Some Numerical Analysis of the Omega Technique

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ABSTRACT

Numerical verifications of the equations deduced by Goodisman for the deviations of the atomic orbital populations and molecular orbital energies from their final self-consistent values have been carried out with six molecules. A generalization has also been introduced, covering thus the frequent case of using an average value as the starting population for the next iteration.

SUMARIO

Se llevaron a cabo verificaciones numéricas de las ecuaciones deducidas por Goodisman para las desviaciones de las poblaciones de los orbitales atómicos y las energías de los orbitales moleculares de sus valores finales auto-consistentes con seis moléculas. También, se introdujo una generalización que abarca el caso frecuente de utilizar un valor promedio como población de partida para la siguiente iteración.

I. INTRODUCCION

Solving a physical system's behavior usually requires the iterative solution of a set of non-linear parametric equations. The computational resolution consists of a cyclical procedure involving these equations until the sets of parameters and of results which they produce are consistent with each other. The Hartree-Fock-Roothaan SCF method [1,2] is a matrix eigenvalue problem of an iterative nature as described above. Semi-empirical methods for molecular electronic structures also involve this technique and self-consistency requirements are set up among Fock matrix elements and density matrix elements /3/.

For this kind of calculation scheme, there exists the possibility that successive parameter adjustment between cycles would produce divergencies of an absolute or oscillatory nature, as well as very slow convergence which, from a practical viewpoint, yields unsatisfactory results, too.

The previous knowledge of these inappropiate behaviours should be desirable in order to avoid unnecessary wasting of computing time. Furthermore, it could be possible to make, in a consistent and formally correct procedure, the necessary arrangements to overcome these shortcomings.

Goodisman analyzed the w-technique algebraically in order to make some statements about its convergence properties /4/. He derived simple equations showing how the deviations of the atomic orbital populations from their final self-consistent values change with succesive iterations. The results of considering these equations in several special cases, imply that the populations oscillate about their final values on successive iterations, as has actually been found experimentally /5/. In turn, this property suggested a simple means of speeding up convergence.

Goodisman's work can be considered as a starting point with respect to the study, in an analytical way, of the convergence properties of semi-empirical methods. Following a suggestion of Goodisman's regarding the interest in subsequent analysis of other molecular orbital theories, one of the present authors extended Goodisman's analysis to the w-β -variable method without /6/ and with /7/ inclusion of overlap integrals. Among several interesting conclusions reached in those two previous works, it was found that the characteristic alternation in sign on successive iterations for deviations of the populations from their final self-consistent values, is lost in those methods where the whole Fock matrix is varied in each iteration.

Only under very restrictive conditions such alternations would take place, so it was suggested a different simple way of speeding up convergence in the iterative cycle.

The three afromentioned communications /4,6,7/ made an analytical study without further numerical verifications of the equations deduced. The purpose of this paper is to compare, in a numerical way, the perturbational equations derived by Goodisman for the w-technique with "experimental" values of some molecules. In order to cover the frequent case of using an average (instead of the previous one), as the starting population for the next iteration, the equations given by Goodisman are generalized.

The paper is organized as follows: in Section II, we give the fundamental definitions and sketch the procedure to obtain the desired formulae for the deviations. The reader who is interested in finer details, has to resort to Refs. 4,6,7, where the complete procedure was originally presented.

Section III deals with the results and discussion. There we show six numerical examples for energy and population deviations.

The obtained values allow us to verife the good agreement between theoretically predicted and "experimental" values. Finally, some future lines of research in this field are indicated.

II. PERTURBATIVE EQUATIONS

As is usual in the w-technique, /8/ we assume that overlap integrals may be neglected. Then the secular equation is

$$\sum_{j=1}^{n} H_{ij}\, c_{ik} = E_k\, c_{ik} \qquad i = 1,2,\ldots,n \qquad (1)$$

where

$$H_{ii} \equiv \alpha_i = \alpha_o + = w\beta \quad (1 = q_i) \qquad (2)$$

$$H_{ij} \equiv \beta \qquad i \neq j \qquad (3)$$

and the population of atomic orbital i is calculated according to

$$q_i = 2 \sum_{k}^{(occ)} c_{ik}\, c_{ik} \equiv 2 \sum_{k}^{'} c_{ik}\, c_{ik} \qquad (4)$$

We are assuming real coefficients and that all molecular orbitals are either doubly occupied or empty to simplify notation.

