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The calculation of the dipole moments of NiH, TiO, and FeO

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Summary. We explore several computational strategies for computing the dipole moment of the $X^2\Delta$ state of NiH, the $X^3\Delta$ state of TiO, and the $X^5\Delta$ state of FeO. The averaged coupled-pair functional (ACPF) method gives consistently the best agreement with experiment, but can become intractable, as rather large zeroth-order reference spaces can be required. At the ACPF level, unlike the multireference configuration-interaction (MRCI) level, the dipole moments determined as an expectation value and by finite-field methods are similar, and are insensitive to natural orbital iteration. Our best theoretical results for NiH are in excellent agreement with experiment, whereas our best dipole moments for TiO and FeO are both about 10%–15% larger than the recently measured values.

Key words: *Ab initio* calculations — Properties — Dipole moment — Correlation methods

1. Introduction

Ab initio quantum mechanical calculations are becoming an increasingly valuable method for determining spectroscopic constants and properties of molecular systems containing transition metals [1]. The dipole moment of a given electronic state of a molecule is a sensitive measure of the degree of mixing of the different metal-atom asymptotes and thus depends critically on the quality of the wave function. This is well illustrated by previous calculations on the $X^2\Delta$ state dipole moment of NiH [2–7], where the value is strongly influenced by the mixing of the nearly degenerate $^3D(3d^94s^1)$ and $^3F(3d^84s^2)$ states of Ni atom, because these atomic states bond to the hydrogen atom in very different ways. The ^3D state of Ni forms a $4s$—$1s$ bond, which is polarized toward the H giving a large dipole moment of Ni^+H^- polarity. In contrast, the ^3F state forms $4s4p\sigma$ hybrid orbitals. While the bonding orbital is polarized toward the H, the other orbital is polarized away from H, thereby balancing the charge movement and giving a very small dipole moment. The magnitude of the $X^2\Delta$ state dipole moment therefore depends critically on the degree to which these two bonding mechanisms contribute to the wave function.

Experimental dipole moments have recently become available for the lowest vibrational level of the ground states of NiH [8], TiO [9], CrO [10], FeO [11], CuO

[12], CuS [13], YO [14], and ZrO [15], as well as the $A^2\Pi$ state of ScO [16]. Thus a theoretical study to determine the optimal computational approaches for determining the dipole moments of transition-metal systems is especially timely. Zeroth-order wave functions such as self-consistent-field (SCF) or complete-active-space SCF (CASSCF) wave functions are often biased toward one metal atomic asymptote and thus an extensive treatment of electron correlation is required to compute an accurate dipole moment. Previous theoretical work on NiH [3] and CrO [10] focused on the iterative natural orbital (INO) method, based on multireference configuration-interaction (MRCI) wave functions, to overcome the orbital bias in the zeroth-order wave function. Although previous results for NiH [3, 5], TiH [17] and CrO [10] indicate that the INO method works well, it can be slowly convergent and thus quite costly. Recently, Marian et al. [7] have applied the averaged coupled-pair functional (ACPF) method [18] as well as the MRCI approach to NiH. They found that the ACPF results were superior to the MRCI, and that relativistic effects were relatively important. Unfortunately, they did not carry out INO calculations for comparison with their ACPF results. In this work we also explore the ACPF method and compare it to the MRCI treatment using a series of CASSCF wave functions as a starting point. In addition we compare the ACPF results to the INO using the same basis. Finally, we evaluate the finite-field method as an alternative for accounting for orbital relaxation effects. We apply these methods to NiH and TiO because accurate experimental values are available for comparison, and to FeO as an example of a system with more d electrons and a high-spin state. In Sect. 2 we describe our one-particle basis sets and methods for incorporating electron correlation. In Sect. 3 we compare our theoretical results for NiH, TiO, and FeO with experiment. Our conclusions are given in Sect. 4.

