

Unexpected CASSCF Bistability Phenomenon

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ABSTRACT

One exhibits a problem in which two strongly nonorthogonal complete active-space self-consistent field (CASSCF) solutions are obtained. The problem concerns a molecular frame which presents two stable geometries at the CASSCF level, quinoidal and diradical forms, in disagreement with experiment which indicates a unique minimum corresponding to an intermediate geometry. Those two stable solutions are obtained in a significant domain of intermediate geometries and are related with the CASSCF wave functions of the two stable structures. Obtaining a reliable potential surface starting from CASSCF solutions (even from larger CAS) appears as a very difficult task. © 1997 John Wiley & Sons, Inc.

Introduction

In molecular problems and for a given geometry of the nuclear frame, the Hartree–Fock (HF) single-determinantal equations have no reason to present a unique solution. Of course, one may quote the symmetry-breaking phenomenon [1–3], which leads to several equivalent and degenerate stable symmetry-broken solutions for symmetrical problems, but this is a special case of limited interest. Referring to catastrophe theory and considering the potential energy as a function of nuclear coordinates (r) and molecular orbital (MO)

parameters (α), the occurrence of the symmetry breaking appears as a bifurcation of a valley in the potential energy surface, $E(r, \alpha)$, into two valleys. It is interesting to notice that in the study of multiple bonds [4, 5] and of atomic cluster [6], one may frequently reach a whole set of nondegenerate stable solutions with different spin and space parts. In such problems, the different stable solutions draw a folding of the potential energy surface $E(r, \alpha)$.

The occurrence of symmetry breaking is related to the intensity of the electronic correlation, as evident for the unrestricted HF (UHF) symmetry breaking in lengthened bonds, which reflects the strength of the left–right correlation [7, 8]. It is frequently hoped that the inclusion of the domi-

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nant nondynamical correlation effects in the multi-configuration (MC) wave function will avoid the symmetry breakings; but due to the nonlinear character of the self-consistent field (SCF), the MC-SCF method has no intrinsic reason to avoid the occurrence of multiple solutions. Actually, there are a few rather well-known problems where the MCSCF solutions are multiple.

Most of them are related to electron transfer problems. As a first case, one may quote a problem where three electrons occupy two lone pairs on remote oxygen atoms [9]. The complete active-space self-consistent field (CASSCF) solutions are symmetry broken when the CAS is of valence nature, and symmetry is only restored when the leading part of the dynamical polarization (i.e., the instantaneous repolarization of the MOs) of the two localized forms $O_1^+ \text{---} O_2$ and $O_1 \text{---} O_2^+$ is incorporated in the CAS of enlarged dimension.

As a second example one may quote the symmetry breaking in the CASSCF treatment of the singlet excited states of ethylene (and larger conjugated centrosymmetric hydrocarbons) for strongly twisted geometries. The resonance between the two valence bond (VB) ionic components $\Phi_1 = |\text{core}(a\bar{a})\rangle(\text{CH}_2^+ \text{---} \text{CH}_2^-)$ and $\Phi_2 = |\text{core}(b\bar{b})\rangle(\text{CH}_2^- \text{---} \text{CH}_2^+)$ becomes weak while these two components would induce strong electrostatic polarizations of opposite directions in the core. A large energy gain (81 kcal/mol) is obtained for a 90° twist at the CASSCF level [10] by removing the symmetry of the wave function. This is the case of CASSCF symmetry breaking for a physical problem involving a simultaneous two-electron transfer.

The problem of double CASSCF solutions appears dramatic in the elementary LiF problem, well studied by Bauschlicher and Langhoff [11], where the CASSCF solutions are discontinuous, even for large active space. The physics of that problem is again a one-electron transfer between two weakly interacting dominant VB forms, namely Li^+F^- and Li^+F^- , which require different MOs. The reason for this discontinuity was discussed in detail in reference [12]. Although it was not searched, it is clear that the two CASSCF solutions coexist in the region of the curve crossing, as do the single-determinantal RHF (for Li^+F^-) and UHF (for Li^+F^-) solutions [13].

In all the above-mentioned examples of CASSCF multistabilities, the stable solutions correspond to two nearly orthogonal VB configurations with

weak direct interaction, each of them inducing strong polarities on the inactive MOs along different directions. Here we want to exhibit a case of MCSCF multiple stability without electron transfer and with strong overlap between the different solutions.

A New MCSCF Bistable Problem

DESCRIPTION OF THE PROBLEM

The chemical frame is a large conjugated hydrocarbon which may be considered as having either a quinoidal structure, with all the electrons paired in short $\text{C}=\text{C}$ double bonds separated by single $\text{C}-\text{C}$ bonds, or a diradical structure. The versatility of the Chichibabin hydrocarbon [14–19] has been known for quite a long time. Our candidate belongs to this class and may be called tetracyano-dipheno-quinodimethane (TCNDQ); it is derived from the famous Chichibabin molecule by replacing the peripheral phenyl groups by nitril groups. The most natural chemical graph may be written as a quinoidal structure (see Fig. 1), but one may expect that the diradical structure (see Fig. 2) is stabilized, despite the occurrence of two unpaired (nonbonding) electrons, by the restored aromaticity of the benzene rings.

