Quantum-chemical study of the properties of the excited states of organic molecules
II. Calculations of transition energies and geometries of molecules in the excited states by the electron-hole potential method

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The electron-hole potential (EHP) one-configuration SCF method, where the energy of the chosen excited state is optimized, has been investigated within semiempirical INDO parametrization. The method has been tested for the calculation of excitation energies and geometry in the lowest excited states of molecules (derivatives of formaldehyde and propinal, benzaldehyde, carbon dioxide, ketene, ammonia, and hydrogen cyanide). A comparison of the results of the EHP method, of an approach of virtual orbitals (VO) and of singly excited configuration interaction (SECI) has shown a qualitative improvement of the EHP results over the VO method. The EHP results are qualitatively comparable with those of SECI; the EHP method has an advantage of simplicity and computer time saving. This advantage is especially important for the larger AO basis (larger systems, *ab initio* calculations in extended AO bases, *etc.*).

Одноконфигурационный SCF метод — метод электрон-дырка потенциала (EHP), в котором энергия выбранного возбужденного состояния минимизирована, был применен в рамках полуэмпирической INDO параметризации. Этот метод был применен для расчета энергий возбужденных состояний и геометрий низших возбужденных состояний молекул — производных формальдегида и пропиналя, бензальдегида, двуокиси углерода, кетена, аммиака и цианистого водорода. Сравнение расчитанных данных EHP методом, данных полученных методом виртуальных орбиталей (VO) и данных метода взаимодействия однократно возбужденных конфигураций (SECI) показало, что данные EHP метода качественно лучше чем данные VO метода и сравнимы с качеством данных получен-

ных методом SECI. Выгода ЕНР метода в его простоте и в меньшей затрате расчетного времени. Эта выгода особенно важна для больших наборов АО (большие системы, *ab initio* расчеты в расширенных наборах АО и т.д.).

One of the ways for obtaining a wavefunction for the excited states of molecules is the EHP method proposed by *Morokuma* and *Iwata* [1]. Because of its formal simplicity and easy applicability as well as potential possibilities of computer time saving (compared with CI), we used this method in its one-configurational version for calculating transition energies of a series of carbonyl compounds and for optimizing geometry of some molecules in the excited states within semiempirical INDO approximation.

Theoretical

The EHP method starts from a set of molecular orbitals $\{\psi_i\}$ which diagonalize a Hartree—Fock operator for the ground state. The total wavefunction of the ground state is represented by Slater determinant

$$\Phi_0 = |\psi_1 \bar{\psi}_1 \psi_2 \bar{\psi}_2 \dots \psi_N \bar{\psi}_N| \tag{1}$$

Let us find a new set of MO's $\{\varphi_i\}$ (in the form of linear combination of MO's $\{\psi_i\}$) which minimize the total energy for the wavefunction describing the excited configuration formed *e.g.* by excitation from the m-th to k-th MO, *i.e.*

$$^{1,3}\Phi_{(m\to k)} = 2^{-1/2} (|\varphi_1 \bar{\varphi}_1 \dots \varphi_m \bar{\varphi}_k \dots \varphi_N \bar{\varphi}_N| \pm$$
$$\pm |\varphi_1 \bar{\varphi}_1 \dots \varphi_k \bar{\varphi}_m \dots \varphi_N \bar{\varphi}_N|) \tag{2}$$

(In this and other relations, the upper sign refers to singlet state and the lower to triplet state.) New MO $\{\varphi_i\}$ are expressed

$$\varphi_m = \sum_i^D a_{mj} \psi_j \tag{3a}$$

$$\varphi_k = \sum_i^V b_{kj} \psi_j \tag{3b}$$

where D is the subspace represented by doubly occupied MO's and the symbol V is assigned to the subspace of unoccupied (virtual) MO's in the ground state. Moreover, the condition of orthonormality of MO has to be retained, *i.e.*

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} \tag{3c}$$

Under these conditions, the wavefunction of the ground state expressed in new MO's $\{\varphi_i\}$, i.e.

