A nonorthogonal CI treatment of symmetry breaking in sigma formyloxyl radical

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Spatial symmetry breaking can occur in Hartree–Fock wave functions when there are two or more close lying configurations that can mix strongly, such as in HCO$_2$, NO$_2$, and allyl radical. Like spin contamination, spatial symmetry breaking can cause sizeable errors when perturbation theory is used to estimate the correlation energy. With conventional methodology, very large MCSCF and MRCI calculations are necessary to overcome the spatial symmetry breaking problem. This paper explores an alternative approach in which a 2×2 nonorthogonal CI is used to recombine the two symmetry broken Hartree–Fock determinants. The necessary matrix elements closely resemble those used in the spin projection calculations. Second order perturbation theory is used to include electron correlation energy in this approach. With perturbative corrections for correlation energy, this approach predicts that the $^2B_2$ structure is a minimum, in agreement with the best available calculations. © 1998 American Institute of Physics.

INTRODUCTION

The formyloxyl radical, HCO$_2$, is of particular interest in atmospheric and combustion chemistry as an intermediate in the OH+CO→H+CO$_2$ reaction. $^1$–$^3$ The formyloxyl radical is also a possible intermediate in the thermal decomposition of formic acid. $^6$–$^8$ Despite its importance, relatively little is known experimentally about HCO$_2$, not even its equilibrium geometry. $^6$–$^8$ Similar to the isoelectronic allyl radical, $^9$, $^10$ C$_3$H$_5$, and nitrogen dioxide, $^{11}$–$^{16}$ NO$_2$, the Hartree–Fock wave function of the formyloxyl radical $^{16}$–$^{22}$ suffers from spatial symmetry breaking (also known as artificial symmetry breaking $^{11}$ or doublet instability $^{21}$,$^{24}$). However, a $C_{2v}$ equilibrium geometry for HCO$_2$ can be obtained with extensive and carefully constructed multiconfiguration self-consistent field (MCSCF) and multireference configuration interaction (MRCI) calculations $^{16}$–$^{20}$ or large EOM-CC calculations using the anion as a reference configuration $^{21}$,$^{22}$.

In this paper we use the broken symmetry Hartree–Fock orbitals to construct a compact, high symmetry wave functions for the $^2B_2$ and $^2A_1$ states of the σ radicals of HCO$_2$, employing a 2×2 nonorthogonal configuration interaction $^{10}$,$^{13}$,$^{26}$,$^{27}$ combined with second order perturbation theory (Scheme 1).

Scheme 1. Localized, broken symmetry configurations combined to form the $^2B_2$ and $^2A_1$ states of σ-HCO$_2$

The breaking of spatial symmetry in SCF wave functions has been examined a number of times during the last few decades by numerous groups. $^9$–$^{46}$ This problem is often studied in the context of polyenes, open shell oxygen containing radicals, excited states and ions. Molecular systems that encounter symmetry-breaking problems in their wave function share a number of features. For a symmetry adapted HF wave function, minute antisymmetric displacements can cause discontinuous changes in the energy. Removal of the symmetry constraints on the HF wave function yields two or more lower energy wave functions and results in extensive relaxation of the molecular orbitals. The potential energy surfaces for these are continuous under distortions to lower symmetry and distortion to lower symmetry is energetically favored. Symmetry breaking in an HF wave function can occur if there are two or more single determinant wave functions that (a) are similar in energy but different in symmetry, (b) differ by a single excitation and (c) can interact when the geometry is distorted to lower symmetry. $^{12}$,$^{13}$

McLean et al. $^{17}$ have used He$_2^+$ to clearly illustrate the problem of symmetry breaking in the SCF solution and especially the effect of orbital relaxation. A symmetry broken Hartree–Fock wave function, $\Psi_0 = |\phi_a^2\phi_b^1\rangle$, is shown in Scheme 2; because the orbital localized on atom $a$ has to accommodate two electrons, $\phi_a$ is significantly larger (more diffuse) than $\phi_b^1$, the one localized on atom $b$. The configuration $|\phi_a\phi_b^2\rangle$ is considerably higher in energy because two electrons are placed in a smaller, more compact orbital. In the other symmetry broken wave function $P\Psi_0 = |\phi_b^2\phi_a^1\rangle$, where $P$ is the appropriate symmetry operator, $\phi_b^2$ is larger than $\phi_a^1$.

$\phi_a$ • ∆

$\phi_b$ ± ∆

Scheme 2. Symmetry broken and symmetry constrained orbitals for He$_2^+$. 

