

## A Remark on the Comparison between the Roothaan Open Shell and Half-Electron Method

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Using Pople  $\pi$ -electron and CNDO/2 approaches for various open-shell ground states, a comparison is made for total SCF energies calculated by the half-electron and Roothaan methods. Types of electronic configurations are ascertained for which the two methods yield identical total energies.

Unter Anwendung der  $\pi$ -Elektronen- und der CNDO/2-Näherung werden die totalen SCF-Energien für verschiedene "open shell"-Grundzustände im "half electron"-Verfahren und im Roothaan-schen Verfahren verglichen. Es werden Typen von elektronischen Konfigurationen ermittelt, für die beide Verfahren zu der gleichen Gesamtenergie führen.

En utilisant les méthodes  $\pi$ -électroniques de Pople et CNDO/2 pour des états fondamentaux avec couche incomplète différente, on fait la comparaison pour les énergies totales de champs autocohérent calculées par la méthode «sémiélectronique» et celle de Roothaan. On a déterminé les types des configurations électroniques pour lesquels ces deux méthodes livrent les énergie totales identiques.

### Introduction

The open shell SCF procedure of Longuet-Higgins and Pople [1] has proved very useful for the study of electronic spectra and ground state properties of radicals [2] having a singly occupied nondegenerate orbital. Dewar and co-workers [3] derived this procedure in a different way, extended it to treatments of triplet states [4] and called it "the half-electron method". Recently a general extension of this method was reported [5] which makes it possible to treat any electronic configuration regardless of symmetry and spin multiplicity.

The half-electron procedure is an approximate open shell method because some singly excited configurations interact with the ground state configuration [2]. Some authors argue that its deficiencies are negligible, inasmuch as its results for heat of formation of radicals are reasonable [2, 3, 6–8], and for many other characteristics are very close [9] to values given by the Roothaan open shell method [10]. Others (e.g. [11]) prefer the Roothaan method, which can be anticipated to give more accurate heats of formation. Nevertheless this method is inferior to the half-electron method in two respects:

1. Open shell calculations require an entirely new computer program, whereas the half-electron method affords open shell SCF results by means of a closed shell program with only slight modifications (cf. the next section).

2. In general the Roothaan SCF procedure is slower to converge, sometimes even diverging [12].

In the present paper we compare the two methods and examine the possibility of performing routine semiempirical calculations on systems with degenerate open shells.

### Calculations

We employed the standard SCF  $\pi$ -electron method of Pople and the standard CNDO/2 method, combining them with the half-electron or Roothaan open shell procedures. In the  $\pi$ -electron calculations we used the following parameters:  $I_C = 11.22$  eV;  $\gamma_{CC} = 10.53$  eV; two-centre repulsion integrals were evaluated by means of the formula of Mataga and Nishimoto. If the half-electron method is adopted, the  $F$  matrix elements in the frame of both computational schemes remain unchanged, except for the new definition of the electron-density and bond-order matrix

$$P_{\mu\nu} = \sum_k 2c_{k\mu}c_{k\nu} + \sum_m 2f c_{m\mu}c_{m\nu}, \quad (1)$$

where  $k$  and  $m$  run over closed shell and open shell MO's respectively, and  $f$  is the fractional occupation [10] of the open shell (cf. Table 1). Both in the  $\pi$ -electron and CNDO/2 treatments, the half-electron total energies of open shell ground states were calculated by means of the following formulas [5]

$$E = E_R - \frac{1}{4}J_{mm} \quad \text{Doublet, nondegenerate } \varphi_m \text{ singly occupied} \quad (2)$$

$$E = E_R - \frac{1}{4}(J_{mm} + J_{nn} + 2K_{mn}) \quad \text{Triplet} \quad (3)$$

$$E = E_R - \frac{1}{16}(J_{mm} + J_{nn} + 4J_{nn} - 2K_{mn}) \quad \text{Doublet } \varphi_m \pm \varphi_n \text{ and } \varphi_m^2\varphi_n \pm \varphi_m\varphi_n^2 \text{ states} \quad (4)$$

where  $\varphi_m$  and  $\varphi_n$  are degenerate,  $J$  and  $K$  have usual meaning of coulomb and exchange integrals, and

$$E_R = \sum_k \varepsilon_k + \sum_m f \varepsilon_m + \frac{1}{2} \sum_{\mu} \sum_{\nu} H_{\mu\nu} P_{\mu\nu}, \quad (5)$$

where  $\varepsilon_k$  and  $\varepsilon_m$  are orbital energies of closed and open shells.

