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Can a Single-Reference Approach Provide a Balanced Description of Ground and Excited States? A Comparison of the Completely Renormalized Equation-of-Motion Coupled-Cluster Method with Multireference Quasidegenerate Perturbation Theory near a Conical Intersection and along a Photodissociation Coordinate in Ammonia

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We calculated the two lowest electronically adiabatic potential energy surfaces of ammonia in the region of the conical intersection and at a sequence of geometries along which one of the N−H bonds is broken. We employed both a multireference (MR) method and a single-reference (SR) method. The MR calculations are based on multiconfiguration quasidegenerate perturbation theory (MC-QDPT) with a 6-311+G(3df,3pd) basis set. The SR calculations, carried out with the same basis, employ the completely renormalized equation-of-motion coupled-cluster method with singles and doubles, and a noniterative treatment of triples, denoted CR-EOMCCSD(T). At 91 geometries used for comparison, including geometries near a conical intersection, the surfaces agree to 7% on average.

1. Introduction

Electronic structure theory of nondegenerate ground electronic states of molecules has made great advances, and many important properties of molecules in the ground electronic state can be calculated more reliably or more conveniently than they can be measured.[1−3] Furthermore, the value of this advance is greatly multiplied by the fact that many of the methods are systematic enough to be meaningfully tested and to be translated into computer codes that can be used even by nonexperts, which has allowed for unprecedented widespread progress. Quasidegenerate electronic states, such as those encountered in studies of bond breaking and biradicals, open-shell states and, of particular interest to us in this work, excited electronic states, are another matter. Although there has also been great progress in the area of single-reference excited-state calculations, particularly after the introduction of the response[4] and equation-of-motion (EOM)[5,6] coupled-cluster (CC) methods in quantum chemistry, traditionally the most successful treatments of quasidegenerate and excited states have been based on a multireference (MR) treatment.[7,8] Multireference treatments are very powerful, but they do have some important disadvantages, mainly related to the choice of reference state. For small systems, these problems are ameliorated and can largely be solved by using a full-valence complete active space. However, for larger systems such a reference space is usually unaffordable, and one must limit the reference space. There is no completely general systematic way to do this, which has two consequences: (i) the methods often require expert users; (ii) in many cases, such as those encountered in transition metal chemistry, one cannot test the methods systematically because each system requires an individual practical decision on the active space that may become too large or difficult to define for practical applications. In this respect a more systematic single-reference procedure for electronically excited states would be a major step toward widespread progress.

Recently, a new class of single-reference (SR) coupled cluster methods with great potential for the description of at least some classes of bond breaking, biradicals, and excited states has been developed; these methods are based on the method of moments of coupled cluster equations (MMCC).[9−11] In the present paper we apply an approximate variant of the MMCC approach for ground and excited states, called the completely renormalized (CR) EOMCC method with singles, doubles, and noniterative triples (CR-EOMCCSD(T)),[11d,12] to a particularly challenging problem, the potential energy surfaces for the photodissociation of ammonia, including geometries near the conical intersection and along the dissociation coordinate, and we compare these calculations to calculations by a powerful multireference method, namely multiconfiguration quasidegenerate perturbation theory[13,14] (MC-QDPT) based on a full-valence complete-active-space self-consistent field[7] (CASSCF, also called FORS) reference function. The CASSCF calculation includes static correlation, and the perturbation calculation adds dynamical correlation. The CR-EOMCCSD(T) approach treats both types of correlations dynamically via excitations from a single-reference determinant.

2. Theory

2.1. MC-QDPT. The MC-QDPT method is based on multireference perturbation theory (MRPT) and involves expansion

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to the second order of perturbation theory. The reference functions for the perturbation calculations are obtained from the CASSCF scheme, optimized for a state average over the lowest-energy states of interest. The energy through the first order is the original CASSCF approximation, and at second order one includes single and double excitations. The MC-QDPT energies are the eigenvalues of the matrix with perturbed matrix elements. We refer the reader to refs 13 and 14 for further details.

2.2. CR-EOMCCSD(T). The CR-EOMCCSD(T) method[12] is a single-reference approach in which suitably defined noniterative corrections due to triple excitations are added to CCSD or EOMCCSD energies. These corrections are derived from the MMCC formalism,[9−11] which, in general, provides us with the expressions for the differences between the CC or EOMCC and exact, full CI energies of the electronic states of interest. The CR-EOMCCSD(T) expressions for the ground-state ($\mu = 0$) and excited-state ($\mu > 0$) energies have the form

$$E_\mu^{\mathrm{CR-EOMCCSD(T)}} = E_\mu^{\mathrm{EOMCCSD}} + N_\mu^{\mathrm{CR(T)}}/D_\mu^{\mathrm{(T)}} \qquad (1)$$

where E_μ^{EOMCCSD} are the CCSD ($\mu = 0$) and EOMCCSD ($\mu > 0$) energies respectively, and the numerator and denominator terms $N_\mu^{\mathrm{CR(T)}}$ and $D_\mu^{\mathrm{(T)}}$, used to calculate the corrections due to triple excitations, have been defined elsewhere.[12] In this paper, we test the performance of the basic variant ID of the CR-EOMCCSD(T) theory.[11d,12]