The MO's ψ_k, as is usual in the LCAO approximation, are given in the form

$$\psi_k \sum_{i=1}^{n} c_{ik}\, \phi_i \equiv \sum_{i} c_{ik}\, \phi_i \qquad (5)$$

where the ϕ_i's are atomic orbitals.

The orthonormalization requirements for AO's under the assumption $S_{ij} = \delta_{ij}$ implies that

$$\sum_{i=1}^{n} c_{ik}\, c_{il} = \delta_{kl} \qquad (6)$$

while the unitary condition is

$$\sum_{k=1}^{n} c_{ik}\, c_{jk} = \delta_{ij} \qquad (7)$$

Denoting the exact, self-consistent values by bars, Eq. (1) has the form

$$\sum_{j} \bar{H}_{ij}\, \bar{c}_{jk} = \bar{E}_k\, \bar{c}_{ik} \qquad (8)$$

At some stage of the iterative procces, suppose we have

$$c_{ik} = \bar{c}_{ik} + \delta c_{ik} \qquad (9)$$

where δc_{ik} is the deviation of the coefficient c_{ik} from its final value "before" solving the secular equations. We use these coefficients to calculate the new Hamiltonian matrix elements H_{ij} according to Eqs. (2) and (4). The resolution of the secular equations leads to new coefficients $\tilde{c}_{ik}$, where

$$\tilde{c}_{ik} = \bar{c}_{ik} + \delta' c_{ik} \tag{10}$$

$\delta' c_{ik}$ indicates deviations of the coefficients from their final values "after" the resolution of the secular equations.

Then, we have the following equations to solve

$$\sum_j (\bar{H}_{ij} + \delta H_{ij})(\bar{c}_{jk} + \delta' c_{jk}) = (\bar{E}_k + \delta' E_k)(\bar{c}_{ik} + \delta' c_{ik}) \tag{11}$$

where $i,k = 1,2,\ldots,n$

Neglecting second-order terms, using Eq. (8), and applying the orthonormalization condition, we arrive at

$$\delta' E_k = - w\beta \sum_i \bar{c}_{ik}^{-2} \delta q_i \tag{12}$$

Then, the deviation of the orbital energy from its final value, **after** the iteration, is thus a weighted mean of the deviations of the populations from their final values **before** the iteration.

Expressing δc_{ik} in terms of the $\bar{c}_{il}$ and after some further algebraic manipulations, we arrive at

$$\delta' q_i = 4w\beta \sum_j \delta q_j \sum_k^{(occ)} \sum_l^{(unocc)} (\bar{E}_l - \bar{E}_k)^{-1} \bar{c}_{ik} \bar{c}_{il} \bar{c}_{jl} \bar{c}_{jk} \tag{13}$$

Eq. (13) gives the deviations of populations from their final values, after an iteration, in terms of their deviations before the iteration.

Eqs. (12) - (13) are a couple of the desired results for numerical testing purposes. For the more general case of using an average as the starting population for the iteration, Eq. (2) changes to

$$H_{ii} = \alpha_o + w\beta \left[1 - \frac{(q_i)_n + (q_i)_{n-1}}{2}\right] \tag{14}$$

Following identical steps as those indicated by Goodisman /4/ for Eq. (14), we found that Eqs. (12) — (13) change to the more general form

$$\delta' E_k = \frac{-w\beta}{2} \sum_i \bar{c}_{ik}^{-2} \left[(q_i)_n + (q_i)_{n-1}\right] \tag{15}$$

$$\delta' q_i = 2w\beta \sum^{occ} \sum^{unocc} \sum (\bar{E}_l - \bar{E}_k)^{-1} \bar{c}_{jl} \bar{c}_{jk} \bar{c}_{ik} \bar{c}_{il} \left[(\delta q_j)_n + (\delta q_j)_{n-1}\right] \tag{16}$$

Eqs. (15) - (16) are the other couple of the desired results for numerical testing purposes. Obviously, if $(\delta q_l)_{n-1} = (\delta q)_n$, then Eqs. (14) - (15) change to Eqs. (12) - (13).

