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# Calculation of barriers to proton transfer using variations of multiconfiguration self-consistent-field methods. II. Configuration interaction

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Various means are tested of including additional electron correlation into multiconfiguration self-consistent-field (MCSCF) methods for computing proton transfer potentials in $HF_2^-$, $H_7N_2^+$, $H_3O_2^-$, and $H_5O_2^+$. Configuration interaction allowing single excitations (CIS) and configuration interaction with single + double excitations (CISD) calculations are performed following MCSCF expansion of the wave function using various different MCSCF reference wave functions. The CISD results are excellent, being fairly independent of choice of reference space although it is important that the occupied orbitals be balanced between the donor and acceptor. Localizing the occupied molecular orbitals prior to the MCSCF part of the calculation results in a further improvement since it is possible to use a smaller number of occupied orbitals and thereby allow more virtuals to be included. These results are compared to configuration interaction computations using the canonical orbitals and which are not preceded by MCSCF preparation of the wave function.

## I. INTRODUCTION

The preceding paper[1] detailed an attempt to compute proton transfer potentials in four symmetric H-bonded systems, $HF_2^-$, $H_3O_2^-$, $H_5O_2^+$, and $H_7N_2^+$, using the multiconfiguration self-consistent-field (MCSCF) method. It was found that reasonable results were obtainable when the interactions included in the active space were limited to those directly involving the central hydrogen atom, but it was not trivial to ensure no other interactions were included. An additional requirement is that the orbitals chosen treat consistently both the starting and midpoint structures of the transfer. Also, it was found that when the occupied canonical molecular orbitals (MOs) are replaced by localized orbitals the calculations become more reliable due to greater ease in eliminating unproductive types of correlation.

It is widely understood that quantitative treatments of chemical processes require inclusion of electron correlation and proton transfers are no exception. The majority of correlated calculations of proton transfers[2–7] have employed the Møller–Plesset approach which takes as its starting point a single determinant. While such an approach would not be wise if the proton were required to transfer a long distance, it is considered quite satisfactory for H-bonded complexes wherein the two subsystems are within 3 Å or so of one another, an assumption which has been verified for a number of systems.[8–10]

An alternate procedure would be to carry out configuration interaction (CI) calculations, taking as a reference point the multiple determinant solution obtained by the MCSCF method. In this paper, we test the accuracy and feasibility of this approach and compare the results to those obtained from a single-configuration starting point. The first variant tested consists of a singles or doubles configuration interaction calculation using the MCSCF wave function as the starting point of the CI expansion. The second variation uses localized orbitals, as in the previous paper, as the basis set for the MCSCF calculation instead of the canonical MOs which are the usual standard. The concentrated nature of these orbitals should allow a more complete treatment of interactions deemed important with a minimum of orbitals needed in the expansion. To provide a point of reference, these calculations are preceded by the results of a single reference CI study.

## II. COMPUTATIONAL DETAILS

Most calculations were performed using the split valence 4-31G basis[11] and the general atomic and molecular electronic structure system (GAMESS) (Ref. 12); some calculations using the polarized 6-311G** basis[13] are also included. The full optimized reaction space (FORS) approach is used for the MCSCF portion of the calculations. FORS includes all possible combinations of electron excitations from the chosen occupied orbitals to the virtual orbitals in the computational procedure.

Both singles and singles + doubles configuration interaction (CIS and CISD) calculations are performed.[14] For both versions, the MCSCF FORS wave function is computed and used as the beginning wave function for the CI expansion, which involves all virtual orbitals that are not included in the MCSCF active space. The CI portion represents a complete active space (CAS) calculation. The CAS CI calculations add a large number of configurations to the already extensive MCSCF calculations, thus significantly reducing the maximum size of the MCSCF active space from approximately ten to four or possibly six orbitals depending upon the particular system. The localized molecular orbitals (LMOs) were obtained by a Boys localization.[15] The occupied LMOs were then substituted for the canonical orbitals in the MCSCF FORS calculation.

The energy barrier for proton transfer is investigated for four symmetrically hydrogen bonded complexes, $HF_2^-$,


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TABLE I. CI energies (hartree) and proton transfer barriers (kcal/mol) for $HF_2^-$.

| Occupied orbitals[a] | Virtual orbitals[b] | Ex.[c] | Midpoint energy | End-point energy | $E^\dagger$ |
|---|---|---|---|---|---|
| All | 11–20 | 2 | −199.479 144 3 | −199.478 999 8 | −0.091 |
| All | 11–20 | 3 | −199.480 321 9 | −199.480 173 1 | −0.093 |
| $2,3\sigma_g\ 2,3\sigma_u\ 1\pi_{gx}\ 1\pi_{gy}\ 1\pi_{ux}\ 1\pi_{uy}$ | 11–20 | 2 | −199.477 269 7 | −199.477 125 2 | −0.091 |
| $2,3\sigma_g\ 2,3\sigma_u\ 1\pi_{gx}\ 1\pi_{gy}\ 1\pi_{ux}\ 1\pi_{uy}$ | 11–20 | 3 | −199.478 432 4 | −199.478 283 8 | −0.093 |
| $2\sigma_g\ 3\sigma_g\ 2\sigma_u\ 3\sigma_u$ | 11–20 | 2 | −199.307 615 8 | −199.307 482 6 | −0.084 |
| $2\sigma_g\ 3\sigma_g\ 2\sigma_u\ 3\sigma_u$ | 11–20 | 3 | −199.307 998 5 | −199.307 863 0 | −0.085 |
| $3\sigma_g\ 3\sigma_u$ | 11–20 | 2 | −199.268 773 4 | −199.268 041 0 | −0.460 |
| $3\sigma_g\ 3\sigma_u$ | 11–20 | 3 | −199.268 901 7 | −199.268 765 2 | −0.084 |
| $3\sigma_g\ 3\sigma_u$ | 11–20 | 4 | −199.269 036 3 | −199.268 902 8 | −0.084 |

[a]Symmetry designations correspond to the midpoint structure.
[b]Virtual orbitals are numbered from lowest energy (11) to highest energy (20).
[c]Ex. represents the maximum allowed excitation level in the CI expansion.

