

History of the development of the Half-Projected Hartree-Fock method. Application to the calculation of excited states of the same symmetry as the ground state

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Abstract

Spin projected wave functions are known as generalizations of the Hartree-Fock wave function. Among them, the Half-Projected Hartree-Fock (HPHF) model represents a good compromise between the restricted (RHF) and unrestricted (UHF) Hartree-Fock methods. The HPHF wave function is a nearly pure wave function of spin and recovers a small part of the spin correlation energy. This paper reviews the history of the HPHF theory, not only from the conceptual point of view but also providing a compilation of the publications of this method over the years until now. In addition, the extension of the HPHF method to the calculation of non-orthogonal excited states to the ground state will be treated. The variational collapse during the calculation of singlet excited states with the same symmetry as the ground state is avoided by orthogonalizing the excited orbital to the corresponding occupied orbital. As an example, the potential energy surface of the S_0 ground and $^1S_1(n, \pi^*)$ first excited state of the formic acid HCOOH are calculated. Formic acid exhibits complex energy surfaces with respect two large amplitude motions, the torsional rotation of the O-H group and the waving out-of-plane angle of the H atom. In the excited state, the molecule adopts a pyramidal structure. The obtained energy results are fitted to curves that can be used for the calculation of the theoretical spectrum.

Keywords: Half-Projected Hartree-Fock method (HPHF); Projected Hartree-Fock method (PHF); Extended Hartree-Fock method (EHF); Restricted Hartree-Fock method (RHF); Unrestricted Hartree-Fock method (UHF)

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†In memoriam Istvan Mayer

I. THE HARTREE-FOCK THEORY AND ITS GENERALIZATIONS

Today we are approaching the celebration of the centenary of the development of the Hartree-Fock (HF) theory. Hartree's first publications on cristallographic applications of atomic theory date back to 1923. His work during the 1920s was based on his proposal of the independent particle model, in which the electron can be considered to move around a central field created by the nucleus and the average field from the repulsion of all the other electrons, neglecting the instantaneous interelectronic interactions. In an atom, this is called the central field approximation. The Hartree method [1], in which the wave function is a product of one-electron orbitals, strictly represents the independent particle model. But the Hartree-Fock wave function [2, 3] is antisymmetrized, taking into account the Pauli principle in the form of a Slater determinant, which will be zero in the case that two rows or columns are equal, so that the probability that two electrons are at the same place at the same time is zero, creating a Fermi hole.

The wave functions that are exact solutions of the Schrödinger equation are eigenvalues of the spin \hat{S}^2 and \hat{S}_z and angular momentum \hat{L}^2 , \hat{L}_z operators. These operators commute with the Hamiltonian \hat{H} and they share the same set of solutions. This ensures that variationally projected wave functions lead to better energy results. However, in the central field approximation we are working with approximated wave functions, which do not fulfill these symmetry properties.

According to the theoretical concept of doubly electronic occupancy of the orbitals, it is possible to impose on the HF wave function the restriction that the spatial parts of the one-electron orbitals belonging to the same atomic or molecular orbital are the same. This restriction leads to the Restricted Hartree-Fock (RHF) wave function, which has the advantage that the single determinant wave function is automatically an eigenfunction of the spin \hat{S}^2 and \hat{S}^z operators, i.e. the RHF wave function is a pure wave function of spin. The RHF wave function is then defined as a Slater determinant, which is constructed with a_i one-electron spin orbitals or basis functions a_i of spin α and \bar{a}_i of spin β :

$$\Psi_{RHF} = |a_1 \bar{a}_1 a_2 \bar{a}_2 \dots a_n \bar{a}_n| \quad (1)$$

where the vertical bar notation represents a normalized Slater determinant, with normalization constant $\frac{1}{\sqrt{N!}}$. In the RHF wave function $N = 2n$. Due to the widespread use of the

RHF model, following Löwdin [4], the correlation energy is defined as the difference between the RHF energy and the exact non-relativistic energy, and the correlation effects are those that are not yet been included in the RHF wave function. In some especial cases the RHF fails, due to the restrictions it contains. For example, the RHF model cannot correctly reproduce molecular dissociation at large distances in neutral fragments.

The methods whose goal is to obtain part of the correlation energy are generalizations of the HF method within the single determinat approximation. These methods are based on the idea of using "different orbitals for diferents spins" (DODS), an idea that was probably first explored by Slater [5] in the solid state physics and generalized by Löwdin to molecular systems. The idea behind the DODS approach is that important correlation effects can be taken into account if pairs of electrons of opposite spin are not forced to occupy identical space orbitals. In this way, the electrons of opposite spin would avoid each other by increasing the interelectronic distances creating the so-called Coulomb hole. Eliminating the restriction of doubly occupancy of the orbitals in the RHF wave function, we obtain the Unrestricted Hartree-Fock (UHF) wave function or DODS wave function, defined as:

$$\Psi_{UHF} = \Psi_{DODS} = D_0 = |a_1\bar{b}_1a_2\bar{b}_2 \dots a_n\bar{b}_n| \quad (2)$$

As in the DODS method the orbitals can be varied independently, the application of the UHF method means more flexibility in the wave function during the variational procedure. Consequently, the UHF method leads to lower/better energies than the RHF method. Therefore the UHF method achieves to recover a small part of the correlation energy and also the molecules dissociate correctly. However, at short or intermediate intranuclear distances, especially at equilibrium distances, there is no difference between using one method or another, being unnecessary to use the UHF one.

Unfortunately, the UHF wave function has the drawback, as single DODS determinant, that is not an eigenfunction of the operator \hat{S}^2 , and therefore, it is not a pure spin eigenfunction because it does not correspond to a defined multiplicity of spin, but it is mixture of different spin multiplicities (singlet, triplet, etc).

Löwdin introduced the term of "symmetry dilema" [6, 7] to describe this situation: If we request the wave function has a required spin symmetry, then this is a constrain that will result variationally in a higher energy result. On the contrary, if we let the wave function to be flexible and get a lower energy, then the wave function has spin contamination. Löwdin

proposed an 'analysis of components' using a project operator. To solve this dilemma, Löwdin [6] proposed to use a more elegant "general spin projection operator", named after him, which allows extracting from a wave function, which is a mixture of multiplicities, the desired multiplicity $S(S + 1)$. Prat [8] in 1953 had constructed a projection operator that produced a singlet state.

The energy of the unrestricted wave function can be considered as a linear combination or weighted averaged energies of the pure components. As these values are usually different, a lower energy than the initial one can be found. So the use of the operator allows not only to have the correct symmetry but also to improve the energy.

A. The Spin-Projected Extended Hartree-Fock Wave Function

The Spin-Projected Extended Hartree-Fock (PHF or EHF) wave function defined by Löwdin in 1955 [6] can be considered as the best single Slater determinant built on one-electron spin orbitals that have flexibility and projected in the appropriate symmetry state of interest. The projected wave function (determinant) is a linear combination of Slater determinants but conceptually one single entity in the same way that the Slater determinant is a linear combination of Hartree products [6, 7]. In this sense, the EHF model is the generalization of the independent particle model.

The spin-projector operator annihilates all the components of the unwanted multiplicity, leaving the spin component S of the desired multiplicity $S(S + 1)$ unchanged. That is, it projects onto the subspace of the spin eigenfunctions, the appropriate eigenfunction. To visualize this, we can imagine a vector in a n -dimensional space, which is the sum or linear combination of the vector components or coordinates on each axis or dimension. The projection on one of the axis corresponds to an eigenvector or component. The projection operator on a state with spin S_k is then:

$$\Theta_{S_k} = \frac{\prod_S (S^2 - S(S + 1))}{\prod_S (S_k(S_k + 1) - S(S + 1))} \quad (3)$$

The action of the full spin projection operator on a DODS Slater determinant D_0 Eq. (2), produces following Löwdin [6, 9] a linear combination of Slater determinants D_j , which are at the same time a linear combination of all Slater determinants obtained from D_0 by exchanging j orbitals of α spin for other j of β spin, whose coefficients are the well-known

Sanibel Coefficients [9],

$$\hat{\Theta}_S D_0 = \sum_{j=0}^n C_j(S, 0, n) D_j \quad (4)$$

The spin-orbitals have complete flexibility and are variationally determined. Although the EHF wave function is conceptually simple, it is computationally complex. The main disadvantage of the EHF wave function is that the number of determinants produced is $\binom{2n}{n}$ where n is the number of electrons. Therefore, the number of Slater determinants depends on the number of electrons and this number grows rapidly with the number of electrons.