$$\Phi_0 = |\varphi_1 \bar{\varphi}_1 \ldots \varphi_N \bar{\varphi}_N| \tag{4}$$

is identical with the original function ψ_0 because it was obtained by unitary transformation of occupied MO's of the ground state ψ_i and is invariant with respect to such transformation. The energy of the excited state described by the wavefunction (2) is

$$^{1,3}E_{(m \to k)} = \langle \Phi_{(m \to k)} | \hat{H} | \Phi_{(m \to k)} \rangle = E_0 + \langle \varphi_k | \hat{F} | \varphi_k \rangle - $$
$$- \langle \varphi_m | \hat{F} | \varphi_m \rangle - J_{km} + K_{km} \pm K_{km} \tag{5}$$

where E_0 is the energy of the ground state and J_{km} and K_{km} are the coulombic and exchange integrals. For the energy minimum $E_{(m \to k)}$ (5) under conditions (3a—3c) we have

$$(\hat{F} + \hat{J}_k - \hat{K}_k \pm \hat{K}_k) \varphi_i = \lambda_i \varphi_i \qquad i \in D$$
$$(\hat{F} - \hat{J}_m + \hat{K}_m \mp \hat{K}_m) \varphi_l = \gamma_l \varphi_l \qquad l \in V \tag{6}$$

which represent a pair of mutually coupled pseudoeigenvalue equations. Eqns (6) are solved by iteration approach. The wavefunction of the excited configuration formed from orbitals $\{\varphi\}$ by solving eqns (6) is orthogonal with respect to a function of the ground state and fulfils the Brillouin's theorem for the ground state, i.e. monoexcited configurations do not interact with the ground state configuration. The wavefunction $^s\Phi_{(m \to k)}$ does not interact with the configurations monoexcited to it, i.e.

$$\langle ^s\Phi_{(m \to k)} | \hat{H} | ^s\Phi_{(m \to l)} \rangle = 0$$
$$\langle ^s\Phi_{(m \to k)} | \hat{H} | ^s\Phi_{(n \to k)} \rangle = 0 \tag{7}$$

$$s = 1, 3$$

If $k \neq l$ and $m \neq n$, then the function $^s\Phi_{(n \to l)}$ is no more singly excited with respect to $^s\Phi_{(m \to k)}$ and the respective matrix element of Hamiltonian is nonzero, i.e.

$$\langle ^s\Phi_{(m \to k)} | \hat{H} | ^s\Phi_{(n \to l)} \rangle \neq 0 \tag{8}$$

This situation complicates the calculation of the monoexcited configuration (towards ground state configuration) degenerated or near degenerated with another monoexcited configuration (with respect to the ground state configuration again).

Eqns (6) can be expressed in the matrix form in the basis of the original MO's $\{\psi_i\}$

$$\mathbf{F}^D \mathbf{A} = \mathbf{A}\lambda$$
$$\mathbf{F}^V \mathbf{B} = \mathbf{B}\gamma \tag{9}$$

where **A** and **B** are matrices of the coefficients a_{ij} and b_{ij}, λ and γ are the diagonal matrices of eigenvalues, $\mathbf{F}^D$ and $\mathbf{F}^V$ are the square matrices with dimensions of subspaces D and V. The elements of these matrices have the form

$$F_{ij}^D = \delta_{ij} F_{ii} + \langle \psi_i | \hat{J}_k - \hat{K}_k \pm \hat{K}_k | \psi_j \rangle$$
$$F_{ij}^V = \delta_{ij} F_{ii} - \langle \psi_i | \hat{J}_m - \hat{K}_m \pm \hat{K}_m | \psi_j \rangle \qquad (10)$$

The energy of the excited state expressed by orbital energies of new MO's $\{\varphi_i\}$ is

$$^{1,3}E_{(m \to k)} = E_0 + \gamma_k - \lambda_m + J_{mk} - K_{mk} \pm K_{mk} \qquad (11)$$

For solving eqns (9), the construction of matrices $\mathbf{F}^D$ and $\mathbf{F}^V$ or matrix elements is substantial. We did this in semiempirical INDO approximation in the original parametrization [2].

