

## Multiple Solutions to the Single-Reference CCSD Equations for NiH

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**Abstract:** It is typically assumed that once a Hartree–Fock (HF) reference wave function is determined, the correlated wave function obtained from that HF wave function describes the same electronic state. In this paper, we report the appearance of multiple CCSD solutions obtained from the UHF reference wave function for the known ground state of a chemically interesting molecule, NiH. To determine a correspondence between the computed CCSD solutions and the physical electronic states, we consider several characteristics of the CCSD wave functions, e.g., potential energy curves, spin density isovalue plots, and excited state studies via EOM-CCSD calculations. Finally, the use of Brueckner orbitals is encouraged as a way to avoid some of the problems highlighted here for HF-based coupled cluster calculations in such challenging systems.

### 1. Introduction

Coupled-cluster theory<sup>1–3</sup> has undoubtedly provided electronic structure theorists with the most useful hierarchy of methods for obtaining highly accurate descriptions of electron correlation for a large variety of molecular systems. However, the nonlinearities in the wave function expansion coefficients makes it highly challenging to enumerate the multiple solutions of the resulting equations and can sometimes lead to complex behavior. For CI (configuration-interaction), which is linear in the coefficients or amplitudes, the lowest energy wave function for a particular set of molecular orbitals (MOs) can be solved for readily, as it requires the diagonalization of a Hermitian matrix. This is not the case for the CC (coupled-cluster) equations, and multiple solutions may be obtained by starting with different sets of initial amplitudes. The reasons responsible for the existence of multiple solutions in the CC case are different than those for the CI problem. The multiple solutions in CI are simply the different eigenvectors of the CI matrix. The multiple solutions to the CC equations arise from the nonlinear nature of the CC amplitude equations.

This problem was perhaps first addressed in 1978 when Monkhorst and Zivkovic<sup>4</sup> explored the mathematical connections between CI and CC solutions. More recently,

Bartlett and co-workers<sup>5</sup> and then Jankowski and co-workers<sup>6–8</sup> studied particular examples of multiple CC solutions with the widely used H4 model<sup>9</sup> system in which the geometry (comprised of four hydrogen atoms) is completely determined by a single chosen parameter. More recently, the existence of multiple CC solutions has been observed in the PPP<sup>10,11</sup> model of conjugated rings.<sup>12–15</sup> From these studies, it was concluded that determining a connection between a physical electronic state and a particular CC solution is a difficult problem and that a given CC solution may not even correspond to a physical state.

Multiple CC solutions also occur in a different context. In addition to obtaining solutions which differ only in the converged parameters of the multideterminantal wavefunction, one may obtain multiple CC solutions by using a different underlying HF (Hartree–Fock) reference wave function. As the HF method also requires one to solve a set of nonlinear equations, the possibility of multiple solutions arises here as well. While the choice of reference does not matter when the full  $n$ -particle  $T$  operator is used (as this is equivalent to a full configuration interaction which is invariant to rotations of all the orbitals), any realistic calculation must approximate  $T$  by a small number of excitation operators, and thus dependence on the reference wave function arises. This has been investigated by Jankowski et al.<sup>16–18</sup> again using the H4 model system.

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**Scheme 1.** Molecular Orbital Diagram for the Lowest Energy States with  $\Delta$  Symmetry<sup>a</sup>

State	(I) ${}^2\Delta$	(I) ${}^4\Delta$	(II) ${}^2\Delta$
Configuration	$d^9s^1 + 1s$	$d^8s^2 + 1s$	$d^8s^2 + 1s$
$\sigma_{4s}$	$\uparrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$\sigma_{3d}$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
$\delta_{3d}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$\pi_{3d}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

<sup>a</sup> The red arrows represent electrons which participate in bonding, e.g., occupy a bonding orbital (covalent) or transfer to the H atom (ionic).

While the H4 model system is well studied and understood, there exists a dearth of information regarding the appearance of multiple CC solutions in well-studied real molecular systems. As a molecule of both chemical and physical interest, NiH has been the focus of computational and experimental investigation for many years.<sup>19–35</sup> In this paper, we report the calculation of multiple solutions to the CCSD amplitude equations for the known ground state of the NiH molecule. We provide an analysis of the resulting wave functions which suggests particular implications for coupled cluster-based applications.