III. RESULTS AND DISCUSSION

Fig. I displays the atomic numbering of the molecules chosen for the calculation by means of the w-technique.

For the allyl cation (a), trimenthyl-ciclopropene (c), and methyl-cyclo-heptatriene (e), we used the previous population in the iterative cycles, while for the allyl cation (a), methyl-cyclo-propene (b) and methyl-cyclo-pentadiene (d), we used an average population value.

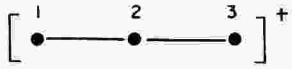
In order to analyse the results in a proper way, we deem it necessary to remember that Eqs. (12) - (13), as well as (15) - (16), were deduced under the assumption that deviations from the final self-consistent results are not too large, so as to allow us to linearize the equations and evaluate some of the unknowns (i.e. neglect of second-order terms in Eq. (11)). Thus, a better agreement is expected for the last cycles of the iteration, where diviations are relatively small.

In every case a factor 1.4 was used for the w-parameter. Tables I-VI show the results for Eqs. (12) - (15) and Tables VII-XII display the values for Eqs. (13) - (16). As it can be seen by direct inspection, there exists an overall good agreement between theoretical and experimental values. As previously stated, the concordance is better for the last cycles in each iterative process. Particularly noticeable is the alternation in sign for deviations on successive iterations, predicted theoretically and in full agreement with what has been found experimentally /5/.

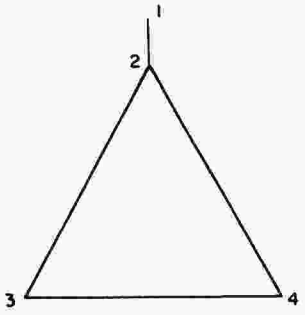
The numerical test thus shows that the chosen way of analysing the convergence properties of the w-techniques is an appropriate one.

The procedure and the analysis given previously as well as the numericla test presented above, should be applicable to any theoretical model, such as CNDO, MINDO, INDO, EHT, PCILO, etc., which, like the simple w-technique, modifiy matrix elements of the Hamiltonian as a function of calculated populations in order to make large populations buildups unfavorable.

At present, works aiming at these models are being carried out in our laboratory. Results will be published elsewhere in the near future.



(a)



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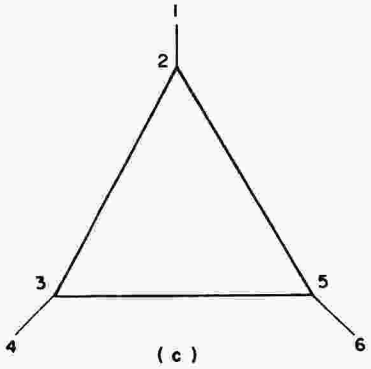

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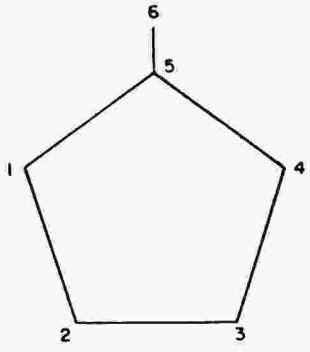

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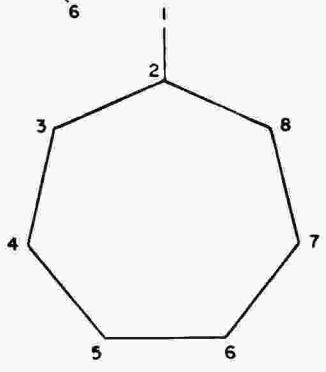

(e)

FIGURA 1.

