

Nonorthonormal CI for molecular excited states. I. The sudden polarization effect in 90° twisted ethylene

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The accurate and efficient calculation of properties of excited states, especially those involved in near-degeneracies and valence-Rydberg mixings, may depend crucially on the zeroth order orbitals employed for the description of a few important configurations. When self-consistent field orbitals specific for the states of interest are employed, one becomes involved with nonorthonormal basis sets, which circumstance has conceptual as well as computational implications. In this work, we have developed a nonorthonormal configuration interaction (NONCI) method and have applied it to the calculation of the "sudden polarization" effect in the zwitterionic excited states of ethylene, in the spirit of a state-specific theory. A very small NONCI, (6×6), yields similar results to those from previous large CI calculations. In particular, the sudden rise of the dipole moment as a function of the pyramidalization angle of the CH_2 group of the 90° twisted Z state is predicted while it is shown that the inclusion of NON at 0° angle (D_{2d} symmetry) is sufficient to recover the correct electronic charge distribution (zero dipole moment).

I. INTRODUCTION

Historical reasons, theoretical constraints, and computational convenience have led to the development and application of many-body methods for excited states of atoms and molecules in terms of single orthonormal basis sets corresponding, most often, to an energy optimized one-electron potential of ground states. With such methods, the emphasis is on efficiency in terms of the manipulation of the one- and two-electron integrals and of potential generality as regards the types of states treatable. Enlargement of the basis set improves the reliability of the computation. However, the n^4 - n^5 dependence of the overall calculation (n is the number of basis functions) quickly puts limitations on the size of possible many-body calculations, even with today's super computers. Furthermore, certain excited state calculations of energetics or other properties can be very sensitive to the choice of basis sets—regardless of the size of the system. This is mainly due to a lack of suitability of the zeroth-order orbitals, whose induced error is difficult to correct subsequently, even with large-scale electron correlation calculations. This fact can be observed easily in atomic structure calculations where the excited state orbitals corresponding to a particular configuration can be computed accurately by a variety of methods, e.g., hydrogenic, configurational average Hartree-Fock, restricted HF, multiconfigurational HF (MCHF). Consider, e.g., the $nsnp$ first excited configurations of the alkaline earths. A HF np for the $^1P^0$ state looks very different from a HF np of the $^3P^0$ or of the $np^2\ ^1S$ configuration. Obviously then, the accuracy, convergence, and interpretation of a many-electron calculation of an excited state property could depend crucially on the choice of the zeroth-order orbitals. Similar situations exist in molecules (al-

though there, the lower symmetry probably reduces the magnitude of *state specificity* of zeroth-order orbitals). For example, Nitzsche and Davidson¹ point out the inadequacy of using ground state or triplet $\pi\pi^*$ orbitals to describe the singlet $\pi\pi^*$ state of amides, and Brooks and Schaefer,² and Bonacic-Koutecky *et al.*³ describe the sensitivity of the "sudden polarization effect" to basis sets, in spite of the magnitude of their calculations.

A computationally *state-specific* theory of excited states has been developed and applied during the past ten years in problems of atomic structure and properties.⁴⁻¹⁰ Such a theory is based on the choice and optimization of the function spaces for each excited state of interest, both at the zeroth order and the correlation level.⁴⁻⁶ This allows the automatic inclusion of relaxation effects and the reliable description of phenomena and calculation of properties with small wave functions. Furthermore, physical and chemical concepts become more transparent while aspects of *transferability* of parts of the energy or of the wave functions and their distinct effects on spectroscopy or chemical bonding in excited states may be systematized.

In the state-specific theory, the zeroth-order and the virtual orbital space for each excited state of interest is optimized separately. In many interesting problems, the corresponding zeroth-order configurations yield near degeneracies and strong mixings—which, in general, are functions of geometry. In such cases their rigorous calculation requires the explicit consideration of nonorthonormality (NON) corrections.

NON situations arise in a variety of chemical physics problems, whenever the overall system or process is conceptually separated into two (or more) distinct parts, with each

part computed within its own function space and an off-diagonal matrix element connecting them. For example, transition probabilities for one or many-electron excitations^{6,7} have been calculated by taking into account NON via the "corresponding orbitals" method of King *et al.*¹¹ In the case of valence Rydberg and pair energy calculations via configuration–interaction methods⁵ or phenomena such as autoionization^{8,9} and shape resonances,¹⁰ brute force evaluation of N -electron integrals, feasible for small-scale, symmetry-adapted atomic structure calculations, has been carried out.