The evaluation of the matrix elements over the EHF wave functions and their programming are enormously complicated. They have been derived by Mayer et al. [7, 10, 11] for even electron systems and Mayer [12] for odd electron systems from the Brillouin's theorem and using corresponding orbitals. In the case of the ground state of the He atom, Lefebvre and Smeyers [13] obtained 90 % of the correlation energy employing only four projected configurations constructed with Slater orbitals. Also, the EHF wave function has a large overlap with the Configuration Interaction (CI) wave function. Some applications of the EHF method to systems with even number of electrons as butadiene [14], cyclobutadiene [7, 15], and some π -electron systems [18] lead to very good energy results, recovering more than 90% of the correlation energy, as a similar full-CI calculation. In systems with odd number of electrons, the results were very good for allyl radical, whereas for larger systems as benzyl radical the method takes into account about only 50% of the correlation energy. For more details, see Ref. [7]. Odd electron systems which cannot be treated well with the RHF method would be a field of application of the EHF method. Another advantage of the EHF method is the correct description of the molecular dissociation into neutral fragments, see Fig. 7 of [7].

Finally, another drawback of the EHF wave function is that the electronic correlation is important only for small electron systems (molecules with up to 25 or 30 electrons) [16]. For larger systems, the EHF energy tends to the UHF energy as noted by Mayer et al. [7, 17–19]. Therefore, the use of the EHF method can be validated for problems in solid state physics, that is, to treat antiferromagnetism, polymers and crystals.

B. The Half-Projected Hartree-Fock Wave Function

Mayer in his landmark review [7, p. 217] wrote "Smeyers and co-workers worked out an extremely simple and ingenious variant of the partial annihilation, called the "half projected HF" (HPHF) method ... The method gives results which are closed to the EHF ones and may be considered as a happy compromise between the spin "symmetry dilemma" and other troubles connected with the UHF method, on the one hand, and the complexity of the EHF equations, on the other".

In fact, the Half-Projecte Hartree-Fock model (HPHF) introduces some correlation effects, beyond the usual RHF. The HPHF model was proposed by Smeyers in 1971 [20, 21] and represents a good compromise between the UHF and the PHF/EHF wave functions, since the HPHF wave-function consists of only two Slater determinants and retains the conceptual simplicity of the RHF method at the same time despite its direct determination, half of the spin contaminants are aniquilated [21]. This model yields results close to those of PHF and better than those of UHF, whereas the method uses only the same computational time of one UHF calculation. In addition, the method can compite with the full-CI procedure, which uses millions of configurations. The full-CI method uses the same basis set for ground and excited states, but the HPHF method can use different basis sets. As is well-known the full-CI method is computationally very expensive to be used in the practice for medium and large systems.

Let us define the HPHF wave fuction and look its properties in detail. The HPHF wave function for a $2n$ electron system, in a ground state of S quantum number, even or odd, is written as a linear combination of two Slater determinants, built up with spinorbitals that minimize the total energy [20, 21]:

$$\Psi = \frac{1}{2}\{|a_1\bar{b}_1a_2\bar{b}_2\dots a_n\bar{b}_n| + (-1)^{S+n}|\bar{a}_1b_1\bar{a}_2b_2\dots \bar{a}_nb_n|\} \quad (5)$$

where a_i and b_i are orbitals of opposite spin belonging to the same electron pair. Here the bar notation implies the normalization factor $\frac{1}{\sqrt{N!}}$.

The linear combination is obtained by projection of one determinant on the spin eigenstates with S even or odd:

$$\hat{A}(S) = \frac{1}{2}[1 + (-1)^{S+n}\hat{P}_{\alpha\beta}] \quad (6)$$

where $\hat{P}_{\alpha\beta}$ is a permutation operator which interchanges all the α and β functions in the determinant.

The $\hat{A}(S)$ is a half-projector operator, its expression can be obtained from the full-projector operator of Löwdin, as is shown in the next lines. The action of the full spin projected operator Eq. (3) over a DODS Slater determinant D_0 , yields a linear combination of Slater determinants D_j obtained from D_0 by changing j orbitals of α spin for other j orbitals of β spin, whose coefficients are the known Sanibel Coefficients, C_j . The sumation Eq. (4) can be also expressed [22]:

$$\hat{\Theta}_S D_0 = \frac{1}{2} \sum_{j=0}^n C_j D_j + \frac{1}{2} \sum_{j=0}^n C_{n-j} D_{n-j} \quad (7)$$

and using the symmetry property of the Sanibel Coefficients:

$$C(S, n - k) = (-1)^{n+S} C(S, n) \quad (8)$$

and the relation among the terms which represent a sum of Slater determinants,

$$D_{n-p} = \hat{P}_{\alpha\beta} D_p \quad (9)$$

one obtains,

$$\hat{\Theta}_S D_0 = \sum_{j=0}^n C_j \hat{A}(S) D_j = \sum_{j=0}^n C_j \Psi_j \quad (10)$$

where $\hat{A}(S)$ is the Half-Projected operator. The spin half-projector fulfill these two properties:

$$\hat{A}(\text{even}) \times \hat{A}(\text{odd}) = \hat{0} \quad (11)$$

$$\hat{A}(\text{even}) + \hat{A}(\text{odd}) = \hat{1} \quad (12)$$

The space of the spin states is split into two subspaces, one for states of even spin and the other for odd spin. Also can be demonstrated that:

$$\Theta_{S=\text{odd}} \hat{A}(\text{even}) D_0 = 0 \quad (13)$$

$$\Theta_{S=\text{even}} \hat{A}(\text{odd}) D_0 = 0 \quad (14)$$

so the HPHF wave function of a spin state $S = 0, 2, 4, \dots$ does not contain contamination of $S = 1, 3, 5, \dots$ and the opposite. When calculating a singlet, the triplet contamination is absent, but a little contamination from quintuplet, nonaplet and higher multiplicity appears [21]. In the same way, the HPHF wave function of a triplet does not contain singlet contamination but does contain heptuplet, and others. These are the reasons that the operator $\hat{A}(S)$ is a half-projector, that $\hat{A}(S)$ annihilates half of the possible spin contaminants.

C. A Historical Review of the HPHF method

The first calculations [21] of the HPHF method on the ground states of the Be atom and its isoelectronic ions Li^- , B^+ and C^{2+} yielded very close results to the corresponding PHF calculations using the same orbitals. The same was the case with molecules as LiH [22, 23], the HPHF energy was very close to the PHF one. In addition, the dissociation curve of LiH was very good with a shape similar of a the CI curve. These results were confirmed with further calculations on small molecules like the BH molecule [24] and H_2O , CO , NH_3 and CH_4 [25]. While the results were close to the PHF ones and the dissociation curves had the correct shape, the correlation energy captured by the HPHF method was relatively small compared with other CI methods. In fact, the HPHF can be considered as a two-determinant CI wave function [23]. This resulted in the assumption that the HPHF wave function is good describing the correlation in a single pair of electrons, which leads to a proper description of bond breaking, but less good for the simultaneous correlation of several pairs. Another problem arised: There were existing several solutions of the HPHF wave function which appeared during the variational procedure [25]. The various solutions included inner or outer correlation effects and occurred as local minima at different geometries, i.e. equilibrium geometries and larger intermolecular distances until dissociation. The problem could be overcome by a careful analysis of the solutions and chosing generally as the best one the lowest solution at every geometry, as can be seen in dissociation curves of the LiH molecule [26–28]. In the case of calculation of molecular properties, usually the solution including the desired type of correlation effects should be chosen. This effect has been also observed in calculations with the PHF wave function [13]. There is a great analogy between the HPHF and PHF wave functions. Both models lead to similar results and have various solutions [23]. They have also the same limitations, whereas the PHF contains less higher

spin contaminants.

The determination of the HPHF wave function was slightly more difficult than the UHF wave function. Two iterative procedures were used. The first was based on the Generalized Brillouin Theorem [13, 29], converged very well and led to accurate results, but it required longer computation times, since matrix elements between Slater determinants had to be calculated. The second one consisted in solving simultaneously two sets of coupled equations as the UHF equation in an iterative way, one for orbitals of α spin and one for spin β [29–31]. The last method is the one used since then. Tested in the case of the dissociation of the Li_2 molecule, the iterative method, similar in time to a UHF, led to a better dissociation curve than UHF, from the variational point of view, for singlet [30] and lowest triplet excited states [31]. Beyond ground singlet states, the HPHF method was successfully applied to the low-lying triplet excited states as it was the case in calculations of the Be atom [32].