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Alternatively one can construct two symmetry adapted Hartree–Fock wave functions \( |\Psi_{a}\rangle \) and \( |\Psi_{b}\rangle \): 

\[
\Psi_{g,m} = \frac{1}{\sqrt{2}} \left( |\phi^{m}_{g,a}\rangle |\phi^{m}_{g,b}\rangle + |\phi^{m}_{g,b}\rangle |\phi^{m}_{g,a}\rangle \right)
\]

where \( \phi^{m}_{g,a}\) and \( \phi^{m}_{g,b}\) refer to the localized orbitals on atoms \( a \) and \( b \). This is effectively a multi-reference determinant. This is used to localize the orbitals on atoms \( a \) and \( b \): 

\[
\Psi_{g,m} = \frac{1}{\sqrt{2}} \left( |\phi^{m}_{g,a}\rangle |\phi^{m}_{g,b}\rangle + |\phi^{m}_{g,b}\rangle |\phi^{m}_{g,a}\rangle \right)
\]

These terms, namely, \( |\phi^{m}_{g,a}\rangle |\phi^{m}_{g,b}\rangle \) and \( |\phi^{m}_{g,b}\rangle |\phi^{m}_{g,a}\rangle \), interact in a resonance fashion. However, \( \Psi_{g,m} \) also contain \( |\phi^{m}_{g,a}\rangle |\phi^{m}_{g,b}\rangle \) and \( |\phi^{m}_{g,b}\rangle |\phi^{m}_{g,a}\rangle \) which correspond to high energy, ionic configurations. These terms are inherent to the symmetry constraints and the SCF process must find optimal orbital sizes that are a compromise between maximizing the resonance effect and minimizing the destabilization effect of the high energy ionic configurations. In the symmetry broken wave functions, such a compromise on orbital size is not necessary. The ordering of the orbital size is \( \phi^{m}_{g,a} > \phi^{m}_{g,b} > \phi^{m}_{g,a} \). This change in orbital size along with the localization constitutes the substantial orbital relaxation that accompanies symmetry breaking. From this, it can be inferred that the artificial symmetry breaking problem appears when the two contradictory objectives of resonance and optimal orbital size cannot be achieved in a single determinant wave function. At shorter internuclear distances the resonance effect dominates and the symmetry adapted wave function is lower in energy; at larger distances the resonance effect is diminished and the broken symmetry wave function with its optimal size orbitals is more stable. Since single reference methods have problems balancing these two objectives, multiconfiguration SCF methods are usually used.

The MCSCF studies of the \( HCO_{2} \) potential energy surface by Feller et al.\(^{19}\) McLean et al.\(^{15}\) and Rauk et al.\(^{18}\) are among the most extensive. Feller, Davidson, and co-workers\(^{19}\) used a split valence plus polarization basis set and 11 orbital/13 electron MCSCF restricted to no more than double excitations, followed by MRCI calculations. McLean et al.\(^{15}\) carefully constructed a larger active space for \( B-HCO_{2} \) that included the CO, CO\(^{2+}\), and CH \( \sigma \) and \( \sigma^{*} \) orbitals, the \( 3\sigma \) orbitals and two in-plane \( \pi \) orbitals of different size on each oxygen to handle the orbital relaxation effect of the \( \sigma \) lone pairs and included dynamic correlation by MRCI calculations constrained to single and double excitations of the 12 most important reference functions. Rauk et al.\(^{18}\) used complete active space MCSCF calculations with 11 electron in 13 orbitals, followed by multireference second order perturbation theory (CASPT2).\(^{47}\) More recently, Stanton et al.\(^{21,22}\) applied the EOM-CC method to \( HCO_{2} \), using the anion as a reference determinant. This is effectively a multiplicity coupled cluster approach starting from all singly ionized determinants that can be generated from \( HCO_{2} \). Small MCSCF and MRCI calculations find the \( 2\beta_{2} \) structure to be a saddle point with respect to asymmetric C–O stretching; however, in larger MCSCF calculations, or with MRCI, CASPT2, or EOM-CC methods, the \( 2\beta_{2} \) state is a minimum with an asymmetric C–O stretching frequency near 1000 cm\(^{-1}\) and, except for the CASPT2 calculations, is lower in energy than the \( 2\alpha_{1} \) structure.\(^{16–22}\) The surface around the \( 2\alpha_{1} \) structure is very flat, and different levels of theory yield different results. With small to medium size basis sets, \( 2\alpha_{1} \) structure is a saddle point with respect to asymmetric C–O stretching, but it may be a minimum with very large basis sets.\(^{22}\) The \( 2\alpha_{1} \) structure can also dissociate to \( H+CO_{2} \), with or without a small barrier, depending on the computational approach.\(^{18,19}\) The \( 2\beta_{2} \) and \( 2\alpha_{1} \) regions of the surface are connected via a pair \( C_{s} \) symmetry reaction paths with unequal C–O bond lengths; there may be minima and/or a small barrier along this path, depending on the level of theory.\(^{16–22}\)