In this paper, we present results of a state-specific, NONCI calculation of the sudden polarization effect in the Z state of ethylene.^{2,3} This is accomplished by a computational method which is based on density matrices and the work of King *et al.*¹¹ A tremendous reduction in the size of the CI required to predict the basic characteristic of this effect is found. Thus, a 6×6 NONCI is in qualitative agreement with large CI^{2,3} (of the order of 5000×5000) which used common orthonormal basis sets for the two states involved in this charge-transfer phenomenon.

II. THE SUDDEN POLARIZATION EFFECT IN ETHYLENE

The sudden polarization effect in the singlet excited zwitterionic states of twisted linear polyenes has been the subject of considerable theoretical work, because its prediction gave rise to many important chemical and biological implications and speculations.^{2,3,12–21}

The two zwitterionic states of twisted alkenes may be expressed mainly as the plus and the minus combinations of two oppositely polarized structures, cf. I and II below for ethylene, corresponding



to configurations of type a^2 and b^2 respectively, which have the two electrons of the broken π bond localized on the one or the other C atom involved.¹²

Any asymmetry existing between the two ends of the twisted bond will induce a difference in the relative contributions of the two structures in the Z_1 and Z_2 states, and consequently these states will possess a permanent dipole moment.

In 90° -twisted ethylene (for which Mulliken,²² first recognized the ionicity of the Z_1 and Z_2 states), the two relevant states are the so called Z and V species, which in the C_s subgroup of D_{2d} are expressed by Eqs. (III) and (IV), where the two states have in common the occupancy $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2$:

$$Z = (1/\sqrt{2})[7a'^2 + 2a''^2], \quad (\text{III})$$

$$V = (1/\sqrt{2})[7a'^2 - 2a''^2]. \quad (\text{IV})$$

These states do not possess any permanent dipole moment in the 90° conformation because of the D_{2d} symmetry of the molecule. However, pyramidalization at one of the C atoms (i.e., bending of one of the CH_2 groups) results in a breaking of the symmetry and in polar Z and V states.^{2,3,13,18–20} The

suddenness and the magnitude of this polarization in the Z and V states of twisted ethylene has been investigated with several methods. The earlier work in the field¹³ made use of a 3×3 CI calculation involving the configurations a^2, b^2 and the diradical ab , with the MO basis set obtained using a Nesbet restricted Hartree–Fock, open-shell calculation on the singlet ab configuration. These early results¹³ as well as extensive CI calculations by Brooks and Schaefer,² Bonacic–Koutecky *et al.*,³ and Buenker *et al.*²⁰ showed that appreciable polarization of the Z and V states was induced even by small bending angles of 5° – 10° . The 3×3 CI approach has been criticized as giving a too crude description, and consequently grossly overestimating the charge separation.^{17,19} On the other hand, in the large CI calculations,^{2,3,20} the one electron basis sets used were again not specific, neither for the Z nor for the V states. Brooks and Schaefer² used the MO's obtained from an SCF procedure constrained to give equal weights to the a^2 and b^2 configuration. In this way, they were able to obtain zero dipole moment for the D_{2d} geometry. However, as the authors of Ref. 2 themselves note, this type of basis set is not necessarily optimal for bent geometries, for which the relative contributions of the two polar structures differ. In the MRD–CI calculations^{3,20} the MO basis set believed to give the best results were the SCF MO of the triplet (ab) state. The authors of Ref. 3 and 20 also note the need of using a basis set more specific for the states of interest. It may be argued that while an equally bad description of the two states gives the correct balance, at least for D_{2d} geometries, it is not optimum for either of the two states. Malrieu and Tringuier¹⁹ state that with such nonpolar one-electron basis sets, a double excitation CI with respect to the two main configurations a^2 and b^2 may not suffice, because higher excitations are required to account for the polarization of the σ bonds accompanying the creation of the π dipole. On the other hand, making use of the a^2 or the b^2 closed-shell MO's (or the appropriate natural orbitals for each state), while possibly being the most appropriate choice of MO for a particular state, at least in the bent geometries,^{3,19,20} leads to incorrect symmetry and erroneous dipole moments at the D_{2d} geometry. As noted in Ref. 19 the best two-determinantal wave functions for the Z and V states of twisted ethylene would be the wave functions (III) and (IV) constructed in terms of two SCF nonorthogonal sets of basis functions, for a^2 (or $7a'^2$) and b^2 (or $2a''^2$), respectively. Analogous situations have come up with similar symmetry-breaking problems such as for inner-hole O_2^+ ²³ and excited NO_2 .²⁴

