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A Study of Possible Applications of the Half-Projected Hartree-Fock Method for Determining Singlet Excited States

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The Half-Projected Hartree-Fock model (HPHF) is proposed for determining open shell singlet states. Some properties of the HPHF wave function are reviewed in order to discuss its application to determining excited states of medium size molecules. A calculation procedure similar to that of the UHF method is described. Some results for the methylene biradical and formic acid are presented. The HPHF model is found to be useful for determining the lowest excited states.

INTRODUCTION

As well known, the Restricted Hartree-Fock model (RHF) is built as an antisymmetrized Hartree product of spinorbitals with the condition of double occupation of the orbitals. The wave function satisfies automatically the Pauli exclusion principle and is an eigenfunction of spin angular momentum operator S^2 . This means that two electrons with the same spin cannot be found at the same point, which is known as the Fermi hole. In each shell, however, two electrons with different spin functions have the same spatial function.

In addition, the Hartree-Fock approximation for atomic systems keeps the central field model, so that the Fock operator commutes with the single particle angular momentum operators, L^2 and \hat{L}_z . The RHF orbitals are then products of a radial part, $R_{nl}(r)$, by a spherical harmonic, $Y(l,m)$. In the same way, the RHF orbitals for molecular systems transform as irreducible representations of the symmetry group of the molecule. The majority of the quantum chemistry approaches are based on the RHF model, which describes well the energy of closed shell systems, but fails in describing open shell systems, as well as molecular dissociation into neutral fragments.

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As well known, the correlation energy is defined as the difference between the exact nonrelativistic energy and the RHF one: as an extension, all the effects that are not included into the RHF model are called electronic correlation effects.

In order to introduce some correlation effects in the wave function, the restrictions introduced into the RHF model have to be dropped. If the electrons of different spins are allowed to move in different orbitals, some correlation effects are introduced in the wave function. The wave function built in this model is called DODS (different orbitals for different spins).

When the wave function is built as a DODS Slater determinant, the model is known as Unrestricted Hartree-Fock (UHF). The energy obtained into the UHF model is expected to be generally lower than the RHF one. Such a DODS wave function, however, sometimes collapses variationally into the RHF one, especially near the equilibrium position in closed shell systems. But, this model predicts correctly the molecular dissociation into neutral fragments.

The UHF wave function is generally not a spin eigenstate of \hat{S}^2 , so that this function may be regarded as a superposition of states of different multiplicities.

To solve this problem, the use of projectors was proposed.¹ Models that use projection operators (orthogonal or nonorthogonal projection, projection over spin state or several states) are called Extended Hartree-Fock models. The projection over one spin eigenstate of a DODS Slater determinant yields a linear combination of determinants. This model is known as the Projected Hartree-Fock model (PHF).¹ Application of the full projection operator to a DODS Slater determinant of a system of $2n$ electrons gives rise to $(2n/n)$ determinants, so that the wave function becomes quickly intractable when the number of electrons increases.

There are other projector methods derived from the PHF model that present a simpler wave function. One of them is the Half-Projected Hartree-Fock model proposed by Smeyers,² in which the wave function is built using only two DODS Slater determinants for any number of electrons. This model yields results close to the PHF ones and better than the UHF ones. Initially, it was applied to small atomic and molecular systems.³⁻⁷ At present, with increasing computer facilities, this model can be a good alternative way to study relatively large systems.

Because the HPHF function is built by only two DODS determinants, this model seems to be suitable for studying open shell excited states of medium size molecules.⁸⁻¹² In the present work, we give some results obtained by using this model applied to methylene and formic acid.

Methylene is chosen as an example for singlet excited states orthogonal by symmetry to the ground state, formic acid as an example for states that are not orthogonal by symmetry to the ground state.

THEORY

The HPHF wave function in the case of $2n$ electron system is a linear combination of only two Slater determinants built up by different orbitals for different spins (DODS).² The first Slater determinant corresponds to the usual configuration of reference ground state and the second one has all its spin functions interchanged. This wave function is written as follows:

$$\Psi^{\text{HPHF}} = \frac{1}{2} \left\{ \left| a_1 \bar{b}_1 a_2 \bar{b}_2 \dots a_n \bar{b}_n \right| + (-1)^{S+n} \left| \bar{a}_1 b_1 \bar{a}_2 b_2 \dots \bar{a}_n b_n \right| \right\} \quad (1)$$

The HPHF wave function is obtained by the application of the half-projection operator on DODS reference function. The half-projection operator introduced in this model possesses the following form:

$$\hat{A}(S) = \frac{1}{2} \left[1 + (-1)^{S+n} \hat{P}_{\alpha\beta} \right] \quad (2)$$

where the $\hat{P}_{\alpha\beta}$ operator interchanges all the α spin functions by β ones, and reciprocally.