Results and discussion

Calculation of transition energies

We tested the EHP method in INDO approximation for calculation of transition energies. Since the transition energies depend strongly on parametrization in semiempirical methods, the comparison with CI results is decisive for evaluating the suitability of the EHP method for computation of the transition energies. It is not our aim to evaluate the suitability of the respective semiempirical parametrization for reproduction of experimental data, although we report on them.

Calculations were done for $n \to \pi^*$ and $\pi \to \pi^*$ transitions on a series of carbonyl compounds and their fluorinated derivatives. This series was studied by *Davies* and *Elvin* [3] in testing the INDO—CI method for transition energies and dipole moments. Geometries of the molecules given in Table 1 are based on experimental data and were taken from Ref. [3]. Geometry of the basic skelet for propinals and acroleins was taken from nonfluorinated derivatives.

Table 2 contains results of calculations and data from [3]. Small differences in CI transition energies may be due to different extent of the used CI (the authors [3] do not give the number of configurations in CI). We used complete singly excited CI (CSECI) for the molecules *I* and *II* and for the rest of molecules we took 49 configurations corresponding to single excitations from seven highest occupied to seven lowest virtual MO's.

The EHP transition energy theoretically represents the upper limit for the CSECI value which may decrease by interactions of the type (8). These interactions are negligible at $n \to \pi^*$ transitions as is especially seen from the data for the molecules *I* and *II*. If CI does not include all singly excited configurations, the EHP wavefunction can be better (in terms of energy) than the CI wavefunction as it is for $n \to \pi^*$ transitions of the molecules *IV—X*.

Table 1

Geometry of molecules (data from Ref. [3])

	Bond length/10^{-10} m						Bond angle			
FCHO	CH	1.095	CF	1.338	CO	1.181	HCF	109.9°	HCO	127.3°
F_2CO	CF	1.312	CO	1.174			FCF	108°		
HC≡C—CH'O	C≡C	1.209	CH	1.055	CH'	1.106	CCO	123°47'	HCO	122°19'
	C—C	1.445	C=O	1.215			CCC	178°24'		
HC≡C—CFO	CF	1.32					*			
FC≡C—CHO	CF	1.28					*			
FC≡C—CFO							*			
H_2C=CH—CHO	CH	1.09	C=C	1.36	C—C	1.45	CCH	120°	CCC	122°5'
	C=O	1.22					CCO	122°5'		
H_2C=CH—CFO	CF	1.32					*			
F_2C=CF—CFO	CF	1.325					FCF	110°		
C_6H_5CHO	CC	1.39	C_6H_5—C	1.465						
	CH	1.08	CO	1.24	OCH	1.09	OCH	122°		

* The geometry of the basic skelets of fluorinated derivatives is the same as that of propinal and acrolein.