There are a number of additional studies on other systems that are related to the present work. Bartlett and co-workers\(^{15,35–37}\) have studied spatial symmetry breaking in \( NO_{2} \) and \( NO_{3} \) using the Brueckner doubles method and coupled cluster wave functions with quasirestricted open shell orbitals. Hiberty et al.\(^{48}\) have used a two configuration valence bond method with breathing orbitals to handle the orbital size effect in two center, three electron bonds. Burton et al.\(^{16}\) have examined the vibrational frequencies in \( NO_{2} \) and \( HCO_{2} \) and have pointed out that the anomalously high frequencies for the asymmetric stretch found for symmetry constrained HF calculations are due to wavefunction instability with respect to symmetry breaking.

**NONORTHOGONAL CI APPROACH**

It would be very desirable to treat the symmetry breaking problem without having to resort to large MCSCF and MRCl calculations. In the two symmetry broken Hartree–Fock solutions for \( HCO_{2} \), the orbitals are optimal size, whereas in the symmetry constrained \( 2\alpha_{1} \) and \( 2\beta_{2} \) solutions, the resonance effect competes with the energy raising effect of intermediate size orbitals. One way to cope with this is to combine the two symmetry broken solutions with a simple \( 2\times2 \) nonorthogonal configuration interaction scheme.\(^{10,13,26,27}\) Jackels and Davidson\(^{13}\) found that a \( 2\times2 \) nonorthogonal CI was not adequate to reproduce a \( C_{2v} \) minimum for the \( 2\beta_{2} \) state of \( NO_{2} \), which is isoelectronic with \( HCO_{2} \). Blahous et al.\(^{14}\) suggest that this is due to the nearby crossing between the \( 2\alpha_{1} \) and \( 2\beta_{2} \) surfaces; extensive CASCC calculations show that additional configurations mix strongly, resulting in a \( C_{2v} \) minimum for the \( 2\beta_{2} \) surface (but with a barrier of less than 1.8 kcal/mol for crossing to the \( 2\alpha_{1} \) surface). The \( HCO_{2} \) surface may show similar difficulties, with added complications arising from transition states for C–H bond dissociation and 1, 2 hydrogen shifts.

A \( 2\times2 \) nonorthogonal configuration interaction approach involves two sets of nonorthogonal orbitals and is similar to spin-coupled valence bond theory\(^{49}\) and resonating GVB theory.\(^{10,26}\) Let \( \Psi_{0} \) and \( \Psi_{0}^{\dagger} \) be the two symmetry broken, normalized Hartree–Fock solutions; a symmetry adapted wave function \( \Phi_{0} \) can be constructed from a linear combination of \( \Psi_{0} \) and \( \Psi_{0}^{\dagger} \) by solving a \( 2\times2 \) nonorthogonal CI problem.
equivalent and molecular orbitals of C applying the appropriate symmetry operator to the molecular

\[ E_0 = \langle \Psi_0 | H | \Psi_0 \rangle, \quad E'_0 = \langle \Psi'_0 | H | \Psi'_0 \rangle, \]

\[ H = \langle \Psi_0 | H | \Psi_0 \rangle, \quad S = \langle \Psi_0 | \Psi_0 \rangle. \]  (1)

The matrix elements can be obtained by expanding one of the wave functions in terms of ground state and excited
determinants of the obtained from the other wave function

\[ \Psi'_0 = a_0 | \Psi_0 \rangle + \sum a_{ij}^{ab} | \Psi_{ij} \rangle + \cdots, \]  (2)

\[ \langle \Psi_0 | H | \Psi'_0 \rangle = a_0 \langle \Psi_0 | H | \Psi_0 \rangle + \sum a_{ij}^{ab} \langle \Psi_0 | H | \Psi_{ij} \rangle. \]  (3)

The coefficients \( a_{ij}^{ab} \) etc. can be obtained from the overlaps between the two sets of orbitals, as outlined in the
Appendix.

For symmetric geometries, \( \Psi_0 \) and \( \Psi'_0 \) are energetically equivalent and molecular orbitals of \( \Psi'_0 \) can be obtained by
applying the appropriate symmetry operator to the molecular orbitals of \( \Psi_0 \). For lower symmetry geometries, the orbitals
are obtained from two separate SCF calculations; however, converging two separate UHF localized solutions can be
difficult. A semiempirical initial guess for the wave function does not necessarily converge to the lowest energy broken
symmetry state, but a suitable initial guess for the second state can be obtained by permuting the orbital coefficients
from the converged solution of the first state. Both solutions are stable with respect to quadratic displacements of the MO
coefficients (i.e., the orbital rotation hessians have only positive eigenvalues).