This operator projects the wave function into the space of spin eigenvalues, even or odd. This operator presents two additional properties:

$$\hat{A}(\text{even}) \hat{A}(\text{odd}) = 0 \quad (3)$$

$$\hat{A}(\text{even}) + \hat{A}(\text{odd}) = 1 \quad (4)$$

The action of this operator on the spin space divides it into two subspaces, one for the states of even spin and the other for those of odd spin.³

The HPHF wave function built for one singlet state contains no triplet contamination, but includes contaminations of quintuplet and states of higher multiplicities, but, as well known, the weight of these highly excited states in the ground state wave function is generally not significant.

In the same way, the HPHF wave function built for one triplet state contains no singlet contamination, but contaminations of heptuplet and states of higher multiplicities.

In order to obtain HPHF equations, the generalized Brillouin theorem is used:³

$$\langle \Psi^{\text{HPHF}} | \hat{H} - E | \Psi_{kt}^{\text{HPHF}} \rangle = 0 \quad (5)$$

where Ψ_{kt}^{HPHF} is an excited wave function in which one occupied a_k orbital has been replaced by an a_t one.

The HPHF wave function can be substituted into equation (5).

$$\langle D_{00} | \hat{H} | (D_{00}^{kt} + (-1)^{n+S} D_{nn}^{kt}) \rangle - E \langle D_{00} | (D_{00}^{kt} + (-1)^{n+S} D_{nn}^{kt}) \rangle = 0 \quad (6)$$

In this expression, D_{00} is a reference DODS Slater determinant and D_{nn} is the reference Slater determinant in which all the α spin functions have been permuted by the β ones. D_{00}^{kt} and D_{nn}^{kt} are corresponding DODS Slater determinants in which one occupied orbital, k has been replaced by virtual orbital t .

In order to deduce the HPHF equations, let us build Ψ^{HPHF} using so called *corresponding orbitals* which satisfy the following conditions:

$$\begin{aligned}\langle a_i | a_i \rangle &= \delta_{ii} \\ \langle b_j | b_j \rangle &= \delta_{jj}\end{aligned}\quad (7)$$

$$\langle a_k | b_m \rangle = \lambda_m \delta_{km} \quad (8)$$

$$(k, k' = 1, \dots, n) \quad (m, m' = 1, \dots, n)$$

Indices k, m, n, l denote occupied orbitals; u, t virtual (excited) orbitals or i, j in a general way. This labelling is important in the development of matrix elements.

The resulting expression can be developed in detail by using the Slater rules for evaluation of matrix elements. New interaction Fock and projection operators are then defined for the expressions of HPHF matrix elements:

$$\begin{aligned}\langle b_m | \hat{F}^{ba} | a_l \rangle &= \langle b_m | \hat{h} | a_l \rangle + \sum_j \frac{1}{\lambda_j} \left[\langle b_m b_j | a_l a_j \rangle + \langle a_l a_j | b_m b_j \rangle + \langle b_m b_j | a_j a_l \rangle \right] \\ \langle a_l | \hat{F}^{ba} | b_m \rangle &= \langle a_l | \hat{h} | b_m \rangle + \sum_j \frac{1}{\lambda_j} \left[\langle a_l a_j | b_m b_j \rangle + \langle b_m b_j | a_l a_j \rangle + \langle a_l a_j | b_j b_m \rangle \right]\end{aligned}\quad (9)$$

$$\hat{R}^{ab} = \sum_i \frac{1}{\lambda_i} |a_i\rangle \langle b_i| \quad \hat{R}^{ba} = \sum_i \frac{1}{\lambda_i} |b_i\rangle \langle a_i| \quad (10)$$

