Theoret. chim. Acta (Berl.) 27, 197—212 (1972)

Simplified Non-Empirical Excited State Calculations

Part I. The Rydberg *ns* and *npσ* Series of Ethylene

I. Fischer-Hjalmars and J. Kowalewski
Institute of Theoretical Physics and Institute of Inorganic and Physical Chemistry
University of Stockholm, Stockholm, Sweden

Received May 12, 1972

A simple non-empirical method for calculating electronic molecular states based on the description of excited states by mixing singly-excited configurations is presented. The complexity of the multiconfigurational wavefunctions is overcome by using the frozen-core approximation combined with natural orbital transformation. The method is tested on some low-lying excited states of the hydrogen molecule and is applied on Rydberg *ns* and *npσ* series of ethylene for $n = 3, 4, 5$, and 6. Transition energies, oscillator strengths and some other properties are computed. Internal consistency of the results and their agreement with available experimental data are good.

Ein einfaches nicht-empirisches Verfahren für die Berechnung angeregter molekularer Zustände, das auf der Darstellung durch Linearkombinationen einfach angeregter Zustände beruht, wird vorgeschlagen. Die Komplexität des Mehrfach-Determinanten-Ansatzes wird durch Verzicht auf die Änderung der Rumpfzustände und Transformation auf natürliche Orbitale gemeistert. Testrechnungen für einige tiefliegende H_2-Zustände und Rydbergzustände von Äthylen werden ausgeführt und Übergangsenergien, Oszillatorstärken und anderes mehr berechnet. Konsistenz untereinander und Übereinstimmung mit dem Experiment sind gut.

Presentation d'une méthode non empirique simple pour le calcul des états électroniques moléculaires fondée sur la description des états excités par interaction de configurations monoexcitées. La complexité des fonctions d'onde multiconfigurationelles est évitée en utilisant l'approximation du coeur fixe combinée avec l'emploi des orbitales naturelles. La méthode est éprouvée sur certains états excités inférieurs de la molécule d'hydrogène et appliquée aux séries de Rydberg *ns* et *npσ* de l'éthylène pour $n = 3, 4, 5$ et 6. Calculs des énergies de transition, des forces oscillatrices et de quelques autres propriétés. La cohérence interne des résultats et l'accord avec les données expérimentales disponibles sont bons.

1. Introduction

During the last decade non-empirical calculations on electronic states of molecules have steadily become more frequent and the quality of results from such calculations has considerably improved. Recently also excited electronic states have been successfully treated by such methods. One goal towards which various attempts have already been made is to develop methods yielding reliable results without requiring excessive computational effort or computer time. This goal forms one of the two aims of the present study. The other aim is to investigate the molecular Rydberg states of ethylene by applying our method to perform calculations on them. This kind of close investigation of the Rydberg states is one of many necessary steps to a better interpretation of the electronic spectra of various molecules. In particular, the calculation of both the excited state energies and the transition probabilities is required since both these quantities are used in making spectral assignments.

Sects. 2 and 3 are a brief outline of the theory, stressing a few points the principles of which are well understood although their applications on performing calculations of this kind seems to have been somewhat neglected. In Sect. 4 our method of computation is presented in detail. In Sect. 5 an application to the hydrogen molecule is carried out in order to illuminate certain features of our method. Sect. 6 describes the application to the Rydberg states of ethylene. The results of the calculations are presented in Sect. 7. Finally we conclude in Sect. 8 with a commentary and evaluations of the present study and its relationship to similar work being done elsewheres.

2. Theory

As is well-known, the Hartree-Fock equations for a closed-shell system can be written

$$F\psi_r = \varepsilon_r \psi_r , \tag{1}$$

$$F = H + \sum_{j=1}^{N} (2J_j - K_j) . \tag{2}$$

As usual, H is the bare-nuclei one-electron operator, and J_j and K_j are the Coulomb and exchange operators. Since F is Hermitian, the eigenfunctions $\{\psi_r\}$ will form a complete orthonormal set. As discussed in detail e.g. by Huzinaga and Arnau [1] this set can be divided into two subsets $\{\psi_0\}$ and $\{\psi_v\}$, representing the occupied and the virtual orbitals. $\{\psi_0\}$ and $\{\psi_v\}$ will span orthogonal subspaces of the complete Hilbert space spanned by $\{\psi_r\}$. As is well-known, the finite set $\{\psi_0\}$ is adequate for construction of a Slater determinant Ψ_0 representing the ground state wavefunction

$$\Psi_0 = \mathscr{A}(\psi_1 \bar{\psi}_1 \psi_2 , \ldots , \bar{\psi}_N) . \tag{3}$$

In principle $\{\psi_v\}$ will be an infinite set. However, in practice the Eqs. (1) are solved by setting

$$\psi_r = \Sigma\, \chi_\mu c_{\mu r} \tag{4}$$

where $\{\chi_\mu\}$ is ome suitably chosen finite basis set, $\mu = 1, 2, \ldots, M$. Consequently, the subsets $\{\psi_v\}$ will now be reduced to $(M - N)$ members.

The simplest way of constructing an excited state wavefunction is to replace one of the ground state orbitals ψ_i, $i \subset 0$, by a virtual orbital ψ_m, $m \subset v$. The resulting wavefunction of the correct multiplicity may be denoted $\Psi(\psi_i \rightarrow \psi_m)$. Usually this wavefunction is not entirely adequate for the description of an excited state, not even when the ψ_r's have emerged from a large basis SCF calculation.

Various suggestions have been made to remedy this deficiency. One way is to keep to the method of replacement of a single orbital of Ψ_0 but to search for other virtual orbitals than those of Eq. (1), i.e. to make a transformation of the subspace $\{\psi_v\}$ without changing the subspace $\{\psi_0\}$.