The use of the Roothaan open shell method in the PPP and CNDO/2 treatments has been described elsewhere [2, 13, 14]. Here we repeat only the formulas for the total energy

$$E = E_R - \sum_{\mu} \sum_{\nu} Q_{\mu\nu}(D_{C,\mu\nu} + f D_{O,\mu\nu}), \quad (6)$$

Table 1. Numerical constants for open shell states ( $\varphi_m$  and  $\varphi_n$  are degenerate) [10]

Configuration	Spin	$f$	$\alpha$	$\beta$
$\varphi_m$	Doublet	$\frac{1}{2}$	0	-2
$\varphi_m\varphi_n$	Triplet	$\frac{1}{2}$	0	-2
$\varphi_m \pm \varphi_n$	Doublet	$\frac{1}{4}$	$\frac{4}{3}$	$\frac{4}{3}$
$\varphi_m^2\varphi_n \pm \varphi_m\varphi_n^2$	Doublet	$\frac{3}{4}$	$\frac{4}{9}$	$\frac{4}{9}$

where  $E_R$  is given by (5) and

$$Q_{\mu\nu} = \delta_{\mu\nu} 2\alpha \sum_{\sigma} D_{0,\sigma\sigma} \gamma_{\mu\sigma} - \beta \gamma_{\mu\nu} D_{0,\mu\nu}, \quad (7)$$

$$D_{C,\mu\nu} = \sum_k c_{k\mu} c_{k\nu}; \quad D_{0,\mu\nu} = f \sum_m c_{m\mu} c_{m\nu}. \quad (8)$$

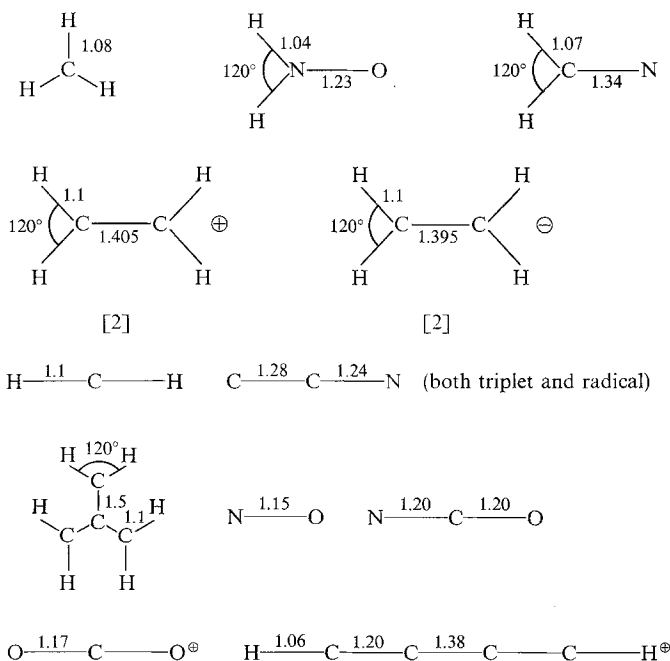
Total density matrix elements used in (5) are given by

$$P_{\mu\nu} = 2(D_{C,\mu\nu} + D_{0,\mu\nu}). \quad (9)$$

Numerical constants  $f$ ,  $\alpha$ ,  $\beta$  depending on the specific case, are summarized in Table 1. Formula (6) can be rewritten as

$$E = E_R - f^3 \sum_m \sum_n (2\alpha J_{mn} - \beta K_{mn}) - f \sum_k \sum_m (2\alpha J_{km} - \beta K_{km}). \quad (10)$$