Using these expressions as well as the well known expressions for \hat{F}^a , \hat{F}^b , \hat{R}^a and \hat{R}^b of usual UHF theory, it is possible to write equation (6) as:

$$\langle D_{00} | \hat{H} (D_{00}^{kt} + (-1)^{n+S} D_{nn}^{kt}) - E (D_{00}^{kt} + (-1)^{n+S} D_{nn}^{kt}) \rangle = \langle \alpha_\kappa | \hat{H}^a | a_i \rangle \quad (11)$$

in which:

$$\hat{H}^a = \hat{F}^a + (\hat{R}^{ab} + \hat{R}^{ba}) (E_2 - \Lambda E) + \Lambda \{ \hat{R}^{ab} \hat{F}^{ba} (1 - \hat{R}^{ab}) + (1 - \hat{R}^{ba}) \hat{F}^{ab} \hat{R}^{ba} \} \quad (12)$$

with

$$\Lambda = (-1)^S \prod_i \lambda_i^2 \quad (13)$$

Taking now (6) into account, the following HPHF equation for the $\{a\}$ orbitals may be written:

$$\langle a_k | \hat{H}^a | a_i \rangle = 0 \quad (14)$$

A similar equation can be expressed for orbitals $\{b\}$ interchanging the a and b indexes in (12).

As Ψ^{HPHF} is invariant with respect to unitary transformations, two canonical sets of $\{a\}$ and $\{b\}$ which diagonalize the matrix representations of \hat{H}^a and \hat{H}^b operators, may be chosen:

$$\begin{aligned}\hat{H}^a |a_i\rangle &= \epsilon_i^a |a_i\rangle \\ \hat{H}^b |b_i\rangle &= \epsilon_i^b |b_i\rangle\end{aligned}\quad (15)$$

Expression (12) was developed in Ref. 6, and it is possible to show⁷ that the diagonal part of this expression is equivalent to the expression given by Smeyers *et al.*:⁵

$$\hat{H}^\alpha = \sum_{k=1}^n (1 - \sum_{i \neq k} \hat{P}_i^{\alpha\alpha}) \hat{H}_k^\alpha \sum_{k=1}^n (1 - \sum_{i \neq k} \hat{P}_i^{\alpha\alpha}) \quad (16)$$

where the operators $\hat{P}^{\alpha\alpha}$ and \hat{H}^α are:

$$\begin{aligned}\hat{P}_i^{\alpha\alpha} &= |a_i\rangle \langle a_i| \\ \hat{H}_k^\alpha &= \hat{F}^\alpha + \frac{\Lambda E_{\text{UHF}} - E_{\text{CROSS}}}{1 + \Lambda} \left[1 - \frac{\hat{P}_k^{\beta\beta}}{\lambda_k^2} \right] + \frac{\Lambda}{\lambda_k^2} \{ (1 - \hat{R}^{\beta\alpha}) \hat{F}^{\alpha\beta} \hat{P}_k^{\beta\beta} + \hat{P}_k^{\beta\beta} \hat{F}^{\beta\alpha} (1 - \hat{R}^{\beta\alpha}) \}\end{aligned}\quad (17)$$

E_{UHF} is the total electronic UHF energy.

The expectation value for this HPHF energy is:

$$E_{\text{HPHF}} = \frac{E_{\text{UHF}} + (-1)^S E_{\text{CROSS}}}{1 + (-1)^S \Lambda} \quad (18)$$

E_{UHF} value is obtained from the first DODS determinant:

$$E_{\text{UHF}} = \frac{1}{2} \sum_{m=1}^n [\langle a_m | \hat{h} + \hat{F}^a | a_m \rangle + \langle b_m | \hat{h} + \hat{F}^b | b_m \rangle] \quad (19)$$

E_{CROSS} value is the cross interaction term between both the first and the second DODS determinants. This term is responsible for the energy lowering of the HPHF model with respect to the UHF one.⁴

$$E_{\text{CROSS}} = \Lambda \left\{ \sum_i^n \frac{2}{\lambda_i} [\langle a_i | \hat{h} | b_i \rangle] + \sum_i^n \sum_j^n \frac{1}{\lambda_i \lambda_j} [2 \langle a_i a_j | b_i b_j \rangle - \langle a_i a_j | b_j b_i \rangle] \right\} \quad (20)$$