Other authors from different groups and countries [33] have also investigated small molecular systems, i.e. H_2O , C_2 , N_2 and CH_2 with the HPHF method. They concluded that the HPHF method performed as a limited Multiconfigurational Self-Consistent Field (MCSCF) treatment, including a small but important fraction of the correlation energy, gave qualitatively correct potential energy surfaces, and provided to good one particle orbital bases. The convergence of the HPHF wave function was also investigated and accelerated employing DIIS algorithms [34]. The HPHF wave function described well the dissociation curves of the molecules F_2 , BH , O_2^+ and BN , where UHF showed ill behaviour due to spin contamination. Also the singlet-triplet energy gap of the CH_2 molecule was correctly described. Therefore, the usage of the HPHF method provides a way to remove serious spin contamination in a referent determinant and provides a reliable wave function on which to introduce correlation. Bone and Pulay [34] pointed out "HPHF is by far the most efficient of projected Hartree-Fock schemes today". At this point, we may mention that the computational times of the HPHF method are about twice or more than the UHF method, since two equations and a cross term should be solved. This computational times are nowadays negligible.

Olivella and Salvador [52] applied the HPHF method to calculate biradicals. For that purpose, they developed the equations of the method when a singularity $\lambda = \langle a_k | b_u \rangle = 0$, representing the overlap between an occupied a_k and virtual orbital b_u , occurs. This singularity was used later as orthogonality condition during the calculation of excited states, see Section II. Note that, orthogonality is automatically achieved when both wave functions

have different spin between singlet and triplet states.

With this extension, the HPHF method was then applied to the calculation of the triplet ground state and singlet excited state of the biradical methylene [36, 37]. Both states are open shells and orthogonal by symmetry (spatial and spin) to each other, what makes easier the calculations during the variational procedure. The results of the singlet-triplet energy gap and the triplet ground state torsion potential energy curves were better than the UHF curve and compared well with the experiments. In the case of methanal and dimethylglyoxal, the excited wave functions were orthogonal to the ground state one and the procedure converged without any complication. The HPHF initial-guess functions were obtained by using mixtures with, or substitutions by, virtual orbitals of RHF occupied orbitals. A criterium for the initial guess and the obtention of the solutions for every spatial geometry was then established [38]. In similar cases, the HPHF method can be regarded as an extension of the UHF method for $M_s = 0$, and employed in calculations of the lowest excited states of medium size molecules.

In large molecules, it is frequent that excited states have same symmetry as the ground state. Therefore the states are non-orthogonal by spin symmetry to each other. When calculating the excited state of the same symmetry than the ground state, it may occur the so-called "variational collapse", that is, the calculation falls down to the one of the ground state. To avoid this, a pair of corresponding orbitals were kept to be zero $\lambda = 0$ at every step of the iterative process [39]. This was an extension of the idea of Ref. [52]. It seemed to be more favourable to orthogonalize a virtual orbital than all the orbitals. As examples of this procedure, the first singlet excited states ($n \rightarrow \pi^*$) of formic acid [40] and cyclobutanone and 3-cyclopenten-1-one [41] were studied, obtaining energies, optimal geometries in both states and potential energy surfaces with respect to the out-of-plane wagging CO-groups. The energy barriers in potential energy surfaces, bond distances and bond angles of medium size molecules are very well described with the HPHF method, comparing well with experimental results. Also nine states of the Li_2 molecule [42] and core excitation energies in the SF_6 molecule have been obtained by the HPHF method [43].

In addition, some methodological improvements of the HPHF methodology took place. One of the simplest was to construct the monoexcited wave function based on the Half-Projected reference wave function [44, 45], and to derive the first and second derivatives of the functional of the energy [44, 45]. These algorithms have not been yet extended compu-

tationally. The analytical gradients for the HPHF wave function were derived [46] starting from the Brillouin theorem. The computational implementation is still missing, and therefore, the analytical gradients have not been yet used. Conversely, the simplex optimization method was implemented [47] leading to remarkably good results. The simplex method is a non-derivative method, which uses the total energy, and therefore it does not depend of the method UHF, RHF or HPHF employed. The simplex method is computationally economical and so it permits the exploration of the potential energy surfaces with a reasonable computational effort. At the same time, it ensures the convergence to conformations with minimal energy. Note that conformations in excited states have usually other geometries than the ones in the ground states. Therefore, the simplex method seems to be appropriate for the calculation of excited states of medium and large systems.

Other important methodological advance was the construction of a Multiconfigurational HPHF wave function (MCHPHF) [48] to treat the problem of spatial symmetry breaking (σ - π separation) which occurs in molecules with extended conjugated π -electron systems, where the excited states are degenerated or quasi-degenerated, what may lead to a mixing of excitations and consequently, to a numerical breakdown during the iterative process. If the spatial symmetry is kept, the HPHF calculations are successful, but if the symmetry is broken, re-orthogonalization of the orbitals in order to keep the condition $\lambda = 0$ does not always work well. The method was implemented computationally and applied to the molecules of ketene, allene and bencene. The calculated excitation energies and geometries of the ground and excited states compared well with the experimental data. Usually, double bonds in excited states become larger, and the carbonyl group too and in addition, it moves out of the plane. In the case of allene in its ground state, the CH_2 groups form an angle of 90° , while in the excited state, allene will relax becoming more planar. Generally, the MCHPHF method employed two to six configurations. With its use, the problems of symmetry breaking can be avoided and the computational cost of geometry optimization does not represent any problem.

The HPHF wave function was defined for the even electron case. For the odd electron case, the HPHF wave function has been obtained in a similar way from the PHF wave function [49]. Also Ref. [25] pointed out the necessity of a HPHF wave function for odd electron systems. However, in the odd-electron case, the HPHF wave function consists on a limited sum of Slater determinants, whose number depends on the number of electrons, as

was the case of the PHF wave function. This fact makes more difficult its computational implementation. For example, in the case of five electrons, the HPHF wave function is a sum of four Slater determinants. The number of determinants grows linearly with the number of electrons. The determinants are constructed using the spin permutation operator, therefore there will be some properties which simplify the matrix equations. The HPHF wave function for the doublet state does not contain contamination of a quadruplet state, which is the one nearest in energy. Similarly, the HPHF wave function for a quadruplet state does not contain contamination of a doublet state. Although the computational difficulty, this implementation seems promising.

In the last decades, methods which introduce more electronic correlation have attracted a major interest and the applications of the HPHF method have had a reduced impact. Nevertheless, the spin contamination is still nowadays a serious problem in the calculations and it is being object of extended investigations. So that in the last years a renewed interest on spin projected wave functions has taken place. The half-projected spin operator is being applied to the wave functions in a variation-after-projection procedure (VAP) and in this way new methods are using the HPHF wave function as reference one. This is the case of the Half-Projected Strongly Localized Geminals (HPSLG) [50], applied to H_4 , diradicals and benzynes, confirming the spin properties already mentioned of the HPHF wave function. In order to get more correlation energy, the HPSLG method has been extended including perturbation theory [51] and tested in the case of singlet - triplet gaps of biradicaloids, leading to very promising results. The HPHF method has been also extended in the variante of semiempirical methods [52, 53] and was employed to calculate biradical species. In the calculation of excited states [54], the HPHF method seems to show great efficiency avoiding the variational collapse high-quality excited-state solutions that exist in a wide range of geometries. These methods make an advantage of the correct spin symmetry of the wave function and improve it with correlation energy, approaching the results of a full-CI wave function, which cannot be applied for such systems.

Recently, there is a renewed interest on the PHF method and efficient computational procedures are being studied in order to be able to apply the method efficiently. That is the case in the method by using the projection operator as integration over the spin-rotation operator, what can be numerically evaluated with grid points. The procedure consists then in determining the appropriate number of grid points, and calculating the rotated Fock

matrix at each grid point [55]. An improvement of the EHF method has been proposed by Pons Viver [56] with the practical use of the expectation value of Löwdins spin projection operator. The methodology seems to be equivalent to the earlier Mayer et al. formulation of the EHF method [7, 10, 11]. In this respect, Yoshizawa [57] pointed out: "Moreover, there is an approach which provides almost EHF quality results at the computational expense of a UHF calculation, and it is called the half-projected HF approach".