3. Calculations and Results

We calculated potential energy curves for the ground state (V_1) and the first excited state (V_2) of ammonia using both MC-QDPT and CR-EOMCCSD(T) with the 6-311+G(3df,3pd)[16,17] basis set. We label the three hydrogen atoms as $\mathrm{H_A}$, $\mathrm{H_B}$, and $\mathrm{H_C}$, and the N−H bond distances are labeled as R_A, R_B, and R_C. The orientation was set with the nitrogen atom at the origin with $\mathrm{H_A}$ along the y-axis. The angles that the N−$\mathrm{H_B}$ and N−$\mathrm{H_C}$ directions make with the y-axis are denoted by ω_B and ω_C, respectively. The out-of-plane angle is denoted by α. The coordinates of the hydrogen atoms are

$$\begin{aligned} H_\mathrm{A}:\ & x = 0 \\ & y = R_\mathrm{A} \cos \alpha \\ & z = R_\mathrm{A} \sin \alpha \\ H_\mathrm{B}:\ & x = R_\mathrm{B} \cos \alpha \sin \omega_\mathrm{B} \\ & y = -R_\mathrm{B} \cos \alpha \cos \omega_\mathrm{B} \\ & z = R_\mathrm{B} \sin \alpha \\ H_\mathrm{C}:\ & x = -R_\mathrm{C} \cos \alpha \sin \omega_\mathrm{C} \\ & y = -R_\mathrm{C} \cos \alpha \cos \omega_\mathrm{C} \\ & z = R_\mathrm{C} \sin \alpha \end{aligned} \qquad (2)$$

We generated four scans for C_{2v} geometries by setting the two distances R_B and R_C equal to 1.020 Å and by setting the angle ω_B equal to ω_C. We then scanned 22 or 23 values of R_A in the 0.8−11 Å range for each of four pairs of ω_B and α:

Scan 1: $\omega_\mathrm{B} = 60°$, $\alpha = 0°$
Scan 2: $\omega_\mathrm{B} = 60°$, $\alpha = 3°$
Scan 3: $\omega_\mathrm{B} = 52°$, $\alpha = 0°$
Scan 4: $\omega_\mathrm{B} = 52°$, $\alpha = 3°$

This yields 91 geometries.

The MC-QDPT calculations were carried out using the HONDOPLUS-v.4.5[18,19] electronic structure package. The active space consisted of 7 orbitals with 8 electrons; for ammonia this corresponds to a full-valence active space. In the MC-QDPT calculation, one inactive orbital corresponding to the 1s core orbital of N was frozen (that is kept doubly occupied in all CSFs). MC-QDPT includes single and double excitations from all of the active orbitals.

The CR-EOMCCSD(T) calculations and the underlying CCSD and EOMCCSD computations were performed with the routines described in refs 12 and 20; these routines form part of the Michigan State University suite of coupled-cluster programs that are incorporated into GAMESS.[21]

Note that because CR-EOMCCSD(T) is a single-reference method and the system shows a conical intersection, the reference configuration is below the “excited” ones at some geometries and above it at others, where the “excitation energy” is negative. The energy values of the lowest two adiabatic states for all 91 geometries in scans 1−4 are provided in the Supporting Information.

To establish a convenient zero of energy, we subtracted E_0 from all energies calculated by either method, where E_0 is −56.467 971 hartrees and is the energy at the ground-state equilibrium geometry of ammonia calculated using the MC-QDPT method. With this zero of energy, we calculate the mean value of the energy for all the points using

$$\bar{E} = \sum \frac{(V_1^{\mathrm{CR-EOMCCSD(T)}} + V_2^{\mathrm{CR-EOMCCSD(T)}}) + (V_1^{\mathrm{MC-QDPT}} + V_2^{\mathrm{MC-QDPT}})}{4 \times 91} \qquad (3)$$

where V_1 and V_2 are the ground- and excited-state energies, and we calculate ϵ, which is the mean unsigned deviation of the MM-EOM-CC energies from the MC-QDPT ones for both adiabatic surfaces, using

$$\epsilon = \sum \frac{|V_1^{\mathrm{CR-EOMCCSD(T)}} - V_1^{\mathrm{MC-QDPT}}| + |V_2^{\mathrm{CR-EOMCCSD(T)}} - V_2^{\mathrm{MC-QDPT}}|}{2 \times 91} \qquad (4)$$