Perturbation theory can be used to estimate the electron correlation contributions to the wave functions associated
with each symmetry broken solution. Let the wave function for the system be a linear combination of the two perturbationally
corrected symmetry broken solutions

\[ \Psi = \Psi_0 + \Psi_1 + \Psi_2 + \cdots; \quad \Psi' = \Psi'_0 + \Psi'_1 + \Psi'_2 + \cdots, \]

\[ \Phi = d \Psi + d' \Psi'. \]  (4)

The coefficients and correlated energy can be obtained by solving a suitable 2×2 eigenvalue problem, in which the matrix
elements are evaluated in the spirit of perturbation theory, i.e., retaining terms up to a given order (in some respects, this is akin to quasidegenerate perturbation theory). The diagonal elements are the respective perturbational energies of the symmetry broken solutions and pose no problems. The off-diagonal matrix elements are taken as the average of the two possible forms so that the matrices are hermitian in the low symmetry cases. For second order the equations are

\[ \begin{bmatrix} E_{MP2} & H \\ H & E'_{MP2} \end{bmatrix} \begin{bmatrix} d \\ d' \end{bmatrix} = \begin{bmatrix} 1 & S \\ S & 1 \end{bmatrix} \begin{bmatrix} d \\ d' \end{bmatrix}, \]

\[ \Phi = d_0 (\Psi_0 + \Psi_1) + d'_0 (\Psi'_0 + \Psi'_1), \]

\[ E_{MP2} = \langle \Psi_0 | H | \Psi_0 + \Psi_1 \rangle, \quad E'_{MP2} = \langle \Psi'_0 | H | \Psi'_0 + \Psi'_1 \rangle. \]  (5)

\[ H = \langle \Psi_0 | H | \Psi'_0 + \Psi'_1 \rangle + \langle \Psi'_0 | H | \Psi_0 + \Psi_1 \rangle/2, \]

\[ S = \langle \Psi_0 | \Psi'_0 + \Psi'_1 \rangle + \langle \Psi'_0 | \Psi_0 + \Psi_1 \rangle/2. \]

The off-diagonal Hamiltonian matrix element \( \langle \Psi'_0 | H | \Psi'_1 \rangle \) requires \( \Psi'_0 \) in Eq. (2) to be expanded up to fourth order. The resulting expression resembles the CCSD equations, and can be evaluated with very little modification of the CCSD code. The computational work is comparable to one CCSD iteration or an MP4SDQ calculation.

The correlation corrections to the 2×2 nonorthogonal CI equations can also be approximated in a manner similar to
spin projected Möller–Plesset perturbation theory. In this approach, the energy expression is very similar to the approximate
spin projected MP2 energy used in a number of previous studies by Schlegel.\(^5\) Equation (2) can be rewritten as

\[ \Psi'_0 = \langle \Psi_0 | \Psi'_0 \rangle \Psi_0 + \bar{\Psi}, \]  (6)

where \( \bar{\Psi} \) is linear combination of excited determinants built from \( \Psi_0 \). An approximate expression for \( \Psi' \) can be obtained
by assuming the perturbative corrections to \( \bar{\Psi} \) are small

\[ \Psi'_0 = \Psi'_0 + \Psi'_1 + \cdots \]

\[ = \langle \Psi_0 | \Psi'_0 \rangle \langle \Psi_0 + \Psi'_1 + \cdots \rangle \]

\[ + \bar{\Psi} (1 - \langle \bar{\Psi} | \bar{\Psi} \rangle) / \langle \bar{\Psi} | \bar{\Psi} \rangle. \]  (7)

The last term is included to remove from \( \bar{\Psi} \) any contributions already contained in \( \Psi_1 \). The approximate off-diagonal
hessian can then be computed relatively simply

\[ \langle \Psi_0 | H | \Psi'_0 \rangle \approx \langle \Psi_0 | \Psi'_0 \rangle \langle \Psi_0 | H | \Psi_0 + \Psi'_1 + \cdots \rangle \]

\[ + \langle \Psi_0 | H | \bar{\Psi} | (1 - \langle \bar{\Psi} | \bar{\Psi} \rangle) / \langle \bar{\Psi} | \bar{\Psi} \rangle \rangle. \]  (8)

For the high symmetry case when \( \langle \Psi_0 | H | \Psi_0 \rangle = \langle \Psi'_0 | H | \Psi'_0 \rangle \), the energy for the 2×2 CI reduces to

\[ E \approx E_{MP2} + \Delta E_0 (1 - \langle \bar{\Psi} | \bar{\Psi} \rangle) / \langle \bar{\Psi} | \bar{\Psi} \rangle, \]  (9)

where \( \Delta E_0 = \langle \Psi_0 | H | \bar{\Psi} \rangle / (1 + \langle \Psi_0 | \Psi'_0 \rangle) \) is the energy lowering given by the 2×2 CI based on Hartree–Fock determinants, Eq. (1). This scheme has a significantly lower computational cost than Eq. (5). These two schemes can be shown to yield a continuous PES, even as the symmetry broken UHF solutions disappear. The energy gradient is continuous except at the onset of the symmetry breaking instability.