To this end, various procedures have been suggested, e.g. by Hunt and Goddard [2] and by Huzinaga and Arnau [1]. However, these treatments imply orthogonality problems or rather lengthy and somewhat arbitrary projection techniques. Another possibility is to carry out separate SCF calculations for each excited state, see e.g. Buenker and Peyerimhoff [3]. These authors have combined the SCF procedures with extensive CI treatments. Their method may be the most adequate for special cases, but becomes very cumbersome when several excited states of the same symmetry are of interest and/or large molecules are considered.

In the present study a rather simple method is presented, though obviously reasonably adequate for certain purposes. The method is a CI method which in the general case means that an excited state is described by combination of several configurations:

$$\Phi^\alpha = \Sigma\, \Psi(\psi_i \psi_j \ldots \to \psi_l \psi_m \ldots)\, C^\alpha_{ij\ldots lm\ldots} \tag{5}$$

where the sum is extended over all possible combinations of occupied orbitals with virtual orbitals. However, in our method the frozen-core approximation has been adopted, i.e. only singly excited configurations are included and the sum is restricted to excitations from a specific occupied orbital ψ_i:

$$\Phi^\alpha = \sum_m \Psi(\psi_i \to \psi_m)\, C^\alpha_{im}\,. \tag{6}$$

The ψ_i's, $i \subset 0$, are eigenfunctions of the ground state Hartree-Fock operator F. Furthermore, all the ψ_m's, $m \subset v$, also belong to this same set $\{\psi_r\}$.

The coefficients C^α_{im} are to be determined by a variational procedure. With the present choice of $\{\psi_r\}$ the matrix elements of the Hamiltonian are composed of ε_r's and two-electron integrals. There is no orthogonality problem and the calculation of transition probabilities is straightforward. However, an attempt to treat several kinds of excited states by use of the same expansion (4) will give rise to either poorly convergent series (6) or unwieldy calculations.

A way out of this dilemma is to limit the interest to a certain class of excited states, e.g. the *ns* series of Rydberg states. The choice of $\{\chi_\mu\}$ has to be made *with particular reference to this class*. Consequently, it may be possible to extend the basis sufficiently for a good description of this particular class, yet keeping the number $(M - N)$ within reasonable limits. Thus, the clue is to choose the set $\{\chi_\mu\}$ to give a good representation of only a special subset $\{\psi_w\}$ of the whole set of virtual orbitals $\{\psi_v\}$. Then, the diagonalisation of the Hamiltonian matrix may provide adequate description of several excited states of the same symmetry.

The adoption of a frozen core implies that the ionization potential can be obtained from Koopmans' theorem within an approximation similar to that of the excitation energies. This expectation is reasonable since both reorganization and correlation are likely to be roughly the same in a Rydberg state as in the corresponding ionized state.

Although the multiconfigurational wavefunctions (6) are not easily surveyable, a simplified interpretation of the excitation process can easily be regained by a transformation to natural orbitals (NO's) ϕ_l [4, 5]. This can be achieved by diagonalization of the first-order density matrix in the ψ-space representation. Then, Eq. (6) can be written

$$\Phi^\alpha = \Sigma\, \Phi(\phi_i \to \phi_m)\, B^\alpha_{im}\,. \tag{7}$$

Since the frozen-core approximation is used this diagonalization leads to $N-1$ doubly occupied NO's identical with the ground state occupied molecular orbitals $\psi_j, j \neq i$, and two singly occupied NO's one being identical with ψ_i, the other one being the orbital occupied in the excited state under consideration but not in the ground state. The values of the diagonal elements of the first order density matrix representation in the NO space satisfy the sufficient condition for Φ^α to be a single-configuration wavefunction, i.e. the sum in (7) is reduced to a single term.

3. Rydberg States

Molecular Rydberg states are commonly defined from the orbital point of view [6–8]. Using this model, a Rydberg state can be described by replacing one of the ground state orbitals by a molecular orbital, called Rydberg orbital, so large in size compared with the molecular core that it can be well described by the united atom (UA) model. Rydberg states fall into series such that the excitation energies, E_n, fit the formula

$$E_n = E(IP) - R/(n-\delta)^2 \tag{8}$$

where R is the Rydberg constant and δ the quantum defect (a positive quantity that varies rather strongly with the azimuthal quantum number l of the UA orbital, but only slightly with the principal quantum number n). In (8), a singly-charged core has been assumed. $E(IP)$ is the energy of ionisation (ionization potential).

4. Computational Details

In the present study the basis set (χ_μ) has been chosen as Gaussian Type Functions (GTF). From the primitive set a smaller set of Contracted Gaussian Type Functions (CGTF) has been obtained as described below. The SCF-MO wavefunctions and the electron repulsion integrals over the CGTF's have been computed with the IBMOL program version 4 [9] using the method described by Clementi and Davis [10]. The CI procedure involves the transformation of the two-electron integrals to the MO basis and construction and diagonalization of the Hamiltonian matrix. The symmetry of the system has been used extensively to bring down the number of integrals to be computed and the size of the matrices to be diagonalized. The computations have been carried out for both singlet and triplet excited states. Dipole matrix elements have been computed by the method of Browne and Poshusta [11].

5. Applications to Hydrogen

A test of the present method has been made by applying it to some lowlying excited states of the hydrogen molecule. The basis chosen in this case included ten GTF's of s-type with exponents optimized by Huzinaga [12], three GTF's of p-type and one of each of the types d_{xx}, d_{yy} and d_{zz} on each atom. No contraction was applied.

Table 1. Energy data for some of the lower states of the H_2 molecule with ground state equilibrium distance, $R = 1.40$ a.u.