$H_3O_2^-$, $H_5O_2^+$, and $H_7N_2^+$. The transfer barrier is evaluated as the difference in energy between the midpoint of the transfer and the starting or ending point (equivalent due to the symmetry). The midpoint structure is that in which the central hydrogen atom is placed halfway along the O–O, N–N, or F–F axis. For the end-point structure, the distance of the bridging hydrogen from the donor atom is determined by a SCF/6-311G** optimization. The rigid molecule approximation is applied so that only the central hydrogen atom is allowed to move during the transfer. All other bond angles and lengths remain constant throughout the optimization. Previous studies have indicated that this is a reasonable approximation for these systems.[16–18] For each complex, the bond angles and lengths used are equivalent to those reported in the previous paper. The midpoint structures have $D_{\infty h}$, $C_{2h}$, $C_{2h}$, and $D_{3d}$ symmetry for $HF_2^-$, $H_3O_2^-$, $H_5O_2^+$, and $H_7N_2^+$, respectively; the end-point symmetries are $C_{\infty v}$, $C_s$, $C_s$, and $C_{3v}$.

## III. CI METHOD

We begin this study with standard CI calculations of the transfer barrier using a single configuration reference. The first two rows of Table I show that when all orbitals of $HF_2^-$ are included, a barrier of −0.09 kcal/mol is calculated at either the double or triple excitation level. Removing the core orbitals has no effect on the calculated barriers while eliminating the occupied $p$ orbitals, which are unable to interact directly with the transferring hydrogen, has virtually no effect either. In fact, the only result that differs appreciably is that obtained when only the $(3\sigma_g,3\sigma_u)$ pair, composed largely of the $2p_z$ atomic orbitals, is used with double excitations, but this 0.4 kcal difference vanishes when triples are added. The last row of the table demonstrates that including quadruple excitations has no further effect on the energy difference between the end and midpoints of $HF_2^-$. The CI barriers in Table I agree nicely with the correlated values obtained by the alternate Møller–Plesset approach, and listed in Table I of the companion paper.[1]

The first few rows of Table II suggest a barrier of 7.5 kcal/mol for $H_7N_2^+$, again unchanged by deletion of the core orbitals. This result is some 1.5 kcal higher than the MP4 value, but quite close to MP3. Removing the occupied $\pi$ ($e$) orbitals raises the calculated barrier to 7.8 kcal (7.6 for triple excitations). The $2a_{1g}$ and $2a_{2u}$ orbitals are composed primarily of the $2s$ atomic orbitals while the $2p_z$ orbitals contribute to $3a_{1g}$ and $3a_{2u}$ extensively. Excitation from the latter pair provides a similar barrier whereas a value several kcal higher is obtained if the former pair is used instead. This finding is unaffected by the level of correlation considered. The last several rows of Table II all involve excitation from the $(3a_{1g},3a_{2u})$ pair. Deletion of the four highest vacant MOs produces only a slight change in barrier, whereas a significant reduction of 3 kcal occurs if eight virtuals are removed; the level of correlation is immaterial. In summary, consistent and accurate barriers may be obtained with even a small number of occupied MOs, provided some care is exercised in their choice.

The results for $H_3O_2^-$ are presented in Table III. A doubles calculation using all orbitals, both occupied and virtual, yields a barrier of 2.74 kcal/mol, a result which is again unaffected by neglect of the core orbitals. The barrier is lowered slightly by removal of the two $2s$ orbitals, but the corresponding triples calculation yields a barrier 0.4 kcal lower. The MP3 barrier for this system is 2.4 kcal/mol, quite close to the 2.3 obtained here with triple excitations in the CI expansion. The occupied $a''$ orbitals have only a small influence, since when they are removed both the doubles and triples barriers increase by only 0.1 kcal. The next several rows show that using only the $a''$ orbitals leaves the SCF barrier unchanged, no matter what level of correlation is applied. On the other hand, limiting the excitations to $a'$ orbitals yields a barrier in good coincidence with that obtained using both $a'$ and $a''$.

As reported in Table IV, a barrier of 2.84 kcal/mol is calculated for $H_5O_2^+$ when all orbitals are included. (Again, the $1s$ core orbitals may be ignored.) Limiting excitations to $a'$ orbitals changes the barrier by only 0.1. As in the previous case of the anion, excitations from only the $a''$ subset produce essentially the SCF barrier. The two $2s$-based or $a''$ orbitals can also be eliminated at little cost in accuracy and raising the level to triples has minimal impact as well. On the other hand, removal of the higher lying virtual orbitals from the excitation list has an appre-



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TABLE II. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_7N_2^+$.

| Occupied orbitals[a] | Virtual orbitals[b] | Ex.[c] | Midpoint energy | End-point energy | $E^\dagger$ |
|---|---|---|---|---|---|
| All | 11–32 | 2 | −112.842 740 7 | −112.854 629 9 | 7.46 |
| $2,3a_{1g}$ $2,3a_{2u}$ $1e_{gx}$ $1e_{gy}$ $1e_{ux}$ $1e_{uy}$ | 11–32 | 2 | −112.840 509 7 | −112.852 378 3 | 7.45 |
| $2a_{1g}$ $3a_{1g}$ $2a_{2u}$ $3a_{2u}$ | 11–32 | 2 | −112.665 019 4 | −112.677 433 9 | 7.79 |
| $2a_{1g}$ $3a_{1g}$ $2a_{2u}$ $3a_{2u}$ | 11–32 | 3 | −112.665 690 7 | −112.677 777 8 | 7.58 |
| $3a_{1g}$ $3a_{2u}$ | 11–32 | 2 | −112.628 204 8 | −112.640 677 8 | 7.83 |
| $3a_{1g}$ $3a_{2u}$ | 11–32 | 3 | −112.628 435 1 | −112.640 754 6 | 7.73 |
| $3a_{1g}$ $3a_{2u}$ | 11–32 | 4 | −112.628 653 4 | −112.640 934 4 | 7.71 |
| $2a_{1g}$ $2a_{2u}$ | 11–32 | 2 | −112.605 254 4 | −112.622 827 0 | 11.03 |
| $2a_{1g}$ $2a_{2u}$ | 11–32 | 3 | −112.605 254 9 | −112.622 827 3 | 11.03 |
| $2a_{1g}$ $2a_{2u}$ | 11–32 | 4 | −112.605 278 4 | −112.622 849 7 | 11.03 |
| $3a_{1g}$ $3a_{2u}$ | 11–28 | 2 | −112.622 016 2 | −112.634 773 1 | 8.00 |
| $3a_{1g}$ $3a_{2u}$ | 11–28 | 3 | −112.622 193 7 | −112.634 957 4 | 8.01 |
| $3a_{1g}$ $3a_{2u}$ | 11–28 | 4 | −112.622 351 5 | −112.635 059 8 | 7.97 |
| $3a_{1g}$ $3a_{2u}$ | 11–24 | 2 | −112.618 844 1 | −112.627 111 2 | 5.19 |
| $3a_{1g}$ $3a_{2u}$ | 11–24 | 3 | −112.619 008 3 | −112.627 314 9 | 5.21 |
| $3a_{1g}$ $3a_{2u}$ | 11–24 | 4 | −112.619 118 0 | −112.627 355 4 | 5.17 |

[a]Symmetry designations correspond to the midpoint structure.
[b]Virtual orbitals are numbered from lowest energy (11) to highest energy (32).
[c]Ex. represents the maximum allowed excitation level in the CI expansion.