## 2. Potential Energy Surfaces

Many of the computational difficulties experienced with NiH ultimately stem from problems in correctly describing the atomic state separations of Ni.<sup>36</sup> Experimentally, the  ${}^3D(d^9s^1)$  and  ${}^3F(d^8s^2)$  states are nearly degenerate, with the  $d^9s^1$  slightly more stable by 0.03 eV.<sup>37</sup> Using unrestricted HF theory (UHF) with the G3Large basis set,<sup>33</sup> the absence of electron correlation among the d electrons causes the  $d^8s^2$  state to lie 1.41 eV lower in energy than the  $d^9s^1$  state. The error in the calculated atomic state separation is reduced dramatically when correlation effects are included with CCSD(T) (0.13 eV).<sup>33</sup> It should be noted that, in addition to correlation effects, relativistic effects are known to contribute significantly to this energy difference (by  $\sim 0.3$  eV).<sup>38</sup> However, as our focus in this paper is on addressing issues related to solving the CC equations, we illustrate our ideas using simple nonrelativistic calculations.

Since the ground electronic state of NiH is known to be  ${}^2\Delta$ , we restrict our study to the low energy states with  $\Delta$  symmetry. The MO diagrams for the three lowest energy states with  $\Delta$  symmetry are given in Scheme 1. On the basis of previous studies on this molecule, these electronic states can be described as follows:

1. Ground State  ${}^2\Delta$ . The nickel hydride molecule has a  ${}^2\Delta$  ground electronic state in which both the  $d^9s^1$  and  $d^8s^2$  atomic states of Ni contribute to the bonding, with the  $d^9s^1$  atomic state as the predominant component.<sup>25</sup> In a covalent bonding model, the Ni–H bond in this electronic state can be thought of principally as a Ni s orbital overlapping with a H s orbital ( $4s+s$ ). Alternatively, in an ionic model, the Ni–H bond can be

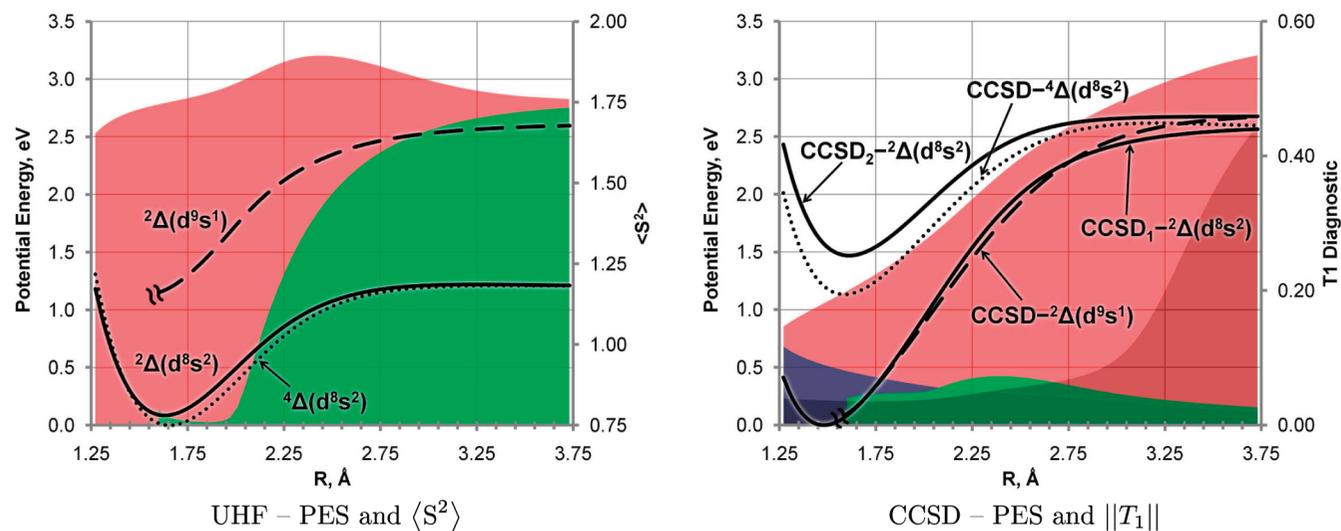
thought of as a bond between a  $Ni^+$  ( $d^9s^0$ ) and a  $H^-$  ( $s^2$ ). We will refer to this state as the  ${}^2\Delta(d^9s^1)$  state.

2. Excited State  ${}^2\Delta$ . An excited  ${}^2\Delta$  state exists which can be thought of as the  $d^8s^2$  atomic Ni state interacting with a hydrogen atom and forming a bond between H s and Ni  $d_{z^2}(d_{z^2}+s)$ .<sup>31</sup> However, recent large scale multireference calculations by Zou and Liu<sup>32</sup> suggest that this state has substantial multiradical character. It may be better considered as a bond between the  $Ni^+$  ( $d^8s^1$ ) and  $H^-$  ( $s^2$ ) ionic fragments resulting in a state with three unpaired electrons, although the overall spin is only 1/2. This state has been experimentally measured at 2.01 eV above the ground state.<sup>39</sup> We will refer to this state as the  ${}^2\Delta(d^8s^2)$  state.
3. Excited State  ${}^4\Delta$ . An excited  ${}^4\Delta$  state can also result from a similar atomic configuration as the  ${}^2\Delta(d^8s^2)$  state above. The arrows shown in red become paired at bond lengths near the equilibrium geometry, and thus the overall multiplicity is 4. Using multireference methods, Zou and Liu calculated this state to lie 1.57 eV higher in energy than the ground state.<sup>32</sup> This state will be denoted as  ${}^4\Delta(d^8s^2)$ .