Calculations were carried out with the GAUSSIAN series of programs\(^5\) using the spin unrestricted Hartree–Fock
(UHF) method with a split valence plus polarization basis set (6-31G*). Additional code was written to compute the matrix
elements needed for the nonorthonormal CI and the MP2 corrections based on the symmetry broken determinants. Vibrational
frequencies were calculated by double numerical differentiation. Because the \( \sigma \) and \( \pi \) states are very close in
energy, converging to the desired \( \sigma \) UHF solutions required some care.
TABLE I. Energies and optimized geometries of $^2B_2$ $\sigma$-HCO$_2$ calculated with single reference, symmetry constrained wave functions and the 6-31G* basis set.

<table>
<thead>
<tr>
<th>Method</th>
<th>CH (Å)</th>
<th>CO (Å)</th>
<th>HCO (degree)</th>
<th>OCO (degree)</th>
<th>Energy (Hartree)</th>
<th>$\Delta E^b$ (kcal/mol)</th>
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<tr>
<td>HF</td>
<td>1.0859</td>
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<td>123.87</td>
<td>112.26</td>
<td>−188.094 168</td>
<td>−9.78</td>
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<td>1.2564</td>
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<td>−189.078 964</td>
<td>0.00</td>
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<tr>
<td>MP2</td>
<td>1.0945</td>
<td>1.2598</td>
<td>124.25</td>
<td>111.50</td>
<td>−188.576 110</td>
<td>10.81</td>
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<td>QCISD</td>
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<td>1.2615</td>
<td>123.78</td>
<td>112.44</td>
<td>−188.592 387</td>
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<tr>
<td>QCISD(T)</td>
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<td>112.60</td>
<td>−188.600 209</td>
<td>14.00</td>
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<td>CCSD</td>
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<td>112.36</td>
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<td>0.93</td>
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<td>1.2647</td>
<td>123.70</td>
<td>112.60</td>
<td>−188.607 549</td>
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<td>BD$^a$</td>
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$^a$Frozen core calculation.
$^b$Energy of the symmetry broken solution minus the symmetry constrained solution at the $C_{2v}$ optimized geometry.

RESULTS AND DISCUSSION

UHF and single reference determinant calculations

The structures and energies of symmetry constrained UHF calculations on the $^2B_2$ and $^2A_1$ states of $\sigma$-HCO$_2$ are collected in Tables I and II, along with the results of correlated methods based on these UHF reference determinants. The results obtained with the hybrid density functional method B3LYP are also given. In the $^2B_2$ state, an $a_1$ orbital is doubly occupied and a $b_2$ orbital is singly occupied; in the $^2A_1$ state, the occupancy is reversed. Sketches of these orbitals are shown in Scheme 3. The $^2B_2$ state is lower in energy and has a smaller OCO angle than the $^2A_1$ state because the $a_1$ orbital is O–O bonding. The $a_1$ orbital also has C–H bonding character; since this orbital singly occupied in $^2A_1$ state, the C–H bond is significantly longer bond than in the $^2B_2$ state. Subsequent improvements of the wavefunctions do not change these qualitative differences between the $^2B_2$ and $^2A_1$ state:

![Scheme 3. $b_2$ and $a_1$ orbitals for HCO$_2$.](image)

At the $C_{2v}$ geometry, the symmetry broken UHF/6-31G* solutions are 9.8 and 6.3 kcal/mol lower than the $^2B_2$ and $^2A_1$ symmetry constrained UHF calculations, respectively (Tables I and II). With UMPn methods, the symmetry broken states are much higher than the symmetry constrained calculations, indicating that perturbative treatment of electron correlation can give rather misleading energetics for spatial symmetry breaking, similar to UMPn calculations on spin contaminated systems$^{59}$ (i.e., spin symmetry broken wave functions). The energy difference between the symmetry broken and constrained wave functions is significantly less for UQCISD calculations, much less for UCCSD and essentially zero for UBD. Perturbative corrections for the triples makes the energy difference significantly worse for UQCISD, but have little or no effect on the CC and BD calculations. This parallels the problems in QCISD(T) calculations for other cases with large $T_1$ amplitudes.$^{52-54}$

Geometry optimization of the symmetry broken solutions results in structures with unequal C–O bond lengths that are 1–13 kcal/mol lower in energy than the symmetric structures (Table III). The changes are largest at the UHF level, with C–O bond lengths that differ by 0.15 Å. The UMP2 calculations reduce this difference slightly. The difference in the C–O bond lengths is much smaller at the UQCISD level, but perturbative triples make matters worse. From the very small energy difference between the symmetry constrained and symmetry broken calculations at the BD level in Tables I and II, one would expect the symmetry broken BD calculations to yield a structure with nearly equal C–O bond lengths. The energy is lower than either the $^2B_2$ or $^2A_1$ solution and the difference in the bond lengths in the BD calculation is nearly as large as at the UHF level. Thus the BD calculations do not solve the symmetry breaking problem.