TABLE III. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_3O_2^-$.

| Occupied orbitals[a] | Virtual orbitals[b] | Ex.[c] | Midpoint energy | End-point energy | $E^\dagger$ |
|---|---|---|---|---|---|
| All | 11–24 | 2 | −151.443 178 6 | −151.447 552 4 | 2.74 |
| $3,4,5,6,7,8a'$ $1,2a''$ | 11–24 | 2 | −151.441 299 5 | −151.445 661 2 | 2.74 |
| $5,6,7,8a'$ $1,2a''$ | 11–24 | 2 | −151.368 202 3 | −151.372 489 9 | 2.69 |
| $5,6,7,8a'$ $1,2a''$ | 11–24 | 3 | −151.370 384 2 | −151.374 078 5 | 2.32 |
| $5,6,7,8a'$ | 11–24 | 2 | −151.297 413 4 | −151.301 876 9 | 2.80 |
| $5,6,7,8a'$ | 11–24 | 3 | −151.299 100 2 | −151.303 027 4 | 2.46 |
| $1,2a''$ | All $a''$ | 2 | −151.208 272 0 | −151.218 902 8 | 6.67 |
| $1,2a''$ | All $a''$ | 3 | −151.207 272 2 | −151.218 903 0 | 6.67 |
| $1,2a''$ | All $a''$ | 4 | −151.208 365 7 | −151.218 995 7 | 6.67 |
| $1,2,3,4,5,6,7,8a'$ | All $a'$ | 2 | −151.358 911 7 | −151.363 320 5 | 2.77 |

[a]Symmetry designations correspond to the midpoint structure.
[b]Virtual orbitals are numbered from lowest energy (11) to highest energy (24).
[c]Ex. represents the maximum allowed excitation level in the CI expansion.

TABLE IV. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_5O_2^+$.

| Occupied orbitals[a] | Virtual orbitals[b] | Ex.[c] | Midpoint energy | End-point energy | $E^\dagger$ |
|---|---|---|---|---|---|
| All | 11–28 | 2 | −152.394 277 0 | −152.398 804 6 | 2.84 |
| $3,4,5,6,7,8a'$ $1,2a''$ | 11–28 | 2 | −152.392 320 3 | −152.396 838 5 | 2.84 |
| $3,4,5,6,7,8a'$ | All $a'$ | 2 | −152.277 961 6 | −152.282 593 3 | 2.91 |
| $1,2a''$ | All $a''$ | 2 | −152.161 765 6 | −152.171 593 1 | 6.17 |
| $5,6,7,8a'$, $1,2a''$ | 11–28 | 2 | −152.316 078 5 | −152.320 826 6 | 2.98 |
| $5,6,7,8a'$ | 11–28 | 2 | −152.224 830 4 | −152.229 422 8 | 2.88 |
| $5,6,7,8a'$ | 11–28 | 3 | −152.225 725 9 | −152.229 982 5 | 2.67 |
| $5,6,7,8a'$ $1,2a''$ | 11–26 | 2 | −152.309 039 7 | −152.314 655 0 | 3.52 |
| $5,6,7,8a'$ $1,2a''$ | 11–24 | 2 | −152.270 708 5 | −152.276 495 1 | 3.63 |
| $5,6,7,8a'$ $1,2''$ | 11–24 | 3 | −152.272 414 9 | −152.277 910 7 | 3.45 |
| $5,6a'$ $1,2a''$ | 11–28 | 2 | −152.230 394 5 | −152.246 169 9 | 9.90 |
| $5,6a'$ $1,2a''$ | 11–28 | 3 | −152.231 347 1 | −152.247 064 0 | 9.86 |

[a]Symmetry designations correspond to the midpoint structure.
[b]Virtual orbitals are numbered from lowest energy (11) to highest energy (28).
[c]Ex. represents the maximum allowed excitation level in the CI expansion.


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TABLE V. CI proton transfer barriers (kcal/mol) for $H_5O_2^+$ using the 6-311G** basis set.

| Occupied orbitals[a] | Virtual orbitals[b] | | | | | |
|---|---|---|---|---|---|---|
| | 11–68 | 11–64 | 11–60 | 11–56 | 11–52 | 11–48 |
| All | | | 7.33 | 6.96 | 7.45 | 6.94 |
| 3,4,5,6,7,8$a'$, 1,2$a''$ | | 6.93 | 7.23 | 6.89 | 7.42 | 6.91 |
| 5,6,7,8$a'$ 1,2$a''$ | 7.27 | 7.27 | 7.52 | 7.20 | 7.52 | 6.99 |
| 5,6,7,8$a'$ | 6.61 | 6.60 | 6.84 | 6.63 | 6.41 | 6.37 |
| 5,6$a'$ 1,2$a''$ | 14.51 | 24.90 | 25.32 | 22.47 | 19.68 | 19.04 |

[a]Symmetry designations correspond to the midpoint structure.
[b]Virtual orbitals are numbered from lowest energy (11) to highest energy (68).

ciable effect, raising the barrier by 1 kcal. The last two rows reveal that unbalanced occupied sets produce overly high barriers, as in all previous studies.

Enlargement of the basis set to 6-311G** increases the number of orbitals from 28 to 68 for $H_5O_2^+$, making complete active space calculations very demanding and precluding all triple excitations. Barriers computed with various combinations of occupied and virtual MOs included in the active space are presented in Table V. These values are consistently higher than those using 4-31G, in agreement with trends noted earlier that larger sets typically yield higher transfer barriers.[8–10] The largest feasible calculation includes all occupied orbitals and all but the eight highest virtual orbitals, and yields a barrier of 7.33 kcal/mol. This value is changed only slightly upon removal of an additional 12 virtuals. Row 2 illustrates that as in the case of the smaller basis set, there is no need to include the occupied core orbitals in the list. The next row documents the effect of removing the 2$s$-based ($3a'4a'$) pair which appears to be a barrier increase of 0.1–0.3 kcal. In this case, the removal of all $a''$ orbitals from the occupied grouping in the active space reduces the calculated barrier by 0.6–1.1 kcal/mol. Finally, an unbalanced set of occupied orbitals again produces high erratic barriers, as evident from the last row of Table V.