**2.1. UHF Solutions.** Both the ground and excited  ${}^2\Delta$  states can be calculated with the UHF method by starting with the appropriate orbital occupations. However, this is not without difficulty since the  $d_{z^2}$  orbital as well as the 4s orbital belong to the  $\sigma$  representation of the  $C_{\infty v}$  point group for NiH. This leads to considerable mixing between them resulting in convergence difficulties, particularly near equilibrium. In fact, all points on the  ${}^2\Delta(d^9s^1)$  potential energy surface (PES) could not be calculated with the UHF method due to convergence problems for bond lengths less than about 1.56 Å. For this region of the PES, the SCF procedure either collapsed to the lower energy  ${}^2\Delta(d^8s^2)$  or simply failed to converge. However, at larger internuclear distances where the two orbitals are fairly distinct, appropriate occupation of the orbitals leads to the two different  ${}^2\Delta$  states. No convergence problems arose, however, for the  ${}^4\Delta(d^8s^2)$  state. In this quartet, the  $\sigma_{d_{z^2}}$  and  $\sigma_{4s}$  orbitals are both singly occupied.

UHF potential energy surfaces of the  ${}^2\Delta(d^9s^1)$  (dashed line),  ${}^4\Delta(d^8s^2)$  (dotted line), and  ${}^2\Delta(d^8s^2)$  (solid line) states are given in Figure 1a. It is immediately obvious that the UHF method does not predict the correct ground state since both of the  ${}^2,4\Delta(d^8s^2)$  states lie over 1 eV lower in energy than the  ${}^2\Delta(d^9s^1)$  state. A stability analysis of the resulting UHF wave functions also reveals that only the lower energy  ${}^2,4\Delta(d^8s^2)$  solutions are stable. *The experimentally observed ground state is unstable using the UHF method* due to the lack of electron correlation, which would preferentially stabilize configurations with a larger number of d electrons (an NBO analysis at  $R = 1.75$  Å yields d populations of 8.0 and 8.9 electrons for the  ${}^2\Delta(d^8s^2)$  and  ${}^2\Delta(d^9s^1)$  states, respectively).

The calculated spin properties of the two UHF solutions are also dramatically different. For example, at a bond distance of 1.75 Å, the  ${}^2\Delta(d^9s^1)$  “ground” state has an  $S^2$  value of 0.76 (close to the expected value of 0.75) but lies much higher in energy. The  ${}^2\Delta(d^8s^2)$  “excited” state has an



**Figure 1.** Potential energy surfaces. (a) UHF solutions for the “ground”  ${}^2\Delta(d^9s^1)$  state (dashed line) and “excited” states  ${}^2\Delta(d^8s^2)$  (solid line) and  ${}^4\Delta(d^8s^2)$  (dotted line). PESs are shown as curves and plotted against the left axis.  $\langle S^2 \rangle$  values are shown for doublet states as areas plotted against the right axis. Pink:  $\langle S^2 \rangle$  for the  ${}^2\Delta(d^8s^2)$  state. Green:  $\langle S^2 \rangle$  for the  ${}^2\Delta(d^9s^1)$  state. (b) Both unique CCSD<sub>1</sub> and CCSD<sub>2</sub> solutions for the  ${}^2\Delta(d^8s^2)$  UHF reference state (solid line). The single CCSD solution for the  ${}^2\Delta(d^9s^1)$  UHF reference state (dashed line). The single CCSD solution for the  ${}^4\Delta(d^8s^2)$  UHF reference state (dotted line).  $\|T_1\|$  values are shown as areas plotted against the right axis. Pink:  $\|T_1\|$  for the CCSD<sub>1</sub> solution. Purple:  $\|T_1\|$  for the CCSD<sub>2</sub> solution. Green:  $\|T_1\|$  for the CCSD-<sup>2</sup> $\Delta(d^9s^1)$  solution. Gray:  $\|T_1\|$  for the CCSD-<sup>4</sup> $\Delta(d^8s^2)$  solution.