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Table 2

Energies for $n \to \pi^*$ and $\pi \to \pi^*$ transitions of a set of molecules

| Structure | Molecule | $E_{n \to \pi^*}$/eV | | | | | | | | | $E_{\pi \to \pi^*}$/eV | | | | | |
| | | Singlet | | | | | | Triplet | | | Singlet | | | Triplet | | |
		VO	VO"	CI	CI^a	EHP	exp^a	VO	CI	EHP	VO	CI	EHP	VO	CI	EHP
I	FCHO	6.17^b	6.60^b	5.87	6.30	5.89	5.60	5.73	5.37	5.37	14.91	10.89	14.90	8.49	7.62	7.64
II	F_2CO	8.01	8.00	7.76	7.80	7.77	6.50	7.61	7.31	7.31	14.64	10.70	14.64	8.41	7.94	7.95
III	$HC \equiv C—CHO$	5.66	5.70	4.39	4.40	4.40	3.70	5.26	3.85	3.86	12.96	10.17	12.95	7.80	6.15	6.38
IV	$FC \equiv C—CHO$	6.01	6.00	4.66	4.50	4.54	—	5.66	4.17	4.01	12.27	9.67	12.25	7.86	6.20	6.31
V	$HC \equiv C—CFO$	6.98	7.00	5.80	5.70	5.74	—	6.59	5.33	5.24	12.94	9.99	12.91	7.64	6.76	6.82
VI	$FC \equiv C—CFO$	7.21	7.20	6.01	5.90	5.86	—	6.87	5.56	5.37	12.41	9.76	12.38	7.84	6.39	6.34
VII	$H_2C = CH—CHO$	5.96	6.00	4.17	4.10	4.17	3.70	5.65	3.65	3.65	11.80	9.98	11.79	6.57	5.18	5.94
VIII	$H_2C = CH—CFO$	7.14	7.10	5.45	5.40	5.43	—	6.85	4.99	4.93	11.86	10.07	—	6.72	5.79	—
IX	$F_2C = CF—CFO$	7.51	7.50	5.54	5.60	5.47	—	7.24	5.08	—	10.06	8.42	9.99	5.72	5.04	5.08
X	$C_6H_5—CHO$	6.72	6.70	4.58	4.40	4.11	3.80	6.49	4.15	—	10.53	9.68	10.45	7.27	5.63	—

a) Data from Ref. [3].

b) The difference 0.43 in the two data is probably caused by a misprint in Ref. [3].

A different situation arises for $\pi \rightarrow \pi^*$ transitions. The EHP transition energies for singlet $\pi \rightarrow \pi^*$ transitions differ only slightly from the values calculated from original orbitals (VO approximation) of the ground state and the CI values are much lower. On the other hand, the energies of transitions from the ground state to the excited triplet $\pi \rightarrow \pi^*$ states computed by the EHP and CI methods have very close values. FCHO and F_2CO can be used for explanation. Table 3 shows CI

Table 3

CI expansion coefficients of the most important configurations for the $^{1,3}A'$ (FCHO) and $^{1,3}A_1$ (F_2CO)

Configurations	$^1A'$	$^3A'$
$2a'' \rightarrow 3a''$ $(\pi \rightarrow \pi^*)$	0.6380	0.9512
$1a'' \rightarrow 3a''$ $(\pi \rightarrow \pi^*)$	0.1023	0.3025
$6a' \rightarrow 8a'$ $(\sigma \rightarrow \sigma^*)$	0.6748	−0.0185
$6a' \rightarrow 9a'$ $(\sigma \rightarrow \sigma^*)$	−0.2635	0.0179
$2b_1 \rightarrow 3b_1$ $(\pi \rightarrow \pi^*)$	−0.7306	0.9777
$1b_1 \rightarrow 3b_1$ $(\pi \rightarrow \pi^*)$	−0.0662	0.2042
$6a_1 \rightarrow 7a_1$ $(\sigma \rightarrow \sigma^*)$	−0.6134	−0.0346
$6a_1 \rightarrow 8a_1$ $(\sigma \rightarrow \sigma^*)$	0.1516	0.0225
$4b_2 \rightarrow 5b_2$ $(n \rightarrow \sigma^*)$	0.1883	0.0175

expansion coefficients corresponding to configurations most contributing to the given state. The dominant configuration of the triplet state is $2\pi \rightarrow 3\pi^*$ and $1\pi \rightarrow 3\pi^*$ is with its contribution in the second place. The interaction of these configurations is also included in the EHP wavefunction. Contributions from other configurations are negligible. For singlets, the configuration $\pi \rightarrow \pi^*$ has the coefficient which is comparable with that in $\sigma \rightarrow \sigma^*$ configurations and contributions of other configurations of this type are not negligible. These configurations are not included in the EHP wavefunction (see eqn (8)). In these cases the use of two-configuration EHP [4] may improve the wavefunction since such modification of the EHP method includes configurations not interacting in single-configuration EHP in terms of eqn (8).