The quinoidal form is well described by a single determinantal wave function:

$$\Phi_0 = |\text{core } h\bar{h}l|, \quad (1)$$

where h stands for highest occupied molecular orbital (HOMO).

The diradical form can only be described in a two-configurational singlet function

$$\Psi = |\text{core}(\lambda h\bar{h} - \mu l\bar{l})|, \quad (2)$$

where l represents the lowest unoccupied molecular orbital (LUMO). The parameter λ and μ are positive. From h and l one may define magnetic orbitals a and b centered on the left and right

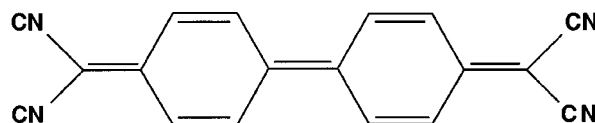


FIGURE 1. TCNDQ molecule represented in the quinoidal structure.

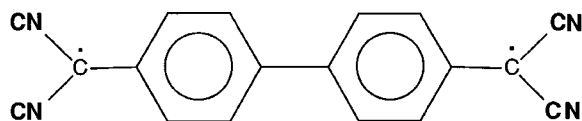


FIGURE 2. TCNDQ molecule represented in the diradical structure.

centers of the molecules:

$$a = (h + l)/\sqrt{2}, \quad b = (h - l)/\sqrt{2}, \quad (3)$$

and if $\lambda = \mu$, the wave function is purely diradical:

$$\Phi_D = \Psi_{(\lambda=\mu)} = |\text{core}(a\bar{b} + b\bar{a})|/\sqrt{2}. \quad (4)$$

In practice $\lambda > \mu$. For the quinoidal form, the two-configuration wave function (2) is, of course, relevant, it reduces to Φ_0 when $\lambda = 1$ and $\mu = 0$. Thus the CASSCF function (2) was first used to study that problem.

MINIMAL CAS STUDY

In the gas phase, the TCNDQ molecule presents a torsional angle around the central bond which is due to the repulsion of the hydrogen atoms linked to the neighbor phenyl rings. In our computations we have compelled the molecule to remain planar by symmetry. Since the experimental results [19] on the Chichibabin molecule show that the central part is planar in the crystal, due to packing effects, we restricted our study to the planar geometries.

A two-configurational CASSCF geometry optimization was first performed using a single-zeta basis set and pseudopotentials [20, 21]. Computations have been carried out using the HONDO8 package [22]. One actually obtains two distinct minima (cf. Figs. 3 and 4) corresponding, respectively, to the quinoidal and diradical chemical structures. The bond lengths are too long, due to

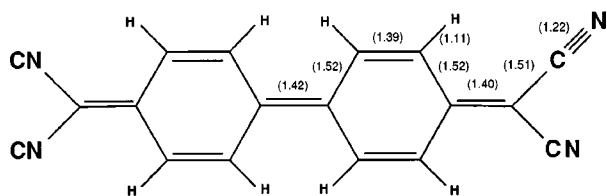


FIGURE 3. Optimized geometry of the TCNDQ molecule in the quinoidal form at the CASSCF level (single-zeta basis set); distances are given in angstroms (Å).

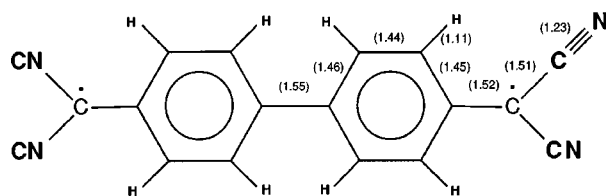


FIGURE 4. Optimized geometry of the TCNDQ molecule in the diradical form at the CASSCF level (single-zeta basis set); distances are given in angstroms (Å).

the use of a single-zeta basis set, but a strong alternation ($\Delta l = 0.13$ Å) in the rings occurs in the quinoidal minimum, while it is very weak ($\Delta l = 0.015$ Å) in the diradical one. The diradical minimum is lower in energy by 0.11 eV and separated from the other minimum by a barrier of 0.32 eV. In order to have more realistic geometries, a double-zeta basis set was used for further computations. Two limit geometries have been optimized at the single configuration level, using a closed-shell restricted Hartree-Fock (RHF) function for the quinoidal structure and a triplet open-shell RHF function for the diradical one. The computations have been performed using the TURBOMOLE package [23]. The geometries are given in Figures 5 and 6, showing the same qualitative contrast. Intermediate geometries were defined using a linear change k of the internal coordinates of the atoms: for $k = -1$ (resp. $k = 1$) we have a quinoidal (resp. diradical) geometry, and for $k = 0$ the geometry is halfway between those of the two structures. The potential energy curve as a function of the parameter k (see Fig. 7) has been computed using the CASSCF algorithm of the MOLCAS package [24].