A. THE NONCI METHOD

In a nonorthogonal CI calculation one is required to solve the secular equation

$$|\mathbf{H} - \mathbf{ES}| = 0, \quad (\text{V})$$

where the overlap matrix S is no longer the unit matrix. The matrix elements of the Hamiltonian operator H_{ij} are taken over many-electron functions φ_i^b and φ_j^a , which are, in general, linear combinations of Slater determinants $\{\Delta_B\}$ and $\{\Delta_A\}$, respectively, constructed with different, nonorthogonal one-electron basis sets $\{b\}$ and $\{a\}$. The matrix ele-

ment H_{ij} is then a sum of N -electron matrix elements over determinants

$$H_{BA}^j = \langle \Delta_B^i | H | \Delta_A^j \rangle. \quad (VI)$$

In the evaluation of Eq. (VI), the well-known Slater–Condon rules are no longer applicable because of the nonorthonormality between the sets $\{a\}$ and $\{b\}$. There are several ways to proceed from here. In this work the method of corresponding orbitals transformation²⁴ is followed, as used by King *et al.*,¹¹ and is adapted here to the specific methods used in carrying out CI calculations on molecules.

For each pair of determinants Δ_B^i, Δ_A^j the overlap matrix D , defined by

$$D_{ij} = \langle b_i | a_j \rangle \quad (VII)$$

for all b_i in Δ_B^i and a_i in Δ_A^j , is diagonalized by a biorthogonal transformation^{11,25}

$$\mathbf{d} = \mathbf{U}^t \mathbf{D} \mathbf{V}. \quad (VIII)$$

The matrices \mathbf{U} and \mathbf{V} are unitary and transform the set $\{b_i\}$ and $\{a_j\}$ into sets of “corresponding orbitals”,²⁴

$$\begin{aligned} \hat{\mathbf{a}} &= \mathbf{a} \mathbf{V}, \\ \hat{\mathbf{b}} &= \mathbf{b} \mathbf{U}, \end{aligned} \quad (IX)$$

where $\langle \hat{a}_i | \hat{b}_j \rangle = d_i \delta_{ij}$, with d_i positive definite. The transformations (IX) leave the determinants invariant, within the factors $\det(\mathbf{U}^t)$ and $\det(\mathbf{V}^t)$,¹¹ and in terms of the corresponding orbital matrix elements for zero-, one-, and two-electron operators can consequently be written in very simple forms (cf. Ref. 11). For example, for the case of zero singularities, i.e., where all d_i are greater than zero, the expressions for the matrix elements are given by Eqs. (Xa)–(Xc) (where N is the number of electrons),

$$S_{BA} = \langle \Delta_B | \Delta_A \rangle = \det(\mathbf{U}) \det(\mathbf{V}^t) \prod_{i=1}^N d_i, \quad (Xa)$$

$$\begin{aligned} O_{BA}^1 &= \langle \Delta_B | O^{(1)} | \Delta_A \rangle \\ &= \det(\mathbf{U}) \det(\mathbf{V}^t) \sum_{i=1}^N \langle \hat{b}_i | O^{(1)} | \hat{a}_i \rangle \prod_{j \neq i}^N d_j, \end{aligned} \quad (Xb)$$

$$\begin{aligned} O_{BA}^2 &= \langle \Delta_B | O^{(2)} | \Delta_A \rangle = \det(\mathbf{U}) \det(\mathbf{V}^t) \sum_{i < j}^N \prod_{k \neq i,j}^N d_k \\ &\quad \times \langle \hat{b}_i \hat{b}_j | O^{(2)}(1,2) | (1 - P_{12}) | \hat{a}_i \hat{a}_j \rangle. \end{aligned} \quad (Xc)$$

