Tetrahedron Vol. 38, No. 6, pp. 737 to 739, 1982
Printed in Great Britain.

0040-4020/82/060737-03$03.00/0
Pergamon Press Ltd.

RHF AND TWO-CONFIGURATION SCF CALCULATIONS ARE INAPPROPRIATE FOR CONJUGATED DIRADICALS

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(*Received in U.S.A.* 6 *April* 1981)

Abstract—Restricted Hartee Fock (RHF) and two-configuration self-consistent field (TCSCF) calculations provide qualitatively correct molecular orbitals for the two open-shell electrons in diradicals. Nevertheless, these calculations fail to give correct relative energies and in some cases they even lead to incorrect geometries. Examples of these failures are given for both singlet and triplet states of some conjugated diradicals. In several cases these failures are related to the "doublet instability problem" in RHF calculations on radicals. It is argued that unrestricted Hartee-Fock (UHF) calculations on triplet states are more likely than RHF to provide accurate geometries.

For closed shell molecules self-consistent field (SCF) calculations provide, in general, a satisfactory method for optimizing geometries and for obtaining relative energies at closely related geometries. Since restricted Hartee-Fock (RHF) and two-configuration SCF (TCSCF) calculations provide reasonable molecular orbitals for the open-shell electrons in diradicals, it might be hoped that these methods could be used to optimize geometries and calculate relative energies on potential surfaces for diradicals. In this paper we present evidence, based on our theoretical studies of fully conjugated diradicals,[1] that RHF and TCSCF calculations cannot be used reliably for either purpose.

SINGLET DIRADICALS

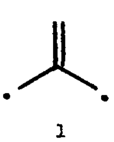
The relative energies of the $^1A_1$ (**1**) and $^1B_2$ (**2**) wavefunctions for trimethylenemethane at their respective equilibrium geometries determine the ease of pseudorotation on the singlet potential surface.[2] Hence, the accurate computation of their relative energies is quite important.[3] A check on the accuracy of any calculation is provided by the fact that at D_{3h} geometries **1** and **2** become the two components of a degenerate $^1E'$ state. Therefore, the wavefunctions should be computed to have the same energy at D_{3h} geometries. However, it can be shown by group theoretical arguments that neither a TCSCF wavefunction for $^1A_1$ nor an RHF wavefunction for $^1B_2$ will become a pure component of $^1E'$ at a D_{3h} geometry.[4] Consequently, D_{3h} degeneracy is not anticipated for the TCSCF and RHF wavefunctions. In fact, this non-degeneracy is computed to amount to almost 8 kcal/mol in calculations carried out with an STO-3G basis set at the equilibrium geometry of the triplet. Thus, at this level of theory the relative energies of the two wavefunctions at their equilibrium geometries can be expected to be prejudiced spuriously in favor of $^1A_1$ by about 8 kcal/mol.

It has been shown that full configuration interaction (CI) in the pi space is necessary[4] and sufficient[5] to provide $^1A_1$ and $^1B_2$ trimethylenemethane wavefunctions that are degenerate at D_{3h} geometries. Therefore, only at this level of theory can one expect to obtain the correct relative energies of the wavefunctions at their equilibrium geometries.

Even full CI in the pi space is not sufficient to provide properly degenerate singlet wavefunctions when a diradical contains a charged pi system that can affect the distribution of sigma electrons. For example, in $(NH)_3^{+2}$ and in the isoelectronic cyclopropenyl anion, $^1A_1$ and $^1B_2$ wavefunctions at both the SCF and pi CI levels of theory are distinctly nondegenerate at D_{3h} geometries.[6] CI in the sigma and in the pi space, which allows for sigma-pi correlation, is necessary in order to obtain wavefunctions with the correct relative energies.

Moreover, both TCSCF and pi CI calculations for $^1A_1$ predict a completely incorrect equilibrium planar geometry for $(NH)_3^{+2}$ and cyclopropenyl anion.[6] An analysis based on Jahn-Teller effects shows that $^1A_1$ should prefer a planar geometry with one long and two short bonds, depicted by **3**, over a planar geometry with one short and two long bonds, represented by **4**. Nevertheless, with both TCSCF and pi CI wavefunctions a geometry of type **4** is found to be the equilibrium planar geometry for $^1A_1$. Distortions from D_{3h} symmetry toward a type **3** geometry actually result in an increase in energy. Only at the sigma-pi CI level of theory does $^1A_1$ show the proper behavior.