Comparison of the columns of Table V reveals the effects of removing certain virtual orbitals. Eliminating the four highest orbitals has little or no effect on the calculated barriers (except in the last row which is eliminated from further consideration due to their unbalanced nature creating erratic behavior). When the next four highest virtual orbitals are removed, the barrier is consistently raised by 0.3 kcal. However, the next removal of four lowers the calculated barrier 0.3 kcal/mol, returning the barrier to its value when all orbitals are included. Further deletions again yield an oscillating effect. Overall, one may obtain a very reasonable result by excluding the 12 highest virtual orbitals. After extrapolating the results to include all of the orbitals and an excitation level of 3, which would lower the values somewhat, the best guess for the barrier in this case would be ~6.75 kcal/mol. This value is slightly above the barrier calculated using MP3, which is 6.1, and above MP4, consistent with the 4-31G results.

In summary, the CI results reported here are in good coincidence with Møller–Plesset computations with the same basis set, especially MP3. Core orbitals need not be included as the results suffer little deterioration in their absence. However, orbitals of more than one symmetry are often necessary; their importance can be determined in each case by performing a few sample calculations. Increasing the excitation level from two to three lowers the calculated barriers by ~0.1–0.3 kcal/mol. An additional but smaller reduction results from inclusion of quadruple excitations. Therefore, calculations using doubles only can provide an excellent upper bound to the barrier.

## IV. MCSCF+CI

In this section, several multiconfigurational wave functions obtained from given collections of occupied and virtual MOs are used as starting points for configuration interaction calculations. As discussed in the preceding paper,[1] each system has ten occupied orbitals; two core, two 2$s$, and six 2$p$-based. The canonical MOs in the midpoint geometry represent either symmetric or antisymmetric combinations of the two subunits, equally weighted. The endpoint MOs are much more localized on one subunit with a corresponding orbital on the other. The important orbital combinations should be included in the MCSCF active space for maximal flexibility. Therefore, the combinations that were found to produce the desired correlated space in the prior MCSCF calculations will be used here as well. In addition, the results from other MCSCF calculations will be utilized as reference wave functions in order to determine the type of reference which produces quality MCSCF+CI results. The same MCSCF reference wave functions are used, whenever possible, for both the singles and singles + doubles configuration interaction calculations so that the effects of changing the excitation level can be evaluated explicitly.

Table VI contains the results obtained for $HF_2^-$ using two fairly well balanced occupied sets. The ($3\sigma_g$,$3\sigma_u$) set contains the two F $2p_z$ orbitals, and the larger occupied group adds the two F 2$s$ orbitals. The virtual combinations utilized are those containing the two, three or four lowest $\sigma_g$ orbitals. Even though none of these combinations were able to produce the proper correlated space for the corresponding MCSCF calculations due to the lack of $\sigma_u$ virtuals, all six combinations produce a negative barrier, correctly indicating that the midpoint geometry is slightly favored. The values agree nicely with the CI calculations in Table I, indicating that neither the multiconfigurational



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TABLE VI. CI energies (hartree) and proton transfer barriers (kcal/mol) for $HF_2^-$ using MCSCF reference wave function.

| Occupied orbitals[a] | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| $3\sigma_g\ 3\sigma_u$ | $4\sigma_g\ 5\sigma_g$ | −199.265 011 7 | −199.264 876 5 | −0.0848 | −199.273 618 7 | −199.273 488 5 | −0.0817 |
| $3\sigma_g\ 3\sigma_u$ | $4\sigma_g\ 5\sigma_g\ 6\sigma_g$ | −199.268 441 4 | −199.268 119 9 | −0.2018 | −199.273 644 5 | −199.273 513 4 | −0.0822 |
| $3\sigma_g\ 3\sigma_u$ | $4\sigma_g\ 5\sigma_g\ 6\sigma_g\ 4\sigma_u$ | −199.270 368 7 | −199.270 235 7 | −0.0834 | −199.273 651 1 | −199.273 520 8 | −0.0817 |
| $2\sigma_g\ 3\sigma_g\ 2\sigma_u\ 3\sigma_u$ | $4\sigma_g\ 5\sigma_g$ | −199.275 372 4 | −199.275 229 3 | −0.0898 | −199.308 400 4 | −199.308 264 4 | −0.0853 |
| $2\sigma_g\ 3\sigma_g\ 2\sigma_u\ 3\sigma_u$ | $4\sigma_g\ 5\sigma_g\ 6\sigma_g$ | −199.290 980 1 | −199.289 884 4 | −0.6880 | −199.308 659 5 | −199.308 523 8 | −0.0852 |
| $2\sigma_g\ 3\sigma_g\ 2\sigma_u\ 3\sigma_u$ | $4\sigma_g\ 5\sigma_g\ 6\sigma_g\ 4\sigma_u$ | −199.300 974 0 | −199.300 834 9 | −0.0872 | −199.308 830 3 | −199.308 695 6 | −0.0846 |

[a]Symmetry designations correspond to the midpoint structure.

nature of the wave function nor the poor MCSCF reference wave function significantly perturbs the character of the potential. There seems to be little sensitivity to either the size or the accuracy of the reference wave function as all barriers are approximately −0.08 kcal/mol. The only exceptions are the CIS computations that use an unbalanced set of three virtuals; the barriers here are still negative but probably overly so.

Unlike the MCSCF calculations where efforts were made to focus on that correlation directly involved in the proton transfer process, inclusion of all or most virtual MOs in the CI calculations leads to a full range of types of correlation. The near agreement between the latter CI barriers and those reported from MCSCF further confirms that the extraneous types of correlation can be ignored as they are fairly constant as the proton translates.