The point of interest here is that, despite a unique form of the wave function, which permits a description of both structures, we do not obtain a smooth potential energy curve $E(k)$ (see Fig. 7). It presents an unexpected cusp at the crossing of the

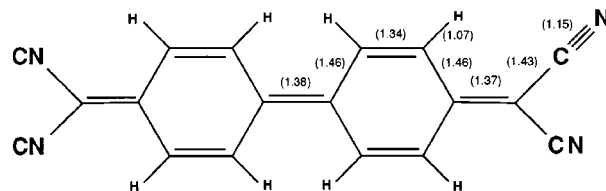


FIGURE 5. Optimized geometry of the TCNDQ molecule in the singlet state (double zeta basis set); distances are given in angstroms (Å).

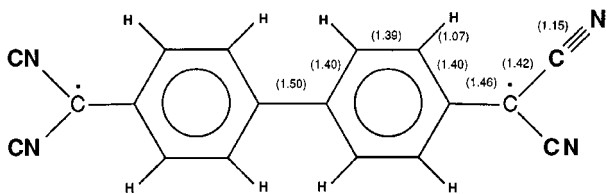


FIGURE 6. Optimized geometry of the TCNDQ molecule in the triplet state (double-zeta basis set); distances are given in angstroms (Å).

potential energy curves, respectively, associated with the quinoidal and the diradical electronic structures. Moreover, for intermediate geometries we have obtained two stable CASSCF solutions (see Fig. 7 and Table I) by using different trial vectors coming from either the quinoidal or the diradical solutions of the neighbor geometries. There is a significant domain of multistability of the CASSCF method. We do not claim that we have explored the whole domain of multistability, but its existence is clear.

The physical nature of the two coexistent solutions may be appreciated from the λ/μ ratio, larger in the quinoidal-type solution than in the

TABLE I
Configuration mixing for the quinoidal- and diradical-type CASSCF solutions along the potential energy curve of Figure 7.

k	$E_{\text{quinoidal}}$	λ/μ	$E_{\text{diradical}}$	λ/μ
-1.2	-903.766888	4.88		
-1	-903.766820	4.81		
-.8	-903.765842	4.75		
-.5	-903.762737	4.64		
-.2	-903.757818	4.52	-903.757970	2.24
0	-903.753602	4.41	-903.758910	1.85
.2	-903.748702	4.23	-903.760203	1.61
.5			-903.762001	1.42
.7			-903.762722	1.34
.8			-903.762881	1.31
1			-903.762741	1.26

diradical-type one (cf. Table I). Notice that we have not found eigenfunctions presenting the halfway ratio $\lambda/\mu = 3$.

The here-presented example of multistability of CASSCF solution is different from the previously reported cases. First of all, it is not an electron transfer problem. Second, the phenomenon cannot

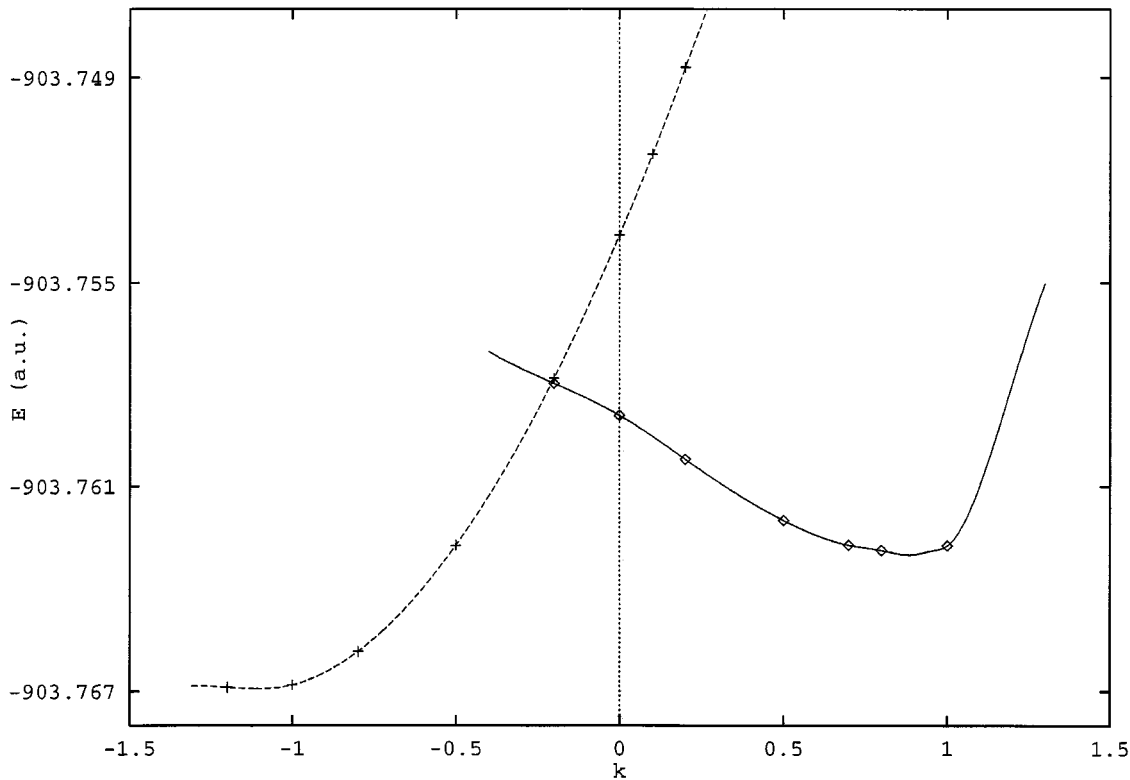


FIGURE 7. Potential energy curve computed using the CASSCF (2 conf.) method.