TABLE I — MOLECULE (a)

δE_k = exp. dev. from final value of the k-th level ($\beta .10^{-4}$ units)

$\delta' E_k$ = same dev. calc. acc. to Eq. (12) ($\beta .10^{-4}$ units)

N° Iter.	δE_1 —	$\delta' E_1$ —	δE_2 —	$\delta' E_2$ —	δE_3 —	$\delta' E_3$ —
0	4137	----	6012	----	3851	----
1	210	285	−988	−988	778	703
2	−238	−200	694	692	−456	−494
3	126	146	−505	−506	380	361
4	−114	−104	360	359	−246	−257
5	69	75	−261	−261	191	186
6	− 57	− 54	187	187	−130	−133
7	37	39	−135	−135	98	96
8	− 29	− 29	98	97	− 68	− 70
9	19	21	− 70	− 68	50	51
10	− 15	− 15	51	50	− 36	− 37
11	10	10	− 36	− 37	26	26
12	− 8	− 7	27	26	− 19	− 19
13	5	5	− 18	− 20	14	14
14	− 4	− 4	14	13	− 10	− 9
15	2	2	− 9	− 10	7	6
16	− 3	− 2	7	6	− 5	− 5
17	1	1	− 5	− 6	4	4
18	− 2	− 1	4	3	− 2	− 3
19	0	0	− 2	− 3	2	2
20	− 1	− 1	2	1	− 1	− 1
21	0	0	− 1	− 2	1	1
22	− 1	− 1	1	0	− 1	− 1
23	1	1	0	− 1	1	1
24	0	− 1	1	0	0	− 1

TABLE II — MOLECULE (c)

See note at the top of Table I.

Levels 2 and 3, 5 and 6, are degenerate.

N° Iter.	δE_1	$\delta' E_1$	δE_2	$\delta' E_2$	δE_4	$\delta' E_4$	δE_5	$\delta' E_5$
0	2862	----	312	----	6021	----	8570	----
1	−1338	211	−126	2407	− 1301	−210	−2513	−2407
2	448	− 81	43	− 926	564	80	968	926
3	− 175	30	− 17	343	− 200	− 30	− 358	− 343
4	65	− 11	6	− 129	77	11	136	129
5	− 24	4	− 3	49	− 29	− 4	− 50	− 49
6	10	− 2	1	− 19	11	2	20	19
7	− 3	1	0	7	− 4	0	− 7	− 7
8	2	0	0	− 3	1	0	3	3
9	0	0	0	1	− 1	0	− 1	− 1
10	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0

TABLE III — MOLECULE (e)

See note at the top of Table I.

Only the first twenty iterations have been taken.

Nº Iter.	δE_1 —	$\delta' E_1$ —	δE_2 —	$\delta' E_2$ —	δE_3 —	$\delta' E_3$ —	δE_4 —	$\delta' E_4$ —
0	220	----	1824	----	1878	----	1873	----
1	— 15	30	2	— 11	16	15	— 21	— 14
2	10	13	— 5	— 5	— 12	— 10	3	5
3	— 8	— 9	4	— 3	7	7	1	0
4	7	8	— 2	— 7	— 3	— 3	— 4	— 4
5	— 5	— 6	2	2	1	2	4	5
6	5	6	— 1	— 1	0	0	— 6	— 4
7	— 4	— 5	1	0	0	— 1	5	4
8	4	4	— 1	— 1	1	0	— 6	— 5
9	— 3	— 5	1	1	— 1	— 1	5	5
10	4	4	— 1	— 1	1	3	— 5	— 5
11	— 3	— 4	1	1	0	0	4	4
12	3	4	0	— 1	1	0	— 4	— 6
13	— 2	— 2	1	1	0	0	3	3
14	3	3	0	— 1	1	1	— 4	— 4
15	— 2	— 2	1	0	0	— 1	3	4
16	2	3	0	— 1	1	1	— 3	— 4
17	— 2	— 1	1	0	0	— 1	2	2
18	2	2	0	— 1	— 1	0	— 3	— 3
19	— 1	— 1	1	— 1	0	0	2	2
20	2	2	0	— 1	1	0	— 2	— 2

TABLE III — MOLECULE (e) (continued)

See note at the top of Table I.

Only the first twenty iterations have been taken.