Another wave function for the ground state of atomic and molecular systems based on a spin projected operator is the Omega function [59]. The operator interchanges the α and β spin-functions of all the electron pairs in the wave-function. This function is roughly equivalent to a closed shell excited configuration expansion. For singlet states, the Omega function is defined as a linear combination of 2^n slater determinants, where n is the number of electron pairs. It has been applied to Be atom [58], finding that the Omega function introduces an important part of the correlation energy. It has been also applied to the LiH molecule [60].

Because the increasing of the computer facilities, the HPHF method is expected to play a more important role in the field of medium-large size systems when no other methods can be even applied. Also the HPHF wave function can serve as reference wave function for other methodologies. Another great field of application of the HPHF wave function is the calculation of potential energy surfaces.

II. THE HPHF METHOD FOR EXCITED STATES.

Theoretically, wave functions which are solutions of the same Hamiltonian are orthogonal to each other. In addition, if they possess different spatial symmetry or different spin, they are orthogonal by symmetry. Since our wave functions are solutions of different Hamiltonian equation, one for the ground state and a different one for the excited state, see eqs. (24) and (37) of Ref. [39], it may happen that during the variational process, the calculation of an excited state falls down to the calculation of the ground state, the so-called "variational collapse". In this work, we present how the HPHF method has been employed to calculate potential energy surfaces of the singlet excited states which are of the same symmetry as the ground state avoiding the variational collapse. In medium size molecules is very frequent that the first excited state possesses the same symmetry that the ground one, in addition, with

the HPHF method the spin contamination of triplet (which is the principal one) is absent in the singlet.

Molecules in the excited state show interesting properties with respect to vibronic and rotational barriers of groups e.g. to mention only the wagging motion of carbonyl groups and ring puckering in cyclobutanone and 3-cyclopenten-1-one [61] and the potential curves for the rotation of the methyl group in fluorinated toluene [62] in its ground and excited state, depending on its position, respectively. The HPHF method has been extended to calculate medium size and large molecules and being applied to the examples mentioned above and the results are in good agreement with experimental spectroscopic data [41]. In this work, we present the calculations carried out about the formic acid molecule with the purpose of obtaining the potential energy function of the first singlet excited and ground states that can be used as starting point for further investigation, in particular, to calculate the theoretical spectra of luminiscence with the help of the Group Theory of Non-Rigid Molecules [63] and so, to compare later with the experimental one in order to check the theories.

The HPHF wave function for an excited state ($b_k \rightarrow b_u$) is constructed substituting in the HPHF ground state wave function (5) an b_k occupied spinorbital by a b_u virtual one,

$$\Psi(b_k \rightarrow b_u) = \frac{1}{2} \{ |a_1 \bar{b}_1 \dots a_k \bar{b}_u \dots a_n \bar{b}_n| + (-1)^{n+S} |\bar{a}_1 b_1 \dots \bar{a}_k b_u \dots \bar{a}_n b_n| \} \quad (15)$$

In order to avoid the possible collapsing of the so-constructed excited wave- function onto the ground state one during the variational process, it is convenient that the excited wave function should be orthogonal to the former. In some cases, this orthogonality is automatically achieved, when both wave functions exhibit different multiplicities or different spatial symmetries. When both wave functions exhibit the same multiplicity and the same spatial symmetry, it is convenient that the excited wave function should be orthogonal to the fundamental one. One way to achieve this requirement is orthogonalizing the excited orbital b_u to its companion a_k , at each step of the iterative procedure.

In any cases, the requirement applied to the orbitals:

$$\lambda = \langle a_k | b_u \rangle = 0 \quad (16)$$

The Brillouin theorem's has been shown to hold in the case of the HPHF wave function [13]. For excited states we have:

$$\frac{\partial E}{\partial \epsilon_{it}} = \langle \Psi(b_k \rightarrow b_u) | \hat{H} - E | \Psi_{it}(b_k \rightarrow b_u) \rangle = 0 \quad (17)$$

where $\Psi_{it}(b_k \rightarrow b_u)$ is the HPHF excited wave function in which an a_i occupied orbital has been replaced for an a_t virtual one.

Introducing the HPHF wave function expression (15) into (17), and taking into account the idempotency of the operator $\hat{A}(S)$, the following equation may be obtained:

$$\frac{\partial E}{\partial \epsilon_{it}} = \langle D_{0k} | \hat{H} | (D_{0k}^{it} + (-1)^{n+S} D_{nk}^{it}) \rangle - E \langle D_{0k} | (D_{0k}^{it} + D_{nk}^{it}) \rangle \quad (18)$$

D_{0k} and D_{nk} are the terms of the bideterminantal HPHF wave function for excited states considered separately. D_{0k}^{it} and D_{nk}^{it} are the Slater determinants D_{0k} and D_{nk} in which one i occupied orbital has been substituted by a t virtual one, respectively.

In order to solve the equation (18), the following matrix elements between Slater determinants have to be considered:

$$\langle D_{0k} | \hat{H} | D_{0k}^{it} \rangle, \quad \langle D_{0k} | D_{0k}^{it} \rangle, \quad (19)$$

$$\langle D_{0k} | \hat{H} | D_{nk}^{it} \rangle, \quad \langle D_{0k} | D_{nk}^{it} \rangle. \quad (20)$$

Since D_{0k} and D_{0k}^{it} are constructed with the same set of orthonormal spinorbitals, the two first matrix elements can easily be rewritten, according to the Slater's rules [64], as:

$$\langle D_{0k} | \hat{H} | D_{0k}^{it} \rangle = \langle a_i | \hat{F}^a | a_t \rangle, \quad (21)$$

$$\langle D_{0k} | D_{0k}^{it} \rangle = 0. \quad (22)$$

In this expression, the \hat{F}^a operator is the usual Fock operator of the Unrestricted Hartree-Fock method:

$$\langle a_i | \hat{F}^a | a_t \rangle = \langle a_i | \hat{h} | a_t \rangle + \sum_{j=1}^n ([a_i a_j | a_t a_j] + [a_i b_j | a_t b_j] - [a_i a_j | a_j a_t]), \quad (23)$$

the notation used for the repulsion integrals is:

$$[a_i a_j | a_k a_l] = \langle a_i(1) a_j(2) | \frac{1}{r_{12}} | a_k(1) a_l(2) \rangle, \quad (24)$$

and \hat{h} stands for the well known one-electron operator:

$$\hat{h}(1) = -\frac{1}{2}\Delta_1 + \sum_A \frac{Z_A}{r_{1A}}. \quad (25)$$

A similar operator as (23) can be written when b_i orbital is substituted by a b_t virtual one:

$$\langle b_i | \hat{F}^b | b_t \rangle = \langle b_i | \hat{h} | b_t \rangle + \sum_{j=1}^n ([b_i a_j | b_t a_j] + [b_i b_j | b_t b_j] - [b_i b_j | b_j b_t]). \quad (26)$$

The calculation of the cross matrix elements (19,20) is somewhat more difficult, because the Slater determinants involved in them are constructed with two sets of non-orthonormal spinorbitals. This calculation, however, may be greatly simplified, if the two sets are assumed to be "corresponding", that is, if they fulfill the following condition [65]:

$$\langle a_i | b_j \rangle = \lambda_i \delta_{ij}. \quad (27)$$

And the orthogonality requirement applied to the orbitals (16) implies some modifications in the formulae of the usual cross HPHF operators [39], which are now redefined as:

$$\begin{aligned} \langle a_i | \hat{F}^{ab} | b_l \rangle &= \langle a_i | \hat{h} | b_l \rangle + \sum_{j \neq k}^n \frac{1}{\lambda_j} ([a_i a_j | b_l b_j] + [a_i b_j | b_l a_j] - [a_i a_j | b_j b_l]), \\ \langle b_l | \hat{F}^{ba} | a_i \rangle &= \langle b_l | \hat{h} | a_i \rangle + \sum_{j \neq k}^n \frac{1}{\lambda_j} ([b_l b_j | a_i a_j] + [b_l a_j | a_i b_j] - [b_l b_j | a_j a_i]), \end{aligned} \quad (28)$$

in which the summations are restricted to the non-orthogonal orbitals.