2. Methods

The Fe and Ni basis sets are derived from the $(20s12p9d)$ basis sets and Ti from the $(21s13p9d)$ basis set optimized by Partridge [19]. Three even-tempered $2p$ functions are added to describe the $4p$ orbital, an even-tempered diffuse $3d$ function is added to describe the $3d^{n+1}4s^1$ and $3d^{n+2}$ occupations, and six even-tempered $4f$ functions are added for polarization. The even-tempered functions are of the form $\alpha = 2.5^n\alpha_0$, with $n = 0, \dots, k$. The $\alpha_0(f)$ values are 0.056, 0.1741, and 0.2024 for Ti, Fe, and Ni, respectively. These large primitive sets are contracted using the atomic natural orbital (ANO) procedure [20] for the average of the lowest atomic state arising from the $3d^n4s^2$, $3d^{n+1}4s^1$, and $3d^{n+2}$ occupations, except that the $3d^8$ occupation was not included for Fe, as it is too high in energy to contribute to the ground state of FeO. The most diffuse s and p primitives are uncontracted to accurately describe the polarizability. For Ti, the most diffuse d primitive was also uncontracted to improve the description of the $3d^4$ occupation. Our final contracted Gaussian basis sets are $[7s6p4d2f]$ for Ti and Ni and $[6s5p4d3f]$ for Fe. For Ti a second ANO set was also developed for the treatment of $3s$ and $3p$ correlation. The ANO contraction is based on the averaged ANOs for a 12-electron SCF/SDCI treatment of the lowest states arising from the $3d^24s^2$, $3d^34d^1$, and $3d^4$ occupations. The outermost s and p functions were again uncontracted yielding a final basis set for the form $(21s16p10d6f)/[8s7p5d3f]$.

The H basis set is derived from the $(8s6p4d)/[4s3p2d]$ set developed by Almlöf and Taylor [20], and has a diffuse s $(\alpha = 0.03)$ and p $(\alpha = 0.04)$ function added to improve the description of H^-. For O atom we used the previously reported

$(13s9p6d4f)/[5s5p2d1f]$ set [10], which is based on the van Duijneveldt [21] $(13s8p)$ set. The ANO contraction is based on the average of O and O^-. Two slightly different contractions were used for oxygen atom. For FeO we used the $[4s4p2d1f]$ ANO set with the outermost s and p functions uncontracted, whereas for TiO we used a $[5s5p2d1f]$ ANO set. The dipole moment of TiO changes by only 0.002 D with the contraction scheme for the oxygen basis. Only the pure spherical harmonic components of the basis functions are used.

For the multireference-based correlation approaches, the orbitals are optimized using CASSCF wave functions, and the specific choice of the active spaces is discussed below. While the calculations are carried out in C_{2v} symmetry, full $C_{\infty v}$ symmetry is imposed on the orbitals [22]. More extensive correlation is added using the MRCI and ACPF approaches. In addition, we perform natural orbital iterations for both the MRCI and ACPF wave functions to overcome the orbital bias of the CASSCF optimization. The reference lists from which single and double excitations were generated included every occupation for which the absolute value of the coefficient of any one of its component spin couplings exceeded a threshold, usually 0.05, in the CASSCF wave function for r values near r_e. For the ACPF wave functions, and when natural orbital iterations were performed, the additional configurations found to have coefficients with absolute values greater than 0.05 in the final wave function are added to the reference list, except for special cases noted later.

The iterative expansion of the ACPF reference list can lead to computational problems and to intractably long CSF expansions. It has been suggested [23] that the single excitations in the valence space, i.e. those that involve only the active and inactive orbitals, are given too much weight in the ACPF approach. In the formulation of the ACPF method [18], it was assumed that the reference wave function is a good approximation to the full CASSCF reference, in which case there are no singles of this type. Recently Siegbahn [23] suggested that the single excitations in the valence space should be treated like the reference wave function instead of the external space. He has found that this new definition of the ACPF energy functional generally requires fewer occupations be added to the reference space compared with the original formulation and that these two ACPF approaches yield similar energies [23]. In this work we compare dipole moments evaluated using these two ACPF formalisms.