In order to calculate the excited states using the Half-Projected Hartree-Fock model, the expressions of \hat{F}^{ab} , $\hat{F}^{\beta\alpha}$, \hat{R}^{ab} and $\hat{R}^{\beta\alpha}$ have to be modified. The summations have to run over all occupied orbitals, except for the orbital pair whose overlap is zero,⁸ in order to avoid singularities. This feature really occurs in the monoexcited configurations:

$$\langle a_k | b_u \rangle = 0$$

$$\hat{R}^{ab} = \sum_{j \neq k}^n \frac{1}{\lambda_j} |a_j\rangle \langle b_j| \quad \hat{R}^{ba} = \sum_{j \neq k}^n \frac{1}{\lambda_j} |b_j\rangle \langle a_j| \quad (21)$$

$$\hat{R}_0^{ab} = |a_k\rangle \langle b_k| \quad \hat{R}_0^{ba} = |b_k\rangle \langle a_k|$$

$$\langle a_l | \hat{F}^{ab} | b_m \rangle = \langle a_l | \hat{H} | b_m \rangle + \sum_{j \neq k}^n \frac{1}{\lambda_j} [\langle a_l a_j | b_m b_j \rangle + \langle b_m b_j | a_l a_j \rangle + \langle a_l a_j | b_j b_m \rangle]$$

$$\langle b_m | \hat{F}^{ab} | a_l \rangle = \langle b_m | \hat{H} | a_l \rangle + \sum_{j \neq k}^n \frac{1}{\lambda_j} [\langle b_m b_j | a_l a_j \rangle + \langle a_l a_j | b_m b_j \rangle + \langle b_m b_j | a_j a_l \rangle] \quad (22)$$

It is also necessary to define the new Fock operators \hat{F}_0^{ab} and \hat{F}_0^{ba} where the orbitals with zero overlap are involved.

$$\langle a_l | \hat{F}_0^{ab} | b_m \rangle = 2\langle a_l a_k | b_m b_u \rangle - \langle a_l a_k | b_u b_m \rangle$$

$$\langle b_m | \hat{F}_0^{ab} | a_l \rangle = 2\langle b_m b_u | a_l a_k \rangle - \langle b_m b_u | a_k a_l \rangle \quad (23)$$

and

$$\Lambda^0 = (-1)^S \prod_{i \neq k}^n \lambda_i^2 \quad (24)$$

The expression found for E_{CROSS}^0 is now much simpler:

$$E_{\text{CROSS}}^0 = \Lambda^0 \langle a_k a_u | b_k b_u \rangle \quad (25)$$

As a result, the somewhat more complicated expression is found for the HPHF equation, which exhibits the following form:

$$\hat{H}_0^a = \hat{F}^a + (\hat{R}^{ab} + \hat{R}^{ba})E_{\text{CROSS}}^0 + \Lambda^0 \{ \hat{R}_0^{ab} \hat{F}_0^{ba} + \hat{R}_0^{ab} \hat{F}_0^{ba} \hat{R}_0^{ab} - \hat{R}_0^{ab} \hat{F}_0^{ba} \hat{R}_0^{ab} - \hat{R}_0^{ab} \hat{F}_0^{ba} \hat{R}_0^{ab} - \hat{F}_0^{ab} \hat{R}_0^{ba} + \hat{F}_0^{ba} \hat{F}_0^{ab} \hat{R}_0^{ba} - \hat{R}_0^{ba} \hat{F}_0^{ab} \hat{R}_0^{ba} - \hat{R}_0^{ba} \hat{F}_0^{ab} \hat{R}_0^{ba} \} \quad (26)$$

A similar expression for \hat{H}_0^b operator is obtained by interchanging the a and b indexes in (26).

COMPUTATIONAL ASPECTS

The HPHF program was initially written for determining the ground state HPHF wave function.⁵ Later, it was extended to excited states with a symmetry different from that of the ground state.⁸⁻⁹ Recently, it was extended to systems with up to 12 atoms, with full geometry optimization.¹⁰ Finally, the program was generalized for excited states with the same symmetry as that of the ground state.¹³ In this last program, the excited electron orbital was orthogonalized to its companion, at each step of the iterative procedure, in order to avoid the variational collapsing of the excited state on the ground state.

The HPHF program structure is similar to UHF program with the presence of additional cross Fock matrixes, F^{ab} and F^{ba} . The corresponding orbitals are built up at each cycle of the iterative process.

The convergency is very fast in the case of excited states. The computational time is not much longer than that of UHF calculation, which suggests that the model can be successfully used in calculations of large systems.

APPLICATIONS

The most recent applications of the HPHF method have been the calculations of singlet excited states.^{9,10} Two systems have been chosen to compare the calculated values with the results obtained into other models, as well as with the available experimental data.

The basis sets used were the Huzinaga-Dunning with polarization orbitals and the 4-31G ones. These basis sets seem to be reasonably good for calculating potential energy curves with full geometry optimization.