2×2 Nonorthogonal CI calculations

Tables IV and V present the results of the 2×2 nonorthogonal CI calculations. The potential energy surfaces are stabilized by about 18 kcal/mol compared to the UHF calculations and the $^2B_2$ state is lower in energy than the $^2A_1$ state. There is a noticeable change in geometry for the minima, especially for the $^2A_1$ state.

TABLE II. Energies and optimized geometries of $^2A_1$ $\sigma$-HCO$_2$ calculated with single reference, symmetry constrained wave functions and the 6-31G* basis set.

<table>
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<tr>
<th>Method</th>
<th>CH (Å)</th>
<th>CO (Å)</th>
<th>HCO (degree)</th>
<th>OCO (degree)</th>
<th>Energy (Hartree)</th>
<th>$\Delta E^b$ (kcal/mol)</th>
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<td>MP2</td>
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<td>107.82</td>
<td>−188.570 267</td>
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</table>

$^a$Frozen core calculation.
$^b$Energy of the symmetry broken solution minus the symmetry constrained solution at the $C_{2v}$ optimized geometry.
Figure 1 shows a series of potential energy curves as a function of the OCO angle. The $^2\text{B}_2$ state is lower in energy at small bond angles, while the $^2\text{A}_1$ state is more stable at larger angles. By varying the OCO angle, the effects of symmetry breaking can be studied without the lowering in symmetry that accompanies asymmetric C–O bond stretching. As expected, the symmetry broken UHF curve is lower in energy than both symmetry constrained solutions and has only one minimum at an intermediate angle. The $2\times2$ nonorthogonal CI calculations yield two potential energy curves of the correct symmetry and energy ordering. Surprisingly, the crossing between the $^2\text{B}_2$ and $^2\text{A}_1$ curves occurs at nearly the same angle at both the symmetry constrained UHF and $2\times2$ nonorthogonal CI levels of theory.

Unlike the symmetry constrained UHF calculations, the $2\times2$ CI calculations are continuous over asymmetric large displacements. In the MR-CI calculations of Peyerimhoff and coworkers, the energy decreases as one CO bond is lengthened and the other shortened. At the $2\times2$ CI level, the $^2\text{B}_2$ state is stable with respect to asymmetric CO stretch. However, a frequency calculation shows that the $^2\text{B}_2$ stationary point is a first order saddle point at the $2\times2$ nonorthogonal CI level of theory. The transition vector contains a large HCO bend component and should be perhaps best described...
as an asymmetric deformation rather than an asymmetric CO stretch.

Similar to Feller’s MCSCF study and Stanton’s EOM-CC calculations with medium size basis sets, the \( ^2A_1 \) structure is a first order saddle point (one imaginary frequency, 2151 cm\(^{-1}\)). The two mirror image \( ^2A' \) minima are found 0.38 kcal/mol below the \( ^2B_2 \) transition state with geometries closely resembling the Hartree–Fock structure. Very large basis set calculations with the EOM-CC method suggest that the \( ^2A_1 \) structure may be a shallow minimum on a very flat potential energy surface. At the UHF level of theory, the \( ^2A_1 \) portion of the potential energy surface shows a very small barrier for CH dissociation (0.12 kcal/mol). In the CASSCF calculations by Rauk et al., the \( ^2A_1 \) structure dissociates to H+CO\(_2\) without a barrier. Attempts to locate the \( ^2A_1 \) transition state for H loss at the \( ^2\)\( \times \)2 CI level were unsuccessful, since the instability of the UHF solution disappeared before a saddle point for dissociation could be reached. One can argue that the \( ^2\)\( \times \)2 CI procedure may be unsuited for this portion of the potential energy surface since inclusion of the C–H bond breaking configuration becomes more and more important and it should at least be treated by a 4\( \times \)4 CI, for example.

