig. 1).

For a deeper insight into the role of the Kekule and orthopolar $^1A_{1g}$ symmetry structures, in calculations of type B we used the contraction coefficients λ_c, λ_i obtained minimizing the energy of the Kekule and orthopolar structures separately. In calculations of type C, the coefficients λ_c, λ_i determined by minimizing the total energy of the 8 selected structures were used.

All VB calculations on the singlet and triplet π-electron states of benzene, and doublet states of the corresponding π cation were performed by meane of our VB program [6]; SCF-MO results for the uncontracted basis set wers obtained using a Univac adapted version of Gaussian 70 [7].

3. GROUND STATE

In Table I, the VB energy results obtained using different contraction coefficients are compared with those relative to STO [1] and Gaussian lobes [2] minimum basis set calculations. The total energy values corresponding to the DZ basis set contracted to SZ (column *d*) confirm the results presented in Ref. [1] (column *b*) which differ from those of Ref. [2] (column *c*) mainly in the fact that the energy of the orthopolar structures alone falls above the SCF value. It is interesting to note that this is also true for columns *e* and *f* of the Table where the orbital split technique was performed. The orbital split improves the total energy by less than 1 kcal/mol (compare the results in columns *d* and *f* corresponding to the 8 selected symmetry structures calculation). The minimum basis set correlation energy (i.e. the energy difference between the full VB calculation and the corresponding SCF result) decreases on improving the quality of the basis set: —2.75 eV for STO, —2.16 for Gaussian lobes, —1.94 for calculation of type A. It is particularly interesting to note that the complete CI total energy value obtained by means of an iterative natural orbital procedure on the π DZ basis set is 0.3 and 0.5 eV lower than the full (22 $^1A_{1g}$ symmetry structures) and the limited VB value corresponding to the calculation including only the 8 most significant structures constructed on the SZ basis set. We can conclude that an optimized contraction of the basis set from DZ to SZ in order to facilitate the interpretation of the VB wave function allows a drastic reduction in computing time without introducing significant differences in the total energy value.

In Table II, the energy values of the most important symmetry structures and the corresponding occupation numbers are reported. The results coming from the different types of calculations (A, B, C) indicate the orthopolar as the most important symmetry structure thus confirming the results obtained

TABLE I

SCF *and* VB *Total Energies for Different Sets of* $^1A_{1g}$ *Symmetry Structures* [a].

	Symmetry structures	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
Kekule	1	—0.077809	—0.2972	—0.527063	—0.541985	—0.521108	
Covalent	2	—0.084216	—0.3026	—0.532579	—0.546730	—0.526755	
Orthopolar	2	—0.146837	—0.3781	—0.614617	—0.620909	—0.622302	
SCF	1	—0.215126	—0.3754	—0.624160	—0.624160	—0.624160	
Covalent + Orthopolar	4	—0.250715	—0.4125	—0.650634	—0.640660	—0.649503	
Covalent + Singly polar	8	—0.280901	—0.4373	—0.676198	—0.662664	—0.675911	
Covalent + Singly + Doubly polar	19	—0.314875		—0.694971			
Full	22	—0.316045	—0.4546	—0.695427			
Selected [h]	8	—0.300331		—0.689041	—0.672852	—0.690074	
CI							—0.706957

(*a*) Energies correspond to E+230 hartree; all VB values refer to minimum basis set calculations.

(*b*) STO: Reference [1].

(*c*) Gaussian lobes: Reference [2].

(*d*) 6–31 G; calculation of type A (see text): $\lambda = 0.739$.

(*e*) 6–31 G; calculation of type B (see text): $\lambda_c = 0.909$, $\lambda_i = 1.029$.

(*f*) 6–31 G; calculation of type C (see text): $\lambda_c = 0.711$, $\lambda_i = 0.862$.

(*g*) Uncontracted 6–31 G; π-electron configuration interaction including 379 configurations constructed using iterative natural orbitals (4 iterative cycles).

(*h*) Selected $^1A_{1g}$ symmetry structures containing at least one covalent bond and without charges of the same sign on adjacent carbon atoms (n. I, II, III, IV, V, VI, VII, XV in fig. 1).