In addition, partial cross Fock operators are also to be defined:

$$\begin{aligned} \langle a_i | \hat{f}^{ab} | b_l \rangle &= (2[a_i a_t | b_l b_u] - [a_i a_t | b_u b_l]), \\ \langle b_l | \hat{f}^{ba} | a_i \rangle &= (2[b_l b_u | a_i a_t] - [b_l b_u | a_t a_i]). \end{aligned} \quad (29)$$

For the same reason, new density projector operators are defined with respect to the usual HPHF ones:

$$\hat{R}^{ab} = \sum_{i \neq k}^n \frac{1}{\lambda_i} |a_i\rangle \langle b_i|, \quad \hat{R}^{ba} = \sum_{i \neq k}^n \frac{1}{\lambda_i} |b_i\rangle \langle a_i| \quad (30)$$

as well as limited projector operators to the k or u orbital space:

$$\hat{r}^{ab} = |a_k\rangle\langle b_u|, \quad \hat{r}^{ba} = |b_u\rangle\langle a_k| \quad (31)$$

Finally, a restricted overlap between the two determinants limited to the non-orthogonal orbitals is defined:

$$\Lambda' = (-1)^S \prod_{i \neq k}^n |\lambda_i|^2. \quad (32)$$

In order to deduce the pseudo-eigenvalue equations, we have to distinguish the two possibilities:

When $a_i \neq a_k$, the Brillouin theorem equation (18) is reduced to:

$$\frac{\partial E}{\partial \epsilon_{it}} = \langle a_i | \hat{F}^a | a_t \rangle + \frac{\langle b_i | a_t \rangle}{\lambda_i} E'_2 - \frac{\Lambda'}{\lambda_i} \langle b_u | a_t \rangle \langle b_i | \hat{F}^{ba} | a_k \rangle, \quad (33)$$

where the cross energy term, E'_2 , between the two Slater determinants, takes the form of a simple repulsion integral:

$$E'_2 = \Lambda' [a_k a_k | b_u b_u]. \quad (34)$$

In contrast, when $a_i = a_k$, the following expression is found:

$$\begin{aligned} \langle a_k | \hat{F}^a | a_t \rangle + \Lambda' \{ \langle b_u | \hat{f}^{ba} | a_t \rangle + \langle b_u | a_t \rangle \langle a_k | \hat{F}^{ab} | b_u \rangle \\ - \sum_{j \neq k}^n \frac{\langle b_j | a_t \rangle}{\lambda_j} \langle b_u | \hat{f}^{ba} | a_j \rangle \} = 0. \end{aligned} \quad (35)$$

From equations (33) and (35), a general HPHF Fock operator for determining the a_i orbitals of excited states can be extracted after some straightforward transformations:

$$\hat{H}^a = \hat{F}^a + \hat{R}^{ab} E'_2 + \Lambda' \{ \hat{r}^{ab} \hat{f}^{ba} + \hat{r}^{ab} \hat{F}^{ba} \hat{r}^{ab} - \hat{r}^{ab} \hat{f}^{ba} \hat{R}^{ab} - \hat{R}^{ab} \hat{f}^{ba} \hat{r}^{ab} \}. \quad (36)$$

Since equation (29) is not symmetric, it is symmetrized by addition of the adjoint of the asymmetric part. We obtain the new expression:

$$\begin{aligned} \hat{H}^a = \hat{F}^a + (\hat{R}^{ab} + \hat{R}^{ba}) E'_2 + \Lambda' \{ \hat{r}^{ab} \hat{f}^{ba} + \hat{r}^{ab} \hat{F}^{ba} \hat{r}^{ab} - \hat{r}^{ab} \hat{f}^{ba} \hat{R}^{ab} \\ - \hat{R}^{ab} \hat{f}^{ba} \hat{r}^{ab} + \hat{f}^{ab} \hat{r}^{ba} + \hat{r}^{ba} \hat{F}^{ab} \hat{r}^{ba} - \hat{R}^{ba} \hat{f}^{ab} \hat{r}^{ba} - \hat{r}^{ba} \hat{f}^{ab} \hat{R}^{ba} \}. \end{aligned} \quad (37)$$

A similar equation can be deduced for the b_i orbitals.

Finally, the expression of the total electronic energy holds:

$$E(b_k \rightarrow b_u) = E_1 + E'_2, \quad (38)$$

with E_1 as a principal contribution to the energy:

$$E_1 = \frac{1}{2} \sum_{i=1}^n \left\{ \langle a_i | (\hat{h} + \hat{F}^a) | a_i \rangle + \langle b_i | (\hat{h} + \hat{F}^b) | b_i \rangle \right\}. \quad (39)$$

It is of interest that the total HPHF electronic energy of a ground state system is:

$$E = \frac{E_1 + E_2}{1 + \Lambda}, \quad (40)$$

with

$$E_2 = \Lambda \left\{ \sum_i^n \frac{2}{\lambda_i} \langle a_i | \hat{h} | b_i \rangle + \sum_i^n \sum_j^n \frac{1}{\lambda_i \lambda_j} (2[a_i a_j | b_i b_j] - [a_i a_j | b_j b_i]) \right\}, \quad (41)$$

and

$$\Lambda = (-1)^S \prod_i^n |\lambda_i|^2. \quad (42)$$

III. COMPUTATIONAL ASPECTS: THE PROGRAM

Based on the original HPHF computer program developed over the years by Smeyers et al. [20–23, 26–32, 36–39, 42, 43], our HPHF computer program has been implemented in an ab-initio molecular program MOLSCF [66], which uses lobe functions to represent atomic orbitals of s-, p- d-, and f-orbitals. The HPHF program has been programmed in Fortran 90 language and developed for vector and parallel multiprocessor systems [67]. In the SCF standard procedure, the methods RHF, UHF, AUHF, MP2 and MCHPHF [48] are included. To ensure convergence of the iterative process, variable damping of charge-bond order and Fock matrices can be optionally chosen. The acceleration of the convergence maybe performed using either 3-, or 4-point extrapolation, the DIIS-method, which is applied independently \hat{H}^a and \hat{H}^b matrices, turns out to be the most efficient for acceleration. The program has been used for the calculations of cyclobutatone, 3-cyclopenten-1-one [41], ketene, allene and bencene [48].

The geometry optimization of molecules in excited states is very important because major changes occur with respect to the ground state. For this purpose, we have developed a program based in the simplex algorithm [47], which has been applied successfully to medium size molecules. The gradients of the HPHF program have been derived [46] and then will be also implemented. The optimization can be performed for all or a part of the degrees of freedom.

The HPHF computer program is parallellized. As the number of processors use to be large, the task have to be defined within a molecular calculation. Each processor calculate part of the integrals and in the following iterative procedure, the processors are working only in their parts of integrals. The diagonalization of the Fock matrices can also be performed in parallel, using a program based on the basis of the QR algorithm [67].

The calculation of excited states of molecules using HPHF has to follow a number of steps. Each one of them has to be treated carefully and frequently one may select among different solutions. Some of the occurring problems will be briefly discussed in the following sections.

A. Choice of the starting HPHF wave function for excited states

Usually, the first step is to perform a RHF calculation of the ground state of the molecule under consideration. After having decided which excitation has to be investigated, an occupied b_k orbital is exchanged by a virtual b_u orbital, while the rest of the a_i, b_i occupied orbitals are taken from the starting wave function. In certain cases, the starting HPHF wave function constructed in this simple way may have difficulties to converge. Then it is recommended to perform an UHF calculation using the configuration of the excited state with the above mentioned replacement. If there are still convergence difficulties, an UHF calculation of the ionic form of the molecule may be performed, in order to generate a splitting between the a_i and b_i sets of orbitals. Another way to introduce a splitting is to change arbitrarily the selected orbitals from the RHF wave function, but then they should be renormalized and make them orthogonal again to the rest of unchanged orbitals by using the Schmidt orthogonalization. Furthermore, the previous virtual orbital b_u , which belongs now to the occupied space of the b_i orbitals, must be made orthogonal to the corresponding occupied a_k orbital. As a consequence of this approach, in the case of π -electron systems, the $\sigma - \pi$

separation maybe broken. According to our experience with many HPHF calculations, we can conclude that the RHF wave function represents a satisfactory initial wave function for the subsequent HPHF calculation of energy levels of excited states.