If there are singularities in the \mathbf{D} matrix, the expressions (Xa)–(Xc) are further simplified, in a manner analogous to that applied for the derivation of the conventional Slater–Condon rules. For more than two singularities in the D matrix the matrix element (VI) is identically zero. It may be noted that in expressions (X), there appear molecular integrals involving the corresponding orbitals. It would seem that there is need for one more integral transformation than is normally required in a CI calculation. Alternatively, as was actually done in this work, the corresponding orbitals can be expressed directly in terms of the AO basis set over which the integrals have been calculated and stored in the first step in any MO calculation. If the original sets of MO's a and b , in terms of the AO basis χ are given by

$$a_k = \sum_{p=1}^m \chi_p f_{pk}, \quad (XI)$$

$$b_l = \sum_{q=1}^m \chi_q c_{ql},$$

the corresponding orbitals (IX), can be expressed as given in

$$\hat{a}_i = \sum_p^m \sum_{k=1}^N f_{pk} V_{ki} \chi_p = \sum_{p=1}^m d'_{pi} \chi_p \quad (XII)$$

and

$$\hat{b}_i = \sum_{q=1}^m \sum_{l=1}^N c_{ql} U_{li} \chi_q = \sum_{q=1}^m c'_{qi} \chi_q.$$

The following density matrices may then be defined:

$$\text{Den}(q, p) = \sum_{i=1}^N c'_{qi} d'_{pi} / d_i, \quad \text{if all } d_i > 0, \quad (XIIIa)$$

$$\begin{aligned} \text{Den}_k(q, p) &= \sum_{i \neq k}^N c'_{qi} d'_{pi} / d_i, \quad d_i > 0, i \neq k \\ & \quad d_k = 0, \end{aligned} \quad (XIIIb)$$

$$E_k(q, p) = c'_{qk} d'_{pk}, \quad d_k = 0. \quad (XIIIc)$$

The matrix elements (X) in terms of the density matrices (XIII) become:

(a) zero singularities,

$$\begin{aligned} O_{BA}^1 &= \det(\mathbf{U}) \det(\mathbf{V}^t) \prod_{j=1}^N d_j \\ &\quad \times \sum_{q=1}^m \sum_{p=1}^m \text{Den}(q, p) \langle q | O^{(1)} | p \rangle, \end{aligned} \quad (XIVa)$$

$$\begin{aligned} O_{BA}^2 &= \det(\mathbf{U}) \det(\mathbf{V}^t) \prod_{i=1}^N d_i \\ &\quad \times \left(\frac{1}{2} \sum_p^m \sum_q^m \sum_r^m \sum_s^m \{ \text{Den}(p, q) \text{Den}(r, s) \right. \\ &\quad \left. - \text{Den}(p, s) \text{Den}(r, q) \} [pqrs] \right), \end{aligned} \quad (XIVb)$$

(b) one singularity ($d_k = 0$),

$$\begin{aligned} O_{BA}^1 &= \det(\mathbf{U}) \det(\mathbf{V}^t) \prod_{j \neq k}^N d_j \\ &\quad \times \sum_q^m \sum_p^m E_k(q, p) \langle q | O^{(1)} | p \rangle, \end{aligned} \quad (XIVc)$$

$$\begin{aligned} O_{BA}^2 &= \det(\mathbf{U}) \det(\mathbf{V}^t) \prod_{i \neq k}^N d_i \\ &\quad \times \left(\sum_p^m \sum_q^m \sum_r^m \sum_s^m \{ \text{Den}_k(p, q) E_k(r, s) \right. \\ &\quad \left. - \text{Den}_k(p, s) E_k(r, q) \} [pqrs] \right), \end{aligned} \quad (XIVd)$$

(c) two singularities ($d_k = d_l = 0$),

only the two-electron matrix element exists,

$$\begin{aligned} O_{BA}^2 &= \det(\mathbf{U}) \det(\mathbf{V}^t) \prod_{i \neq k,l}^N d_i \sum_{p=1}^m \sum_{q=1}^m \sum_{r=1}^m \sum_{s=1}^m \\ &\quad \times \{ E_k(p, q) E_l(r, s) - E_k(p, s) E_l(r, q) \} [pqrs]. \end{aligned} \quad (XIVe)$$

It is obvious that the present implementation of the method requires processing of the two-electron integral file for each pair of determinants. Making use of any existing symmetry in the system as well as processing groups of matrix elements

simultaneously is expected to improve the speed of the program. At present the only symmetry that is utilized is the spin symmetry, separating the α set from the β set of MO, since these are mutually orthogonal. Another way of improving the speed of the NONCI calculation would be to work with integrals over molecular orbitals, define a set of common orbitals, and deal rigorously in a NONCI scheme only with a few strongly nonorthonormal MO's.