In the case of $H_7N_2^+$, the two occupied combinations included in Table VII are first the two $2p_z$ orbitals and then the four $2s$ and $2p_z$ orbitals. Both combinations have a good balance between the donor and acceptor N atoms. All of the MCSCF reference wave functions using the two $2p_z$ orbitals produced the desired correlated space. Those including all four occupied orbitals gave the proper correlation with two virtuals but not with three virtuals. With the $2p_z$ orbitals and the lowest two virtual orbitals, the CIS barrier is fairly high but is reduced after including an additional virtual. Similar results are obtained with the $2s$ and $2p_z$ orbitals except the values are lower. Singles and doubles calculations using the $2p_z$ orbitals and either virtual combination yields a barrier of 8 kcal. (The corresponding calculations using the second occupied pair were too large to be performed.) These results indicate good consistency at the CISD level, as compared to much greater sensitivity of barriers to orbital choice for CIS. The CISD barrier of 8 kcal/mol is in accord with the best CI result of some 7.5 in Table II.

The results for $H_3O_2^-$ are presented in Table VIII. The first two sets of occupied orbitals listed are unbalanced in the sense that there is considerably greater electron density on one oxygen atom compared to the other in the end-point geometry. The consequent transfer barriers are quite large, as with all previous unbalanced occupied groups, particularly at the CISD level. Much more reasonable results are obtained for the balanced ($5a'6a'7a'8a'$) quartet of occupied orbitals. Although the CIS barriers are somewhat erratic with respect to choice of virtuals, the data are much more consistent at the CISD level, with barriers all right around 2 kcal/mol. Unlike the CIS case, even the unbalanced ($13a'15a'$) virtual pair produces a value similar to the others, indicating that raising the order of correlation to singles + doubles can overcome an unbalanced set of virtuals. These CISD barriers following MCSCF are quite similar to the single configuration CI results in Table III, reconfirming that a single configuration is sufficient as a starting point for CI.

The first group of occupied orbitals for $H_5O_2^+$ in Table IX is not balanced and yielded MCSCF results that contained inconsistent and unproductive correlation. The second combination of occupied orbitals, which includes all those that can interact directly with the central hydrogen, was not sufficiently balanced for the MCSCF calculations, but yielded slightly more consistent MCSCF wave functions. The third combination adds the oxygen lone pairs, which helped balance the orbitals in the MCSCF calculations. Three different pairs of virtual orbitals are tested with each occupied combination. Two of these pairs

TABLE VII. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_7N_2^+$ using MCSCF reference wave function.

| Occupied orbitals[a] | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| $3a_{1g}\ 3a_{2u}$ | $4a_{1g}\ 4a_{2u}$ | −112.601 699 2 | −112.618 819 8 | 10.74 | −112.631 298 0 | −112.644 162 7 | 8.07 |
| $3a_{1g}\ 3a_{2u}$ | $4a_{1g}\ 4a_{2u}\ 5a_{1g}$ | −112.620 337 1 | −112.629 492 2 | 5.74 | −112.631 575 4 | −112.644 293 5 | 7.98 |
| $2a_{1g}\ 2a_{2u}\ 3a_{1g}\ 3a_{2u}$ | $4a_{1g}\ 4a_{2u}$ | −112.615 143 7 | −112.627 686 7 | 7.87 | | | |
| $2a_{1g}\ 2a_{2u}\ 3a_{1g}\ 3a_{2u}$ | $4a_{1g}\ 4a_{2u}\ 5a_{1g}$ | −112.639 458 5 | −112.647 520 3 | 5.06 | | | |

[a]Symmetry designations correspond to the midpoint structure.


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TABLE VIII. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_3O_2^-$ using MCSCF reference wave function.

| Occupied orbitals[a] | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| 5a′ 7a′ | 11a′ 12a′ | −151.202 085 0 | −151.224 366 3 | 13.98 | −151.215 752 4 | −151.256 882 6 | 25.81 |
| 6a′ 8a′ | 13a′ 14a′ | −151.193 108 7 | −151.209 948 8 | 10.57 | −151.225 454 6 | −151.255 370 1 | 18.77 |
| 5a′ 6a′ 7a′ 8a′ | 9a′ 10a′ | −151.233 707 1 | −151.239 527 1 | 3.65 | −151.311 223 8 | −151.314 746 1 | 2.21 |
| 5a′ 6a′ 7a′ 8a′ | 11a′ 12a′ | −151.242 529 7 | −151.243 800 3 | 0.80 | −151.311 711 4 | −151.314 679 5 | 1.86 |
| 5a′ 6a′ 7a′ 8a′ | 13a′ 14a′ | −151.215 260 9 | −151.221 442 3 | 3.88 | −151.310 142 8 | −151.313 518 9 | 2.11 |
| 5a′ 6a′ 7a′ 8a′ | 14a′ 15a′ | −151.232 886 0 | −151.239 826 2 | 4.36 | −151.310 077 3 | −151.313 886 2 | 2.39 |
| 5a′ 6a′ 7a′ 8a′ | 13a′ 15a′ | −151.230 496 1 | −151.247 909 0 | 10.93 | −151.309 926 2 | −151.313 971 9 | 2.54 |

[a]Symmetry designations correspond to the midpoint structure.

(9a′10a′) and (11a′12a′) are balanced; the third (14a′15a′) is not. At the CIS level, the unbalanced (7a′8a′) pair leads to fairly high barriers, which are further elevated when doubles are also included. The imbalance prevents the second-order computations from relieving the problem, similar to $H_3O_2^-$. Results are improved when (5a′6a′) are added to the occupied MOs, with barriers calculated in the 2–3 kcal/mol range at either level and with any of the virtual combinations. [The CISD calculation using (14a′15a′) would not converge because of the imbalance of the virtual orbitals.] Addition of the 1a″2a″ oxygen lone pairs reduces the barriers somewhat (although in this case, a high barrier occurs with the unbalanced virtual set). The best quality CISD barriers again are in accord with the CI barrier in Table IV wherein all MOs are included.

Overall, the MCSCF+CI results are quite successful. The singles results are fairly consistent, although in a couple of instances the barrier is unreliable because the MCSCF active space is too small for a CIS calculation to include all of the necessary virtual orbital interactions. This inconsistency may be partially the result of starting with different MCSCF reference spaces. The CISD results are excellent. In all cases, the values are nearly independent of the MCSCF reference space employed, and are comparable to those found using other correlation methods. The method's success is due to the extra configuration interaction compensating for any omission of important orbitals from the MCSCF active space, largely negating the need for balanced virtual orbitals. The CAS CI procedure results in all types of correlation being treated in an accurate and complete fashion. The overall success is also due to the other types of correlation which are included in the CAS CI calculations not affecting the calculation of the proton transfer barrier. In any event, the occupied orbitals must still be balanced or the resulting barriers are unreliable and excessively large. Neither a prior MCSCF calculation nor the quality of that prior calculation appears to produce any significant perturbations upon these correlated potentials.