$S^2$  value of 1.76 and lies lower in energy by 1.2 eV. As depicted in Scheme 1, this state has the following electron configuration  $\delta_{3d}^\alpha\sigma_{3d}^\alpha\sigma_{4s}^\beta$ . The corresponding  $\langle S^2 \rangle$  values are shown as areas and plotted as a function of Ni–H bond length. The pink  $\langle S^2 \rangle$  area shown in Figure 1a illustrates the extreme amount of spin contamination which is found to exist at all bond lengths for the stable  ${}^2\Delta(d^8s^2)$  state, an observation which has been known for some time.<sup>19</sup> The source of spin contamination is also clear from the similarity in the potential energy curves for the  ${}^2,{}^4\Delta(d^8s^2)$  states. The result of this spin contamination is that the calculated bond length for the lowest energy  ${}^2\Delta$  state at the UHF level (1.63 Å) is substantially larger than the ground state experimental value of 1.47 Å.<sup>39</sup> As expected, very little spin contamination is observed for the  ${}^4\Delta(d^8s^2)$  UHF solution. Overall, the poor performance of UHF is striking.

**2.2. Multiple CCSD Solutions.** The different UHF solutions were then used to obtain potential energy surfaces (PES) at the CCSD level, leading to unanticipated results. Our most exciting result is that for a single UHF reference wave function, we found two different converged CCSD solutions. Starting from the stable UHF solution for the  ${}^2\Delta(d^8s^2)$  state, we have been able to converge to two CCSD wave functions and energies. To the best of our knowledge, this is the first example of the existence of multiple solutions to the CCSD equations for a chemically interesting molecule with available experimental data. In Figure 1b, the two unique CCSD PESs using the same  ${}^2\Delta(d^8s^2)$  UHF reference state are given as solid curves, while the CCSD solution found for the unstable  ${}^2\Delta(d^9s^1)$  UHF reference state is given as a dashed line (note that since the UHF  ${}^2\Delta(d^9s^1)$  state could not be found for small bond lengths, the CCSD curve also cannot be found). The quartet surface is represented with a dotted line. For all three PESs, we also plot, as areas, the  $T_1$  diagnostic ( $\|T_1\|$ ) of Lee and co-workers<sup>40</sup> as a function of the Ni–H bond

length. The pink, purple, green, and gray areas represent the  $\|T_1\|$  values for the CCSD<sub>1</sub>, CCSD<sub>2</sub>, CCSD-<sup>2</sup> $\Delta(d^9s^1)$ , and CCSD-<sup>4</sup> $\Delta(d^8s^2)$  wave functions, respectively.

As pointed out by previous authors studying the H4 model system,<sup>6</sup> while finding one solution is typically easy, the others are often more difficult. The easily obtained solution is referred to as the “standard” solution, whereas the more difficult solutions are referred to as “alternate” solutions. Of the two CCSD solutions sharing the same UHF reference orbitals, CCSD<sub>1</sub> was found readily using the standard convergence algorithms (using coefficients from first-order perturbation theory (from an MP2 calculation) as the initial set of amplitudes). Therefore, CCSD<sub>1</sub> is considered our “standard” solution. To obtain CCSD<sub>2</sub>, we first ran a CCD calculation to obtain a set of amplitudes that were expected to be closer to the converged CCSD amplitudes than the perturbation theory coefficients, though the orbital relaxation effects from the  $T_1$  amplitudes are still neglected. Using the converged CCD amplitudes as our initial guess for the CCSD amplitudes, we were able to converge to a second CCSD solution (CCSD<sub>2</sub>) at a stretched bond length. These converged amplitudes were then used as the initial amplitude guess for the next point on the potential energy surface. This was repeated to compute the full CCSD<sub>2</sub> PES. Both the “standard” solution and the “alternate” solution are shown in Figure 1b with solid black lines.

### 3. CCSD Solution—Electronic State Correspondence

Upon finding multiple CCSD solutions, one must address the following questions:

- Do the CC solutions correspond to actual physical states?
- Which solution corresponds to the same electronic state as the reference wave function?

**Table 1.** Calculated Spectroscopic Parameters for the  ${}^2\Delta$  State

solution	reference	dissociation	$R_{\text{eq}}$ (Å)	$D_e$ (eV)
UHF <sub>1</sub>		$d^8s^2 + s^1$	1.630	1.12
CCSD <sub>2</sub>	${}^2\Delta(d^8s^2)$	$d^8s^2 + s^1$	1.611	1.21
CCSD <sub>1</sub>	${}^2\Delta(d^8s^2)$	$d^9s^1 + s^1$	1.477	2.71
UHF <sub>2</sub>		$d^9s^1 + s^1$		
CCSD	${}^2\Delta(d^9s^1)$	$d^9s^1 + s^1$		

• To which electronic states do the remaining solutions correspond?