In eqs 3 and 4, the sum is over all 91 geometries. The percentage error is defined as

$$P = \frac{\epsilon}{\bar{E}} \times 100 \qquad (5)$$

4. Discussion and Concluding Remarks

The MC-QDPT method[13,14] has several advantages including an ability to describe potential energy surfaces along bond breaking coordinates, applicability to open-shell excited states, stability of both ground and excited states over wide regions of configuration space, and applicability to degenerate and quasidegenerate systems. The CASSCF energies include nondynamical correlation, and dynamical correlation is added by the second-order MC-QDPT step. A key element of this procedure is that it is a perturb-then-diagonalize procedure. This has the advantage over the popular diagonalize-then-perturb procedures that the final step is a diagonalization. As a consequence, one expects to obtain consistent approximations to coupled potential energy surfaces even at or near intersections or avoided crossings, and our results show that this expectation is born out.

According to the MMCC theory, the energy differences between the EOMCC and full CI energies and the noniterative corrections to EOMCC energies that result from them can be expressed in terms of the generalized moments of the EOMCC equations. The projections of the EOMCCSD equations on triply excited determinants defining the corresponding moments of

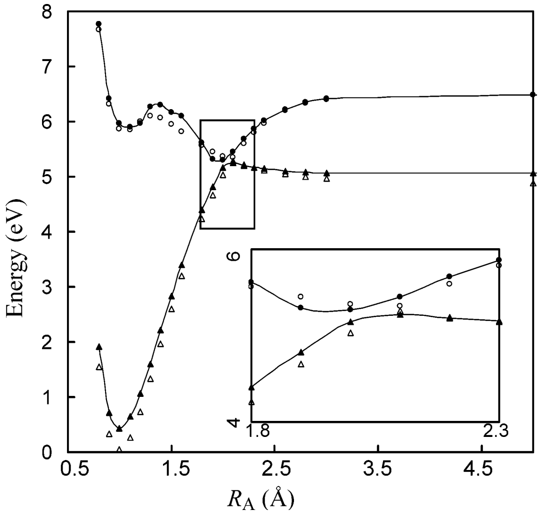

Figure 1. Plots of the ground-state (triangles) and first-excited-state (circles) energies for ammonia calculated using MC-QDPT (solid) and CR-EOMCCSD(T) (open) methods. The solid symbols are connected by curves to guide the eye. For all calculations we set $R_B = R_C = 1.020$ Å and $\omega_B = \omega_C$, and we vary the internuclear distance R_A. The values of the remaining internal coordinates are $\omega_B = 60°$, $\alpha = 0°$. The region near the conical intersection (marked in the rectangular box) is shown as an enlarged inset plot.

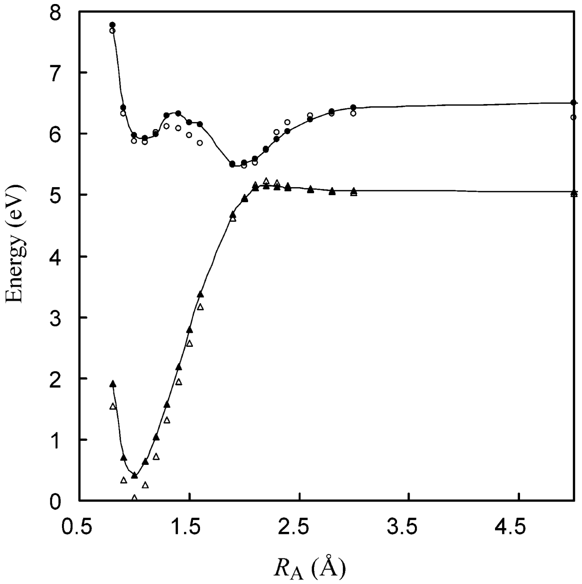

Figure 2. Plots of the ground-state (triangles) and first-excited-state (circles) energies for ammonia calculated using MC-QDPT (solid) and CR-EOMCCSD(T) (open) methods. The solid symbols are connected by curves to guide the eye. For all calculations we set $R_B = R_C = 1.020$ Å and $\omega_B = \omega_C$, and we vary the internuclear distance R_A. The values of the remaining internal coordinates are $\omega_B = 60°$, $\alpha = 3°$.