In the above description the other methods available for dealing with the problem of nonorthonormality have not been discussed. The main alternative to the method presented in this work involves evaluating cofactors of the overlap matrix.^{23,26-28} In Refs. 23 and 28 the procedure employed is the factorized cofactor method, which also involves using the original integral file over AO's. In general, the various methods available require either calculating and storing a very large file of cofactors, or doing integral transformation or reading through the two-electron integral file over AO's for each pair of determinants.

IV. DETAILS OF THE CALCULATIONS

The molecular geometry used is that given by Brooks and Schaefer,² with a C-C distance of 1.416 Å and HCH angles of 116°. Calculations have been carried out for values of the pyramidalization angle φ of 0°, 5°, 10°, 15°, and 20°. The AO basis set employed consists of the 9s5p/5s3p set for carbon and the 5s/3s set for hydrogen of Gaussian-type functions of Huzinaga²⁹ with Dunning's contraction coefficients.^{30,31} The nonorthogonal CI part of the calculation involves calculation of the matrix elements H_{12} of the Hamiltonian operator

$$H_{12} = \langle \varphi_1 | H | \varphi_2 \rangle \quad (\text{XV})$$

the corresponding overlap S_{12} and the solution of a 2×2 secular equation [cf. Eq. (V)]. An alternative NONCI formulation in which individual symmetry adapted configurations serve as the basis functions will be discussed subsequently (INONCI). The functions φ_1 and φ_2 in Eq. (XV) are CI vectors for the Z state of twisted ethylene, obtained with two different MO basis sets, one for configuration $7a'^2$ and one for configuration $2a''^2$ (where these configurations have in common the occupancy $1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2$). It is well known that at the Hartree-Fock level or even at a modest CI level, the ordering of the V and Z states is opposite to that obtained with large CI calculations.^{2,32} It would appear then that one would need to do large CI calculations followed by NONCI to obtain both the ordering and the interaction between the states. In the present work several test calculations have been carried out using the MRD-CI method^{32,33} with various sets of main configurations and different values of the selection threshold T , in order to find small expansions for φ_1 and φ_2 which place the Z state correctly below Eq. (V). It has been found that with $2M/2R$ (two reference configurations and selection with respect to two roots) involving the $7a'^2$ and $1a''^2$ configurations as well as $4M/2R$ treatments for which the four main configurations are taken from the work of Bonacic-Koutecky *et al.*,³ relatively small threshold values are required in order to obtain the Z state as the first root. On the other hand, it is also found that only six

TABLE I. The six configurations required to obtain the correct ordering of the V and Z states.*

MO1 ($7a'^2$)	1	$3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 1a''^2$
	2	$3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 2a''^2$
	3	$4a'^2 5a'^2 6a'^2 7a'^2 1a''^2 2a''^2$
	4	$3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 2a''^2$
	5	$3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 1a''^2$
	6	$3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 1a''^2 2a''^2$
MO2 ($2a''^2$)	1-3	as above
	4	$3a'^2 4a'^2 5a'^2 7a'^2 1a''^2 2a''^2$
	5	$3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 5a''^2$
	6	$3a'^2 4a'^2 5a'^2 6a'^2 7a'^2 1a''^2 2a''^2$

* All have $1a'^2 2a'^2$ in common.

properly selected configurations are sufficient to give the correct ordering of states in the geometries used. These six configurations for each set of MO's given in Table I, are chosen on the basis of their coefficients in the large CI vectors as calculated with the appropriate set of MO's. NONCI calculations have been carried out using these six-term expansions for φ_1 and φ_2 , as well as for larger expansions, always keeping the sets of configurations of Table I as the main configuration. In addition, MRD-CI calculations^{33,34} were carried out using each of the two sets of MO's and $2M/2R$, $T = 10 \mu\text{H}$. These calculations are used to check the effect of electron correlation on the calculated dipole moments for φ angles larger than zero.

V. RESULTS AND DISCUSSION

In Table II the z components of the dipole moments calculated for the Z state using the six-term CI wave functions are compared to those obtained with the large MRD-CI wave functions ($2M/2R$, $T = 10 \mu\text{H}$) and to some of the results of Bonacic-Koutecky *et al.*³ and Brooks and Schaefer.² As expected, for the $\varphi = 0^\circ$ geometry, neither MO1 (from $7a'^2$ SCF) nor MO2 (from $2a''^2$ SCF) alone gives the correct symmetric charge distribution, with the result that large dipole moments are computed, even though none can exist because of symmetry. The NONCI calculation corrects this problem quite effectively, giving virtually zero dipole moment for the $\varphi = 0$ geometry. For geometries with nonzero φ , basis set MO1 gives the correct polarity of the Z state, with the pyramidal carbon at the negative end of the dipole. With basis set MO2, while the first root has coefficients of equal sign for configurations (I) and (II); the resulting dipole moment nonetheless has its positive end at the pyramidal carbon, indicating it is the V state, i.e., of opposite polarity as the previous (Z) state.