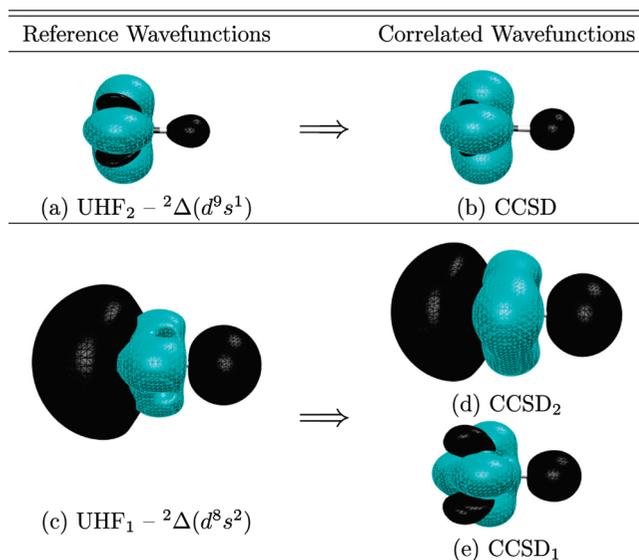
In the absence of a mathematically rigorous way to obtain a physical state correspondence for the different CCSD solutions, we have investigated many aspects related to the CCSD wave functions to make our determinations. As the multiple CCSD solutions arise from a doublet UHF solution, we only concern ourselves with the doublet solutions for electronic state determination.

Considering that the PESs for both CCSD solutions appear reasonable on initial inspection (i.e., separation into atomic states, appropriate equilibrium bond lengths, and binding energies), it seems as though both solutions correspond to physical states. Simple analysis of the PESs shows that the “standard” solution (CCSD<sub>1</sub>) actually corresponds to a different electronic state ( ${}^2\Delta(d^9s^1)$ ) than is described by the reference wave function ( ${}^2\Delta(d^8s^2)$ ), and the “alternate” solution (CCSD<sub>2</sub>) corresponds to the same  ${}^2\Delta(d^8s^2)$  state as the reference UHF wave function. Some of the characteristics of the different PESs are summarized in Table 1. As shown in this table, the UHF wave function values for  $R_{\text{eq}}$  and  $D_e$  are similar to CCSD<sub>2</sub>, whereas the parameters for CCSD<sub>1</sub> are very different.

**3.1. Spin Densities.** Determining the electronic state for a single determinant wave function is normally rather straightforward via direct inspection of the molecular orbitals. However, this type of analysis is more complicated with a correlated, multideterminantal wave function. In Figure 2, we report isodensity plots of the spin densities ( $\rho^\alpha - \rho^\beta$ ) using both the reference wave function density and the associated CCSD response density(ies). Blue surfaces indicate excess  $\alpha$  density, and black surfaces indicate regions of excess  $\beta$  density. Therefore, a pure doublet spin state would have no visible black surface shown.

In Figure 2a and b, respectively, the UHF<sub>2</sub> and associated CCSD spin densities are shown. As shown in Figure 1a, the UHF<sub>2</sub> wave function is already rather close to a pure doublet ( $\langle S^2 \rangle = 0.763$ ), so little is required of the  $T_1$  amplitudes in terms of cleaning up the spin contamination, and thus the resulting CCSD spin density looks rather similar to the UHF spin density and the  $T_1$  diagnostic is small ( $\|T_1\| = 0.05$ ). Both the UHF<sub>2</sub> and resulting CCSD results clearly resemble  ${}^2\Delta$  states, with a single unpaired electron occupying a  $d$ -type orbital.

In Figure 2c,d,e, spin densities are given for the UHF<sub>1</sub> reference wave function ( $d^8s^2$ ) and associated CCSD<sub>2</sub> and CCSD<sub>1</sub> solutions. In addition to the similarities in the spectroscopic parameters shown in Table 1, inspection of the spin densities provides further evidence that the “alternate” solution (CCSD<sub>2</sub>) more closely resembles the reference



**Figure 2.** Spin density plots ( $\rho^\alpha - \rho^\beta$ , isovalue = 0.002) shown at a Ni–H bond length  $R = 1.75$  Å. Excess  $\alpha$  density (blue). Excess  $\beta$  density (black). Left column, a and c, shows the spin densities of the different reference wave function spin densities. Right column shows the different correlated wave function spin densities. (b) CCSD solution using the UHF<sub>2</sub> reference. (d and e) The two different CCSD solutions for the same reference (UHF<sub>1</sub>).

wavefunction. The extreme amount of spin polarization resulting in the high degree of spin contamination can be immediately seen in the spin densities for UHF<sub>1</sub> and CCSD<sub>2</sub>. It is most interesting that the “standard” solution (CCSD<sub>1</sub>) starting from UHF<sub>1</sub> describes a different electronic state ( $d^9s^1$ ) that more closely resembles UHF<sub>2</sub>. These results are quite surprising as it means that the *CCSD solution which was most easily obtained actually corresponds to a different electronic state than the original starting point*. This reinforces the need to employ caution when studying highly correlated chemical systems, even with well-calibrated “black box” methods such as CCSD.