In addition to the CASSCF/MRCI and ACPF methods, we also consider the SCF based coupled-pair functional (CPF) method [24] and the modified CPF (MCPF) method [4]. This allows us to address the question of the effect of $3s$ and $3p$ correlation on the dipole moment of TiO.

We evaluate the dipole moment both as an expectation value and as an energy derivative (using fields of from ± 0.005 a.u. to ± 0.002 a.u.). Based on the CASSCF results, where these two methods should agree, we conclude that the computed dipole moments are precise to better than 0.001 a.u. The calculations were carried out using the MOLECULE-SWEDEN [25] program system on the NASA Ames Research Center CRAY X-MP/14se and CRAY Y-MP/832 computers and at Cray Research, Inc.

3. Results and discussion

3.1. NiH

In a previous study [2] of the bonding in the ground state of the transition metal hydrides, the CASSCF active space contained the metal $3d$, $4s$ and $4p$ orbitals and the hydrogen 1*s* orbital. The second active π orbital became a 3*d* correlating orbital instead of a 4*p* orbital, due to the importance of $3d\pi$ to $3d\pi'$ correlation for the metals on the right half of the row. In the σ space the composition of the active orbitals was less distinct, as there was significant contribution from all of the 3*d*, 4*s*, 4*p*, 3*d*′ and H 1*s* orbitals. While the 3*d* to 3*d*′ excitation is a very important atomic correlation effect, it was assumed to have a smaller differential effect on the dipole moment than the correlation of the NiH bond. Therefore, in an earlier study [3] of the dipole moment of NiH, the active space was reduced to only the Ni $3d\sigma$, $3d\delta$, and 4*s* orbitals, and the H 1*s* orbital.

In this work we consider four active spaces. The first active space is the same as used in the previous study of the dipole moment; i.e. only the Ni $3d\sigma$, $3d\delta$, and 4*s* orbitals, and the H 1*s* orbital are active. Following the notation of Marian et al. [7], this is called CAS4, and the MRCI and ACPF calculations based on it are denoted as MRCI4 and ACPF4. This active space suffers from having more σ electrons than orbitals so that the correlating orbital is forced to serve two purposes. In our CAS5 space this lack of σ orbitals is rectified by adding another orbital, which is principally of Ni $4p\sigma$ character. In the third active space, we add all three components of the 4*p* orbital to the active space, which we denote CAS(4*p*); Marian et al. have no analogous calculation. The larger active space accounts for both $\sigma \rightarrow \sigma^*$ and the $\sigma \rightarrow \pi$ angular correlation of the NiH bond. Since the $3d\pi$ orbitals are inactive, the added active orbital is predominantly of Ni 4*p* character, as desired. This active space leads to MRCI and ACPF results that are very similar to those based on the CAS5 reference. The fourth active space accounts for $3d-3d'$ correlation in addition to the $\sigma \rightarrow \sigma^*$ correlation. It was not possible to include the full 3*d* and 3*d*′ shells in the CASSCF active space. However, the dominant effect of $3d-3d'$ correlation on the orbital optimization can be achieved by adding the 3*d*′ shell to the active space with the following restrictions on the orbital occupancies:

$$(3d\sigma 3d\sigma' 4s 4p\sigma 1s)^4(3d\pi_x 3d\pi_x')^2(3d\pi_y 3d\pi_y')^2(3d\delta_{x^2-y^2} 3d\delta_{x^2-y^2}')^2(3d\delta_{xy} 3d\delta_{xy}')^1.$$

This CASSCF calculation (denoted CAS($3d-3d'$)) results in an expansion of 6944 CSFs, which is the same as the CAS12 calculation of Marian et al. [7]. (Note, however, we have explicitly given the partitioning within the π and δ spaces.) While the two components of the $3d\delta$ orbital appear to be different as the occupation is written, the averaging procedure guarantees their equivalence [22].