The results of the NONCI calculations (cf. Table II) differ significantly from those obtained with the MRD-CI calculations (with MO1) only for the D_{2d} geometry. The general agreement of NONCI with large CI calculations with MO1 for the Z state, except for the $\varphi = 0^\circ$ geometry, can also be seen in the coefficients of the configurations (given in Table III). As shown for $\varphi = 0^\circ$, the NONCI results have equal c_1 and c_2 (where the 2×2 NONCI results refer to the V state, which is the lower root in this level of treatment). For $\varphi = 5^\circ$, the NONCI wave functions have still fairly large c_2 values.

TABLE II. Dipole moments in Debye of the Z state (μ_z) calculated with 6×6 CI and NONCI and by large CI methods.

φ No. of SAF	0°	5°	10°	15°	20°
6×6 MO ₁	3.648	3.655	3.675	3.709	3.756
6×6 MO ₂ ^a	-3.648	-3.649	-3.654	-3.660	-3.668
large CI MO ₁	3.341	3.349	3.378	3.423	3.473
large CI MO ₂ ^a	-3.341	-3.340	-3.332	-3.322	-3.291
NONCI 2×2 ^a	0.000	-0.690	-2.251	-3.264	-3.635
NONCI 6×6	0.005	2.320	3.579	3.691	3.753
INONCI 12×12	-0.001	2.533	3.436		
Ref. 2	0.00	1.25	2.77	3.19	3.30
Ref. 3 ^b	-0.05	0.57	1.77		3.62
	-0.21 ^c	0.99 ^c	2.86 ^c		3.36 ^c

^a Values correspond to the V state.

^b Value obtained using triplet MO and $2M/2R$ treatment.

^c Obtained by Bonacic-Koutecky *et al.* (Ref. 3) using the NO of S_1 .

However the CI wave functions obtained with MO1 alone uniformly show only c_1 large for all values of φ .

In general the present NONCI results for $\varphi = 5^\circ$ – 15° tend to be notably higher than have been found in any of the previous large-scale CI treatments based on a single set of one-electron functions,^{2,3} particularly in comparison with the triplet state SCF MO findings of Bonacic-Koutecky *et al.*³ Although the largest NONCI treatment carried out is between two CI functions containing only 21 symmetry adapted functions (SAF's) each, there is good evidence that still further expansion of the treatment would not change matters greatly, with the possible exception of the $\varphi = 5^\circ$ results. To test the influence of freezing the CI coefficients within the individual pair of NONCI basis functions, an alternative treatment was also carried out (INONCI) in which the individual SAF's in these CI species themselves were taken as basis functions for the super CI. For example, instead of a 2×2 NONCI basis of six-vector CI functions based on MO1 and MO2, respectively, an order 12×12 INONCI has been carried out to see what effect the additional freedom thereby allowed will have. As the results in Table II show, such an improvement in the treatment leads to very little change in computed dipole moments, while en-

ergy lowerings relative to the corresponding (frozen) NONCI results in the order of 0.002 hartree are noted. Since the NONCI treatment leads to the correct result at zero dipole moment in the unpolarized (D_{2d}) geometry, the indication then is that the suddenness in the rise in polarity of the Z and V states of ethylene as φ increases is even larger than previously assumed on the basis of large-scale conventional CI treatments based on a single set of one-electron functions for both electronic states.

In Table IV are given the total energies for the lowest root (Z or V) computed with the six-term CI and the large-scale conventional CI methods, as well as those for the Z and V states obtained with the NONCI method. As shown, use of the set MO1 results in CI energies for the Z state which decrease monotonically with the angle φ (see also the work Trinquier and Malrieu¹⁹). However, use of MO2 results in CI energies which increase monotonically with φ , behavior which is characteristic of the V state.^{3,20}

The NONCI 6×6 results (which are typical of all the NONCI results obtained here) show that the energy of the Z state increases slightly at φ of 5° with respect to that at $\varphi = 0^\circ$ and then slowly decreases for φ values greater than 5° , while that of the V state is monotonically increasing with φ . The

TABLE III. Coefficients of configurations $7a'^2$ and $2a''^2$ in the final wave functions in the lowest root of the CI.