The behavior of the $^1A_1$ state in $(NH)_3^{+2}$ and in the cyclopropenyl anion sounds a strong cautionary note. It is currently standard theoretical practice to locate equilibrium geometries at the SCF level of theory. When CI is carried out, it is rare that the SCF geometry is reoptimized at the CI level. As the behavior of $^1A_1$ in $(NH)_3^{+2}$ and in the cyclopropenyl anion demonstrates, SCF and


1


2


3


4

even pi CI calculations can provide totally incorrect equilibrium geometries for singlet diradicals.

TRIPLET DIRADICALS

That RHF calculations on conjugated triplet diradicals suffer from the same types of problems that plague RHF and TCSCF calculations on singlets was first indicated by our calculations on triplet trimethylenemethane.[2] Using an STO-3G basis set and standard geometries at the methylene groups, RHF calculations showed that the triplet tended to distort away from D_{3h} symmetry toward a geometry resembling that of **1**, with one short C–C bond and two long ones. That this result was spurious was clearly demonstrated by pi space CI calculations which showed a D_{3h} geometry to be an energy minimum. Subsequent RHF calculations by Hood, Pitzer and Schaefer[7] with a double ζ quality basis set and optimized methylene group geometries apparently did find a D_{3h} equilibrium geometry for the triplet; but their published results reveal that it remains significantly less costly at the RHF level to shorten one C–C bond and lengthen two than to perform the reverse distortion from D_{3h} symmetry.

More recently, as part of an exploration of the global potential surface for 1,3-dimethylenecyclobutadiene (**5**), we had occasion to optimize the geometry of the triplet state using energy gradients computed analytically from RHF calculations.[8] We found the triplet state to be planar but with C–C bond lengths significantly different from those obtained previously[9] by pi space CI calculations. The optimal lengths of the ring and external C–C bonds at both levels of theory are shown in Table 1. The RHF ring bond lengths are significantly longer (0.015 Å) and the external ones shorter (0.053 Å) than those obtained from pi CI calculations.

The fact that the RHF geometry is rather different than that obtained by pi CI has an effect on the CI energy calculated for the triplet. The pi CI energy at the RHF geometry is −227.8228 hartrees, 0.0054 hartrees higher than at the optimal pi CI geometry.[10] This would lead to the energy of the triplet being overestimated by 3.4 kcal/mol if the CI energy of the triplet were determined at the RHF geometry.

DISCUSSION

Some of the difficulties encountered with RHF calculations on diradicals are related to what is known as the "doublet instability problem" in radicals.[11] Most simply stated, the doublet instability problem causes radicals like allyl to be computed to have unequal bond lengths at the RHF level of theory.[12] The problem is most severe for calculations with small basis sets. It arises because at the RHF level no correlation is provided between the unpaired electron in the nonbonding MO of allyl and the one of opposite spin in the lowest pi MO. A wavefunction consisting of a double bond between two carbons in allyl, with the odd electron localized at the third, confines these two electrons to different regions of space, thus minimizing their mutual Coulomb repulsion energy. It is the lower Coulomb repulsion energy in such a wavefunction that makes it, at its equilibrium geometry with unequal C–C bond lengths, lower in energy than the delocalized allyl RHF wavefunction with equal C–C bond lengths.

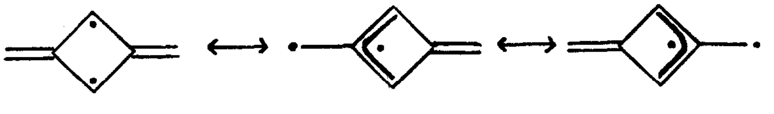
The doublet instability problem disappears when correlation is provided between the unpaired electron and the one of opposite spin in the lowest pi MO. Such correlation can be furnished either by carrying out an unrestricted Hartree–Fock (UHF) calculation,[13] in which the electrons of opposite spin in the lowest pi MO are allowed to have different spatial wavefunctions, or by inclusion of pi CI.[12,14]

There is every reason to believe that an analog of the doublet instability problem should manifest itself in fully conjugated diradicals. Indeed, the bond lengths found at the RHF level for the triplet state of **5** suggest that resonance structures like **5b** and **c** contribute much less than **5a**. However, the longer external and shorter internal bond lengths found at the pi CI level indicate that, with the inclusion of electron correlation, the pi electrons become more delocalized.