be interpreted as due to a weak resonance between two dominant strongly nonorthogonal VB structures requiring different polarities of the core MOs. Here, the overlap between the pure quinoidal and the pure diradical functions is close to $1/\sqrt{2}$ as may be seen from Eqs. (1) and (4), if the core MOs are identical. Nevertheless, one should notice that the “inactive” (different from l and h) π MOs are certainly significantly different in the two solutions, and their opposite relaxations inhibits the resonance between the two forms. Therefore, the whole potential curve of Figure 7 is questionable, and the proper existence of two minima might be an artifact of the poor quality of the wave function. Notice that according to experimental results [19], the analogous Chichibabin molecule presents a unique geometry halfway between those of the two limit structures (bond alternation in the benzene rings $\Delta l = .05$ Å). Computations using a geometry-dependent magnetic (Heisenberg) model Hamiltonian [25] on the Chichibabin-like molecules reveal also a unique intermediate geometry ($\Delta l = 0.05$ Å) resulting from a strong mixing of the two leading forms. It is therefore necessary to go to a further level of treatment.

Beyond the Minimal CASSCF Description

A temptation might consist in performing a state average CASSCF treatment, without increasing the number of active electrons. This procedure has solved the difficulty of the cusp of the ground-state potential energy curve in the LiF problem [11]. It is not relevant here since there is no nearly degenerate excited state of the same symmetry (remember that in a degenerate nonorthogonal two-configuration problem, if h and S are, respectively, the Hamiltonian interaction and the overlap, the eigenenergies are $h/\sqrt{2(1+S)}$ and $h/\sqrt{2(1-S)}$, so that the overlap pushes the upper state to a high energy). Moreover the other symmetrical singlet state is of dominant ionic character

$$\begin{aligned}\Psi^* &= |\text{core}(\lambda h\bar{h} + \mu l\bar{l})| \\ &= \left| \text{core} \left[\frac{\lambda + \mu}{2} (a\bar{a} + b\bar{b}) + \frac{\lambda - \mu}{2} (a\bar{b} + b\bar{a}) \right] \right| \quad (5)\end{aligned}$$

and plays no role in the problem. Actually over-

coming the bistability defect requires involving more π electrons.

As a first improvement, one may treat the effect of the inactive electrons in a perturbative mode through the CASPT2 algorithm [24]. The results appear in Figure 8 and are desperately unreliable, the perturbation is unable to produce consistent matching potential energy curves.

As a next step, larger CASSCF computations were performed. The system is too large to be treated through a CAS concerning 22 electrons in 22 valence MOs. However, we can assume that the deeper bonding and higher antibonding MOs are less crucial than those close to the Fermi level. The HOMO and LUMO, respectively, belong to the B_{1u} and B_{2g} symmetry. We have first performed computations taking all the active orbitals in these symmetries. In Figures 9 and 10 are, respectively, represented the potential energy curves obtained by CASSCF computations concerning 6 electrons in 6 orbitals, and 6 electrons in 8 orbitals. The number of inactive orbitals in the B_{1u} and B_{2g} symmetries are (2, 2) in both cases. We have then used an energetic criterion and considered the orbitals in all the symmetries which are closest to the Fermi level. A CASSCF computation concerning 8 electrons in 10 orbitals has been performed (see Fig. 11); the number of inactive orbitals in the B_{1u} , B_{2g} , B_{3g} , and A_u symmetries being, respectively, 3, 2, 1, and 1. All the potential energy curves present the same qualitative features, namely a single minimum close to the quinoidal structure and an inflection in the diradical domain ($k > 0$). Although we did not perform a systematic research of multiple solutions for the same value of k , the shape of the curve suggests that the wave function changes qualitatively between $k = 0.0$ and $k = 0.5$.

When the remaining electrons and MOs are involved in a subsequent CASPT2 (6 electrons in 6 orbitals), the potential curve presents two minima centered near $k = -0.5$ and $k = 0.5$. The results are presented on Figure 12. The qualitative differences between the CASSCF and CASPT2 shapes indicate that a sufficient accuracy has not been obtained and that the effect of the bistability has not been overcome.