State	Total energy, a.u.			Vertical transition energy from the ground state, e.V.			
	CI	SCF	Accurate	Single configuration	CI	SCF	Accurate
$X\,^1\Sigma_g^+$ (ground)	-1.133595	-1.133595	-1.174442[a]				
$B\,^1\Sigma_u^+$	-0.665456	-0.699693	-0.703744[a]	13.43	12.73	11.81	12.81[a]
$E\,^1\Sigma_g^+$	-0.622893		-0.681254[a]	13.27	13.08		13.42[a]
$b\,^3\Sigma_u^+$	-0.767200		-0.783150[a]	13.21	9.97		10.65[a]
$a\,^3\Sigma_g^+$	-0.691346		-0.71294[b]	12.93	12.03		12.56[b]
$H_2^+\,^2\Sigma_g^+$		-0.569979	-0.569979[c]		16.18[d]	15.34	16.45[c]

[a] Ref. [13]. – [b] Ref. [14]. – [c] Ref. [15]. – [d] Koopmans' theorem value.

To compare the present CI method with the above-mentioned method including SCF calculations for excited states the Hartree-Fock equations were solved both for the ground state $X^1\Sigma_g^+$ and for the lowest excited singlet $B^1\Sigma_u^+$. The total energy of the ground state was found to be -1.133595 a.u., cf. Table 1. According to Kolos and Roothaan [13] the Hartree-Fock limit is -1.133630 a.u., 0.040812 a.u. (1.11 eV) above the accurate energy value [13], the difference being the correlation energy. For the $B^1\Sigma_u^+$ state we obtained an SCF energy of -0.699693 a.u. only 0.00405 a.u. (0.11 eV) above the accurate value. Our basis set was not particularly well adapted to describe this state which is a Rydberg state [16], since our lowest orbital exponent was 0.0285649 and more diffuse basis functions may be required for a good description. The correlation energy of this state is therefore surely smaller than 0.1 eV. This result is in strong support of the above-mentioned conjecture about equality of the correlation energy of a Rydberg state and the corresponding ionized state.

Our CI method with fifteen singly excited configurations produced an energy value of -0.665456 a.u., cf. Table 1. The transformation to NO's showed that the state can be described as built from a ground state $1s\sigma_g$ orbital and a $2p\sigma_u$ NO. The latter orbital was found to be rather similar to the $2p\sigma_u$ orbital, obtained from our SCF calculation. Since we have used the frozen-core approximation, the total energy difference between the results of the SCF and the CI calculations, 0.034237 a.u. (0.9 eV), can be interpreted as reorganization energy.

This value may be compared with the reorganisation energy of the H_2^+ ion. Using Koopmans' theorem, the orbital energy of the ground state, $\varepsilon = -0.594485$, the correlation energy of this state and the accurate energy of the H_2^+ ground state, the ionic reorganisation energy is found to be 0.030834 a.u. (0.84 eV). Thus, it is borne out that also the conjecture about the reorganisation energies is correct in this case. Moreover, it is noticeable that the change in correlation energy between the ground state and the excited state has almost the same value as the reorganisation energy so that these two quantities almost cancel. This cancellation is also obvious from the vertical transition energies, listed in Table 1, showing that the CI-values are very close to the accurate values, in particular for the first excited singlet. A similar cancellation has been found also in other calculations of ionization potentials using Koopmans' theorem.

Finally, vertical transition energies found from the single configuration description using ground state optimized MO's should be compared with the CI result, cf. Table 1. Obviously, this kind of single configuration is not entirely adequate for the description of excited states. As discussed by previous authors [2, 3] some kind of improvement is called for. The present scheme for CI calculations seems to show one possibility for the desired improvement.

6. Applications to Ethylene

The electronic spectrum of ethylene is of great interest and has been studied both experimentally and theoretically by many authors. A comprehensive review of the literature until 1968 has been given by Merer and Mulliken [17]. Several new theoretical [18–21] and experimental [22, 23] investigations have been reported in recent years. Most interest has been devoted to the valence excited T and V states and the lowest Rydberg states, while studies of higher Rydberg states have been more infrequent. The present investigation concerns two different Rydberg series, viz. the well-known ns series and a $np\sigma$ series, including states with $n = 3, 4, 5$, and 6.

6.1. Basis Set

The choice of suitable GTF's for the description of molecular Rydberg states is a rather complicated matter. Preliminary computations on ethylene with some different basis sets indicated that the basis functions actually can be separated into two subsets:

1. Ground state (Normal state) basis functions, NGTF's, with exponents and contraction coefficients optimized in the usual way;
2. Rydberg state basis functions, RGTF's.

These two sets seem to be rather independent. Inclusion of the RGTF's has an insignificant effect both on the total energy of the ground state and on the orbital energies of the occupied orbitals. On the other hand, computations using quite different NGTF's but the same set of RGTF's display very small changes in the orbital energies of the lower virtual orbitals. The influence of the NGTF's on the Rydberg state energies E_n of Eq. (8) appears almost solely in the values of ε_i. Since the same ε_i is responsible for the value of $E(IP)$ the values computed for the quantum defects are effectively independent of the NGTF's. A change of the RGTF's, however, was found to have a drastic effect on the energies of both virtual orbitals and Rydberg states.

As a consequence, the choice of basis set was divided into two separate problems. The set of NGTF's was chosen as the ethylene-optimized basis set of Schulman *et al.* [24], including eight GTF's of s-type and four of p-type on each carbon atom and four GTF's of s-type on each hydrogen. All basis functions composing σ-orbitals were contracted to a minimal basis set as given by Schulman *et al.* [24]. Since we aimed at a rather good description of the occupied π-orbital, only a four-to-two contraction was used for the π-type GTF's.