**MP2 corrections to the \( ^2\)\( \times \)2 nonorthogonal CI calculations**

Tables IV and V list the optimized geometries for the \( ^2B_2 \) and \( ^2A_1 \) structures using the MP2 corrected \( ^2\)\( \times \)2 CI. Both procedures outlined in Eq. (5) and in Eq. (9) are in good agreement with the CASPT2 results of Rauk et al., the MRCI results of McLean et al., and the EOM-CC calculations of Stanton. The geometries obtained with the correlated methods based on single reference determinants (Tables I and II) are also in good agreement with these calculations. Vibrational frequencies in Tables VI show that the \( ^2B_2 \) configuration is a minimum at both MP2 corrected \( ^2\)\( \times \)2 CI levels, confirming that the \( C_{2v} \) symmetry structure is a minimum. The vibrational frequencies are in good agreement with the MRCI, CASPT2 and EOM-CC values. The largest difference is for the asymmetric deformation mode. The calculations listed in Tables VI, along with larger basis set EOM-CC calculations indicate the frequency for this mode should be between 1000 and 1300 cm\(^{-1}\).

The CASPT2 and EOM-CC calculations of the \( ^2A_1 \) structure are minima with respect to C–H dissociation. However, a stationary point could not be located on the \( ^2A_1 \) potential energy with the MP2 corrected \( ^2\)\( \times \)2 CI calculations. At larger CH distances and OCO angles, there is a single

![FIG. 1. Energy curves for the \( ^2B_2 \), \( ^2A_1 \), and \( ^2A' \) states of \( \sigma \)-HCO\(_2\) as a function of the OCO angle. (a) UHF and \( ^2\)\( \times \)2 nonorthogonal CI, (b) UMP2 and \( ^2\)\( \times \)2 nonorthogonal CI with MP2 corrections [Eq. (5)].](https://example.com/fig1.png)

**TABLE VI. Vibrational frequencies of \( ^2B_2 \) \( \sigma \)-HCO\(_2\) calculated with various theories.**

<table>
<thead>
<tr>
<th>Method</th>
<th>( b_2 )</th>
<th>( a_1 )</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( a_1 )</th>
<th>( a_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^2)( \times )2 CI</td>
<td>703i</td>
<td>790</td>
<td>1165</td>
<td>1426</td>
<td>1594</td>
<td>3328</td>
</tr>
<tr>
<td>( ^2)( \times )2 CI(approx MP2)</td>
<td>986</td>
<td>629</td>
<td>989</td>
<td>1228</td>
<td>1486</td>
<td>3259</td>
</tr>
<tr>
<td>( ^2)( \times )2 CI(MP2)</td>
<td>1215</td>
<td>701</td>
<td>1030</td>
<td>1332</td>
<td>1516</td>
<td>3186</td>
</tr>
<tr>
<td>MRCI</td>
<td>649</td>
<td>594</td>
<td>n/a</td>
<td>1313</td>
<td>1479</td>
<td>3184</td>
</tr>
<tr>
<td>MRCI</td>
<td>961</td>
<td>646</td>
<td>n/a</td>
<td>1314</td>
<td>1477</td>
<td>3197</td>
</tr>
<tr>
<td>CASPT2</td>
<td>1287</td>
<td>624</td>
<td>1008</td>
<td>1287</td>
<td>1437</td>
<td>3053</td>
</tr>
<tr>
<td>EOM-CC</td>
<td>1010</td>
<td>650</td>
<td>1027</td>
<td>1318</td>
<td>1513</td>
<td>3170</td>
</tr>
<tr>
<td>B3LYP</td>
<td>1125</td>
<td>646</td>
<td>1029</td>
<td>1306</td>
<td>1509</td>
<td>3080</td>
</tr>
</tbody>
</table>

\( ^a \)Using the 6-31G* basis set.
\( ^b \)Approximate MP2 corrected \( ^2\)\( \times \)2 CI using Eq. (9).
\( ^c \)MP2 corrected \( ^2\)\( \times \)2 CI using Eq. (5).
\( ^d \)From Ref. 17 using a Dunning DZP basis set.
\( ^e \)From Ref. 18 using an ANO DZP basis set.
\( ^f \)From Ref. 22 using a Dunning DZP basis set.
minimum with respect to asymmetric deformation. At short CH distances and small OCO angles, the $^2A_1$ state is a maximum with respect to asymmetric deformation and there are two valleys either side of the ridge. Between these extremes there is a branching point or valley—ridge inflection point. The approximate location of this point (Table V) was obtained by performing constrained optimizations at various OCO bond lengths and the HCO angle. Surprisingly, the branching structure is very similar to the stationary point found by other methods. This apparent coincidence deserves further study.

CONCLUSIONS

This study shows that a $2 \times 2$ nonorthogonal CI along with MP2 corrections can successfully treat systems that have spatial symmetry breaking of the SCF wave function. The most important features of the $^2B_2$-HCO$_2$ potential energy surface are properly described by this procedure. Compared to the large MCSCF, MRCl, CASPT2, or EOM-CC calculations typically needed for these systems, the $2 \times 2$ nonorthogonal CI with perturbative corrections for dynamic correlation requires little computational effort, similar to one or two MP4SDQ calculations or CCSD iterations. The cost of the simpler model is comparable to two MP2 calculations. This procedure may be useful in the studies of chemical systems with symmetry breaking problems or Jahn–Teller interactions.