In order to go beyond the perturbation second-order scheme and to avoid the constraint of the contraction of the model space function (inherent to the CASPT2 formalism), it may be useful to perform a variational configuration interaction (CI)

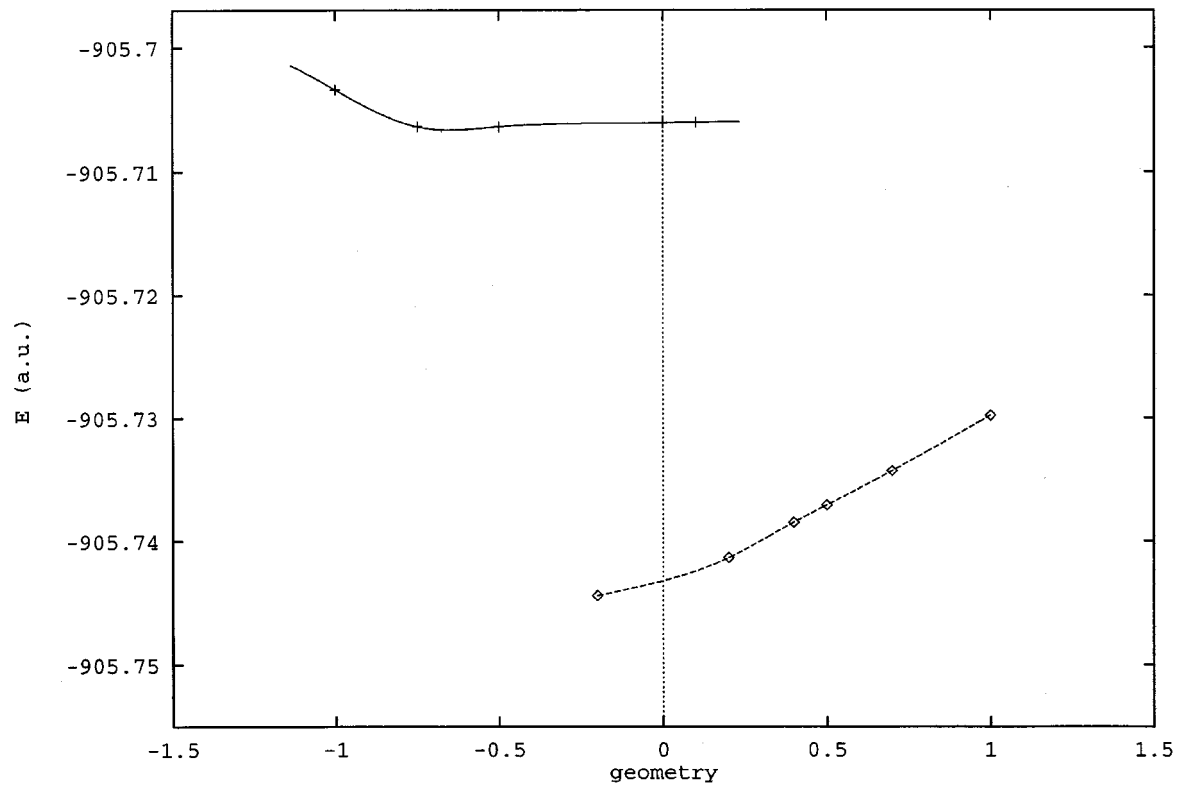


FIGURE 8. Potential energy curve computed using the CASPT2 (2 conf.) method.