Table 2. RGTF's for the *ns* and *npσ* Rydberg series in ethylene

Center	Orbital exponent	
	s-functions	*p*-functions
Carbon atoms	0.048708[a] 0.019631[a]	0.028858[a]
Molecular midpoint	0.00791 0.00319 0.00129 0.00052	0.01582 0.00638 0.00258 0.00104
Hydrogen atoms	0.0413[a]	

[a] Ref. [25].

The choice of a RGTF set is less straightforward. In a study of Rydberg states of the methyl radical McDiarmid [25] has reported orbital exponents suitable for two 3*s*-type and one 3*p*-type GTF on carbon and for one 2*s*-type GTF on hydrogen. Gaussians with still smaller exponents can hardly be centered on the carbons since this would cause so large overlap integrals that convergence of the SCF calculations might be prohibited. We therefore chose to center the most diffuse GTF's at the midpoint of the C–C bond. Refraining from the complicated procedure of optimizing the exponents of these functions we adopted the method of obtaining the exponents simply by division with a constant factor, starting with the most diffuse of the carbon 3*s* functions and using the ratio of the two 3*s* exponents as our constant. In this way we constructed four *s*-type GTF's. To get GTF's of p_z-type (along the C–C bond) we multiplied the *s*-type exponents by two. The RGTF's thus obtained (eighteen) are listed in Table 2. A calculation of the radial distribution functions of these RGTF's indicated that this basis set should be adequate also for higher members of the Rydberg series.

It should be stressed that the present set of RGTF's is chosen to be a *subset* $\{\chi_w\}$ of the whole set $\{\chi_v\}$ necessary to represent all kinds of virtual orbitals, cf. Sect. 2 above. Using this subset we cannot expect to obtain good results for all kinds of excited states, only for the Rydberg *ns* and *npσ* series we had in mind making our choice of $\{\chi_w\}$. For a study of e.g. the *T* and *V* states or other Rydberg series a different subset $\{\chi_w\}$ must be constructed.

6.2. *Ground State* SCF *Calculation*

All the calculations on ethylene have been carried out with the ground state equilibrium geometry as given by Allen and Plyler [26]. With this geometry the ethylene molecule belongs to the point group D_{2h}. The coordinate system was chosen according to the recommendation by Mulliken [27], the molecule lying in the *yz* plane with the CC and *z* axes collinear. The notations B_1, B_2, and B_3 of the symmetry species are referred to this particular choice of axes. Then the ground state electronic configuration is $(1a_g)^2\ (1b_{1u})^2\ (2a_g)^2\ (2b_{1u})^2\ (1b_{2u})^2\ (3a_g)^2\ (1b_{3g})^2\ (1b_{3u})^2$. The first seven orbitals constitute the σ-core while the $1b_{3u}$ orbital is the carbon-carbon bonding π-orbital.

Table 3. Orbital energies for some low-lying virtual orbitals of ethylene

Orbital	Orbital energy, a.u.
$4a_g$	0.00066
$5a_g$	0.00323
$6a_g$	0.01029
$7a_g$	0.02924
$8a_g$	0.08168
$9a_g$	0.09734
$3b_{1u}$	0.00217
$4b_{1u}$	0.00799
$5b_{1u}$	0.02181
$6b_{1u}$	0.05153

With our basis set of 74 GTF's, contracted to 34 CGTF's, the computation of the electron repulsion integrals with IBMOL 4 was by far the most computer-time-consuming part of this study. The total energy obtained from the SCF treatment was -77.91451 a.u. to be compared with the value -77.90830 obtained by Schulman *et al.* [24] with a basis set of NGTF's only and four-to-one contraction of all the *p*-functions. The Hartree-Fock energy of ethylene is close to the best value computed by Siegbahn [28], -78.062 a.u. The present values of the ε_i's of the occupied orbitals are very close to those of Schulman *et al.* [24]. The energy of the π-orbital, -0.3873 a.u. (10.54 eV), is of particular interest since Koopmans' theorem has been used in the discussion of the results for the Rydberg states. The experimental value of the vertical ionization potential reported by Eland [29] is 10.51 eV.

The ε-values found for the virtual orbitals are very low; as many as ten of them lie below 0.1 a.u. Some of the values are listed in Table 3. They are throughout lower than the corresponding values obtained by Buenker *et al.* [20] from their ground state SCF calculation to be used in a subsequent CI treatment. We do not expect these virtual orbitals to have any physical significance individually. Nevertheless, they may constitute an adequate subset $\{\psi_w\}$ for a CI description of certain excited states, cf. Sect. 2.

6.3. Choice of Configurations for the CI *Procedure*

According to the frozen-core approximation the configurations to be included in the CI treatment should be singly-excited and originating from a chosen occupied orbital ψ_i, cf. Eq. (6). In case of the present Rydberg series this occupied orbital should be the π-orbital. The computation is extremely fast. It requires less than one minute computer time on an IBM 360/75 computer for both the Rydberg series, singlets and triplets included.

In the special case of ethylene other kinds of CI treatments are also feasible. One possibility would be to include all singly-excited configurations of appropriate symmetry, excluding only excitations from the carbon inner shells. Such an approach would allow for some reorganization, the amount of which being strongly basis set dependent. Also a partly valence character of the excited states may be described in this way. The wavefunctions obtained will, however, be multiconfigurational both in the (MO) ψ-basis of Eq. (5) and in the (NO) ϕ-basis of Eq. (7). Natural orbitals may still be used for computation of one-electron properties, but the clearness of the model will be lost, at least partly. The interpretation of Eq. (8) will become obscured. Ionization potentials cannot be obtained in a consistent manner neither from Koopmans' theorem nor from SCF computations.