The MRCI reference list is determined using a 0.05 selection threshold, which gives four, four, eight, and six reference occupations based on the CAS4, CAS5, CAS(4*p*), and CAS($3d-3d'$) zeroth-order wave functions, respectively. The number of references increases dramatically when the threshold is reduced to 0.025 or 0.01. For example, a 0.025 threshold for the CAS($3d-3d'$) treatment yields 27 reference occupations. In the ACPF treatments, several additional occupations had CSFs with coefficients larger than 0.05 in the final wave functions. Note that we add only those occupations with a coefficient greater than 0.05, even if the original threshold for the CASSCF wave functions was less. Furthermore, only those occupations that involve the inactive and active orbitals (i.e. valence occupations) are added. The ACPF treatments based on the CAS4, CAS5, and CAS(4*p*) calculations indicated that $3d\pi \rightarrow 3d\pi'$ and $3d\delta \rightarrow 3d\delta'$ excitations were above the threshold. In addition, the ACPF calculations based on the CAS4, CAS5 and CAS($3d-3d'$) treatments showed the importance of $\sigma \rightarrow 4p\pi$ excitations. These effects were addressed by expanding the active space in the CASSCF calculations, instead of including these non-valence configurations in the ACPF reference wave function.

The spectroscopic constants for the $X^2\Delta$ state of NiH are summarized in Table 1.

Table 1. Spectroscopic constants for the $X^2\Delta$ state of NiH

Calculation	r_e (a_0)	ω_e (cm^{-1})	μ (D)	$d\mu/dr$ (D/a_0)
CAS4	2.975	1580	1.544	−0.854
MRCI4	2.663	3096	2.241	−0.278
MRCI4 + Q	2.681	2883		
ACPF4	2.707	2603	2.493	1.063
CAS5	3.036	1508	0.876	0.287
MRCI5	2.659	2016	1.861	−0.004
MRCI5 + Q	2.689	2085		
ACPF5	2.721	2107	2.559	0.590
CAS(4*p*)	2.997	1460	1.024	−0.147
MRCI(4*p*)(0.05)	2.677	2022	1.830	−0.174
MRCI(4*p*) + Q	2.695	2072		
ACPF(4*p*)	2.727	2060	2.515	1.060
MRCI(4*p*)(0.025)	2.679	2074	1.988	0.012
MRCI(4*p*) + Q	2.698	2110		
ACPF(4*p*)	2.728	2066	2.479	0.899
MRCI(4*p*)(0.01)	2.685	2078	2.041	0.122
MRCI(4*p*) + Q	2.700	2128		
ACPF(4*p*)	2.724	2100	2.453	0.786
CAS(3*d* − 3*d*′)	2.912	1664	3.310	0.917
MRCI(3*d* − 3*d*′)(0.05)	2.778	1894	3.056	0.950
MRCI(3*d* − 3*d*′) + Q	2.768	1940		
ACPF(3*d* − 3*d*′)	2.780	1918	2.355	0.289
MRCI(3*d* − 3*d*′)(0.025)	2.779	1921	2.954	0.900
MRCI(3*d* − 3*d*′) + Q	2.765	1948		
ACPF(3*d* − 3*d*′)	2.767	1949	2.522	0.758
Expt.	2.76[a]	2003[a]	2.4 ± 0.1[b]	

[a] Attributed to J. A. Gray by Marian et al. [7]
[b] Gray et al. [8]