φ No. of SAF		0°	5°	10°	15°	20°
6×6 MO ₁	c_1	0.9924	0.9943	0.9943	0.9944	0.9945
	c_2	0.0012	0.0012	0.0011	0.0010	0.0009
6×6 NONCI	c_1	0.7055	0.9043	0.9932	0.9988	0.9997
	c_2	0.7065	0.4241	0.1133	0.0470	0.0208
large CI MO ₁	c_1	0.9547	0.9550	0.9558	0.9566	0.9575
	c_2	0.0850	0.0837	0.0768	0.0674	0.0571
2×2 MO ₁	c_1	0.9999	0.9999	0.9999	0.9999	0.9999
	c_2	-0.0104	-0.0104	-0.0104	-0.0103	-0.0102
2×2 NONCI	c_1	0.7003	0.7618	0.8854	0.9575	0.9825
	c_2	-0.7003	-0.6331	0.4478	0.2699	0.1672

TABLE IV. Computed total energy (hartree) for the Z and V states of twisted ethylene.

φ No. of SAF		0°	5°	10°	15°	20°
6 MO ₁	E_z	-77.823 904	-77.823 952	-77.824 101	-77.824 349	-77.824 703
6 MO ₂	E_v	-77.823 905	-77.823 367	-77.821 754	-77.819 068	-77.815 315
CI ^a MO ₁	E_z	-77.999 708	-77.999 805	-78.000 040	-78.000 677	-78.000 999
CI ^a MO ₂	E_v	-77.999 713	-77.999 247	-77.997 807	-77.995 236	-77.991 741
NONCI	E_z	-77.824 238	-77.824 117	-77.824 132	-77.824 361	-77.824 707
6×6	E_v	-77.823 569	-77.823 200	-77.821 721	-77.819 055	-77.815 310
INONCI	E_z	-77.827 140	-77.827 009	-77.827 093		
12×12	E_v	-77.826 006	-77.826 190	-77.824 693		

^a Large CI.

existence of a slight barrier to pyramidalization in the Z state was also found in the calculations of Bonacic-Koutecky *et al.*³ and Buenker *et al.*,²⁰ when they used the MO of the triplet state as basis set. However, the lack of geometry optimizations in the present calculations and the small differences in energy make it difficult to decide whether the barrier obtained here is significant.

In the course of the calculations of H_{12} and S_{12} it was noted that, for a given set of configurations, the ratio H_{12}/S_{12} in the NONCI treatment remains nearly constant, to the extent that it is possible to estimate H_{12} for a value of φ , ω_2 using the ratio $H_{12}^{(\omega_1)}/S_{12}^{(\omega_1)}$ at ω_1 and the $S_{12}^{(\omega_2)}$. The computational effort required to obtain S_{12} is trivial while the calculation of H_{12} becomes very costly for multiconfiguration expansions φ_1 and φ_2 . In Table V the calculated and the estimated H_{12} are given for some of the cases studied. As shown, the difference is generally in the sixth decimal place. The effect on the calculated dipole moments of using the estimated rather than the calculated H_{12} is negligible, being at most 0.1 D, compared to the differences in dipole mo-

ments obtained with different methods (here and also in Refs. 2, 3, and 20). Estimated H_{12} values were used for φ of 10°, 15°, and 20° in the NONCI calculation involving 21-term expansions for φ_1 and φ_2 . These expansions were obtained with the MRD-CI method with $6M/1R$, $T = 0.001$ hartree.

Finally, in Table VI are collected the computed total dipole moments for the Z state obtained with the NONCI method and different expansions for φ_1 and φ_2 . As shown, once the 6×6 level is passed, from which point the correct ordering of the Z and V states is obtained, the calculated dipole moments converge for φ of 10° or larger, while for $\varphi = 0^\circ$, the correct symmetric distribution (i.e., zero dipole) is obtained even at the 2×2 level. For φ of 5° convergence is slower.