Geometry of molecules in excited states

To test the EHP method (in INDO parametrization) for optimization of geometry we have chosen five molecules in which one or two parameters were optimized. The obtained values were compared with the data calculated in VO

Table 4

Calculated and experimental values of some geometrical parameters

Molecule (Symmetry)	Optimized parameter	State	EHP INDO	VO^k INDO	exp^i	Other data	exp Ground state^j
NH$_3$ (C_{3v})	≮HNH	$^1A_1(n\to\pi^*)$	120°	120°	120°		107.8°
		$^3A_1(n\to\pi^*)$	120°	120°			
HCN (C_s)	≮HCN	$^1A''(a''\to a')$	127.5°	126.5°	125°	127.2^{oh} 127^{od}	180°
		$^1A'(a'\to a')$	106°	117°	—	108^{oc}	
	($R_{CN}/10^{-10}$ m)^a	$^1A''(a''\to a')$	1.300	1.302	1.297	1.318^b 1.300^d	1.156
		$^1A'(a'\to a')$	1.230	1.205	—	1.232^c	
CO$_2$ (C_{2v})	≮OCO	$^1B_2(b_2\to a_1)$	132.5°	132.5°	122°	132^{od}	180°
	($R_{CO}/10^{-10}$ m)^a	$^1B_2(b_2\to a_1)$	1.267	1.267	1.246	1.265^d	1.162
H$_2$CO (C_s)	α^e	$^1A''(n\to\pi^*)$	32°	0°	31°	31^{od}	
		$^3A''(n\to\pi^*)$	37°	0°	35.6^{of}		0°
		$^3A'(\pi\to\pi^*)$	28°	—	—		
	($R_{CO}/10^{-10}$ m)^a	$^1A''(n\to\pi^*)$	1.280	1.280	1.323	1.280^d	
		$^3A''(n\to\pi^*)$	1.280	1.280	1.291^f		1.21
		$^3A'(\pi\to\pi^*)$	1.380	—	—		

<div align="center">Table 4 (Continued)</div>

Molecule (Symmetry)	Optimized parameter	State	EHP INDO	VO[k] INDO	exp[i]	Other data	exp Ground state[i]
H_2CCO (C_s)	∢CCO	$^1A''(\pi \to \pi^*)$	128°	132°	—	127°[g] 138°[h] 147°[d]	
		$^3A''(\pi \to \pi^*)$	125°	130°	—		
		$^1A'(\pi \to \pi^*)$	115°	—	—		
		$^3A'(\pi \to \pi^*)$	120°	121°			180°

a) Bond lengths; b) *ab initio* CI results [10]; c) INDO/S CI results [9]; d) CNDO CI results [5]; e) α — angle of deviation of CO bond from the plane HCH; f) data from Ref. [11]; g) STO-3G [7]; h) *ab initio* CI [12]; i) experimental data from Ref. [6] if not stated otherwise; j) Other geometrical parameters were taken from experimental data [6]. k) Values obtained from MO's of the ground state.

approximation, with the experimental data, if available, and with other literature data obtained by different theoretical methods.

Optimization of one parameter (x) was done so that quadratic minimum was determined from three energies $E_2 (x)$, $E_1 (x - h)$, $E_3 (x + h)$ according to the relation

$$x_i = x_{i-1} + \frac{h}{2} \frac{E_1 - E_2}{E_1 + E_3 - 2E_2} \qquad (12)$$

The minimum was the starting point of the next three-point minimization which continued until the quantities obtained from the two subsequent steps differed by less than 0.005×10^{-10} m for bond lengths and $0.5°$ for bond angles. The value of h gradually decreased for bond lengths between 0.05×10^{-10} m and 0.005×10^{-10} m and for bond angles between $5°$ and $1°$. Optimization of the two parameters was repeated alternatively for both parameters.