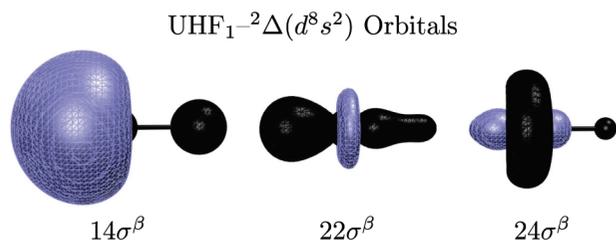
**3.2. EOM-CCSD.** To determine the electronic state correspondence for the “standard” solution (CCSD<sub>1</sub>), we note the resemblance between the PES for CCSD<sub>1</sub> and the PES for the CCSD calculation starting from the UHF<sub>2</sub> reference (comparing regions of the PES for which both solutions could be obtained). This suggests that the CCSD<sub>1</sub> solution corresponds to the experimental ground state (and UHF<sub>2</sub> excited state)  ${}^2\Delta(d^9s^1)$ . This implies that the cluster operators within the spin-orbital formulation act upon the spin-symmetry-broken UHF<sub>1</sub> solution to produce a correlated wave function where the spin symmetry is mostly restored. However, the similarities in the energy alone are not sufficient to make our determination, as there are multiple low lying electronic states for NiH. To make a more definitive connection, we have calculated EOM-CCSD excited states using both the “standard” and “alternate” solutions, the results of which are listed in Table 2.

Table 2 shows the similarities in excitation energy between the lowest energy  ${}^2\Delta$  excited states from both of the EOM-CCSD calculations. If we compute the excited states for the “standard” solution (CCSD<sub>1</sub>), we find an excited  ${}^2\Delta$  state

**Table 2.** EOM-CCSD Calculations with Both the Standard and Alternate CCSD Solutions<sup>a</sup>

solution	lowest ${}^2\delta$ state (ev)	occ $\rightarrow$ virt	coefficient
EOM-CCSD <sub>2</sub>	-1.327	$14\sigma^\beta\rightarrow 22\sigma^\beta$	-0.561
		$14\sigma^\beta\rightarrow 24\sigma^\beta$	+0.530
EOM-CCSD <sub>1</sub>	+1.343	$14\sigma^\beta\rightarrow 22\sigma^\beta$	+0.642
		$14\sigma^\beta\rightarrow 24\sigma^\beta$	-0.601

<sup>a</sup> Both CCSD solutions use the UHF<sub>1</sub> ( ${}^2\Delta(d^8s^2)$ ) reference. Ni-H bond length,  $R = 1.75$  Å.

**Figure 3.** Molecular orbitals which have significant contributions to the EOM-CCSD excited states.

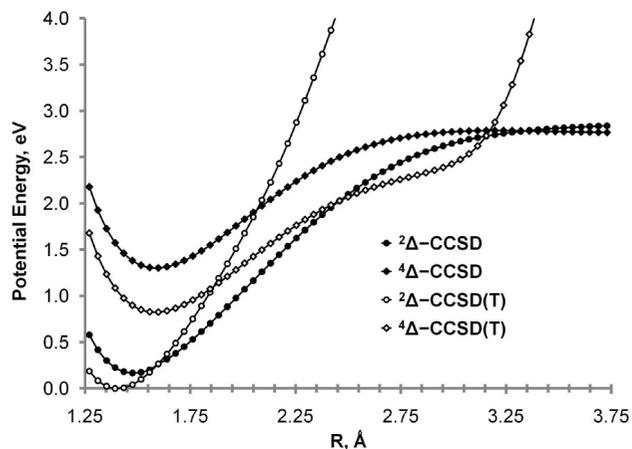
1.34 eV higher in energy. Likewise, if we calculate the excited states for the “alternate” solution (CCSD<sub>2</sub>), we find that a  ${}^2\Delta$  state lies 1.33 eV lower in energy. If we look at the results more closely, we see that for both excited states the largest coefficients are in front of determinants which involve switching the same UHF<sub>1</sub> orbitals (i.e.,  $14\sigma^\beta\rightarrow 22\sigma^\beta$  and  $14\sigma^\beta\rightarrow 24\sigma^\beta$ ). These orbitals are shown in Figure 3.