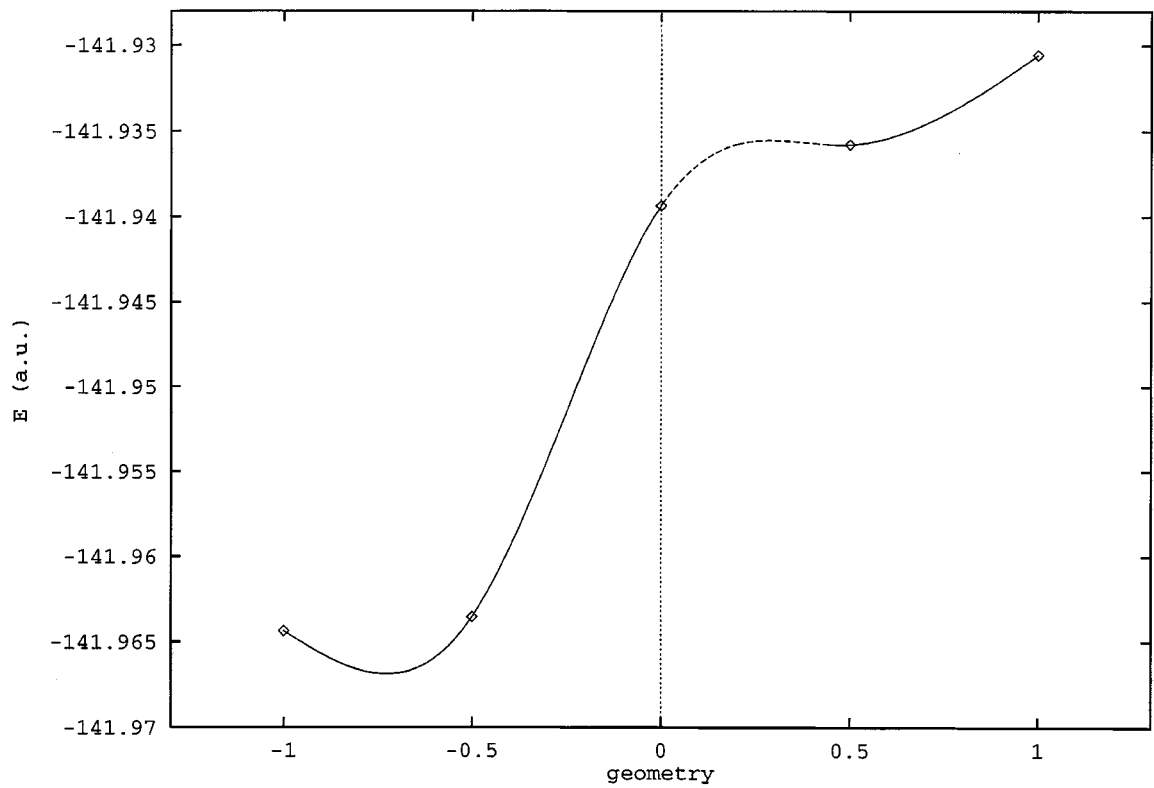


FIGURE 9. Potential energy curve computed using the CASSCF (6 electrons in 6 orbitals) method.

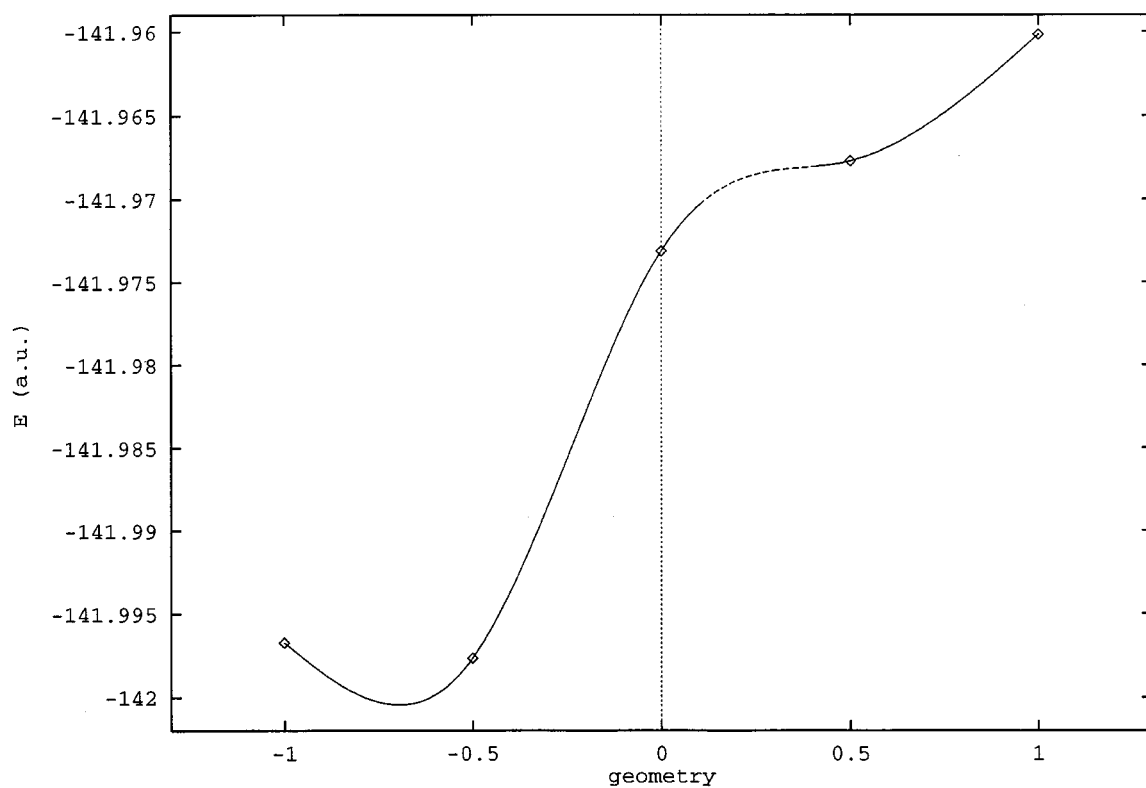


FIGURE 10. Potential energy curve computed using the CASSCF (8 electrons in 6 orbitals) method.

