Theoret. Chim. Acta (Berl.) 33, 263—268 (1974)

SCF–CI MO Treatment of Radicals Having Degenerate Ground States

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Received September 27, 1973/January 23, 1974

A form of the configuration interaction method is described which accommodates radicals having a doubly degenerate molecular orbital occupied by one or three electrons. The procedure covers all types of excited configurations corresponding formally to one-electron promotions from the ground state. The matrix elements derived are based on the SCF MO's given by the half-electron method. The computational scheme is applied, in the CNDO and PPP-like approaches, to the interpretation of the electronic spectrum of the cyclopentadienyl radical.

Key words: Radicals with degenerate ground states

Introduction

The open shell MO studies of radicals have become so successful (for recent reviews see e.g. Refs. [1, 2]) that the accuracy achieved in predicting molecular properties can be compared with that given by MO treatments of closed shell molecules. In spite of some special features of the open shell MO theory, computational procedures have been developed which are useful for routine calculations of radicals. In the most common case, that of radicals having a nondegenerate open shell molecular orbital, the present state of the theory is particularly satisfactory. With radicals having degenerate ground states the situation seems less satisfactory. Here the SCF solution is difficultly accessible because the Roothaan procedure [3] usually diverges for this type of configuration [4–6]. This difficulty can probably also be expected with other methods that use coupling operators. A promising degree of progress was achieved by developing the SCF procedures [7, 8] related to the "second" method of Huzinaga [9] which were reported to converge rapidly. Unfortunately, it has been recently demonstrated [10] that methods of this type do not satisfy all necessary conditions for the energy to be stationary. It can be argued that, in general, one can use any set of arbitrary molecular orbitals and subject it to configuration interaction. In such a procedure, however, the construction of the CI matrix is not a simple task and requires much computer time. Because there are rather numerous chemically interesting radicals which have in their ground state a doubly degenerate MO occupied by one or three electrons, we considered it expedient to formulate a more convenient computational scheme for these structural types. We have selected the half-electron

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* Postdoctoral fellow of the Swiss National Foundation.

method [11] (i.e., the approximate SCF method of Longuet-Higgins and Pople [12]) in its extended form [13] because it is reasonably rapidly convergent and, in conjunction with the limited CI treatment gives results for radicals with non-degenerate ground states which are very close to CI results based on Roothaan's MO's [14, 15].

In this paper we present a description of the computational scheme and a model calculation on the cyclopentadienyl radical in the PPP and CNDO approximations. Explicit formulas for the CI matrix elements and applications to the electronic spectra of a series of highly symmetric conjugated and small linear radicals will be given in the following papers.

Theoretical

For the sake of convenience, we use the same notation for the case where the doubly degenerate MO is occupied in the ground state by one electron (hereafter referred to as the case $n = 1$) or by three electrons (hereafter referred to as the case $n = 3$).

The half-electron method in its extended form [13] works with F matrix elements which are formally the same as those used in the usual Roothaan SCF procedure for closed shell molecules, the only difference being a new definition of the density matrix

$$P_{\mu\nu} = \sum_{i} 2c_{i\mu}c^*_{i\nu} + \sum_{m} 2f\, c_{m\mu}c^*_{m\nu}\,,$$

where i and m run over closed shell and open shell MO's respectively, and the fractional occupancy of the open shell, f, is $\frac{1}{4}$ for the case $n = 1$ and $\frac{3}{4}$ for the case $n = 3$.

In the configuration interaction treatment, we account for all excited states which arise formally from one-electron promotions from the ground state. These are of the A–E types as defined in Fig. 1. The corresponding doublet functions are given in Tables 1 and 2; the formulas for the CI matrix elements will be pub-

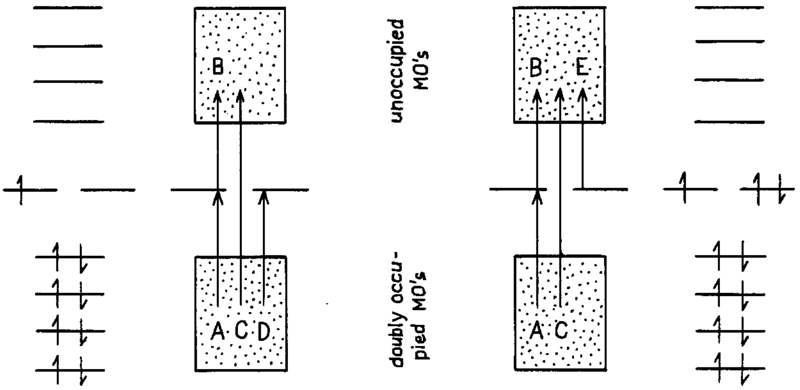

Fig. 1. Types of electron promotions leading to singly excited states for the cases $n = 1$ (left) and $n = 3$ (right)