B. Reordering of the molecular orbitals

After the diagonalization in each SCF-cycle of the Fock matrices \hat{H}^a and \hat{H}^b , Eq. (37) it is necessary to ensure that the subspace of occupied orbitals b_i still contains the so-called excited orbital. This special orbital is identified by the maximum overlap with one of the orbitals of the wave function of the previous iteration step. For the sake of convenience, we put this orbital as well as the a_i which has been replaced by the excited b_u configuration at the position of the HOMO. Further ordering of the rest of the orbitals in both a_i and b_i sets and also between them is not necessary, though corresponding orbitals are calculated in the next step. In any case one has to check whether the two HOMO orbitals (of a_i and b_i electrons) are still orthogonal to each other. If this is not fulfilled, a Schmidt orthogonalization is performed. According to the algorithm the a_k orbital is unchanged and b_k orbital modified. The program offers the possibility of orthogonalize the rest of the b_i orbitals to the new HOMO β -orbital.

C. Calculation of corresponding orbitals

As it has already been mentioned, no ordering of the orbitals is necessary to determine the corresponding orbitals by suitable transformation. It can be shown that the unitary matrix \mathbf{U} for the α -wave function corresponds to the eigenvector matrix obtained from the eigenvalue problem:

$$\mathbf{S}^\dagger \mathbf{S} \mathbf{U} = \mathbf{U} \mathbf{a}, \quad (43)$$

where one of the eigenvalues is zero (or small). The transformation matrix for the β -wave function is the same than \mathbf{U} except that the eigenvector of the zero-eigenvalue is replaced by the eigenvector to the same eigenvalue of the matrix $\mathbf{S} \mathbf{S}^\dagger$:

$$\mathbf{S}^\dagger \mathbf{S} \mathbf{V} = \mathbf{V} \mathbf{b}. \quad (44)$$

During the iteration process, it is required to test the orthogonality of the two HOMO orbitals. A Schmidt orthogonalization is performed when the overlap exceeds a threshold value and the corresponding orbitals have to be recalculated. In this case, both transformation matrices are the same and only one diagonalization has to be performed.

IV. RESULTS

Formic acid, the smallest of the carboxylic acids, is an interesting case in spectroscopy, with complex potential energy surfaces for ground S_0 and excited states. Its singlet excited state $^1S_1(n, \pi^*)$ has the same symmetry as its ground state S_0 . Thus, the wave function for the excited state is no longer orthogonal by symmetry to that of the ground state. Formic acid exhibits two large amplitude motions: the angle torsion of the hydroxylic group (θ) and the out-of-plane wagging (α) of the aldehydic hydrogen atom, as shown in Fig. 1. In order to obtain the theoretical spectrum of luminiscency of formic acid and further comparison with the spectroscopical data, it is necessary to determine not only the potential energy surface of its low-lying excited state, but also the ground state potential energy surface.

A. The S_0 Ground state

We have calculated the potential energy surface of the ground state of formic acid with respect to the torsion θ and the wagging α motions in the RHF approximation using 4-31G and 6-31G** basis sets and full optimization of the geometry, except for the torsional angles θ and α . The RHF method has been used instead of the HPHF method because the formid acid molecule in its ground state has an even number of electrons, it then is a closed shell system, and the calculated conformations are near to the molecular equilibrium (since optimization of the geometry is used). In those cases, the RHF method leads to a good description of the potential energy surface. In addition, the potential energy surface is also calculated with the 6-31G** basis, which is the same basis that will be employed in the calculation of the excited state.

There are two planar conformations in formic acid, the *anti* and *syn* that represent two minima. The ground state configuration is the *anti* conformation, where the hydroxylic hydrogen is on the same side than the carbonyl oxygen ($\theta = 0, \alpha = 0$). The reason is

due to two effects: on the one hand, the delocalization of a π molecular orbital. On the other hand, an intermolecular hydrogen bridge of the hydrogen from the hydroxylic group with the carbonyl oxygen. The *syn* conformation ($\theta = 180, \alpha = 0$) is a relative minimum about 2000 cm^{-1} above the *anti* conformation. The energy results, presented in Table 1, show a potential energy surface with high walls when the wagging angle becomes large, and oscillating values which change smoothly with the torsional angle θ . Our calculated energy values and torsional barrier compare well with GVB calculations using 6-31G* basis [68], see Table 2.

The geometrical parameters for these conformations are listed in Table 3. Among them, the bond distance C=O, is shorter in the *syn* conformation and the bond distance C-O is greater. During the torsion, the C=O bond distance shortens (less interaction with the hydroxylic hydrogen) while the C-O bond distance becomes larger. The other distances are not changing appreciably. The calculated geometrical parameters compare very well with those of the *anti* and *syn* conformations calculated by other methods, see Table 4.

It is useful to express the potential energy surface depending on the variables that have not been optimized in order to use this function for further investigations. The electronic energy V in the formic acid molecule, due to the presence of a symmetry plane between the fixed structure and the movable parts, is invariant with respect to a simultaneous change of both rotations, therefore it fulfills the next symmetry relation:

$$V(\theta, \alpha) = V(-\theta, -\alpha) \quad (45)$$

with this, it is necessary the calculation of the symmetry irreducible points of the potential energy surface. Using this relation, we can extend the potential energy surface of Table 1 with additional points, i.e. $V(-30, -30) = V(30, 30)$, and so on. The energy values of the ground state have been fitted to a potential function composed by terms which are products of trigonometrical functions (easier integration) and has the following form:

$$V(\theta, \alpha) = \sum_{KL} A_{KL}^{CC} \cos(K\theta) \cos(L\alpha) + \sum_{KL} B_{KL}^{CC} \sin(K\theta) \sin(L\alpha) \quad (46)$$

where A_{KL}^{CC} are the coefficients of the $\cos(\theta) \times \cos(\alpha)$ functions and B_{KL}^{CC} the coefficients of the $\sin(\theta) \times \sin(\alpha)$ functions. K, L are whole numbers that indicate periodicity. The coefficients and periodicity are determined by the fitting of the potential energy surface. This type of

form is a Fourier series of symmetry adapted and has been chosen because the integrals between such functions are very easy to evaluate and they are further used in the Theory of Non-Rigid Molecules [63]. The potential energy curve for the ground state obtained by the calculations using a 6-31G** basis set is:

$$\begin{aligned}
V(\theta, \alpha) = & 27332.55 - 857.91 \cos(\theta) - 25176.78 \cos(\alpha) + 2363.10 \sin(\theta) \sin(\alpha) \\
& - 1041.49 \cos(2\theta) - 755.59 \cos(2\theta) \cos(\alpha) + 1138.65 \sin(2\theta) \sin(\alpha) - 545.57 \sin(\theta) \sin(2\alpha) \\
& + 619.85 \cos(3\alpha) - 120.64 \cos(3\theta) \cos(\alpha) + 104.70 \sin(3\theta) \sin(\alpha) \quad (47)
\end{aligned}$$

The energies are related to the minimum energy and expressed in cm^{-1} . The standard deviation is 37 cm^{-1} , with a correlation coefficient of 1.0000 and a tolerancy of the variables 0.01. This function can be used for the calculation of the theoretical energy levels of internal rotation of the formic acid molecule.

B. The $^1S_1(n, \pi^*)$ single excited state

The potential energy surface of the single excited state has been calculated using the 4-31G and 6-31G** basis sets and full optimization of the geometry except the torsion and wagging angles. We found two conformations which are pyramidal in agreement with the geometry of the carboxylic group in excited state, $\theta = -47.91, \alpha = 41.32$ and $\theta = 63.66, \alpha = 45.76$, which are only slightly more stable, about 119 cm^{-1} , one than the other. The carbon atom of the preferred conformations exhibits an sp^3 hybridization due to the destabilization of the π electronic bond by occupation of the π^* antibonding orbital ($n \rightarrow \pi^*$). The bond distance of the C=O is considerably larger than in the molecule in its ground state. The C atom of the C-O bond maintains its sp^2 character, although the C-O distance is also larger than in the case of the ground state. In addition, the O-H group is rotated up or down of the O=C-O plane. In Tables 5 and 6, the conformations and energies employing the two different basis sets are listed. The relative energies are smaller than in the ground state. The calculations of the diedral angles of the preferred conformations are in good accordance with calculations using the GVB approximation [68] and 6-31G* basis set (-47.91 and 41.32 , the most stable, and 63.66 and 45.76 the next one in energy). It can be seen that they are only a few degrees different of our results.