## V. LOCALIZED MCSCF+CI

Localization simplifies the choice of which orbitals to include in the MCSCF expansion to achieve the proper correlation and reduces the number of occupied orbitals that are necessary.[1] CI makes much less critical the choice of which orbitals to include in the MCSCF reference space. It was therefore deemed worthwhile to investigate the efficacy of employing both methods simultaneously.

Following localization of $HF_2^-$, the two F–$H_c$ orbitals were used in the MCSCF expansion. The data in Table X suggest very low sensitivity to choice of virtuals included in the MCSCF reference space. All barriers are correctly negative, even those which fail to include an active virtual $\sigma_u$ orbital, which was required to produce a good MCSCF wave function. Indeed, there is minimal dependence for CIS. The calculations which include a virtual $\sigma_u$ yield a

TABLE IX. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_5O_2^+$ using MCSCF reference wave function.

| Occupied orbitals[a] | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| 7a′ 8a′ | 9a′ 10a′ | −152.144 127 7 | −152.153 881 4 | 6.12 | −152.170 411 8 | −152.189 433 0 | 11.94 |
| 7a′ 8a′ | 14a′ 15a′ | −152.145 694 3 | −152.159 887 8 | 8.19 | −152.170 544 5 | −152.189 537 2 | 11.92 |
| 5a′ 6a′ 7a′ 8a′ | 9a′ 10a′ | −152.165 406 4 | −152.165 958 1 | 2.23 | −152.231 220 2 | −152.235 447 2 | 2.65 |
| 5a′ 6a′ 7a′ 8a′ | 11a′ 12a′ | −152.174 078 0 | −152.176 687 9 | 1.64 | −152.231 622 4 | −152.235 754 9 | 2.59 |
| 5a′ 6a′ 7a′ 8a′ | 14a′ 15a′ | −152.176 517 8 | −152.181 140 4 | 2.90 | | | |
| 5a′ 6a′ 7a′ 8a′ 1a″ 2a″ | 9a′ 10a′ | −152.183 715 7 | −152.186 493 1 | 1.74 | | | |
| 5a′ 6a′ 7a′ 8a′ 1a″ 2a″ | 11a′ 12a′ | −152.189 850 2 | −152.191 463 7 | 1.01 | | | |
| 5a′ 6a′ 7a′ 8a′ 1a″ 2a″ | 14a′ 15a′ | −152.202 024 9 | −152.213 432 6 | 7.16 | | | |

[a]Symmetry designations correspond to the midpoint structure.



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TABLE X. CI energies (hartree) and proton transfer barriers (kcal/mol) for $HF_2^-$ using MCSCF reference wave function and localized occupied orbitals.

| Occupied orbitals[a] | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| 2 F–$H_c$ | $4\sigma_g$ $5\sigma_g$ | −199.265 011 6 | −199.264 876 4 | −0.085 | −199.273 618 8 | −199.273 488 6 | −0.082 |
| 2 F–$H_c$ | $6\sigma_g$ $4\sigma_u$ | −199.257 841 2 | −199.257 736 3 | −0.066 | −199.273 468 1 | −199.273 338 5 | −0.081 |
| 2 F–$H_c$ | $7\sigma_g$ $5\sigma_u$ | −199.250 971 2 | −199.250 873 7 | −0.061 | −199.273 497 0 | −199.273 367 6 | −0.081 |
| 2 F–$H_c$ | $4\sigma_g$ $5\sigma_g$ $6\sigma_g$ $4\sigma_u$ | −199.270 368 7 | −199.270 235 8 | −0.083 | −199.273 651 7 | −199.273 520 8 | −0.082 |
| 2 F–$H_c$ | $4\sigma_g$ $5\sigma_g$ $7\sigma_g$ $5\sigma_u$ | −199.271 200 7 | −199.271 071 9 | −0.081 | −199.273 654 5 | −199.273 524 2 | −0.082 |
| 2 F–$H_c$ | $6\sigma_g$ $7\sigma_g$ $4\sigma_u$ $5\sigma_u$ | −199.258 427 4 | −199.258 324 4 | −0.065 | −199.273 605 1 | −199.273 475 2 | −0.082 |
| 2 F–$H_c$ | $2\pi_{ux}$ $2\pi_{uy}$ $2\pi_{gx}$ $2\pi_{gy}$ | −199.274 715 9 | −199.274 690 8 | −0.016 | −199.273 367 2 | −199.273 238 2 | −0.081 |

[a]Symmetry designations correspond to the midpoint structure.

barrier of −0.06 and those without yield −0.08. There is no dependence at all at the CISD level where all reported values are −0.08 kcal, comparable to the previous results.

Table XI shows the singles results obtained for $H_3O_2^-$ are rather poor, with either occupied combination exhibiting a 13 kcal range of barrier relative to choice of virtuals, even though the MCSCF reference wave functions are equivalent for all of the virtual combinations of a given size. However, the CISD data are in excellent coincidence, all around 3.2–3.3 kcal/mol, although a bit more variance and barrier decrease is noted if the two O–$H_t$ bonds, which significantly change the reference wave function, are included along with the two O–$H_c$ bonds. Tables XII and XIII contain results for $H_5O_2^+$ and $H_7N_2^+$ that are nearly identical to $H_3O_2^-$. CIS yields quite inconsistent barriers, which are improved after double excitations are included, with barriers of 3.6–3.7 and 8.0–8.1 kcal/mol, respectively. However, again for $H_5O_2^+$ the results are consistent only if the occupied MOs are the two O–$H_c$ bonds. Overall, application of CISD, following localization, provides results that are superior to those obtained by CIS from the canonical MCSCF or by MCSCF from a localized set of occupied MOs.

## VI. CONCLUSIONS

Whereas it was shown in the preceding paper that MCSCF calculations are generally able to calculate consistent proton transfer barriers when restricted to correlation directly involved in the transfer itself, results are improved dramatically by following the MCSCF calculation with CI. The CI removes much of the sensitivity to the choice of correlated space within the MCSCF reference wave function. When a single electron is allowed to be excited from the MCSCF reference (CIS), the results depend slightly on the quality of the MCSCF calculation, and are not completely reliable. Excellent and consistent barriers are obtained when two electrons are allowed to be excited (CISD).