N° Iter.	δE_5	$\delta' E_5$	δE_6	$\delta' E_6$	δE_7	$\delta' E_7$	δE_8	$\delta' E_8$
0	1850	----	1970	----	1988	----	1948	----
1	54	52	— 68	— 71	7	6	— 23	— 24
2	— 54	— 56	55	56	5	— 6	7	5
3	52	41	— 51	— 49	— 2	2	— 2	— 2
4	— 45	— 47	46	47	0	0	1	1
5	44	42	— 43	— 46	0	— 2	0	— 1
6	— 38	— 40	39	40	1	1	— 1	0
7	37	34	— 37	— 36	— 1	— 2	1	1
8	— 32	— 34	33	33	1	0	— 1	— 1
9	31	30	— 31	— 30	— 1	— 2	1	1
10	— 27	— 28	28	29	1	0	— 1	— 1
11	27	25	— 26	— 25	0	— 1	1	0
12	— 23	— 25	23	24	1	0	— 1	— 1
13	23	21	— 22	— 21	0	— 1	1	1
14	— 19	— 21	20	21	1	1	— 1	0
15	19	17	— 19	— 17	0	— 1	0	0
16	— 16	— 18	17	17	1	0	— 1	0
17	16	15	— 16	— 14	0	— 1	0	0
18	— 13	— 15	14	13	1	0	— 1	— 1
19	14	12	— 14	— 13	0	— 2	0	— 1
20	— 11	— 13	12	13	1	0	— 1	0

TABLE IV — MOLECULE (a)

δE_k = exp. dev. from final value of the k-th level ($\beta .10^{-3}$ units).

$\delta' E_k$ = same deviation calc. acc. to Eq. (13) ($\beta .10^{-3}$ units)

N° Iter.	δE_1	$\delta' E_1$	δE_2	$\delta' E_2$	δE_3	$\delta' E_3$
0	414	---	601	---	385	---
1	21	14	—99	—50	78	35
2	4	4	—15	—15	11	10
3	1	0	— 2	— 3	2	1
4	0	0	0	— 1	0	0
5	0	0	0	— 1	0	0

TABLE V — MOLECULE (b)

See note at the top of Table IV.

N° Iter.	δE_1	$\delta' E_1$	δE_2	$\delta' E_2$	δE_3	$\delta' E_3$	δE_4	$\delta' E_4$
0	70	---	384	---	435	---	444	---
1	—2	5	— 2	0	1	0	— 3	—3
2	—1	5	— 1	—1	0	—1	— 1	0
3	0	3	0	1	0	—1	0	0
4	0	1	0	0	0	—1	0	0

TABLE VI — MOLECULE (d)

See note at the top of Table IV.

N° Iter.	δE_1	$\delta' E_1$	δE_2	$\delta' E_2$	δE_3	$\delta' E_3$	δE_4	$\delta' E_4$	δE_5	$\delta' E_5$	δE_6	$\delta' E_6$
0	−21	---	56	---	85	---	118	---	−68	---	0	---
1	24	14	50	−19	37	19	−89	−52	42	22	37	16
2	− 6	− 5	− 5	− 4	9		13	13	− 5	− 4	−6	− 6
3	0	− 1	− 1	− 1	2	2	− 4	− 4	3	4	−1	− 2
4	0	− 1	0	− 1	1	1	0	0	0	1	−0	− 1
5	0	0	0	− 1	0	− 1	0	0	0	1	0	0

TABLE VII — MOLECULE (a)

δq_i = exp. dev. from final value referring to atom i . (10^{-4} scale)

$\delta' q_i$ = same dev. calc. acc. to Eq. (15) (10^{-4} scale)

N° Iter.	δq_1	$\delta' q_1$	δq_2	$\delta' q_2$
0	702	----	—1412	----
1	—499	— 502	990	1017
2	357	362	— 723	— 713
3	—261	— 254	514	521
4	182	191	— 373	— 370
5	—138	— 128	267	269
6	92	102	— 193	— 192
7	— 73	— 64	139	139
8	46	55	— 100	— 100
9	— 40	— 32	72	71
10	22	32	— 52	— 52
11	— 23	— 13	37	38
12	9	19	— 27	— 27
13	— 14	— 3	19	20
14	3	13	— 14	— 14
15	— 9	1	10	10
16	— 1	9	— 7	— 7
17	— 6	4	5	5
18	— 3	7	— 4	— 3
19	— 5	5	3	3
20	— 4	6	— 2	— 2
21	— 3	6	1	2
22	— 6	4	— 1	— 1
23	— 2	8	1	1
24	— 7	3	0	1

TABLE VIII — MOLECULE (c)

See note at the top of Table VII.