Providing electron correlation through a UHF calculation gives, as shown in Table 1, a geometry for **5**

Table 1. Ring and external C–C bond lengths (Å) calculated at different levels of theory for $^3B_{2u}$ and ^1A_g 1,3-dimethylenecyclobutadiene (**5**)

	$^3B_{2u}$ ring	$^3B_{2u}$ external	^1A_g ring	^1A_g external
RHF	1.486	1.321	1.501	1.311
Pi CI	1.471	1.374	1.506	1.342
UHF	1.470	1.394	---	---



5a b c

similar to that obtained by pi CI, except that the external C–C bonds are even longer at the UHF level of theory. A pi CI calculation at the optimal UHF geometry yields a CI energy only 0.0007 hartree (0.4 kcal/mol) above that at the optimal pi CI geometry. This finding suggests that it may be possible in general to optimize triplet geometries with UHF calculations, instead of at the CI level. At the least, UHF geometries for triplets should be much closer than RHF geometries to those that would be obtained by CI calculations.

The doublet instability problem manifests itself not only in RHF calculations on triplet diradicals but also in calculations on singlets. For instance, the doublet instability problem would be expected to affect the allylic portion of the $^1B_2$ wavefunction for trimethylenemethane. Localization of the odd electron on one carbon should be favourable at the RHF level, if permitted by the symmetry imposed. Such localization would simply lead to the $^1A_1$ wavefunction with the molecule rotated by 120°. This explains the lower energy spuriously calculated for the $^1A_1$ wavefunction at the RHF/TCSCF level of theory. A similar effect is responsible for the tendency of triplet trimethylenemethane at the RHF level to shorten two bonds and lengthen one, leading to pi electron localization analogous to that found in $^1A_1$.

Unfortunately, singlet diradicals cannot be represented by single Slater determinants. Therefore, UHF calculations cannot be carried out on singlets in order to attempt to solve the problems caused by the lack of correlation between electrons of opposite spin at the RHF level.

Minimization of Coulombic repulsion between the open-shell electrons usually causes the bonding in singlet diradicals to be more localized than in the corresponding triplets.[15] This may tend in some cases to make RHF and TCSCF calculations yield satisfactory equilibrium geometries for singlets, especially when symmetry constraints are imposed in the geometry optimization. For instance, the TCSCF and pi CI geometries for the ^1A_g state of **5**[9] have similar ring bond lengths; and external C–C bonds differ by 0.032 Å. This is considerably less than the 0.053 Å difference between the RHF and pi CI lengths for the external bonds in the triplet. Nevertheless, our results on $(NH)_3^{+2}$ and the cyclopropenyl anion warn of the possible dangers inherent in optimizing the geometries of singlet diradicals without the inclusion of substantial amounts of electron correlation in the calculations.[16]

Acknowledgements—Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

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[3] The wavefunction for $^1B_2$ is closely related to that ($^1B_1$) for the "orthogonal" or "bisected" conformation of trimethylenemethane, in which one group is twisted out of conjugation. This conformation has been implicated in the thermal rearrangements of methylenecyclopropanes. If the relative energies of $^1A_1$ and $^1B_2$ are not computed correctly, it is unlikely that those of $^1A_1$ and $^1B_1$ will be.

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[10] For this calculation we used the optimal C–C pi CI bond lengths determined previously;[9] but for the C–H bond lengths and the bond angles we employed the values obtained from the RHF geometry optimization, instead of the standard set we used before.

[11] For a discussion and leading references see J. Paldus and A. Veillard, *Mol. Phys.* **35**, 445 (1978).

[12] The same problem arises in unsaturated triplet carbenes like cyanomethylene, where the two unpaired electrons can be delocalized over two mutually orthogonal pi systems. J. F. Harrison, A. Dendramis and G. E. Leroi. *J. Am. Chem. Soc.* **100**, 4352 (1978).

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[16] The difficulty in these molecules has some features in common with the doublet instability problem. With an SCF wavefunction for the sigma electrons, Coulomb repulsion between the sigma and pi electrons is lower for the more localized pi wavefunction.[6] The more delocalized wavefunction becomes competitive in energy only when sigma–pi electron correlation is explicitly included through CI. The same phenomenon is encountered in charged radicals like the cyclobutadiene radical cation.[17] In this radical the energy at square geometries is found to depend strongly on the supposedly arbitrary choice of whether a localized or delocalized e_g pi MO is occupied by the odd electron. This is true at the RHF, UHF and pi CI levels of theory. Sigma–pi CI is necessary to render the energy invariant to the choice of representation of the singly occupied e_u MO.

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