In  $\pi$ -electron calculations, idealized molecular geometries were assumed, i.e.  $r_{CC} = 1.4 \text{ \AA}$  and  $\angle CCC = 120^\circ$ . In nonalternant hydrocarbons, regular five and seven-membered rings were considered. For  $\text{BH}_2$ ,  $\text{NH}_2$ ,  $\text{HCO}$ ,  $\text{NO}_2$ ,  $\text{NF}_2$ ,  $\text{CNC}$ ,  $\text{N}_2\text{O}^+$ ,  $\text{N}_3$ ,  $\text{BO}_2$  [15],  $\text{O}_2$ ,  $\text{O}_2^+$  [16] radicals, experimental geometries were employed. The  $\text{CNC}$  anion was calculated for the same geometry as the  $\text{CNC}$  radical. In the cyclopropenyl anion and radical, and in the cyclopentadienyl cation the idealized geometry ( $r_{CH} = 1.1 \text{ \AA}$ ,  $r_{CC} = 1.4 \text{ \AA}$ ) was considered. For the remaining systems, the following geometries were assumed (the order is the same as in Tables 3–6):



### Results and Discussion

The results of  $\pi$  electron calculations for unsaturated radicals having a singly occupied nondegenerate orbital are summarized in Table 2. Here both methods yield very similar results; except for the fulvene anion, the differences are negligible from the practical point of view. In light of these results, one can understand why

Table 2. Total SCF energies obtained by the open shell calculation in the  $\pi$  electron approximation for conjugated systems having a nondegenerate singly occupied molecular orbital. (All entries are in eV)

Radical	LHP <sup>a</sup>	R <sup>b</sup>	Difference
Butadiene <sup>+</sup>	- 40.074	- 40.077	0.003
Butadiene <sup>-</sup>	- 51.984	- 51.987	0.003
Hexatriene <sup>-</sup>	- 78.001	- 78.004	0.003
Octatetraene <sup>-</sup>	- 103.799	- 103.806	0.007
Decapentaene <sup>-</sup>	- 129.480	- 129.491	0.011
Dodecahexaene <sup>-</sup>	- 155.091	- 155.106	0.015
Allyl	- 36.711	- 36.711	0.0
Pentadienyl	- 62.153	- 62.175	0.022
Naphthalene <sup>-</sup>	- 132.436	- 132.441	0.005
Anthracene <sup>-</sup>	- 185.310	- 185.331	0.021
Tetracene <sup>-</sup>	- 237.885	- 237.910	0.025
Pentacene <sup>-</sup>	- 290.300	- 290.330	0.030
Phenanthrene <sup>-</sup>	- 185.167	- 185.188	0.021
Benz-[a]-anthracene <sup>-</sup>	- 237.923	- 237.960	0.037
Chrysene <sup>-</sup>	- 237.995	- 238.011	0.016
Pyrene <sup>-</sup>	- 212.274	- 212.274	0.0
Phenalenyl	- 169.022	- 169.022	0.0
Fulvene <sup>+</sup>	- 66.785	- 66.797	0.012
Fulvene <sup>-</sup>	- 79.661	- 79.859	0.198
Azulene <sup>+</sup>	- 120.092	- 120.159	0.067
Azulene <sup>-</sup>	- 132.176	- 132.198	0.022
Acenaphthylene <sup>-</sup>	- 159.681	- 159.685	0.004

<sup>a</sup> The method of Longuet-Higgins and Pople, i.e. the half-electron method.

<sup>b</sup> The Roothaan method.

heats of atomization of conjugated radicals are so well interpreted by the half-electron method [2, 3]. The radicals listed in Table 3 have formally the same electronic configuration – the nondegenerate frontier orbital is occupied by one electron. A somewhat more complicated picture of CNDO/2 results in Table 3 can be explained in part by examination of the formula for the open shell Roothaan total energy. On putting  $f = \frac{1}{2}$ ,  $\alpha = 0$ , and  $\beta = -2$ , (10) reduces to

$$E = E_R - \frac{1}{4} J_{mm} - \sum_k K_{km}. \quad (11)$$

If all exchange  $K_{km}$  integrals vanish, (11) becomes equivalent to (2) and the Roothaan SCF procedure becomes equivalent to that of the half-electron method, the

corresponding SCF eigen-values and eigen-vectors being identical. This is the case with  $\text{CH}_3$  and  $\text{NH}_2$  where an unpaired electron occupies a  $2p_z$  atomic orbital of carbon and nitrogen, respectively, and with the ethylene cation where an unpaired electron occupies a bonding  $\pi$  molecular orbital. The same situation