N° Iter	δq_1	$\delta' q_1$	δq_2	$\delta' q_2$
0	—1885	----	1885	----
1	722	1116	— 722	—865
2	— 268	— 427	268	331
3	101	159	— 101	—122
4	— 38	— 60	38	46
5	14	23	— 14	— 18
6	— 5	— 8	5	7
7	2	3	— 2	— 2
8	— 1	0	1	1
9	0	0	0	0
10	0	0	0	0
11	0	0	0	0

TABLE IX — MOLECULE (e)

See note at the top of Table VII.

Only the first twenty iterations have been taken.

N° Iter.	δg_1	$\delta' g_1$	δg_2	$\delta' g_2$	δg_3	$\delta' g_3$	δg_4	$\delta' g_4$	δg_5	$\delta' g_5$
0	−36	---	143	---	−67	---	−24	---	11	---
1	− 2	− 1	−104	− 102	71	39	− 30	− 30	14	13
2	1	1	82	83	− 65	− 67	35	37	−12	−12
3	− 2	− 1	− 70	− 68	61	60	−38	− 36	12	11
4	1	1	59	60	− 55	− 56	36	37	−11	−11
5	− 1	− 1	− 54	− 52	52	51	−35	− 33	11	10
6	1	1	47	48	− 46	− 48	32	32	− 9	−10
7	− 1	− 1	− 42	− 42	44	43	−31	− 30	10	8
8	1	1	39	40	− 39	− 41	28	28	− 8	− 9
9	− 1	− 1	− 37	− 35	37	36	−27	− 26	9	8
10	1	1	33	34	− 33	− 34	23	24	− 7	− 8
11	− 1	− 1	− 31	− 30	32	29	−23	− 20	8	7
12	0	1	27	28	− 28	− 29	20	20	− 6	− 7
13	− 1	− 1	− 27	25	27	26	− 20	− 18	7	5
14	0	1	23	25	− 23	− 25	17	17	− 5	− 6
15	− 1	0	− 23	20	23	21	− 17	− 15	6	5
16	0	0	19	20	− 19	− 21	14	15	− 4	− 5
17	− 1	0	− 19	− 17	20	21	− 14	− 13	5	3
18	0	0	16	17	− 16	− 17	12	14	− 3	− 3
19	− 1	0	− 16	− 15	17	15	− 12	− 11	4	2
20	0	0	14	15	− 14	− 16	10	12	− 3	− 2

TABLE X — MOLECULE (a)

δq_i = exp. dev. from final value referring to atom i . (10^{-3} scale)

$\delta' q_i$ = same dev. calc. acc. to Eq. (16) (10^{-3} scale)

N° Iter.	δq_1 —	$\delta' q_1$	δq_2 —	$\delta' q_2$
0	71	----	—141	----
1	—49	—25	99	51
2	— 7	— 8	15	15
3	— 1	— 1	2	2
4	0	0	1	1
5	0	0	0	0

TABLE XI — MOLECULE (b)

See note at the top of Table X.

N° Iter.	δq_1 —	$\delta' q_1$	δq_2 —	$\delta' q_2$	δq_3 —	$\delta' q_3$
0	—10	---	10	---	0	---
1	0	0	— 5	— 2	2	1
2	0	0	—1	— 1	0	1
3	0	0	—1	0	0	0
4	0	0	0	0	0	0

TABLE XII — MOLECULE (d)

See at the top of Table X.

N° Iter.	δq_1	$\delta' q_1$	δq_2	$\delta' q_2$	δq_5	$\delta' q_5$	δq_6	$\delta' q_6$
0	—23	---	33	---	—68	---	181	---
1	— 2	—1	51	24	122	58	—221	—107
2	11	11	—16	—15	—24	—24	35	33
3	0	—1	2	4	2	2	— 6	— 7
4	1	0	— 1	1	— 1	—1	1	1
5	0	0	0	1	0	0	0	0

BIBLIOGRAFIA

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