All of the CASSCF calculations yield properties that are significantly in error. The r_e values are consistently too large, whereas the ω_e values are too small. Excluding the CAS(3*d* − 3*d*′) calculation, μ is too small, because the CAS4, CAS5, and CAS(4*p*) wave functions, which include little of the Ni atomic correlation, contain too much $3d^8 4s^2$ character. In fact, the active space in the CAS4 calculation corresponds to an SCF calculation for Ni atom, which results in a $^3D - {}^3F$ separation of -1.28 eV, as compared with the experimental value of 0.03 eV [26]. Including the 4*p* orbital in the CASSCF active space increases the degree of $3d^8 4s^2$ character in the wave function, because of the improved treatment of the $4s^2 \rightarrow 4p^2$ near degeneracy effect. At the CAS(4*p*) level the $^3D - {}^3F$ separation is -1.91 eV, resulting in a dipole moment that is 0.5 D smaller than when the 4*p* orbital is excluded from the active space. In contrast, the CAS(3*d* − 3*d*′) treatment, which includes 3*d* − 3*d*′ correlation, is biased more towards the $3d^9$ asymptote, thus yielding a dipole moment that is too large.

The inclusion of more extensive correlation improves the spectroscopic constants, but all of the correlated treatments based on the CAS4, CAS5, and CAS(4*p*) wave functions now yield r_e values that are too small. Corrections for higher excitations (+Q and ACPF) improve r_e, but even the best value is still in error by 0.03 a_0.

Tightening the threshold in the MRCI(4*p*) and ACPF(4*p*) calculations makes little difference. Our MRCI5 and ACPF5 treatments yield r_e values that are about 0.03 a_0 shorter than the non-relativistic values of Marian et al. [7], probably due to the better basis set used in the present work. The calculations based on the CAS5 treatment yield much better results than those based on the CAS4 wave function—see, for example, the ω_e values in Table 1. The r_e values increase and the ω_e values decrease when based on the CAS($3d-3d'$) wave function. Although both values are in good agreement with experiment, we have neglected relativistic effects, the discussion of which we defer till later. The MRCI and ACPF results change only slightly when the threshold is decreased from 0.05 to 0.025; this represents a large increase in the computational effort, however, as the MRCI and ACPF wave functions involve 3.3 million CSFs.

Correlation improves the dipole moment, but the MRCI4, MRCI5, and MRCI(4*p*) μ values are still too small, while the MRCI($3d-3d'$) value is too large. Clearly none of the MRCI calculations can overcome the orbital bias introduced in the CASSCF calculation. While the MRCI values range from 1.83 to 2.95 D, the ACPF values only vary from 2.36 to 2.56 D. Thus the ACPF treatment, which includes the effect of higher excitations, overcomes the orbital bias much more effectively than the MRCI. Unlike the r_e and ω_e values, the dipole moments are somewhat sensitive to the threshold, changing by up to 0.2 D as the selection threshold is tightened. For the CAS(4*p*) reference, the ACPF dipole moment is unaffected by changing the threshold. However, it is more sensitive to selection when based on the CAS($3d-3d'$) active space, probably because the $3d-3d'$ correlation arises from many small contributions, whereas for the CAS(4*p*) treatment only the NiH bond is correlated in the CASSCF zeroth-order reference.

The dipole derivative at r_e is even more sensitive to the level of treatment than the dipole moment. Given that the ACPF(4*p*)(0.01), MRCI($3d-3d'$)(0.025), and ACPF($3d-3d'$)(0.025) values are comparable, the correct dipole derivative is probably near 0.8 D/a_0. In the best calculations the $3d$ population increases with increasing r, so that both the reduction in importance of the $3d^84s^2$ occupation and the ionic contribution to the bonding make a positive contribution to the derivative. Lower levels of theory, which are biased towards the $3d^84s^2$ occupation, mix in even more $3d^84s^2$ character with increasing r, thereby yielding a dipole derivative of the wrong sign.