TABLE II

Diagonal Energies (E_i) (a), *Total Energy Variations* (ΔE_i) (b) *and Occupation Numbers* (n_i) (c) *for* $^1A_{1g}$ *Symmetry Structures.*

Symmetry structure (d)	Calculation A				Calculation B		Calculation C	
	E_i	ΔE_i	n_i (e)	n_i (f)	E_i	n_i (f)	E_i	n_i (f)
I	—0.527063	2.37	0.220	0.227	—0.541985	0.229	—0.521108	0.209
II	—0.512998	0.63	0.109	0.098	—0.529114	0.096	—0.506860	0.088
III	—0.584586	5.03	0.247	0.260	—0.597879	0.240	—0.594116	0.261
IV	—0.499830	1.80	0.111	0.147	—0.530578	0.144	—0.512943	0.150
V	—0.231394	1.05	0.047	0.063	—0.297504	0.071	—0.250896	0.068
VI	—0.202906	0.83	0.040	0.051	—0.275830	0.053	—0.227667	0.051
VII	—0.100110	0.69	0.027	0.023	—0.170000	0.021	—0.120230	0.023
XV	—0.340539	1.93	0.093	0.130	—0.404304	0.145	—0.381688	0.149

(*a*) The energy values correspond to $E_i + 230$ hartree.

(*b*) ΔE_i is the total energy increase in kcal/mol when eliminating the *i*-th symmetry structure from the full calculation (22 $^1A_{1g}$ symmetry structures).

(*c*) $n_i = C_i^* \Sigma_j C_j S_{ij}$ (Ref. [8]); S_{ij} is the overlap integral between structures *i* and *j*, C_i and C_j are the variational coefficients.

(*d*) For the numbering of the structures see fig. 1.

(*e*) Full calculation (22 $^1A_{1g}$ symmetry structures).

(*f*) Calculation limited to 8 selected structures (see Table I footnote *h*).

TABLE III

Diagonal Energies (E_i) [(a)], *Occupation Numbers* (n_i) [(b)], *Overlap Charges* (q_{rs}) [(c)] *for the Kekule, Dewar and Orthopolar Structures* [(d)].

	E_i	n_i	q_{12}	q_{23}	q_{34}	q_{45}	q_{56}	q_{61}	$q_{r,r+1}$ [(e)]
Kekule	—230.482513	0.110	0.1844	—0.0938	0.1844	—0.0938	0.1844	—0.0938	0.0721
Dewar	—230.415310	0.036	—0.0847	0.1829	—0.0847	—0.0847	0.1829	—0.0847	0.0636
Orthopolar	—230.163457	0.021	—0.2053	0.1884	—0.0951	0.1802	0.0	0.0	0.2062

(*a*) In hartree.

(*b*) Refer to full calculation; see Table II footnote *c*.

(*c*) $q_{rs} = \gamma_{rs} S_{rs} + \gamma_{sr} S_{sr}$; $\gamma_{rs} = (r, s)$-element of the charge density matrix, S_{rs} = overlap integral between orbitals on carbons r and s (atoms are numbered counterclockwise starting from the top vertex).

(*d*) Calculation of type A; if not otherwise specified the values refer to individual structures.

(*e*) Refer to ${}^1A_{1g}$, symmetry structures.

with STO [1] and Gaussian lobes [2] basis sets. On the other hand, if we consider the results of Table III concerning the total energy, the occupation numbers and the overlap charges for the individual Kekule, Dewar and orthopolar structures, the indication is again that the Kekule structure is the most important and the most binding one ($\Sigma_r q_{r,r+1} = 0.2717$ for the Kekule, 0.0268 for the Dewar and 0.0682 for the orthopolar). The overlap charges of Table III are always greater than the corresponding values reported in Ref. [1] and [2]. In particular, a covalent bond between adjacent atoms has a degree of bonding (~ 0.18) which is remarkably higher than the value (~ 0.10) corresponding to STO and Gaussian lobes. Coming to symmetry structures, the overlap charges $q_{r,r+1}$ reported in Table III indicate the orthopolar as the most binding one.