Table 4 contains the results of calculations. The valence angle HNH was optimized for the NH_3 molecule in the excited states $^1A_1$ and $^3A_1$. According to experimental data in the first excited state, the originally pyramidal structure of the ground state of ammonia changes into planar; this change is well reproduced at the VO approximation level and the identical result was obtained by the EHP method.

We optimized the angle HCN and the bond R_{CN} in a HCN molecule. The HCN molecule is linear in the ground state. The value of the bond angle of $125°$ is reported for the excited state $^1A''$ The calculated VO value of $126.5°$ is closer to the experimental one than the EHP value of $127.5°$ which, however, approximates the *ab initio* CI value ($127.2°$), differences between the values being not important. The length of the CN bond increases during excitation from 1.156×10^{-10} m to 1.297×10^{-10} m. The EHP value calculated by us is identical with the CNDO CI value [5] and only slightly differs from the experimental value. Greater differences between VO and EHP data occur in the $^1A'$ state. The bond angle changes from $117°$ to $106°$ and the bond length from 1.205×10^{-10} m to 1.230×10^{-10} m. Although the experimental data are not available*, EHP values are very close to INDO CI data in contrast to VO results.

The linear structure of the CO_2 molecule also changes during excitation to the bent one. The bond angle calculated from VO ($132.5°$) and the bond length (1.267×10^{-10} m) do not vary in the EHP method and are in principle identical with the CNDO CI values.

Formaldehyde, which is planar in the ground state becomes pyramidal in the excited state. The CO bond lengthens simultaneously. The planar structure of the excited state (singlet and triplet) is, however, retained in VO approximation. The

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* Experimental value for the state $^1A'$ $141°$ [6] corresponds to configuration $\quad a' (a')^2 (a'')^2 a'$ but we considered configuration $\quad (a')^2 a' (a'')^2 a'$

"half electron" method in CNDO/2 parametrization predicts planar structure [5]. The minimum energy for pyramidal form is obtained only on inclusion of CI and the out-of-plane angle α in the $^1A''$ state assumes the value of 31° [5]. By using the EHP method, the expected change in geometry agrees well with experiment. The singlet $^1A''$ shows minimum at 32° and the triplet $^3A''$ at 37°. The experimental data are 31° and 35.6°. The optimal out-of-plane angle for the $^3A'$ state corresponding to $\pi \rightarrow \pi^*$ excitation is 28°. There is no experimental value for this state available because no $\pi \rightarrow \pi^*$ transition is observed in the spectrum of formaldehyde. The CO bond elongates in the singlet and triplet states $^{1,3}A''$ to 1.280×10^{-10} m already in VO approximation. Neither EHP method nor CI changes this value.

The change of the bond angle CCO in ketene was examined during excitation to the $^{1,3}A''$ and $^{1,3}A'$ states. There is no experimental evidence of this angle and, as seen from Table 4, different authors report different theoretical data for the $^1A''$ state. The angle of 128° calculated by us for this state is closest to the *ab initio* (STO-3G) value [7]. A relatively great difference between the EHP (128°) and CNDO CI value (147°) is surprising. The bond angle for the $^{1,3}A''$, $^3A'$ states decreases in the EHP method as compared with VO values. The state $^1A'$ is interesting; here the minimum is attained at 115° by the EHP method but no minimum occurs in this region for the VO energy curve (Fig. 1). The second
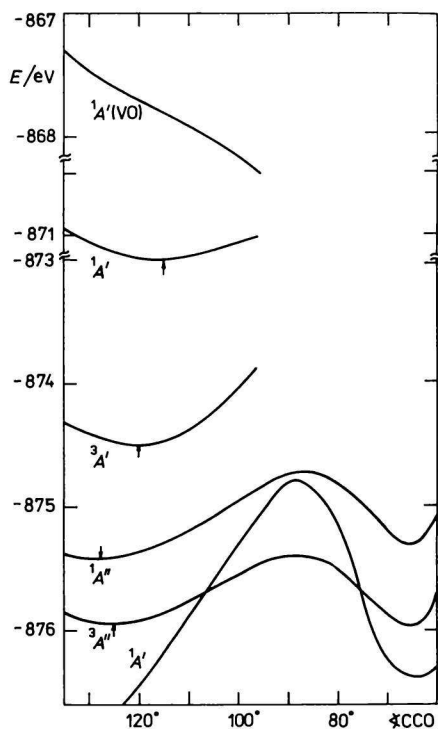