Methylene

Methylene is a biradical system with six electrons, which exhibits a triplet ground state 3B_1 . By using the HPHF model, the second singlet excited state, 1B_1 , has been calculated. This state is orthogonal by spin symmetry to the ground state, 3B_1 , as well as to the first singlet state 1A_1 . The interest of studying this system stands in the electronic transition $^1A_1 \rightarrow ^1B_1$.

For this purpose, the HPHF wave function has been built up by replacing the occupied orbital $3a_1$ by the first virtual $1b_1$, in the RHF one, 1A_1 , to have the wave function of correct symmetry.

The potential energy curve for inversion in methylene was determined. Bond lengths were optimized for each bond angle. The obtained results are summarized in Table I.

The potential energy curves are given in Figure 1.

By comparison with the experimental data, it is seen that the geometry found for the minimum 1B_1

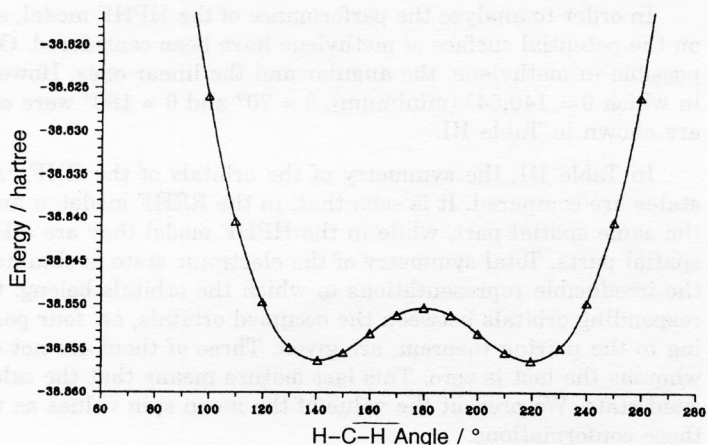


Figure 1. Potential energy curves for the bending angle in methylene in its first triplet and singlet excited states.

TABLE I
 Potential energy values of the 1B_1 singlet excited state of methylene as a function of the bond lengths C-H (r) and bond angle HCH (θ)

1B_1		
$\theta/^\circ$	$r/\text{\AA}$	$E_{\text{HPHF}} / \text{hartree}$
180	1.056	-38.850284
170	1.057	-38.851125
160	1.060	-38.853195
150	1.063	-38.855367
140	1.068	-38.856294
140.54	1.068	-38.856296
130	1.073	-38.854753
120	1.078	-38.849740
110	1.084	-38.840415
100	1.091	-38.826023
90	1.000	-38.805808
80	1.109	-38.778970
70	1.120	-38.744633

TABLE II
 Comparison of theoretical and experimental data

Calculation*		Experimental		$\langle \hat{S}^2 \rangle$	Ref.
HPHF 1B_1	$\theta = 140.54^\circ$	$\theta = 140.3^\circ$			14
barr. 1B_1	1319.48 cm^{-1}	1617 cm^{-1}	$r = 1.068 \text{ \AA}$	0.0126	14
			$r = 1.070 \text{ \AA}$		

* Basis set Huzinga-Dunning + pol (25 basis function)

state is in agreement with the high resolution calculations based on laser magnetic resonance.¹⁴ It is remarkable that HPHF calculations describe adequately the torsional barrier of the 1B_1 state.

In order to analyze the performance of the HPHF model, some significant points on the potential surface of methylene have been considered. Only two structures are possible in methylene, the angular and the linear ones. However, the conformations in which $\theta = 140.54^\circ$ (minimum), $\theta = 70^\circ$ and $\theta = 180^\circ$ were considered. The results are shown in Table III.

In Table III, the symmetry of the orbitals of the RHF, 1A_1 and the HPHF, 1B_1 states are compared. It is seen that, in the RRHF model, α and β spin orbitals have the same spatial part, while in the HPHF model they are allowed to have different spatial parts. Total symmetry of the electronic state is obtained by direct product of the irreducible representations to which the orbitals belong. Overlaps between corresponding orbitals between the occupied orbitals, *i.e.* four possible overlaps according to the pairing theorem, are given. Three of them are not exactly equal to unity, whereas the last is zero. This last feature means that the calculated state is an excited state. We present the value of the mean spin values as well as the energies of these conformations.