As illustrated in Scheme 1, the  ${}^2\Delta(d^9s^1)$  and  ${}^2\Delta(d^8s^2)$  UHF solutions differ primarily in the  $\beta$  occupancy of the  $\sigma_{3d_z}$  and  $\sigma_{4s}$  orbitals. These are precisely the orbitals upon which a change in occupation connects the two excited  ${}^2\Delta$  states in Table 2. It can be seen from Figure 3 that the molecular orbital  $14\sigma^\beta$  is primarily of 4s character, and the  $22\sigma^\beta$  and  $24\sigma^\beta$  each have significant  $3d_z$  character. We therefore conclude the following:

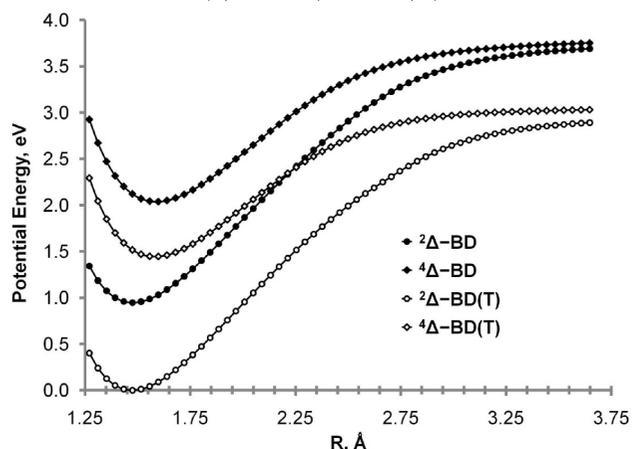
- Both the “standard” (CCSD<sub>1</sub>) and “alternate” (CCSD<sub>2</sub>) solutions correspond to physical states.
- The “standard” solution is assigned to the  ${}^2\Delta(d^9s^1)$  state, and the “alternate” solution is assigned to the  ${}^2\Delta(d^8s^2)$  state.
- The “alternate” solution describes the same electronic state as the reference UHF wave function.

#### 4. Corrections to Correlated Wave Functions

As we have just noted, if one treats this system in a “black box” fashion and first obtains a stable  ${}^2\Delta$ UHF solution, then employs standard convergence procedures to obtain a CCSD energy, the solution will have extremely large  $T_1$  amplitudes related to the orbital rotations required to describe the  ${}^2\Delta(d^9s^1)$  state from a  ${}^2\Delta(d^8s^2)$  reference wave function. If one is only concerned with the CCSD energies, then this provides at least a qualitatively acceptable PES. However, often it is recognized that triple excitations are necessary to describe the system to a satisfactory degree of quantitative accuracy. This is commonly done via a perturbational correction to the correlated wave function using the well-known CCSD(T) method.<sup>41,42</sup> We now explore some of the implications related to using CCSD(T) to describe an



(a) CCSD/CCSD(T)



(b) BD/BD(T)

**Figure 4.** Potential energy surfaces. (a) CCSD (solid line), CCSD(T) (dashed line). As this uses the  ${}^2\Delta(d^8s^2)$  UHF reference wave function, the CCSD curve is the same as the CCSD<sub>1</sub> curve given in Figure 1. (b) BD (solid line), BD(T) (dashed line).

electronic state whose character is substantially different from the orbital occupations that define the reference wave function.

In Figure 4a, we show the lowest energy  ${}^2\Delta$  and  ${}^4\Delta$  potential energy curves for both CCSD and CCSD(T). While the CCSD curves are qualitatively correct, inclusion of triple excitations by means of a perturbational correction results in unphysical potential energy curves. This unrealistic rising of energy with the bond length is a direct result of the incredibly large  $T_1$  amplitudes in the CCSD wave functions which are used to compute the triples correction. In Figure 1b, the  $T_1$  diagnostic is given for the CCSD- ${}^2\Delta$  curve (pink) and the CCSD- ${}^4\Delta$  curve (gray). For both of these CCSD solutions, the  $\|T_1\|$  becomes very large at long bond lengths. However, as a matrix norm, the  $\|T_1\|$  metric does not fully indicate the nature of the individual  $T_1$  amplitudes. Table 3 lists the largest amplitudes (greater than 0.2) for the CCSD<sub>1</sub> and CCSD<sub>2</sub> solutions. While there are many significantly large  $T_1$  amplitudes, two particular components of the CCSD<sub>1</sub> wave function have coefficients greater than 1. The singly excited determinants  $|\Psi_{14\sigma^\beta}^{22\sigma^\beta}\rangle$  and  $|\Psi_{14\sigma^\beta}^{24\sigma^\beta}\rangle$  have coefficients of 1.05 and  $-1.01$ , respectively. These incredibly large  $T_1$

**Table 3.** Dominant Configurations in the CCSD<sub>1</sub> and CCSD<sub>2</sub> Wavefunctions<sup>a</sup>

orbitals		amplitude
	CCSD <sub>1</sub>	
14σ <sup>β</sup> →22σ <sup>β</sup>		1.05
14σ <sup>β</sup> →24σ <sup>β</sup>		-1.01
14σ <sup>β</sup> →21σ <sup>β</sup>		-0.55
14σ <sup>β</sup> →27σ <sup>β</sup>		0.53
14σ <sup>β</sup> →18σ <sup>β</sup>		-0.45
14σ <sup>β</sup> →40σ <sup>β</sup>		-0.33
14σ <sup>β</sup> →30σ <sup>β</sup>		0.30
14σ <sup>β</sup> →37σ <sup>β</sup>		-0.26
14σ <sup>β</sup> →17σ <sup>β</sup>		0.20
	CCSD <sub>2</sub>	
14σ <sup>β</sup> →22σ <sup>β</sup>		-0.29
14σ <sup>β</sup> →24σ <sup>β</sup>		0.26