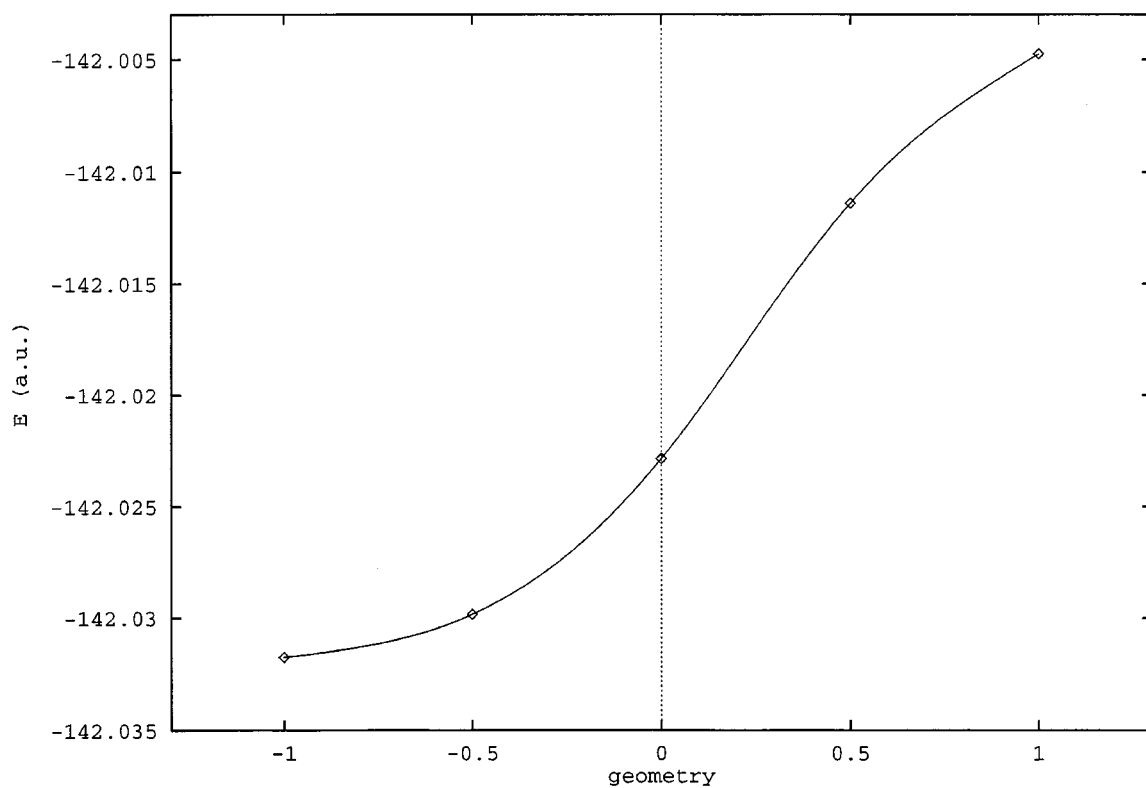


FIGURE 11. Potential energy curve computed using the CASSCF (8 electrons in 10 orbitals) method.

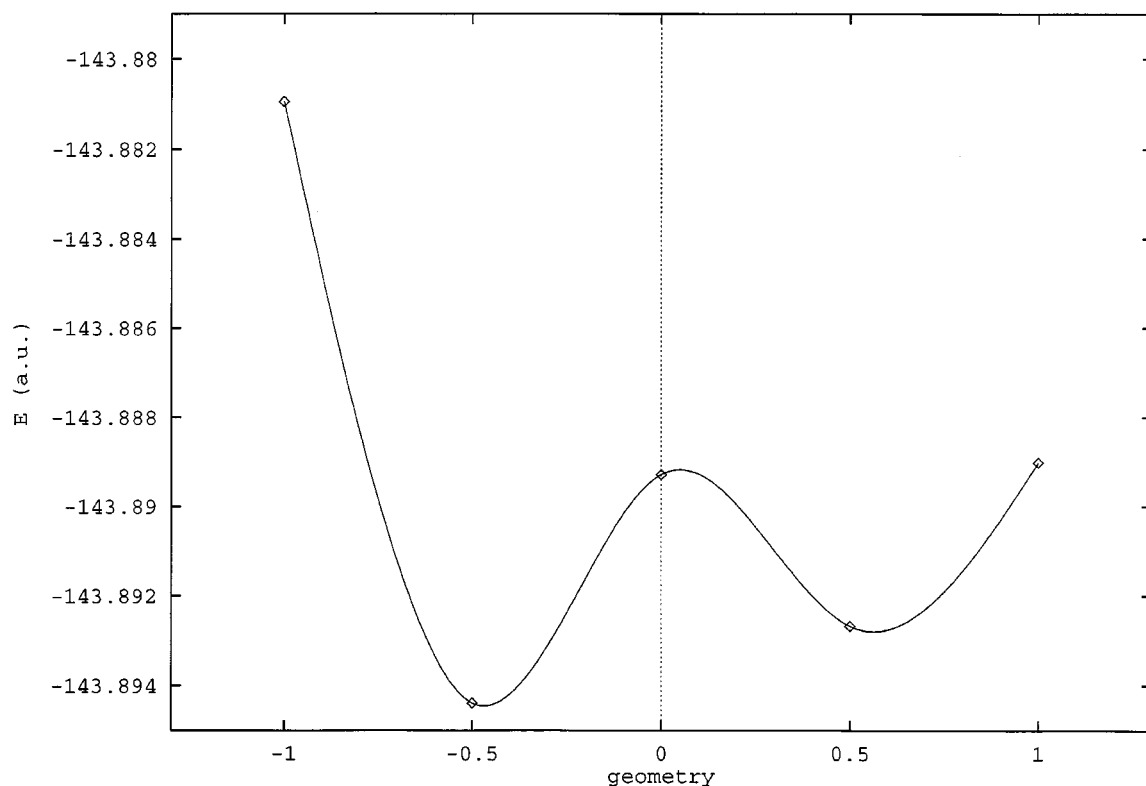


FIGURE 12. Potential energy curve computed using the CASPT2 (6 electrons in 6 orbitals) method.

over all π electrons and π valence MOs. The full CI is of course impossible, and even a CI limited to singles and doubles (CISD) would be very expensive. We have frozen the σ MOs and have performed a CISD limited to the π electrons and MOs. The number of π electrons is large (22) and size inconsistency may result in serious errors, so that ACPF formalism [26] was used.