The potential energy curve for the excited state (6-31G** basis set) is:

$$\begin{aligned}
V(\theta, \alpha) = & 20229.83 - 27604.30 \cos(\alpha) - 44.27 \cos(\theta) \cos(\alpha) + 168.71 \sin(\theta) \sin(\alpha) \\
& - 0.06 \cos(2\theta) + 9877.11 \cos(2\alpha) + 1350.00 \sin(3\theta) \sin(3\alpha) - 10.21 \cos(5\theta) \cos(3\alpha) \\
& - 23.84 \cos(\theta) \cos(6\alpha) + 790.86 \cos(6\theta) \cos(3\alpha) + 235.30 \cos(3\theta) \cos(6\alpha) \\
& - 110.86 \cos(6\theta) \cos(4\alpha) + 148.17 \cos(4\theta) \cos(6\alpha) + 5.85 \cos(6\theta) \cos(5\alpha) \quad (48)
\end{aligned}$$

The standard deviation is about 30 cm^{-1} , the correlation coefficient 1.0000 and the tolerancy of the variables is 0.01. Knowing the potential energy surfaces, it is possible to calculate the theoretical rotational spectra of the molecule of formic acid and to compare with the experimental fluorescence spectrum.

V. DISCUSSION AND CONCLUSIONS

In the present paper, the necessity of spin projected wave functions is discussed and the HPHF wave function is derived from the PHF wave function, and its main properties with respect to the spin elimination/contamination are proved. An historical review including all the references and main contributions over the years is done. As further application of the HPHF method, the calculation of excited states of the same symmetry as the ground state is reviewed and the method is applied to the calculation of the first singlet excited state S_1 of formic acid. For this, an orthogonalization of the excited orbital to its corresponding occupied orbital is made, in order to avoid the variational collapse of the excited state into the fundamental one. Note, that the excited wave function is not necessarily orthogonal to the fundamental one because the wave functions are eigenfunctions of different Hamiltonian equations, see i.e. Eqs. (24,37) of Ref. [39] and Eqs. (17,23) of Ref. [41]. Nevertheless, the wave functions are nearly orthogonal. This procedure is preferred to the complete orthogonalization of all the envolved orbitals, which might led to worse results.

Formic acid is small molecule but it has been chosen due to its complex spectra. To study the spectrum of formic acid, potential energy surfaces of the molecule in its ground and excited state with respect to the slow motions are needed. These motions are the torsion of the hydroxilic group and the waving out-of plane of the aldehydic hydrogen. The potential energy surface of the ground state has two minima, the *anti/trans* and *sin/cis* conformations.

In the *anti* conformation, the hydroxilic hydrogen interacts with the carboxylic oxygen by hydrogen bonding, making more stable, about 2000 cm^{-1} this conformation. In addition, the surface shows many relative minima.

In the S_1 excited state, two minimum conformations have been found with pyramidal geometries, which are in concordance with other theoretical calculations. Contrary to the ground state, they are separated by a smaller barrier of about 119 cm^{-1} . The bond distance of the C-O groups are larger. The carboxylic carbon seems to be in a sp^3 hybridization while the other C atom is in a sp^2 one. The obtained potential energy surface and geometrical parameters can be employed to calculate the theoretical spectrum of this molecule.

It can be concluded that the HPHF method, appart of introducing small spin correlation effects and provide almost pure state wave functions, can be advantageously employed in the calculation of the lowest singlet and triplet excited states of medium size to large molecules.

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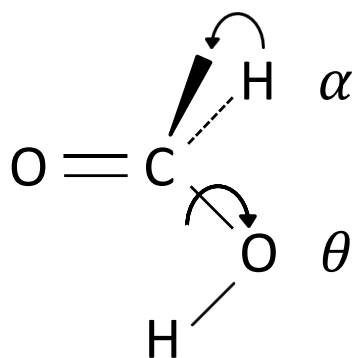


Figure 1: The formic acid molecule with its motions of torsion of the hydroxylic group (θ) and the out-of-plane wagging (α) of the aldehydic hydrogen atom.

TABLE I: Potential energy surface of the S_0 ground state of formic acid molecule with respect to the torsion θ of the hydroxylic group and the out-of-plane wagging α of the aldehydic hydrogen atom. The angles are defined in Fig. 1. The molecular conformations have been optimized using a 4-31G basis and the fixed conformations were calculated using a 6-31G** basis set. Energies in a.u., relative energy in cm^{-1} and bond and diedral angles in degrees.

$\theta(\text{tor.})$	$\alpha(\text{wag.})$	E(RHF/4-31G)	E(RHF/6-31G**)	E rel. (RHF/6-31G**)
0	0	-188.475615	-188.767056	0.00
30	0	-188.470908	-188.761748	1164.97
60	0	-188.461790	-188.751644	3382.54
90	0	-188.456326	-188.746200	4577.36
120	0	-188.457521	-188.748718	4024.73
150	0	-188.462181	-188.754910	2665.74
180	0	-188.464635	-188.757967	1994.80
0	30	-188.463221	-188.754128	2837.37
30	30	-188.454621	-188.744940	4853.90
30	-30	-188.463119	-188.753494	2976.51
60	30	-188.444947	-188.734622	7118.44
90	30	-188.441525	-188.731700	7759.75
90	-30	-188.448790	-188.737534	6479.33
120	30	-188.444879	-188.736391	6738.56
120	-30	-188.447250	-188.737145	6564.71
150	30	-188.450292	-188.743008	5277.93
150	-30	-188.450267	-188.742081	5481.38
180	30	-188.452578	-188.745984	4624.77
0	60	-188.424328	-188.713229	11813.66
30	60	-188.412716	-188.701357	14419.26
30	-60	-188.428407	-188.716832	11022.89
60	60	-188.402374	-188.691024	16687.10
60	-60	-188.423932	-188.711090	12283.12

Continuation Table I.

$\theta(tor.)$	$\alpha(wag.)$	E(RHF/4-31G)	E(RHF/6-31G**)	E rel. (RHF/6-31G**)
90	60	-188.400008	-188.689427	17037.60
90	-60	-188.416679	-188.703031	14051.86
120	60	-188.404514	-188.695059	15801.51
120	-60	-188.412656	-188.699901	12544.07
150	60	-188.410892	-188.702447	14180.04
150	-60	-188.413169	-188.702713	14121.66
180	60	-188.414088	-188.705467	13517.22

TABLE II: Comparison of the energies and relative energies of the S_0 ground state *anti* and *syn* conformations obtained by the RHF method and a 6-31G** basis with the HPHF program package and results obtained by Ref. [68] using the GVB approximation and a 6-31G* basis. The angles are defined in Fig. 1. Energies in a.u., relative energies in cm^{-1} and bond and diedral angles in degrees.

Ref.	Conform.	$\theta(tor.)$	$\alpha(wag.)$	E(a.u.)	E rel. (cm^{-1})
This work (RHF/6-31G**)	<i>anti</i>	0	0	-188.767056	0.00
Ref. [68] (GVB/6-31G*)	<i>anti</i>	0	0	-188.7747569936	0.00
This work (RHF/6-31G**)	<i>syn</i>	180	0	-188.757967	1994.80
Ref. [68] (GVB/6-31G*)	<i>syn</i>	180	0	-188.7648402037	2175.00

TABLE III: Conformations of the potential energy surface of the S_0 ground state of formic acid molecule with respect to the torsion θ of the hydroxylic group and the out-of-plane wagging α of the aldehydic hydrogen atom. The angles and distances are referred to Fig. 1. They have been optimized with a 4-31G basis set. Lengths are expressed in Å and bond and diedral angles in degrees.

θ (tor.)	α (wag.)	r(C=O)	r(C-O)	r(O-H)	r(C-H)	α (O=C-O)	α (C-O-H)	α (H-C-O)
0	0	1.200	1.341	0.956	1.072	124.62	114.89	124.93
30	0	1.199	1.348	0.955	1.073	124.70	116.09	124.52
60	0	1.195	1.360	0.954	1.074	124.48	118.19	123.74
90	0	1.193	1.365	0.954	1.076	123.69	118.83	123.14
120	0	1.192	1.360	0.953	1.078	123.00	117.97	122.87
150	0	1.193	1.351	0.952	1.080	122.63	116.99	122.88
180	0	1.193	1.347	0.951	1.080	122.46	116.65	122.89
0	30	1.201	1.352	0.956	1.076	123.37	114.95	125.04
30	30	1.980	1.364	0.955	1.077	123.06	115.79	124.70
60	30	1.195	1.374	0.954	1.079	122.85	116.71	123.59
90	30	1.194	1.374	0.954	1.081	122.61	116.28	122.41
120	30	1.195	1.365	0.953	1.083	122.39	115.96	121.87
150	30	1.195	1.356	0.951	1.083	121.91	116.03	122.04
180	30	1.194	1.316	0.951	1.083	121.39	116.41	122.56
0	60	1.201	1.396	0.957	1.085	118.86	114.59	127.43
30	60	1.197	1.414	0.955	1.085	118.22	114.35	127.65
60	60	1.195	1.423	0.955	1.086	118.48	113.38	124.94
90	60	1.197	1.414	0.955	1.089	119.14	112.77	121.89
120	60	1.198	1.399	0.952	1.091	119.23	114.06	120.55
150	60	1.197	1.391	0.951	1.093	118.50	114.95	121.08
180	60	1.195	1.396	0.952	1.092	117.57	115.94	122.52
30	-30	1.201	1.353	0.956	1.076	124.11	116.22	124.18
60	-30	1.198	1.364	0.954	1.076	124.24	118.88	123.24

Continuation Table II.