Fig. 1. A plot of the energies of the excited states of ketene against the bond angle CCO.

minimum appears for the $^{1,3}A''$ states and for the $^1A'$ ground state at about 65°. This structure accompanied with migration of one hydrogen leads to formation of oxirene

H—C=C—H (with O bridging the two carbons)

regarded as a possible intermediate of photochemical decomposition of ketene.

Conclusion

The significant advantage of the EHP method is that it is less time consuming as compared with CI. Even the operation memory demands are lower because of lower order of $\mathbf{F}^D$ and $\mathbf{F}^V$ matrices as compared to CI matrix. Table 5 shows that the computation time is substantially shorter than in CI, although the EHP method is iterative. The program for EHP computation was not optimized and thus the given time data could be lowered. The time saving would become more evident in *ab initio* calculations in an extensive AO basis where for larger systems the number of virtual MO's progressively increases. The most time consuming step in CI calculation is here the transformation of two-electron integrals from AO basis to MO basis. This transformation is a function of m^5—m^8 [8] (m is the number of functions of AO basis) and thus the computing time strongly increases with the

Table 5

Time data for EHP and CI calculations

	t_0 Ground state	$^{1,3}n \to \pi^*$ EHP			$^{1,3}\pi \to \pi^*$ EHP			CI	
		IS	IT	t_1	IS	IT	t_2	n	t_3
FCHO	25 s	3	3	45 s	3	3	45 s	36	2 min 35 s
F₂CO	38 s	3	3	1 min 24 s	1	3	56 s	48	5 min 23 s
HCCCHO	1 min 5 s	4	4	2 min 24 s	3	6	2 min 29 s	49	7 min 50 s
HCCCFO	1 min 15 s	3	3	3 min 2 s	4	5	5 min 12 s	49	8 min 17 s
FCCCHO	1 min 27 s	4	4	3 min 50 s	3	6	4 min 35 s	49	8 min 29 s
FCCCFO	1 min 39 s	3	3	5 min 56 s	3	5	6 min 35 s	49	9 min 17 s

IS — number of iterations in calculation of singlet.
IT — number of iterations in calculation of triplet.
n — number of configurations in CI calculation.
These timing data were obtained on a CDC 3300 computer. Calculations for other molecules (*VII—X*) were done on a Siemens 4004 computer. No partial timing data were available for these computations.

increasing basis. Operators $\hat{F}^V$ and $\hat{F}^D$ in the EHP method can be formulated directly in AO basis and the respective transformations are then not necessary.

But while in the EHP calculation we obtain a wavefunction for one excited state, CI calculation gives usually a spectrum of states. Advantages of the EHP method become evident in solutions of problems concerning one concrete excited state, like *e.g.* in optimization of geometry of molecules in the excited state or in studying the effect of medium on transition energies.

We see from optimization of the geometry of a limited set of molecules that the EHP method can yield results comparable and often identical *e.g.* with CI results obtained by the same semiempirical parametrization but also with the results of other methods. An optimal value of the respective parameter is sometimes obtained already at VO level, which does not vary by using the EHP or CI methods (*e.g.* HNH angle in NH_3, CN bond in HCN, OCO angle and CO bond in CO_2, CO bond in H_2CO). On the other hand, if the VO method fails, as *e.g.* in determining the out-of-plane angle in the excited states of H_2CO, the EHP method gives values comparable with CI results or with experimental data. This, together with the mentioned time saving advantage of the EHP method favours the applications of the EHP method to optimization of geometry in the excited states using the known gradient or gradientless methods.

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