Table 1. Configurations for the case $n = 1$

Designation	Occupation of		Wave function
	m	m'	
G^1	1	0	$\vert \ldots \varphi_m \vert$
G^2	0	1	$\vert \ldots \varphi_{m'} \vert$
$A^1(i \to m)$	2	0	$\vert \ldots \varphi_i \bar{\varphi}_m \ldots \varphi_m \vert$
$A^2(i \to m')$	0	2	$\vert \ldots \varphi_i \bar{\varphi}_{m'} \ldots \varphi_{m'} \vert$
$C_\alpha^1(i \to k)$	1	0	$\frac{1}{\sqrt{2}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_m \vert + \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_m \vert]$
$C_\alpha^2(i \to k)$	0	1	$\frac{1}{\sqrt{2}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_{m'} \vert + \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_{m'} \vert]$
$C_\beta^1(i \to k)$	1	0	$\frac{1}{\sqrt{6}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_m \vert - \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_m \vert + 2 \vert \ldots \varphi_i \bar{\varphi}_m \ldots \varphi_k \vert]$
$C_\beta^2(i \to k)$	0	1	$\frac{1}{\sqrt{6}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_{m'} \vert - \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_{m'} \vert + 2 \vert \ldots \varphi_i \bar{\varphi}_{m'} \ldots \varphi_k \vert]$
$B^3(m, m' \to k)$	0	0	$\vert \ldots \varphi_k \vert$
$D_\alpha(i \to m, m')$	1	1	$\frac{1}{\sqrt{2}} [\vert \ldots \varphi_i \bar{\varphi}_{m'} \ldots \varphi_m \vert + \vert \ldots \varphi_i \bar{\varphi}_m \ldots \varphi_{m'} \vert]$
$D_\beta(i \to m, m')$	1	1	$\frac{1}{\sqrt{6}} [\vert \ldots \varphi_i \bar{\varphi}_{m'} \ldots \varphi_m \vert - \vert \ldots \varphi_i \bar{\varphi}_m \ldots \varphi_{m'} \vert + 2 \vert \ldots \varphi_{m'} \bar{\varphi}_i \ldots \varphi_m \vert]$

Table 2. Configurations for the case $n = 3$

Designation	Occupation of		Wave function
	m	m'	
G^1	1	2	$\vert \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_m \vert$
G^2	2	1	$\vert \ldots \varphi_m \bar{\varphi}_m \varphi_{m'} \vert$
$B^1(m \to k)$	0	2	$\vert \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_k \vert$
$B^2(m' \to k)$	2	0	$\vert \ldots \varphi_m \bar{\varphi}_m \varphi_k \vert$
$C_\alpha^1(i \to k)$	1	2	$\frac{1}{\sqrt{2}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_m \vert + \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_m \vert]$
$C_\alpha^2(i \to k)$	2	1	$\frac{1}{\sqrt{2}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_m \bar{\varphi}_m \varphi_{m'} \vert + \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_m \bar{\varphi}_m \varphi_{m'} \vert]$
$C_\beta^1(i \to k)$	1	2	$\frac{1}{\sqrt{6}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_m \vert - \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_m \vert$ $+ 2 \vert \ldots \varphi_i \bar{\varphi}_m \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_k \vert]$
$C_\beta^2(i \to k)$	2	1	$\frac{1}{\sqrt{6}} [\vert \ldots \varphi_i \bar{\varphi}_k \ldots \varphi_m \bar{\varphi}_m \varphi_{m'} \vert - \vert \ldots \varphi_k \bar{\varphi}_i \ldots \varphi_m \bar{\varphi}_m \varphi_{m'} \vert$ $+ 2 \vert \ldots \varphi_i \bar{\varphi}_{m'} \ldots \varphi_m \bar{\varphi}_m \varphi_k \vert]$
$A^3(i \to m, m')$	2	2	$\vert \ldots \varphi_i \bar{\varphi}_m \ldots \varphi_{m'} \bar{\varphi}_{m'} \varphi_m \vert$
$E_\alpha(m, m' \to k)$	1	1	$\frac{1}{\sqrt{2}} [\vert \ldots \varphi_k \bar{\varphi}_m \varphi_{m'} \vert + \vert \ldots \varphi_k \bar{\varphi}_{m'} \varphi_m \vert]$
$E_\beta(m, m' \to k)$	1	1	$\frac{1}{\sqrt{6}} [\vert \ldots \varphi_k \bar{\varphi}_m \varphi_{m'} \vert - \vert \ldots \varphi_k \bar{\varphi}_{m'} \varphi_m \vert + 2 \vert \ldots \varphi_m \bar{\varphi}_k \varphi_{m'} \vert]$

lished elsewhere [16]. In all cases the indices m, m' represent a pair of degenerate MO's constituing the open shell.