θ (tor.)	α (wag.)	r(C=O)	r(C-O)	r(O-H)	r(C-H)	α (O=C-O)	α (O-C-H)	α (H-C=O)
90	-30	1.194	1.374	0.954	1.078	123.21	120.56	122.82
120	-30	1.192	1.374	0.953	1.080	121.89	119.80	122.82
150	-30	1.193	1.365	0.953	1.082	121.26	117.80	122.89
30	-60	1.202	1.388	0.958	1.085	120.49	116.39	124.98
60	-60	1.200	1.395	0.956	1.085	121.58	119.51	122.77
90	-60	1.196	1.409	0.955	1.086	120.67	121.83	122.20
120	-60	1.193	1.415	0.954	1.087	118.62	121.25	122.81
150	-60	1.193	1.409	0.953	1.090	117.34	118.29	123.32

TABLE IV: Comparison of the obtained ground state S_0 geometries of the most stable conformeres *anti/trans* ($\theta = 0, \alpha = 0$) and *syn/cis* ($\theta = 180, \alpha = 0$) of formic acid with SCF-MO ab initio calculations using the Gaussian 82 program package with a 6-3G* basis and experimental values. In this work, the molecular conformations have been optimized using a 4-31G basis. The angles are defined in Fig. 1. Energies in a.u., bond distances in \AA and dihedral angles in degrees. Note, in Ref. [69] bond distances are given in *pm*.

Method	θ (tor.)	α (wag.)	r(C=O)	r(C-O)	r(O-H)	r(C-H)	α (O=C-O)	α (C-O-H)	α (H-C=O)
RHF	0	0	1.200	1.341	0.956	1.072	124.62	114.89	124.93
Exp. [70]	0	0	1.203	1.342	0.972	1.097	124.8	106.3	123.2
SCF-MO [69]	0	0	1.182	1.323	0.953	1.084	124.9	108.7	124.7
RHF	180	0	1.193	1.347	0.951	1.080	122.46	116.65	122.89
Exp. [71]	180	0	1.195	1.352	0.956	1.105	122.1	109.7	123.3
SCF-MO [69]	180	0	1.175	1.328	0.948	1.090	122.0	111.6	124.1

TABLE V: Potential energy surface of the S_1 singlet excited state of formic acid molecule with respect to the of torsion θ of the hydroxylic group and the out-of-plane wagging α of the adehydic hydrogen atom calculated by the HPHF method. The molecular conformations have been optimized using a 4-31G basis. The angles are defined in Fig. 1. Energies in a.u., relative energies in cm^{-1} , bond distances in \AA and diedral angles in degrees.

θ	α	r(C=O)	r(CO)	r(OH)	r(CH)	α (OCO)	α (COH)	α (HCO)	E(RHF/4-31G)	E rel.
-47.91	41.32	1.417	1.385	0.957	1.073	109.29	115.20	120.93	-188.371380	0.00
63.66	45.76	1.397	1.385	0.957	1.077	109.32	115.20	120.88	-188.367798	786.23
0	0	1.408	1.373	0.961	1.064	123.97	114.71	116.91	-188.361620	2142.10
45	0	1.408	1.364	0.952	1.063	117.21	115.47	120.38	-188.364681	1470.35
90	0	1.405	1.368	0.955	1.063	115.25	115.50	119.93	-188.364987	1403.11
135	0	1.399	1.366	0.952	1.066	114.16	115.34	119.68	-188.362674	1910.83
180	0	1.392	1.369	0.948	1.068	111.86	114.90	120.98	-188.361081	2260.52
0	45	1.397	1.400	0.956	1.069	111.30	115.56	116.42	-188.369582	394.69
90	45	1.394	1.382	0.955	1.074	109.55	116.05	114.28	-188.368744	578.67
180	45	1.389	1.396	0.954	1.073	108.15	113.96	114.41	-188.369099	500.73
150	-45	1.388	1.381	0.950	1.075	107.60	114.70	114.67	-188.369775	352.36
0	90	1.389	1.483	0.956	1.081	101.95	114.14	117.30	-188.326282	9821.95
90	90	1.378	1.537	0.956	1.078	98.92	110.53	118.07	-188.315520	12259.87
-90	90	1.396	1.484	0.957	1.081	101.69	116.15	113.72	-188.331551	8741.47

TABLE VI: Potential energy surface of the S_1 singlet excited state of formic acid molecule with respect to the of torsion θ of the hydroxylic group and the out-of-plane wagging α of the aldehydic hydrogen atom calculated by the HPHF method. The molecular conformations have been optimized using a 6-31G** basis. The angles are defined in Fig. 1. Energies in a.u., relative energies in cm^{-1} , bond distance in \AA and angles in degrees.

θ	α	r(C=O)	r(CO)	r(OH)	r(CH)	α (OCO)	α (COH)	α (HCO)	E(RHF/6-31G**)	E rel.
-41.93	46.57	1.370	1.351	0.946	1.071	109.17	115.15	119.96	-188.645986	0.00
67.38	39.67	1.362	1.348	0.950	1.084	109.45	115.25	120.15	-188.644483	119.79
0	0	1.376	1.347	0.941	1.067	123.88	114.74	117.34	-188.631843	3512.60
45	0	1.370	1.343	0.950	1.065	117.01	115.42	120.83	-188.636122	2164.83
90	0	1.375	1.345	0.944	1.062	115.20	115.49	120.33	-188.636949	1983.54
135	0	1.369	1.343	0.942	1.068	114.09	115.38	120.12	-188.634223	2581.16
180	0	1.370	1.347	0.940	1.066	111.80	114.90	121.26	-188.631414	3198.16
0	45	1.378	1.349	0.946	1.080	111.46	115.38	116.86	-188.645211	170.25
90	45	1.368	1.346	0.944	1.081	109.61	116.17	114.73	-188.644777	265.48
180	45	1.359	1.350	0.940	1.064	108.16	113.93	114.91	-188.644990	218.62
150	-45	1.364	1.351	0.941	1.079	107.77	114.71	115.11	-188.645440	119.79
0	90	1.354	1.437	0.947	1.089	102.02	114.34	117.95	-188.600875	9900.69
90	90	1.337	1.458	0.948	1.081	99.06	110.65	118.90	-188.591982	11852.64
-90	90	1.356	1.421	0.951	1.087	101.72	116.19	114.47	-188.605821	8815.33

TABLE VII: Comparison of the obtained singlet excited state S_1 geometries of the most stable conformeres of formic acid with another ab initio calculations using a 6-3G* basis and Gaussian 98 (GVB) computer program. In this work, the molecular conformations have been optimized using a 6-31G** basis. The angles are defined in Fig. 1. Energies in a.u., relative energies in cm^{-1} and bond distances in \AA and diedral angles in degrees.

Method	θ	α	r(C=O)	r(CO)	r(OH)	r(CH)	α (OCO)	α (COH)	α (HCO)	E	E rel.
HPHF	-41.93	46.57	1.370	1.351	0.946	1.071	109.17	115.15	119.96	-188.645986	0.00
GVB [68]	-47.91	41.32	1.3701	1.3499	0.9524	1.0821	112.35	-118.72	111.50	-188.6336441178	0.00
HPHF	67.38	39.67	1.362	1.348	0.950	1.084	109.45	115.25	120.15	-188.644483	119.79
GVB [68]	63.66	45.76	1.3743	1.3515	0.9492	1.0771	112.87	-122.63	110.71	-188.6321054319	338.00

The disagreement between the angles α (COH) is maybe due to a different reference direction of the angles calculation.