TABLE III

A comparison of the symmetry of the singlet excited states orbitals for three points on the potential energy surface

	$\theta = 140.54^\circ$	$\theta = 70.00^\circ$	$\theta = 180.00^\circ$
Point group	C_{2v}	C_{2v}	$D_{\infty h}$
RHF configuration (in 1A_1 state)	(α) $a_1a_1b_2a_1$ (β) $a_1a_1b_2a_1$	(α) $a_1a_1b_2a_1$ (β) $a_1a_1b_2a_1$	(α) $\sigma_g\sigma_g\pi_u\sigma_u$ (β) $\sigma_g\sigma_g\pi_u\sigma_u$
HPHF configuration	(α) $a_1a_1b_2a_1$ (β) $a_1a_1b_2a_1$	(α) $a_1a_1a_1b_2$ (β) $a_1a_1b_2b_1$	(α) $\sigma_g\sigma_g\pi_u\sigma_u$ (β) $\sigma_g\sigma_g\pi_u\pi_u$
Total HPHF symmetry	1B_1	1B_1	Asymmetric singlet
Overlaps between corresponding orbitals	1.00000 0.99703 0.99980 0.00000	1.00000 0.99167 0.99840 0.00000	1.00000 0.99776 1.00000 0.00000
$\langle \hat{S}^2 \rangle$	0.012639	0.039534	0.008929
$E_{\text{RHF}} (^1A_1 \text{ state})/\text{hartree}$	-38.84802	-38.84421	-38.81789
$E_{\text{HPHF}}/\text{hartree}$	-38.85629	-38.74463	-38.85028
$r_{\text{HPHF}}/\text{\AA}$	1.068	1.120	1.056

The 1B_1 state is the second excited state of methylene. Its symmetry is different from that of the ground state 3B_1 , and first singlet excited state, 1A_1 , so these states are orthogonal by symmetry. Thus, it is seen that the HPHF model is able to determine at least the excited states which are orthogonal by symmetry to the ground state.

Formic Acid

Formic acid is a molecule of five atoms. In random conformation, formic acid is a good example of molecules in which the singlet excited state, $^1A(n,\pi^*)$ possesses the same symmetry as that of the ground state. Thus, the wave function for the singlet excited state is no more orthogonal by symmetry to that of the singlet ground state. Most of the more complex molecules of organic chemistry indeed possess their ground and excited states with the same symmetry.

Formic acid exhibits two large amplitude motions: the angle torsion of the hydroxylic group and the out-of-plane wagging of the aldehydic hydrogen atom.

In Table IV, the energies of *anti* and *syn* planar conformation of the ground state of formic acid are shown. They correspond to the two minima on the potential energy surface of this state. These were obtained in the RHF approximation using a 4-31G basis set.

The conformations chosen were the planar *syn* and *anti*, which correspond to the minimum energy in the ground state, and two non-planar conformations which correspond to the minima in the singlet excited state into the GVB approximation.¹⁵ The HPHF energy values found for formic acid in these conformations are presented in Table V.

TABLE IV

RHF potential energy for anti and syn conformations of the 1A_1 ground state of formic acid

Torsion angle (θ)/°	Out-of-plane angle (α)/°	E_{RHF} /hartree	ΔE_{RHF} /cm ⁻¹
0.0	0.0	-188.47562	0.0
180.0	0.0	-188.46464	2409.8

TABLE V

HPHF potential energy calculations of the $^1A(n - \pi^)$ first singlet excited state of formic acid*

Torsion angle (θ)/°	Aleto angle (α)/°	E_{HPHF} /hartree	ΔE_{HPHF} /cm ⁻¹
-47.91	41.32	-188.371380	0.000
63.66	45.76	-188.367798	786.226
0.0	0.0	-188.361620	2142.102
180.	0.0	-188.361081	2260.518

A number of calculations on this molecule have been carried out, and in the future, it will be desirable to compare the theoretical results with experiments. The complete study of the potential energy surfaces of formic acid in its ground and first singlet excited states will be published.

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SAŽETAK

**Moguće primjene poluprojeciranog Hartree-Fockova postupka
za određivanje singletnih pobuđenih stanja**

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Za određivanje singletnih stanja otvorene ljuske predložen je poluprojecirani Hartree-Fockov (HPHF) model. Dan je pregled nekih svojstava HPHF valnih funkcija i prodiskutirana njihova moguća primjena za određivanje pobuđenih stanja molekula srednje veličine. Postupak je kombiniran Hartree-Fockovom metodom bez ograničenja (UHF). Prikazani su rezultati primjene HPHF postupka na metilenski biradikal i mravlju kiselinu koji upućuje na to da bi metoda mogla biti korisna u određivanju nižih singletnih pobuđenih stanja.