The expressions for the diagonal matrix elements and those between ground and excited states of Table 1 have already been published by Hobey [17]. Upon rederivation, we have found a minor error in his Eq. (A3). It should be taken into account that the configurations in Tables 1 and 2 are not unambigously determined, because the degenerate open shell orbitals φ_m and $\varphi_{m'}$ are given only up to a unitary transformation between themselves. To get further insight into this, let us use degenerate open shell orbitals φ_n and $\varphi_{n'}$, which are related to the orbitals φ_m and $\varphi_{m'}$ by the following unitary transformation

$$\begin{pmatrix}\varphi_n\\ \varphi_{n'}\end{pmatrix}=\begin{pmatrix}\alpha & \beta\\ -\varepsilon\beta^* & \varepsilon\alpha^*\end{pmatrix}\begin{pmatrix}\varphi_m\\ \varphi_{m'}\end{pmatrix}\quad \begin{aligned}\alpha\alpha^*+\beta\beta^*&=1\\ |\varepsilon|&=1\,.\end{aligned}$$

We then obtain (for the case $n=1$) the following relations between the new configurations $\bar{X}$ (with φ_n, $\varphi_{n'}$) and the original ones (with φ_m, $\varphi_{m'}$):

$$\begin{aligned}
\bar{X}^1&=\alpha X^1+\beta X^2 \qquad\qquad X=G,\,C_\alpha,\,C_\beta\\
\bar{X}^2&=\varepsilon(-\beta^* X^1+\alpha^* X^2)\\
\bar{A}^1&=\alpha^2A^1+\beta^2A^2+\sqrt{2}\alpha\beta D_\alpha\\
\bar{A}^2&=\varepsilon^2(\beta^{*2}A^1+\alpha^{*2}A^2-\sqrt{2}\alpha^*\beta^*D_\alpha)\\
\bar{D}_\alpha&=\varepsilon[-\sqrt{2}(\alpha\beta^*A^1-\alpha^*\beta A^2)+(\alpha\alpha^*-\beta\beta^*)\,D_\alpha]\\
\bar{D}_\beta&=\varepsilon D_\beta\\
\bar{B}^3&=B^3\,.
\end{aligned}$$

On changing B for A, A for B, and D for E we get the same results for the case $n=3$.

Therefore, in the CI calculation the following two conditions are to be fulfilled:

a) if an orbital participating in the excitation is degenerate, we must include the configuration of the same type, where the second degenerate orbital participates in the excitation

b) if we take into account a configuration of the type A, we must include the corresponding configuration of the type D_α (B and E_α for the case $n=3$).

Model Calculations on the Cyclopentadienyl Radical

The above SCF CI computational scheme has been applied to the cyclopentadienyl radical within the framework of the PPP and CNDO methods. In the former we use the following semiempirical parameters: $I_C(\text{VSIP}, 2\pi)=11.22$ eV, $\gamma_{CC}=10.53$ eV, $\beta_{CC}=-2.318$ eV; two-centre $\gamma_{\mu\nu}$ are evaluated by the Mataga-Nishimoto formula. In the CNDO calculation we follow closely the original version of the method of Del Beñe and Jaffé [18], with a modification suggested later [19], i.e., using the Mataga-Nishimoto approximation for repulsion integrals.

Table 3. Electronic transitions in the cyclopentadienyl radical

Transition	Transition energy E (eV) and oscillator strength f						
	PPP[a]		CNDO DBJ[a]		Ref. [20]	Ref. [21]	Observed[b]
	E	f	E	f	E	E	E
$^2A_2'' \leftarrow {}^2E_1''$	2.99	0.015	3.70	0.001	4.02	4.92	3.69
$^2E_1'' \leftarrow {}^2E_1''$	5.55	0.000	4.94	0.000	5.34	6.54	
$^2E_2' \leftarrow {}^2E_1''$			5.13	0.000			
$^2E_1' \leftarrow {}^2E_1''$			5.29	0.004			
$^2A_1'' \leftarrow {}^2E_1''$	6.28	0.190	5.54	0.138	6.06	8.28	
$^2E_2'' \leftarrow {}^2E_1''$	6.42	0.010	5.83	0.002	5.79	8.16	

[a] This paper.
[b] Ref. [22].

In both calculations we assumed idealized geometries of a regular pentagon with $r_{CC} = 1.40$ Å and $r_{CH} = 1.10$ Å.

In the PPP approximation, we performed a complete CI calculation with all possible one-electron excitations, whereas in the CNDO calculation we took into account all one-electron excitations from the five occupied orbitals just below the open shell to the five virtual orbitals just above the open shell. The results of our calculations are summarized in Table 3.

Our results agree rather closely with those of Longuet-Higgins and McEwen [20] and Bouman [21], which were computed in the single transition approximation. All calculations predict only one $^2A_2'' \leftarrow {}^2E_1''$ transition in the visible region of the spectrum.

Acknowledgements. One of the authors (J.K.) thanks the Swiss National Foundation for a grant.

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