For the sake of comparison, some Rydberg state energy calculations have been carried out by the more extended CI method. However, most of the results presented below refer to first method described above being the one we judge suitable for future development and applications.

7. Results

7.1. B_{3u} States – ns Rydberg Series

Excitations from the occupied π-orbital to a virtual σ-orbital and belonging to the B_{3u} species are of the type $1b_{3u} \rightarrow ma_g$, with $m = 4, 5, \ldots, 12$. Excitations from an occupied σ-orbital to a virtual π-orbital belonging to the same species and included in the extended CI treatment are $2a_g \rightarrow 2b_{3u}$, $3a_g \rightarrow 2b_{3u}$, $2b_{1u} \rightarrow 1b_{2g}$ and $2b_{1u} \rightarrow 2b_{2g}$.

The energies obtained for the five lowest Rydberg singlets and triplets and the singlet-triplet splittings are summarized in Table 4, which also displays experimental data for the singlets [30, 31]. Results from the frozen-core approximation (nine configurations) as well as results from an extended CI treatment (thirteen configurations) are given. It is seen that the extension to $\sigma \rightarrow \pi$ excitations has an almost negligible effect on the energy values. The agreement between calculated and experimental values is rather good, which seems to confirm the expectation that correlation and reorganization energies should almost cancel for Rydberg states. The somewhat inferior agreement for the first member of the series may be due to some valence character of this state.

The singlet-triplet splittings are small for all the states and in particular for the higher ones. This may be interpreted as a result of the very small differential overlap between the occupied π-orbital and the very diffuse Rydberg NO's of these states.

Table 4. Some lower B_{3u} states of ethylene

Frozen core CI				Experimental	Extended CI	
Vertical transition energies, eV		Singlet-triplet splitting eV	Oscillator strength of singlet	0–0 transition energies, eV	Vertical transition energies, eV	
Singlet	Triplet				Singlet	Triplet
7.523	7.376	0.157	0.045	7.11[a]	7.522	7.363
9.090	9.025	0.065	0.022	8.90[b]	9.089	9.020
9.404	9.377	0.027	0.003	—	9.403	9.376
9.770	9.758	0.012	0.003	9.62[b]	9.770	9.757
10.049	10.026	0.023	0.004	9.95[a]	10.048	10.021

[a] Ref. [30]. – [b] Ref. [31].

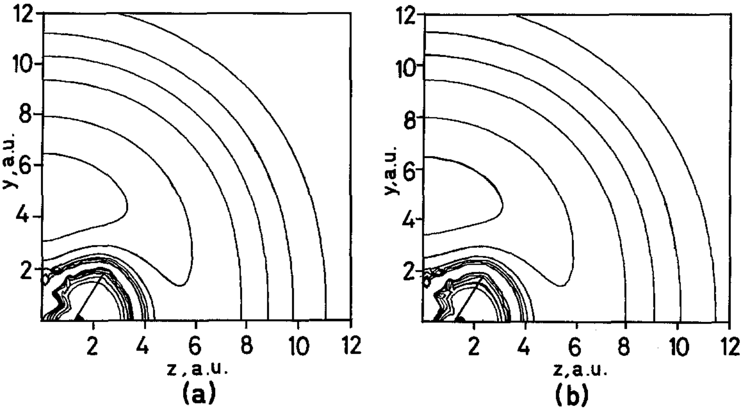

Fig. 1. Charge density contours for (a) $3s$ natural orbital and (b) corresponding $4a_g$ MO obtained from the open shell SCF calculation

To compare the present method with other possible methods we have carried out a restricted Hartree-Fock open shell calculation for the lowest $^1B_{3u}$ state using the same basis set as described above. The total energy was found to be 6.734 eV above the ground state energy. As could be anticipated, this energy difference is too small since reorganization but not correlation is taken into account by this kind of SCF method. An interesting result of this calculation is that the $4a_g$ orbital obtained by the SCF method is very similar to the Rydberg $4a_g$ orbital obtained by a very different procedure, viz. by the transformation to natural orbitals of the CI result for the lowest $^1B_{3u}$ state. Charge density contours in the molecular plane of these two differently computed $4a_g$ orbitals are presented in Fig. 1.

Table 4 also includes the computed oscillator strengths of the $^1A_g \rightarrow {}^1B_{3u}$ transitions which are fully allowed. No experimental values of the oscillator strengths are available. It is not very helpful to quote the experimental intensity values since the Rydberg transitions are found in the same region as a strong absorption continuum. Nevertheless, the experimental values strongly indicate that the intensity is considerably larger for the first members of the series than for the higher ones in good accord with the calculated values.

The $(n-\delta)^2$ values listed in Table 5 were found for all singlets by use of Eq. (8). The necessary value of the ionization potential, $E(IP)$, was calculated from Koopmans' theorem to be 10.539 eV. As discussed above the use of this theorem is consistent with our method of finding the energy values E_n of the Rydberg states. In order to obtain quantum defects δ which are reasonably constant within the series and of proper magnitude for Rydberg states of ns type the third state with $(n-\delta)^2 = 12.0$ must be excluded. Still, the composition of the CI vector of the third state does not immediately call for an exclusion. The motivation is however easily provided by inspection of the natural orbitals. The NO's of this state indicate that it should be interpreted as originating from a $\pi \rightarrow 4d\sigma$ transition. The Rydberg NO is mainly a $3p_z - 3p_z$ orbital. Its charge density contours in the molecular plane are presented in Fig. 2. It is easily seen that the orbital has a

Table 5. Properties of Rydberg natural orbitals found for some of the lower ${}^1B_{3u}$ states of ethylene