The results appear in Figure 13. They indicate an unique minimum for an intermediate geometry ($k_{\min} = 0$). In order to check the reliability of the results, we have calculated the energy for the same geometry $k = 0$ starting from the two sets of CASSCF MOs. The resulting energies were almost identical (fortuitously as small as 2.7×10^{-4} eV). These results, which suppress the bistability behavior, are in qualitative agreement with both the magnetic picture and the experimental evidence [19] of an intermediate geometry.

Conclusion

The present study has exhibited a new case of bistability of CASSCF solutions. It differs from the

previous cases reported in the literature by the fact that it does not involve electron transfer nor two nearly degenerate VB configurations. The two CASSCF solutions correspond, respectively, to a Kékulé-type (quinoidal) function and to a diradical function and have in principle a strong overlap. The physical nature of the problem suggests that a small CAS (two electrons in two MOs) is sufficient, but the polarization of the inactive orbitals is such that it prevents the resonance between the two leading structures to play freely.

The inclusion of further correlation effects should repair the defect of the CASSCF functions, but it appears that larger CASSCF functions of moderate size do not give a satisfactory potential energy curve and that the corresponding CASPT2 results are not sufficient. It seems necessary to go to a variational CI involving all the π electrons to suppress the artifactual double minima of the CASSCF or CASPT2 potential energy curves and to obtain the expected intermediate equilibrium geometry. The present computations are not perfectly conclusive and accurate MOCI calculations remain desirable on this unexpectedly difficult problem.

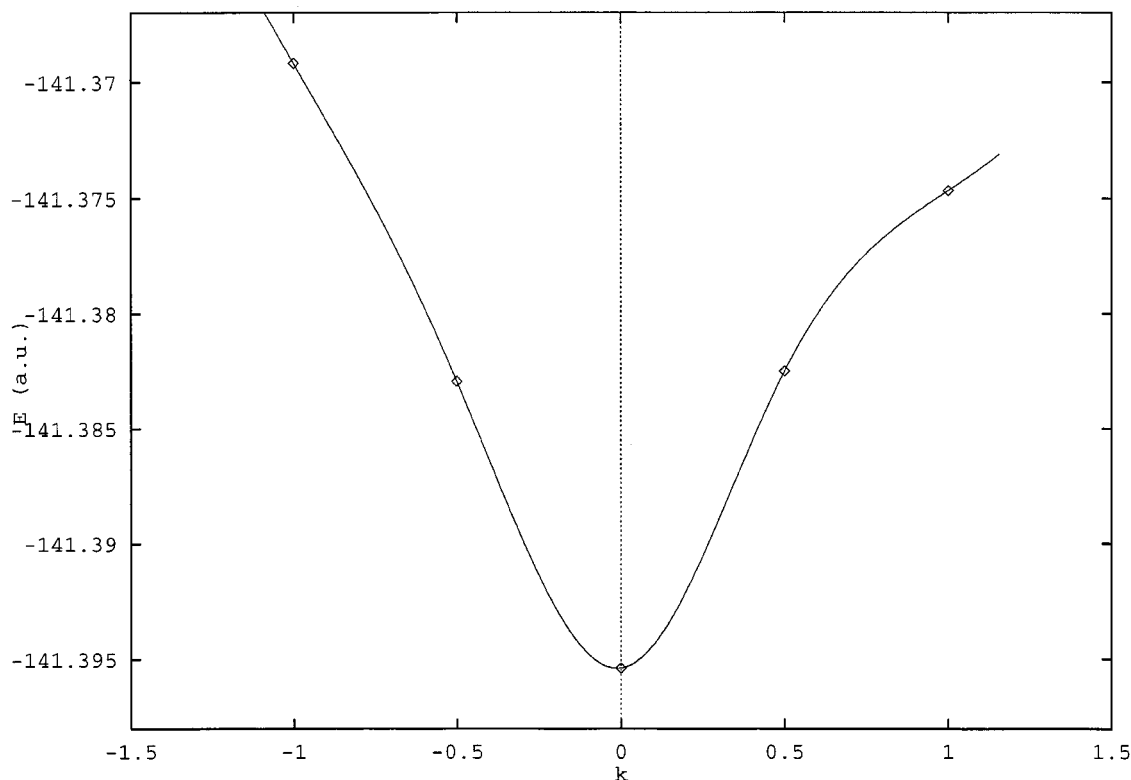


FIGURE 13. Potential energy curve computed using the CISD method (restricted to π electrons).

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