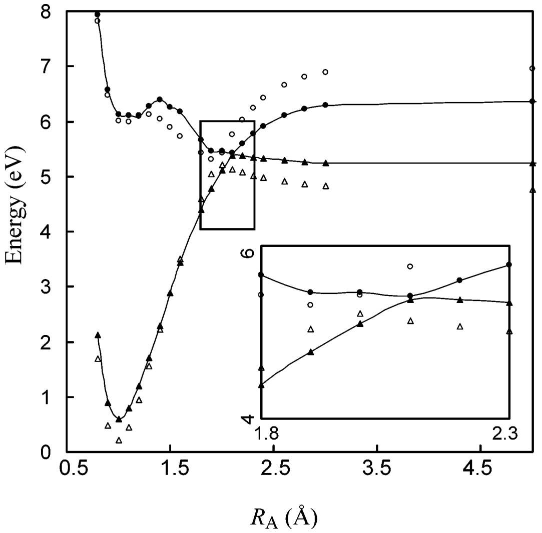

Figure 3. Same as Figure 1 except $\omega_B = 52°$, $\alpha = 0°$.

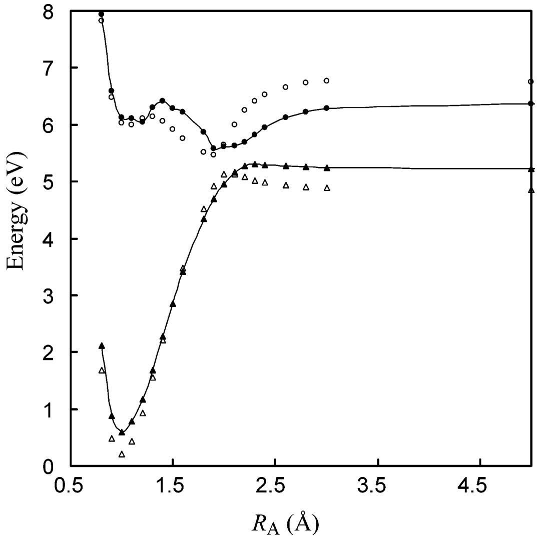

Figure 4. Same as Figure 2 except $\omega_B = 52°$, $\alpha = 3°$.

these equations enter the numerator term of eq 1. The denominator in eq 1 renormalizes the triples corrections, and this renormalization allows the CR-EOMCCSD(T) method to improve the results in the bond breaking region. Thus we expect improved performance for potential energy surfaces of photodissociation processes, and a comparison of the MC-QDPT and CR-EOMCCSD(T) results shows that this is achieved. In particular, results for scans 1−4 are shown in Figures 1−4, respectively. In the case of planar ammonia (scans 1 and 3), we find that the CR-EOMCCSD(T) and MC-QDPT values of the V_1 and V_2 potential energy curves are in excellent qualitative agreement. Figure 1 shows that both methods yield a conical intersection at an N−H distance of 2.10 Å. The potential energy curves for N−H distances between 1.8 and 2.3 Å are enlarged and shown as an inset plot in Figures 1 and 3. In the case of nonplanar geometries (scans 2 and 4) the potential curves have an avoided crossing for both MC-QDPT and CR-EOMCCSD(T) methods, as shown in Figures 2 and 4.

The adiabatic energies for the ground and the first excited state of ammonia obtained using the multireference MC-QDPT and single-reference CR-EOMCCSD(T) methods agree within 7% on average (calculated using eq 5; in particular, $\epsilon = 0.35$ eV and $\bar{E} = 4.92$ eV). The potential energy curves along key one-dimensional cuts that pass through conical intersection and avoided crossings show similar features. EOMCCSD results obtained without the triples correction are given in Supporting Information, and they are much less accurate than the CR-EOMCCSD(T) results.

It is particularly encouraging that the CR-EOMCCSD(T) results behave in a reasonable and smooth way near the conical intersection and that it tends to the asymptotic limit of dissociation in a reasonable way. In analogy to the standard CCSD(T) approach for the ground-state problem, the CR-EOMCCSD(T) method is a single-reference "black-box" scheme that can be used by nonexperts. In particular, the numerator and denominator terms, $N_\mu^{\mathrm{CR(T)}}$ and $D_\mu^{\mathrm{(T)}}$, respectively, defining the triples energy corrections of CR-EOMCCSD(T) are expressed in terms of the singly and doubly excited clusters obtained in the CCSD calculations and, in the case of excited-state calculations, the zero-, one-, and two-body components of the linear excitation operator that defines the excited-state wave function in the EOMCCSD ansatz (see ref 12 for the details). The computer costs of the CR-EOMCCSD(T) calculations per electronic state of interest are essentially identical to the costs of standard CCSD(T) calculations. Thus, in analogy to the CCSD(T) approach,[1,15] the CR-EOMCCSD(T) method is an $n_o^2 n_u^4$ procedure in the iterative CCSD/EOMCCSD steps and an $n_o^3 n_u^4$ procedure in the noniterative steps involving triples (n_o and n_u are the numbers of correlated occupied and unoccupied orbitals, respectively).

The ability to obtain accurate results for this kind of a problem can have a profound affect on our future ability to develop systematic, validated methods for photodissociation problems as well as making it much more straightforward to carry out specific applications.

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Supporting Information Available: Adiabatic energies for scans 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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