Table IV gives the atomic and overlap charges for calculations corresponding to different sets of symmetry structures; it can be pointed out that the convergence toward the full VB result and the validity of the chemical criterion to select VB structures parallel the conclusions drawn in Ref. [1].

TABLE IV

Atomic and Overlap Charges for Different Sets of $^1A_{1g}$ *Symmetry Structures* (a).

	Symmetry structures	q_{11}	q_{12}	q_{13}	q_{14}
Covalent	2	0.9363	0.0754	—0.0105	—0.0025
Orthopolar	2	0.8005	0.2187	—0.0123	—0.0137
Covalent + Orthopolar	4	0.8184	0.2000	—0.0134	—0.0100
Covalent + Singly polar	8	0.7939	0.2254	—0.0108	—0.0170
Covalent + Singly + Doubly polar . . .	19	0.7711	0.2495	—0.0113	—0.0185
Full	22	0.7704	0.2502	—0.0113	—0.0186
Selected (b)	8	0.7798	0.2403	—0.0109	—0.0184

(*a*) Calculation of type A; $q_{rr} = \gamma_{rr} S_{rr}$, see Table III footnote *c*.
(*b*) See Table I footnote *h*.

Finally, the resonance energy, as defined in Ref. [2] that is, including the effect of the orthopolar structures, is: 62.94, 57.17 and 63.59 kcal/mol for calculations of type A, B and C, respectively, in agreement with the values: 67.4 kcal/mol of Ref. [1], 61.4 kcal/mol of Ref. [2], and 66 kcal/mol of experiment [1].

4. EXCITED STATES AND IONIZATION POTENTIALS

In Table V, the VB data concerning singlet and triplet excited states and vertical Ionization Potentials (IP) for the π electrons of benzene (calculation of type A) are compared with the experiment and with the corresponding results obtained using a STO basis set [1]. The extension of the basis set does not lead to substantial modifications in the positions of the peaks in the singlet and triplet spectra; for the photoelectron spectrum, a nice agreement between the computed and the experimental values of the first and the second IP can be observed. On analyzing the singlet and triplet excited states of benzene and the doublet states of the π cation to have indications of the relative importance of the different VB structures, it can be pointed out that the conclusions that can be drawn from this kind of analysis are pratically independent of the starting basis set [1].

TABLE V

π-*Electron Singlet and Triplet Spectra and Vertical Ionization Potentials* [(a)].

Singlet spectrum			Triplet spectrum			Ionization Pot.		
(*b*)	(*c*)	(*d*)	(*b*)	(*c*)	(*d*)	(*b*)	(*c*)	(*e*)
5.31	5.43	4.9	3.96	4.14	3.9	8.38	9.13	9.3
8.75	8.92	6.2	5.53	5.55	4.7	11.36	12.09	11.8
10.45	9.54	6.98	7.52	7.76	5.6	14.15	14.84	12.5
11.48	10.72	7.3	9.44	8.67	6.55	15.36	15.95	
13.20	12.93		11.42	11.77		16.70	17.11	
13.54	13.51					17.17	17.59	
14.97	14.03					17.38	18.10	
						17.49	18.20	

(*a*) All values are in eV.
(*b*) STO, Reference [1].
(*c*) Calculation of type A.
(*d*) Experiment, Reference [9].
(*e*) Experiment, Reference [10].

5. CONCLUSIONS

The VB results reported in the present paper obtained after contraction of a DZ basis set (6–31 G) to SZ are perfectly comparable with those obtained using minimum basis sets of different kinds (STO and Gaussian lobes) and lead to the same conclusions drawn in Ref. [1]. In particular, the validity of the qualitative picture given by simple VB theories of the chemical bond in delocalized systems such as benzene is once more confirmed.

As a final remark, we want to point out that owing to the good qualitative (and quantitative) agreement between the results obtained in Ref. [1] using the two different basis sets STO and GTO (3 G), this last one can be successfully used instead of the much more expensive 6–31 G basis set.

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