Table 3. Total CNDO/2 energies for systems having a non-degenerate singly occupied molecular orbital. (All entries are in eV)

Radical	LHP <sup>a</sup>	R <sup>a</sup>	Difference
$\text{BH}_2$	- 133.856	- 134.493	0.637
$\text{NH}_2$	- 352.391	- 352.391	0.0
$\text{HCO}$	- 704.143	- 704.178	0.035
$\text{NO}_2$	- 1317.506	- 1317.632	0.126
$\text{NF}_2$	- 1824.938	- 1825.070	0.132
$\text{CH}_3$	- 248.021	- 248.021	0.0
$\text{H}_2\text{CN}$	- 541.969	- 542.220	0.251
$\text{H}_2\text{NO}$	- 858.385	- 858.521	0.136
Ethylene <sup>+</sup>	- 449.570	- 449.570	0.0
Ethylene <sup>-</sup>	- 460.189	- 460.189	0.0

<sup>a</sup> See footnotes in Table 2.

occurs, if *one* from the  $K_{km}$  integrals, say  $K_{im}$ , is non-zero and the singly occupied orbital,  $\varphi_m$ , is *unambiguously* determined by molecular symmetry. By considering the forms of the  $\hat{F}$  operators [5, 10]

$$\hat{F}_{\text{half-electron}} = \hat{H}_c + \sum_k (2\hat{J}_k - \hat{K}_k) + f \sum_m (2\hat{J}_m - \hat{K}_m), \quad (12)$$

$$\begin{aligned} \hat{F}_{\text{Roothaan}} = \hat{H}_c + \sum_k (2\hat{J}_k - \hat{K}_k) + f \sum_m (2\hat{J}_m - \hat{K}_m) \\ + 2\alpha(\hat{L}_T - \hat{J}_0) - \beta(\hat{M}_T - \hat{K}_0) \end{aligned} \quad (13)$$

and by comparing the respective expanded  $\langle \varphi | \hat{F} | \varphi \rangle$  terms, we obtain for orbital energies

$$\epsilon_k^{\text{Roothaan}} = \epsilon_k^{\text{half-electron}} + K_{km}, \quad (14)$$

$$\epsilon_m^{\text{Roothaan}} = \epsilon_m^{\text{half-electron}}. \quad (15)$$

Thus the effect of both  $\hat{F}$  operators on closed shell and open shell orbitals is the same with exception of  $\varphi_i$ . Moreover,  $\varphi_m$  being unambiguously determined by molecular symmetry, all corresponding eigen-vectors (including  $\varphi_i$ ) yielded by the two methods are identical. Also orbital energies of all closed and open shells are identical, except  $\varphi_i$  for which (14) holds. By introducing (14) and (15) into (5) and (11),  $K_{im}$  cancels and the total energy in both computational schemes becomes identical. This is the case of the ethylene anion,  $\varphi_i$  and  $\varphi_m$  being the bonding and antibonding  $\pi$  MO's and of the allyl radical (cf. Table 2), where  $\varphi_i$  and  $\varphi_m$  are bonding and nonbonding  $\pi$  MO's. For the remaining six radicals in Table 3, the

average difference between the total energies given by the two methods amounts to 0.22 eV, i.e. to about 5 kcal/mole. In actual calculations on the heats of formation of radicals, as e.g. in the MINDO/2 treatment, this difference will probably be smaller. From (11) and (14) it can be inferred that the total energy differences are proportional to the  $K_{km}$  terms. As a consequence, replacement of theoretically calculated repulsion integrals by the smaller semiempirical values in the computation should give a smaller total energy difference. If the energy difference were still greater than the range of experimental errors, a small scaling factor could be employed as the half-electron values are always higher (or equal) to Roothaan values. Another way how to arrive at more accurate total energies is to mix the half-electron SCF ground state with several A-type and B-type singly excited configurations (for a description of the CI treatment see [2]).