For $H_3O_2^-$ and $H_7N_2^+$, the results using Boys localized orbitals are extremely consistent. For the other complexes, there is some variability, but a consistent value can be determined nonetheless. Once again, the calculated barriers are similar to those of other correlation methods, including the CISD results. The barriers are approximately −0.80 kcal/mol for $HF_2^-$, 3.3 kcal/mol for $H_3O_2^-$, 4.0 kcal/mol for $H_5O_2^+$, and 8.0 kcal/mol for $H_7N_2^+$.

TABLE XI. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_3O_2^-$ using MCSCF reference wave function and localized occupied orbitals.

| Occupied orbitals | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| 2 O–$H_c$ | $9a'$ $10a'$ | −151.211 525 2 | −151.222 608 5 | 6.95 | −151.229 881 7 | −151.235 110 4 | 3.28 |
| 2 O–$H_c$ | $11a'$ $12a'$ | −151.218 690 6 | −151.219 860 2 | 0.73 | −151.230 199 5 | −151.235 244 2 | 3.17 |
| 2 O–$H_c$ | $13a'$ $14a'$ | −151.210 266 0 | −151.220 199 1 | 6.23 | −151.229 805 8 | −151.235 131 6 | 3.34 |
| 2 O–$H_c$ | $15a'$ $16a'$ | −151.209 123 5 | −151.217 828 0 | 5.46 | −151.229 852 1 | −151.235 093 0 | 3.29 |
| 2 O–$H_c$ | $14a'$ $15a'$ | −151.210 094 0 | −151.220 760 5 | 6.69 | −151.229 818 2 | −151.235 095 8 | 3.31 |
| 2 O–$H_c$ | $13a'$ $15a'$ | −151.207 845 6 | −151.228 001 0 | 12.65 | −151.229 811 0 | −151.235 131 8 | 3.34 |
| 2 O–$H_c$ | $9a'$ $10a'$ $11a'$ $12a'$ | −151.221 865 4 | −151.227 037 8 | 3.25 | −151.230 267 8 | −151.235 281 8 | 3.15 |
| 2 O–$H_c$ | $9a'$ $10a'$ $13a'$ $14a'$ | −151.229 821 8 | −151.228 860 6 | −0.60 | −151.229 911 4 | −151.235 177 5 | 3.30 |
| 2 O–$H_c$ | $11a'$ $12a'$ $13a'$ $14a'$ | −151.219 637 8 | −151.225 039 0 | 3.39 | −151.230 211 3 | −151.235 315 6 | 3.20 |
| 2 O–$H_c$+2 O–$H_t$ | $9a'$ $10a'$ | −151.233 706 7 | −151.239 526 8 | 3.65 | −151.311 235 2 | −151.314 756 6 | 2.21 |
| 2 O–$H_c$+2 O–$H_t$ | $11a'$ $12a'$ | −151.242 532 2 | −151.243 800 1 | 0.79 | −151.311 730 3 | −151.314 698 7 | 1.86 |
| 2 O–$H_c$+2 O–$H_t$ | $13a'$ $14a'$ | −151.215 328 1 | −151.236 111 2 | 13.04 | −151.310 155 3 | −151.314 002 5 | 2.41 |

[a]Symmetry designations correspond to the midpoint structure.



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TABLE XII. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_5O_2^+$ using MCSCF reference wave function and localized occupied orbitals.

| Occupied orbitals | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| 2 O–$H_c$ | 9a′ 10a′ | −152.144 130 4 | −152.153 889 3 | 6.12 | −152.170 418 8 | −152.176 290 6 | 3.68 |
| 2 O–$H_c$ | 11a′ 12a′ | −152.156 027 9 | −152.162 493 4 | 4.06 | −152.170 589 8 | −152.176 414 2 | 3.65 |
| 2 O–$H_c$ | 15a′ 16a′ | −152.144 462 1 | −152.158 668 9 | 8.91 | | | |
| 2 O–$H_c$ | 9a′ 10a′ 11a′ 12a′ | −152.161 304 7 | −152.165 082 8 | 2.37 | −152.170 686 1 | −152.176 452 0 | 3.62 |
| 2 O–$H_c$ | 9a′ 10a′ 15a′ 16a′ | −152.151 233 0 | −152.160 691 8 | 5.94 | −152.170 450 6 | −152.176 410 0 | 3.74 |
| 2 O lone pairs | 9a′ 10a′ | −152.144 130 2 | −152.153 877 7 | 6.12 | −152.144 127 9 | −152.155 104 8 | 6.89 |
| 2 O lone pairs | 11a′ 12a′ | −152.156 031 2 | −152.161 806 3 | 3.62 | −152.132 691 2 | −152.161 803 7 | 18.27 |
| 2 O–$H_c$+2 O l.p. | 9a′ 10a′ | −152.165 405 4 | −152.168 956 9 | 2.23 | | | |
| 2 O–$H_c$+2 O l.p. | 3a″ 4a″ | −152.171 743 4 | −152.180 887 6 | 5.74 | | | |

[a]Symmetry designations correspond to the midpoint structure.

Although both variations offer improved results, they take advantage of different aspects of the MCSCF procedure. The MCSCF+CI calculations alleviate the difficulty in choosing the virtual orbitals by allowing all of them to interact in some way. However, the overall quality is still sensitive to the occupied orbitals chosen; they must have similar contributions from the donor and acceptor in both structures. In contrast, the localized MCSCF eliminates some of the uncertainty in choosing occupied orbitals. Only the orbitals involving the transferring hydrogen, usually two of them, need to be included in the MCSCF active space. Therefore, additional virtual orbitals can be included, making it easier to include all important interactions.

Combining the methods results in easier choices for both sets of orbitals. The localized CIS results are not a significant improvement over the other methods, but the localized CISD results are comparable to or better than either approach by itself in terms of both consistency and accuracy of the calculated barriers. The best values obtained in this way are −0.08, 3.26, 3.68, and 8.02 kcal/mol for $HF_2^-$, $H_3O_2^-$, $H_5O_2^+$, and $H_7N_2^+$, respectively.

The disadvantage of the CISD calculations from a MCSCF reference, either localized or canonical, is that they take significantly more computer time, especially when compared to the single reference CI or MP calculations. For example, a CISD calculation on $H_7N_2^+$ can require an order of magnitude more computer time in comparison to the others. On the other hand, it requires a smaller group of orbitals to achieve consistent results, economizing on computer resources in that way. In addition, the CISD calculation gives a great deal of useful information pertaining to orbital interactions and the contributions of individual configurations that are not available from the Møller–Plesset perturbation data.