<sup>a</sup>All amplitudes greater than 0.2 are shown. Bond length, 1.75 Å.

amplitudes, required to obtain the  ${}^2\Delta(d^9s^1)$  state from a  ${}^2\Delta(d^8s^2)$  reference wave function, render any correction based on perturbation theory inappropriate. Note that these two excited determinants are obtained by swapping the exact same orbitals that are active in the EOM-CCSD calculations, as shown in Table 2.

If, however, one opts to use a different MO basis, one in which all the  $T_1$  amplitudes are zero by design, better behavior might be expected. The BD method (Brueckner Doubles) is defined as a CCSD approach in which all of the  $T_1$  amplitudes have been driven to zero via orbital rotations.<sup>43</sup> In Figure 4b, the BD and BD(T) potential energy curves are given for both the lowest energy  ${}^2\Delta$  and  ${}^4\Delta$  potential energy curves. While the BD and CCSD methods yield very similar potential energy curves, the triples correction for BD behaves far better. Because the  $T_1$  amplitudes in a BD wave function are zero, the singles–doubles terms in the (T) correction are also zero, and thus there are no terms which may provide a destabilizing effect on the energy.

Note that Figure 4a shows CCSD underestimating the 1.57 eV  ${}^2\Delta$ – ${}^4\Delta$  energy separation by 0.47 eV.<sup>32</sup> Performance worsens significantly when the triples correction is added to CCSD (calculated energy separation of only 0.82 eV). As seen in Figure 4b, the performance of BD is very similar to that of CCSD (BD underestimates this state separation by 0.48 eV). However, due to the reasons just outlined, the BD wave function does not suffer from the accumulation of large  $T_1$  amplitudes, and thus BD(T) performs quite well, yielding a  ${}^2\Delta$ – ${}^4\Delta$  energy separation of 1.44 eV. This is in good agreement with the results from the multireference calculations.<sup>32</sup> The calculated BD(T) bond lengths for the  ${}^2\Delta$  and  ${}^4\Delta$  states (1.479 Å and 1.587 Å) are also in good agreement with the multireference results.

The energy difference between the  ${}^2\Delta(d^9s^1)$  and  ${}^2\Delta(d^8s^2)$  states (experimentally measured to be 2.01 eV)<sup>39</sup> is more difficult to compute. At the CCSD level, the calculated difference is too small, 1.5 eV, since the  ${}^2\Delta(d^9s^1)$  ground state is described poorly. However, since the  ${}^2\Delta(d^8s^2)$  and  ${}^4\Delta(d^8s^2)$  states are somewhat similar, the calculated energy difference between them at the CCSD level (0.3 eV) is likely to be more reasonable. If this energy difference is added to the computed  ${}^2\Delta(d^9s^1)$  –  ${}^4\Delta(d^8s^2)$  energy difference (1.44

eV at the BD(T) level), we determine the energy difference between the two lowest  ${}^2\Delta$  states as 1.74 eV, in reasonable agreement with the experimental value of 2.01 eV.

## 5. Conclusions

In this article, we report the calculation of multiple solutions to the CCSD equations and subsequent analysis of the results, which suggest interesting implications for coupled cluster-based applications. From this work we have drawn the following conclusions:

1. The ability to find alternate solutions to the CCSD equations largely depends on the underlying wave function. For systems whose ground state orbital occupations change after the inclusion of electron correlation, one needs to be wary of the resulting wave function, as it may not correspond to the same electronic state. Analysis of the  $T_1$  diagnostic is useful in determining if the correlated wave function is describing a different electronic state. This has implications for deliberately using unstable UHF wave functions as references in CCSD calculations for the purpose of modeling excited states.
2. EOM-CCSD is useful as a test to determine if lower energy CCSD solutions exist.
3. We have found that using the converged CCD amplitudes as a set of initial guess amplitudes for a CCSD calculation improves the ability to converge to a solution which describes the same state as the reference.
4. The use of a Brueckner orbital reference wave function reduces the possibility of converging to CCSD solutions which describe different electronic states than the reference.
5. In addition to other beneficial aspects, obtaining a correlated wave function from a set of Brueckner orbitals yields a correlated wave function which is much more appropriate for use in perturbative treatments for higher order corrections such as BD(T).
6. NiH is an interesting molecule which exhibits many characteristics which are often very difficult to describe theoretically. Thus, its use as a test molecule is further encouraged.

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