$(n-\delta)^2$	Rydberg natural orbital	Quantum defect	$r_{\max}$ of the outermost loop, a.u.	Expectation values of second moment components, a.u.		
				$\langle x^2\rangle$	$\langle y^2\rangle$	$\langle z^2\rangle$
4.51	3*s*	0.88	5.7	18.18	21.29	14.89
9.40	4*s*	0.93	8.3	59.12	59.25	74.07
12.00	(4$d\sigma$)	(0.54)	—	47.86	47.89	62.47
17.72	5*s*	0.79	25.5	267.2	266.8	264.9
27.8	6*s*	0.7	42	740	740	739

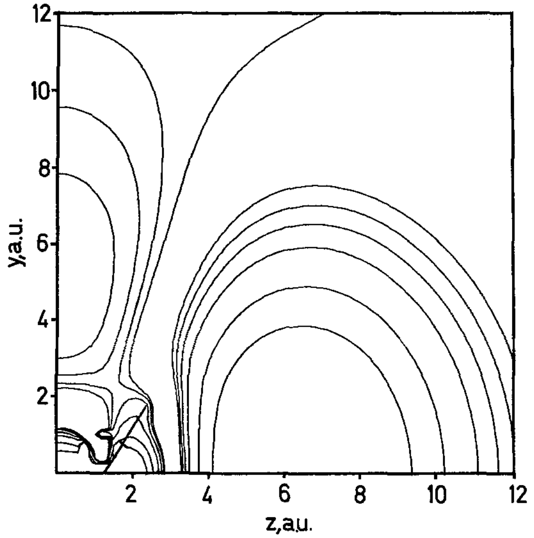

Fig. 2. Charge density contours for the natural Rydberg orbital of the third ${}^1B_{3u}$ state

clear *d* character. The presence of a transition of this type is by no means surprising and has actually been reported by Buenker *et al.* [20].

The present description of this state is however rather poor since our choice of the subset $\{\chi_w\}$ was made with the *ns* and $np\sigma$ Rydberg orbitals in mind and not $nd\sigma$ orbitals.

The assignments of the Rydberg orbitals and their quantum defects are listed in Table 5. In accord with Merer and Mulliken [17] we assume the lowest Rydberg *ns* orbital to be the 3*s* orbital. This assignment is at variance with the interpretation of Buenker *et al.* [20] who argue that this orbital must be the 4*s* since they assume all the three ground state occupied a_g orbitals to be united-atom *s* orbitals. Merer and Mulliken [17] on the other hand assumed the $3a_g$ orbital to be the united-atom $3d\sigma$ orbital. This latter assignment is strongly supported by our results. In Fig. 3 the charge density contours for the $3a_g$ orbital are displayed. This picture is very similar to the one for the $5a_g$ MO obtained by Buenker *et al.* [20] and assigned as united-atom $d\sigma$ by themselves.

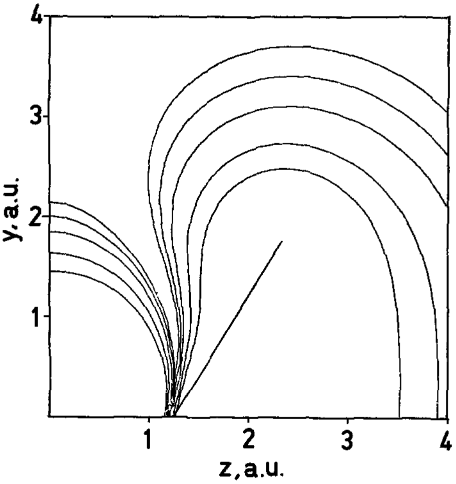

Fig. 3. Charge density contours for the $3a_g$ orbital

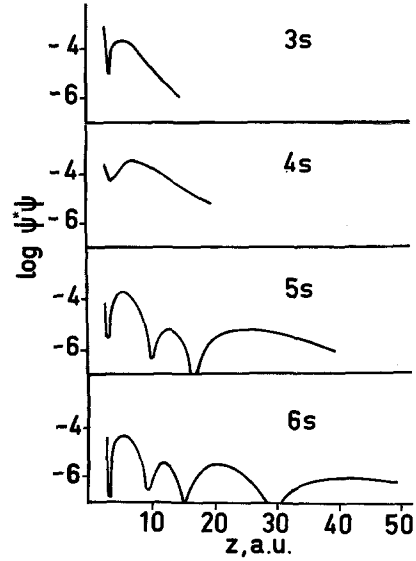

Fig. 4. Logarithm of charge density *vs.* distance from the molecular midpoint along the z-axis (C–C axis) for *ns* natural orbitals

The charge densities of the Rydberg natural orbitals of *ns* type have been computed along the z-axis and are presented in Fig. 4. We have chosen to plot the logarithm of the density since we wanted to display the whole range of interest including all the loops. It should be mentioned that the curves have been obtained by computing $\psi^*\psi$ at rather arbitrarily chosen points so that neither the maxima nor the minima are very accurate. A rough estimate of the z-value, corresponding to the maximum of the outermost loop and called $r_{\max}$, is given in Table 5. According to Mulliken [6] this $r_{\max}$ should be related to the effective quantum number: $r_{\max} \approx (n-\delta)^2$. This relation holds moderately well for the first two orbitals but not so well for the highest ones. The outermost loop is found well outside the molecular core even for the 3*s* orbital. The 4*s* NO seems to have one loop missing, but an additional loop was observed on an analogous curve along the y-axis. The spherical symmetry of the 3*s* and 4*s* orbitals is somewhat distorted, as could be anticipated. This is clearly shown by the expectation values $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ listed in Table 5. The 5*s* and 6*s* orbitals are however very closely spherical. They are also very diffuse. It should be noted that all the *ns* NO's were found to be C–H antibonding in agreement with the maintainance of Merer and Mulliken [17].