One may conclude then that the CISD method, using localized orbitals, is a reliable and cost-effective choice, particularly if analysis in terms of orbital interactions is desirable. MP3 or MP4 calculations are cheaper and may be run on a tighter budget. MCSCF using localized orbitals can be accurate, providing proper care is taken. On the other hand, MCSCF calculations are not the best choice if neither prior localization nor subsequent CI is attempted because of the care that is needed in obtaining the proper

TABLE XIII. CI energies (hartree) and proton transfer barriers (kcal/mol) for $H_7N_2^+$ using MCSCF reference wave function and localized occupied orbitals.

| Occupied orbitals | Virtual orbitals[a] | CIS Midpoint energy | CIS End-point energy | CIS $E^\dagger$ | CISD Midpoint energy | CISD End-point energy | CISD $E^\dagger$ |
|---|---|---|---|---|---|---|---|
| 2 N–$H_c$ | $4a_{1g}$ $4a_{2u}$ | −112.601 699 2 | −112.619 209 6 | 10.99 | −112.631 297 0 | −112.644 162 7 | 8.07 |
| 2 N–$H_c$ | $6a_{1g}$ $5a_{2u}$ | −112.604 170 8 | −112.619 797 7 | 9.81 | −112.631 515 2 | −112.644 235 0 | 7.98 |
| 2 N–$H_c$ | $7a_{1g}$ $6a_{2u}$ | | | | −112.631 352 0 | −112.644 262 5 | 8.10 |
| 2 N–$H_c$ | $4a_{1g}$ $5a_{1g}$ $4a_{2u}$ | −112.620 336 8 | −112.629 491 9 | 5.74 | −112.631 575 7 | −112.644 293 8 | 7.98 |
| 2 N–$H_c$ | $5a_{1g}$ $6a_{1g}$ $5a_{2u}$ | −112.623 433 3 | −112.634 747 8 | 7.10 | −112.631 643 3 | −112.644 346 9 | 7.97 |
| 2 N–$H_c$ | $5a_{1g}$ $7a_{1g}$ $6a_{2u}$ | −112.621 765 0 | −112.635 703 8 | 8.75 | −112.631 565 6 | −112.643 368 7 | 8.03 |
| 2 N–$H_c$ | $4a_{1g}$ $6a_{1g}$ $4a_{2u}$ $5a_{2u}$ | −112.611 694 1 | −112.622 524 4 | 6.80 | −112.631 555 7 | −112.644 251 4 | 7.97 |
| 2 N–$H_c$ | $4a_{1g}$ $7a_{1g}$ $4a_{2u}$ $6a_{2u}$ | −112.607 951 0 | −112.624 977 0 | 10.68 | −112.631 423 4 | −112.644 283 5 | 8.07 |
| 2 N–$H_c$ | $6a_{1g}$ $7a_{1g}$ $5a_{2u}$ $6a_{2u}$ | −112.610 092 4 | −112.629 926 7 | 12.45 | −112.631 591 2 | −112.644 351 0 | 8.01 |
| 2 N–$H_c$ | $4a_{1g}$ $6a_{1g}$ $7a_{1g}$ $4a_{2u}$ | −112.609 847 0 | −112.626 923 2 | 10.72 | −112.631 480 3 | −112.644 222 6 | 8.00 |
| 2 N–$H_c$ | $4a_{1g}$ $4a_{2u}$ $5a_{2u}$ $6a_{2u}$ | −112.609 618 2 | −112.629 306 0 | 12.35 | −112.631 491 3 | −112.644 322 3 | 8.05 |

[a]Symmetry designations correspond to the midpoint structure.



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correlated space. MCSCF, followed by CIS, is not recommended either, since much more consistent results can be achieved by increasing the CI to include doubles at only a moderate additional effort.

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[1] K. Luth and S. Scheiner, J. Chem. Phys. **97**, 7507 (1992).
[2] L. Jaroszewski, B. Lesyng, J. J. Tanner, and J. A. McCammon, Chem. Phys. Lett. **175**, 282 (1990).
[3] T. N. Truong, and J. A. McCammon, J. Am. Chem. Soc. **113**, 7504 (1991).
[4] S. P. Gejji, O. E. Taurian, and S. Lunell, J. Phys. Chem. **94**, 4449 (1990).
[5] H. Basch and W. J. Stevens, J. Am. Chem. Soc. **113**, 95 (1991).
[6] E. Bosch, J. M. Lluch, and J. Bertran, J. Am. Chem. Soc. **112**, 3868 (1990).
[7] M. J. Frisch, A. C. Scheiner, H. F. Schaefer III, and J. S. Binkley, J. Chem. Phys. **82**, 4194 (1985).
[8] Z. Latajka and S. Scheiner, J. Mol. Struct. **234**, 373 (1991).
[9] S. Scheiner, M. M. Szczesniak, and L. D. Bigham, Int. J. Quantum Chem. **23**, 739 (1983).
[10] M. M. Szczesniak and S. Scheiner, J. Chem. Phys. **77**, 4586 (1982).
[11] R. Dirchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971); W. J. Hehre, R. Ditchfield, and J. A. Pople, *ibid.* **56**, 2257 (1972); J. B. Collins, P. V. R. Schleyer, J. S. Binkley, and J. A. Pople, J. Phys. Chem. **86**, 1529 (1982).
[12] M. Dupuis, D. Spangler, and J. J. Wendoloski, General Atomic and Molecular Electronic Structure System, National Resource for Computational Chemistry, Lawrence Berkeley Laboratory, Berkeley, California, 1980, as modified by M. W. Schmidt, North Dakota State University; S. T. Elbert, Iowa State University.
[13] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
[14] B. Brooks and H. F. Schaefer, J. Chem. Phys. **70**, 5092 (1979); B. Brooks, W. Laidig, P. Saxe, N. Handy, and H. F. Schaefer, Phys. Scr. **21**, 312 (1980).
[15] S. F. Boys, Rev. Mod. Phys. **32**, 296 (1960).
[16] S. Scheiner, Acc. Chem. Res. **18**, 174 (1985).
[17] S. Scheiner, J. Am. Chem. Soc. **103**, 315 (1981).
[18] S. Scheiner, J. Phys. Chem. **86**, 376 (1982).


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