ACKNOWLEDGMENT

This work was supported by a Grant from the National Science Foundation (CHE 94-00678).

APPENDIX

The matrix elements between nonorthogonal determinants can be evaluated by expanding the orbitals for one determinant in terms of the orbitals for the other determinant. The spin orbitals for both wavefunctions can be written in terms of basis functions $x_\mu$

$$
\phi_i = \sum c_{\mu i} x_\mu; \\
\langle \phi_i | \phi_j \rangle = \delta_{ij};
$$

(A1)

$$
\phi'_i = \sum c'_{\mu i} x_\mu; \\
\langle \phi'_i | \phi'_j \rangle = \delta_{ij}.
$$

The spin orbitals of one wave function can then be expressed in terms of the spin orbitals of the other wave function and the overlap between the orbitals

$$
\phi'_i = \sum S_{ip} \phi_p = \sum s_{ij} \phi_j + \sum \bar{s}_{ia} \phi_a;
$$

(A2)

$$
S_{pq} = \langle \phi'_p | \phi_q \rangle = \sum c'_{\mu p} c_{\nu q} \langle x_\mu | x_\nu \rangle,
$$

where indices $i, j, \ldots$, etc., run over occupied orbitals, $a, b, \ldots$, etc., run over unoccupied orbitals and $p, q, \ldots$, etc., run over all orbitals. For convenience, the overlap between $\phi$ and $\phi'$ is split into the occupied—occupied block, $s$, and the occupied—virtual block, $\bar{s}$. The wave function $\Psi'_0$ can be expanded in terms of $\Psi_0$ and single, double and higher excitations of $\Psi_0$

$$
\Psi'_0 = \left[ \sum S_{1p} \phi_p \right] \left[ \sum S_{2q} \phi_q \right] \cdots \left[ \sum S_{n} \phi_r \right]
$$

$$
= a_0 \Psi_0 + \sum a^a_i \Psi_i + \sum a^{ab}_{ij} \Psi^{ab} + \cdots. \tag{A3}
$$

The matrix elements between two nonorthogonal configurations is given by

$$
\langle \Psi_0 | H | \Psi'_0 \rangle = \sum \langle \phi_i | H | \phi_j \rangle C(i | j)
$$

$$
+ \sum \langle \phi_i | H | \phi_i \rangle C(i | j | k | l), \tag{A4}
$$

$$
\langle \Psi'_0 | \Psi'_0 \rangle = \text{Det}(s),
$$

where $C(i | j)$ is the cofactor arising from $s$ by deleting row $i$ and column $j$, and $C(i | j | k | l)$ from deleting rows $i$ and $j$, and columns $k$ and $l$. $C(i | j)$ is given by

$$
C(i | j) = (s^{-1})_{ij} \text{Det}(s) = (s^{-1})_{ij} \langle \Psi'_0 | \Psi'_0 \rangle. \tag{A5}
$$

By further application of Kramer rule for matrix inversion or by use of the Jacobi ratio theorem $^56$ $C(i | j | k | l)$ can be expressed as

$$
C(i | j | k | l) = [C(i | k) C(j | l) - C(i | l) C(j | k)] / \text{Det}(s)
$$

$$
= \left((s^{-1})_{ik} (s^{-1})_{jl} - (s^{-1})_{il} (s^{-1})_{jk}\right) \langle \Psi'_0 | \Psi'_0 \rangle. \tag{A6}
$$

Alternatively, the necessary matrix elements can be evaluated readily if the amplitudes are known

$$
\langle \Psi_0 | H | \Psi'_0 \rangle = a_0 \langle \Psi_0 | H | \Psi_0 \rangle + \sum a^{ab}_{ij} \langle \Psi_0 | H | \Psi^{ab}_{ij} \rangle. \tag{A7}
$$

After rearrangement of the expressions for the cofactors, the amplitudes can be written as:

$$
a_0 = \text{Det}(s),
$$

$$
a^i_i = \sum C(k | i) \bar{s}_{ka} = \sum (s^{-1})_{ki} \bar{s}_{ka} a_0, \tag{A8}
$$

$$
a^{ab}_{ij} = (a^a_i a^b_j - a^b_i a^a_j) / a_0.
$$

This result can be shown more directly by considering the overlap between $\Psi'_0$ and each excited determinant of interest. Figari and Magnesco $^{57}$ and VerBeek and VanLenthe $^{58,59}$ have given more general expressions for matrix elements between nonorthogonal configurations. Once the expansion coefficients are known, the off-diagonal CI matrix elements can be constructed in a way similar to the MP2 procedure.