7.2. B_{2g} States – $np\sigma$ Rydberg Series

Excitations from the occupied π-orbital to a virtual σ-orbital and belonging to the B_{2g} species are of the type $1b_{3u} \rightarrow mb_{1u}$ with $m = 3, 4, \ldots, 12$. Excitations from an occupied σ-orbital to a virtual π-orbital belonging to the same species and included in the extended CI treatment are $2a_g - 1b_{2g}$, $2a_g \rightarrow 2b_{2g}$, $3a_g \rightarrow 1b_{2g}$, $3a_g \rightarrow 2b_{2g}$, and $2b_{1u} \rightarrow 2b_{3u}$. The energies obtained for the four lowest singlets and the corresponding triplets are presented in Table 6 together with the singlet-triplet splittings. Results from the frozen-core approximation (ten configurations) as well as from an extended CI treatment (fifteen configurations) are given. Also for this series the extension to $\sigma \rightarrow \pi$ excitations has a negligible effect. No experimental data are available since the ${}^1A_g \rightarrow {}^1B_{2g}$ transitions are dipole forbidden. Also in this case a restricted SCF open shell calculation was carried out for the lowest state of the series. The total energy was found to be 7.374 eV above the ground state energy. With the same argument as above this energy difference is presumably too small. A comparison of the SCF $3p\sigma$ orbital with the Rydberg NO orbital again shows large similarity between the two counterparts, cf. Fig. 5. The values of the singlet-triplet splitting, given in Table 6, seem to be reasonable for all the states.

Some properties of the $np\sigma$ natural orbitals are presented in Table 7. The quantum defects are quite constant and of proper magnitude for a Rydberg series of p-type. The values of $r_{\max}$, found from the densities displayed in Fig. 6, fit in with Mulliken's relation slightly better than in the *ns* series.

Table 6. Some lower B_{2g} states of ethylene

Frozen core CI			Extended CI	
Vertical transition energies, eV		Singlet-triplet splitting eV	Vertical transition energies, eV	
Singlet	Triplet		Singlet	Triplet
8.224	8.153	0.079	8.222	8.143
9.406	9.381	0.025	9.405	9.375
9.864	9.851	0.013	9.863	9.852
10.098	10.088	0.010	10.096	10.087

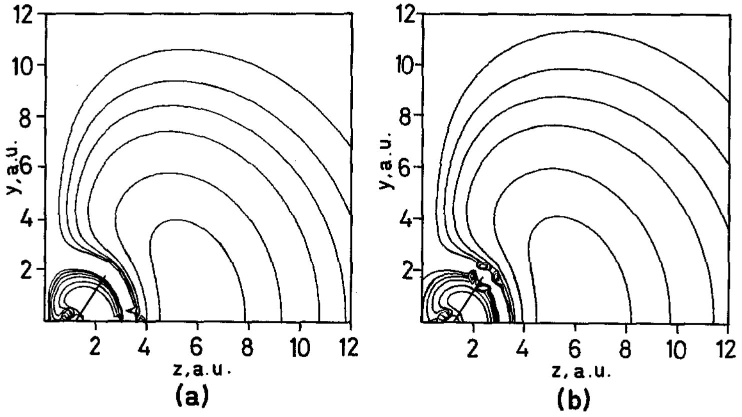

Fig. 5. Charge density contours for (a) $3p\sigma$ natural orbital and (b) corresponding $3b_{1u}$ MO obtained from the open shell SCF calculation

Table 7. Properties of some Rydberg $np\sigma$ natural orbitals in ethylene singlets

$(n-\delta)^2$	Principal quantum number n	Quantum defect δ	$r_{\max}$ for outermost loop, a.u.	Expectation values of second moment components, a.u. $\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$
5.88	3	0.58	5.9	14.56	16.06	46.79
12.01	4	0.53	15.2	67.60	67.65	203.52
20.16	5	0.51	27.5	197.5	197.4	592.7
30.9	6	0.4	43	332	331	995

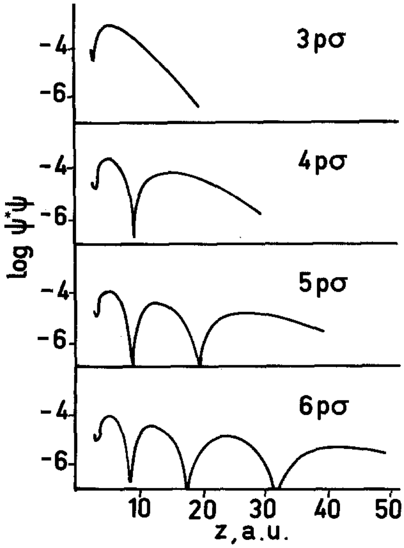

Fig. 6. Logarithm of charge density vs. distance from the molecular midpoint along the z-axis (C–C axis) for $np\sigma$ natural orbitals

It should be noted that the number of nodes in this series is in complete agreement with the assignments of principal quantum numbers provided that all the density minima indicated in Fig. 6 do represent nodes. The expectation values $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$ show that the orbitals are very nearly ellipsoids of revolution. Further, it was found that also all the $np\sigma$ orbitals are C–H antibonding.

8. Discussion

The present study has been carried out in search for an excited state treatment, intermediate between very elaborate methods, such as the combined SCF and CI method [3], and drastically simplified methods, such as pseudopotential methods [32]. The drawback of the elaborate methods is that long experience and great care is needed in order to treat all states considered at equal levels of accuracy, including equal amounts of correlation, etc. Further, even if the principles of the treatment have been disentangled, the application to large systems will easily give rise to an unwieldy complexity. Also, liberal access to a large computer is a necessary pre-requisite for using such a method. Moreover, even the most extended (and costly) treatments have hitherto given only limited physical information.