It should be noted that for the D_{2d} geometry, the computed results are very sensitive to the balance between functions φ_1 and φ_2 . Only when the two functions give nearly identical energies, is it possible to get zero dipole moment with the NONCI calculation. For the calculations shown in

TABLE V. Calculated (H_{12}) and estimated (H'_{12}) values of the interaction matrix elements.^a

No. of SAF	φ	0°	5°	10°	15°	20°
2×2	H_{12}	1.516 527	1.521 525	1.536 128	1.560 145	1.596 038
	H'_{12}		1.521 526	1.536 133	1.560 157	1.596 060
4×4	H_{12}	2.955 792	2.970 766	3.015 946	3.093 279	3.209 370
	H'_{12}		2.970 773	3.015 972	3.093 338	3.209 481
6×6	H_{12}	-0.244 702	-0.238 727	-0.220 747	-0.190 919	-0.150 008
	H'_{12}		-0.238 725	-0.220 741	-0.190 907	-0.149 989
8×8	H_{12}		-0.213 304	-0.196 106		
	H'_{12}	-0.219 090		-0.196 087		
9×9	H_{12}	-0.670 293	-0.659 168	-0.625 925	-0.568 833	-0.486 619
	H'_{12}		-0.659 154	-0.625 892	-0.568 873	-0.486 615
13×13	H_{12}	-0.582 235	-0.571 713	-0.540 168		
	H'_{12}		-0.571 718	-0.540 168	-0.485 793	-0.407 113
6×9	H_{12} ^b	-0.359 099	-0.355 730	-0.345 110	-0.326 327	-0.299 022
	H'_{12} ^c		-0.355 733	-0.345 112	-0.326 326	-0.299 014
21×21	H_{12}	-0.121 225	-0.116 921			
	H'_{12}		-0.116 940	-0.104 319	-0.163 685	-0.139 845

^a H_{12}/S_{12} has the value of -77.899 283 for 2×2, -77.899 336 for 4×4, -77.928 569 for 6×6, -77.905 040 for 8×8 and -77.908 098 for 6×6 + CI with threshold $T = 0.001$ H.

^b In this calculation six configurations are chosen employing MO1 and nine using MO2.

^c The configuration set was chosen on the basis of a $T = 0.001$ H selection criterion for an MRD-CI calculation employing six reference species.

TABLE VI. Total dipole moments^a computed for the Z state of twisted ethylene, with the NONCI method.

φ No. of SAF	0°	5°	10°	15°	20°
2×2	0.000	0.700	2.255	3.267	3.638
4×4	0.001	0.478	1.667	2.790	3.378
6×6	0.006	2.340	3.606	3.750	3.852
8×8	0.000	2.995	3.673		
21×21	0.018	3.344	3.548	3.627	3.726
12×12 ^b	0.002	2.540	3.463		

^a In Debye.^b INONCI.

Table VI, the difference in the total CI energies obtained at this geometry with φ_1 and with φ_2 is at most 1×10^{-6} hartree, while that of the large CI is 5×10^{-6} hartree. If the balance of treatment for φ_1 and φ_2 is disturbed, such as by using a six-term function for φ_1 and a nine-term function for φ_2 (where these nine configurations are again selected on the basis of their coefficients in the large CI wave function), the φ_2 description is favored resulting in a difference in energy of about 5×10^{-3} hartree and in an incorrect dipole moment of 3.5 D for the D_{2d} geometry.

VI. CONCLUSION

A variety of interesting and important molecular excited states have a crucial geometry dependence, especially as regards the character of their wave functions. This is caused mainly by near-degeneracy effects of configurations which describe different "physical situations", such as localization of charge on one part of the molecule, or valence-Rydberg, ionic-covalent, and bound-continuum mixings. Rather than using a common, but not necessarily suitable, basis set to describe the principal configurations entering the wave functions of such excited states, separately optimized basis sets for each main configuration can be adopted. Since the zeroth order approximation is thus improved considerably, relaxation and correlation corrections of the errors introduced via the common basis set approach become unnecessary. However, now one must incorporate into the CI calculations the effects of basis set nonorthonormality (NON). In this work, this has been done by modifying the MRD-CI programs through the application of the corresponding-orbitals method.

The first case of the application of our state specific, NONCI approach to molecular excited states has been the sudden polarization effect in the Z state of 90° twisted ethylene. Here, in C_2 symmetry, the major configurations are the $7a'^2$ and the $2a''^2$. A 6×6 NONCI predicts all the important energy and dipole moment effects from 0° angle of pyramidalization (where, due to the D_{2d} symmetry the system is rigorously without a dipole moment) to 20° where the dipole moment, having increased rapidly, levels off (see Table II). For angles larger than 10°, the $7a'^2$ MOs are a good basis for the Z state while the $2a''^2$ MOs are better for the V state.

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