Table 4. Total CNDO/2 energies for triplet state configurations having a doubly degenerate frontier orbitals. (All entries are in eV)

System	Half-electron method	Roothaan method	Difference
CNC <sup>-</sup>	- 677.587	- 677.587	0
CCN <sup>-</sup>	- 681.278 <sup>a</sup>	no convergence	—
O <sub>2</sub>	-1000.588	-1000.588	0
CH <sub>2</sub>	- 219.921	- 219.921	0
Trimethylenemethane	- 884.967	- 884.967	0
Cyclopropenyl <sup>-</sup>	- 627.996	- 627.996	0
Cyclopentadienyl <sup>+</sup>	-1052.505	-1052.505	0

<sup>a</sup> No convergence unless the damping [17] with the factor 0.5 is employed.

Table 4 comprises data for several triplet state configurations having frontier  $\varphi_m$  and  $\varphi_n$  degenerate. Here analogous expressions to (11), (14) and (15) hold:

$$E = E_R - \frac{1}{4}(J_{mm} + J_{nn} + 2K_{mn}) - \sum_k K_{km} - \sum_k K_{kn}, \quad (16)$$

$$\varepsilon_k^{\text{Roothaan}} = \varepsilon_k^{\text{half-electron}} + K_{km} + K_{kn}, \quad (17)$$

$$\varepsilon_m^{\text{Roothaan}} = \varepsilon_m^{\text{half-electron}} \quad (18)$$

For all systems considered in Table 4 except CCN<sup>-</sup> the open shell  $\varphi_m$  and  $\varphi_n$  orbitals are unambiguously determined by molecular symmetry and all exchange integrals  $K_{km}$  and  $K_{kn}$  vanish except one  $K_{im}$  and one  $K_{in}$  integral. In CH<sub>2</sub> all these exchange integrals vanish. By comparing (3) and (16) and by making use of arguments given above in the discussion of doublet states, one can understand why both open shell treatments give the same total energies here also. In less symmetrical molecules such as CCN<sup>-</sup>, where a total energy difference is to be expected, the divergence of the Roothaan SCF procedure precludes any comparison.

Divergence of the Roothaan procedure was also found with all  $\phi_m \pm \phi_n$  and  $\phi_m^2 \phi_n \pm \phi_m \phi_n^2$  doublet systems listed in Tables 5 and 6. Either the oscillation of orbital levels reported by Sleeman [12] occurred (as in the case of  $O_2^+$ ), or the electronic configuration changed in the first iteration, the frontier open shell becoming nondegenerate. Neither damping [17] nor continuation in the SCF procedure with changed  $f$ ,  $\alpha$ , and  $\beta$  values lead to convergence. Unfortunately, no simple comparison of (4) and (10) serves to show where the Roothaan method can safely be replaced by the half-electron method. Therefore it seems the total energies obtained by the half-electron calculations for such systems as those in Tables 5 and 6 must be tested by means of the observed heats of formation.

Table 5. Total CNDO/2 energies calculated by the half-electron method for doublet state  $\phi_m \pm \phi_n$  configurations having a doubly degenerate frontier orbital occupied by one electron (in eV)

System	Half-electron method
CNC	-678.666
CCN	-680.763
$O_2^+$	-986.723
NO	-813.424
Cyclopropenyl	-631.014

Table 6. Total CNDO/2 energies calculated by the half-electron method for doublet  $\phi_m^2 \phi_n \pm \phi_m \phi_n^2$  configurations having a doubly degenerate frontier orbital occupied by three electrons (in eV)

System	Half-electron method
NCO	no convergence
$NNO^+$	no convergence
NNN	-941.576
$OCO^+$	-1171.165
OBO	-1090.641
Diacetylene <sup>+</sup>	-783.753

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