At present, the most interesting results concerning excited Rydberg states seem to have emerged from the opposite kind of approach, viz. from the use of model potentials. As an example, Betts and McKoy [32] have presented calculations including sizable series of term values for both diatomic and polyatomic molecules, apparently in excellent agreement with experiments, using a one-particle model with a drastically simplified potential. Their results are indeed very encouraging. However, even their approach has certain drawbacks. Singlet and triplet states ought to be treated separately. A more serious deficiency is that the handling of the potential from hydrogen atoms seems to be rather casual. In its present form the method is seemingly unable to distinguish between Rydberg states of e.g. ethane and acetylene.

The present method is non-empirical and the application to any system is straightforward. Some consideration must be given to the choice of basis functions, but this part of the procedure can easily be handled after some more experience of various systems. More serious may be the necessity to carry out an SCF calculation for the ground state with the chosen basis set. However, the present rapid development of efficient programs may be helpful in this respect. Since the single necessary SCF calculation is by far the most computer-time-consuming part of the procedure, the whole calculation may hopefully become a rather modest operation, even for comparatively large molecules. In view of the completely non-empirical character of the method, the results obtained so far are rather promising. Both energies, transition probabilities, description of orbitals and other properties seem to come out with very reasonable values. Furthermore, the method is very flexible since it is easy to modify the accuracy in keeping with the actual need by extension or contraction of the basis set.

In conclusion, the present method seems to offer a useful alternative for studies of molecular excited states. Further applications are currently being performed in our Laboratories and will be published in the near future.

Acknowledgments. We are indebted to Dr. Björn Roos and Mr. Per Siegbahn for valuable discussions and information about unpublished results and to Mrs. Janina Kowalewska for drawing the figures. One of us (J.K.) gratefully acknowledges support from Professor Ragnar Vestin.

References

1. Huzinaga, S., Arnau, C.: Physic. Rev. A **1**, 1285 (1970); J. chem. Physics **54**, 1948 (1971).
2. Hunt, W. J., Goddard III, W. A.: Chem. Physics Letters **3**, 414 (1969).
3. Buenker, R. J., Peyerimhoff, S. D.: J. chem. Physics **53**, 1368 (1970).
4. Löwdin, P.-O.: Physic. Rev. **97**, 1474 (1955).
5. Fischer-Hjalmars, I.: Trans. International Symp. Mol. Structure and Spectroscopy, B **205** (1962).
6. Mulliken, R. S.: J. Amer. chem. Soc. **86**, 3183 (1964).
7. Mulliken, R. S.: J. Amer. chem. Soc. **88**, 1849 (1966).
8. Mulliken, R. S.: J. Amer. chem. Soc. **91**, 4615 (1969).
9. Veillard, A.: IBMOL Version 4, Special IBM Technical Report, San José (1968).
10. Clementi, E., Davis, D. R.: J. comput. Physics **2**, 223 (1967).
11. Browne, J. C., Poshusta, R. O.: J. chem. Physics **36**, 1933 (1962).
12. Huzinaga, S.: J. chem. Physics **42**, 1293 (1965).
13. Kolos, W., Roothaan, C. C. J.: Rev. mod. Physics **32**, 219 (1960).
14. Wakefield, C. B., Davidson, E. R.: J. chem. Physics **43**, 834 (1965).
15. Bates, D. R., Ledsham, K., Stewart, A. L.: Philos. Trans. Roy. Soc. (London) A **246**, 215 (1953).
16. Herzberg, G.: Molecular spectra and molecular structure, Vol. I. Spectra of diatomic molecules, 2nd Ed. Princeton, N. J.: Van Nostrand 1950.
17. Merer, A. J., Mulliken, R. S.: Chem. Reviews **69**, 639 (1969).
18. Dunning Jr., T. H., Hunt, W. J., Goddard III, W. A.: Chem. Physics Letters **4**, 147 (1969).
19. Basch, H., McKoy, W.: J. chem. Physics **53**, 1628 (1970).
20. Buenker, R. J., Peyerimhoff, S. D., Kammer, W. E.: J. chem. Physics **55**, 814 (1971).
21. Buenker, R. J., Peyerimhoff, S. D., Hsu, H. L.: Chem. Physics Letters **11**, 65 (1971).
22. Merer, A. J., Schoonveld, L.: Canad. J. Physics **47**, 1731 (1969).
23. Hubin-Franskin, M. J., Collin, J. E.: Int. J. Mass Spectrom. Ion Physics **5**, 163 (1970).
24. Schulman, J. M., Hornback, C. J., Moskowitz, J. W.: Chem. Physics Letters **8**, 361 (1971).
25. McDiarmid, R.: Theoret. chim. Acta (Berl.) **20**, 282 (1971).
26. Allen, H. C., Plyler, E. K.: J. Amer. chem. Soc. **80**, 2673 (1958).
27. Mulliken, R. S.: J. chem. Physics **23**, 1997 (1955).
28. Siegbahn, P.: Private Communication.
29. Eland, J. H. D.: Int. J. Mass Spectrom. Ion Physics **2**, 471 (1969).
30. Price, W. C., Tutte, W. T.: Proc. Roy. Soc. (London) A **174**, 207 (1940).
31. Wilkinson, P. G.: Canad. J. Physics **34**, 643 (1956).
32. Betts, T., McKoy, V.: J. chem. Physics **54**, 113 (1971).

Prof. I. Fischer-Hjalmars
Institute of Theoretical Physics
University of Stockholm
Vanadisvägen 9
S-113 46 Stockholm
Sweden