One approach to overcoming the CASSCF bias towards the $3d^84s^2$ occupation is natural orbital iterations based on the MRCI wave functions. In Table 2 we show the

Table 2. The effect of MRCI-NO iterations on the energy (E_h) and dipole moment(D) of NiH

Iteration	MRCI(4*p*)			MRCI4		
	Energy[a]	Ref%[b]	Dipole	Energy[a]	Ref%[b]	Dipole
0	−0.763167	91.5	1.827	−0.764796	92.0	2.229
1	−0.764271	92.0	2.116	−0.763719	92.6	2.375
2	−0.768125	92.5	2.398	−0.767488	92.9	2.478
3	−0.768049	92.6	2.515	−0.767619	93.0	2.534
4	−0.768080	92.7	2.588	−0.767650	93.0	2.568
5	−0.768336	92.7	2.637	−0.767657	93.0	2.588
6	−0.768488	92.7	2.667	−0.767658	93.0	2.601
7	−0.768563	92.8	2.686	−0.767568	93.0	2.609

[a] Energy relative to −1507

[b] Percent of reference in final wave function

convergence of the NO iteration procedure for the CAS4 and CAS(4*p*) choices of the active space. One additional valence occupation was added to the reference list after the first natural orbital iteration, since it had a coefficient larger than 0.05 in the MRCI wave function. The NO iterations increase the dipole moment, resulting in converged values that are nearly the same for both active spaces, although both are slightly larger than experiment.

In Table 3 we summarize the results of NO iterations based on the ACPF(4*p*) wave function. In the first series of calculations, configurations found to be important for a given NO iteration were added to the reference list for all subsequent NO iterations. This procedure results in a slowly convergent and oscillating dipole moment, which is probably a manifestation of the tendency of the ACPF method to give too much weight to the external space and hence overshoot the correct result when the reference list is deficient. Thus a second series of NO iterations was performed using the final reference list from the first series. In this case convergence is much better and NO iterations change the dipole moment only slightly, unlike when NO iterations are based on MRCI wave functions. The converged value is in excellent agreement with experiment.

In Table 4 we summarize our study of the dipole moment of NiH as a function of the level of correlation treatment at $r = 2.7\,a_0$. The MRCI(4*p*) dipole moment computed using the finite-field approach is more than 1 D larger than the value computed as an expectation value, and 0.4 D larger than the converged INO-MRCI

Table 3. The effect of ACPF(4*p*) NO iterations on the properties of NiH

Iteration	Energy (E_h)[a]	Ref%[b]	Dipole (D)
ACPF with variable reference list			
0	−0.797531	85.8	2.486
1	−0.798829	87.6	2.077
2	−0.798429	88.4	2.869
3	−0.799584	84.4	1.513
4	−0.798827	87.8	2.662
5	−0.797972	88.4	2.002
6	−0.797699	89.4	2.539
7	−0.797475	89.7	2.225
8	−0.797336	89.9	2.511
9	−0.797330	89.9	2.287
10	−0.797279	90.0	2.483
11	−0.797280	90.0	2.320
ACPF with full reference list			
0	−0.797531	85.8	2.486
1	−0.797782	88.9	2.162
2	−0.798015	89.7	2.491
3	−0.797707	90.0	2.376
4	−0.797601	89.9	2.441
5	−0.797535	90.0	2.406
6	−0.797507	90.0	2.415
7	−0.797457	90.0	2.410
8	−0.797429	90.0	2.405

[a] Energy relative to −1507

[b] Percent of reference in final wave function

Table 4. Summary of NiH dipole moments at $r = 2.7\ a_0$

Method	Dipole (D)
CAS4	2.170
MRCI4(0.05)	2.229
ACPF4(0.05)	2.491
INO-MRCI4	2.61
CAS5	0.973
MRCI5(0.05)	1.863
ACPF5(0.05)	2.547
CAS($4p$)	1.165
MRCI($4p$)(0.05)	1.827
MRCI($4p$)(0.05) field	3.098
MRCI($4p$)(0.05) + Q field	3.051
INO-MRCI($4p$)	2.69
ACPF($4p$)(0.05)	2.486
ACPF($4p$)(0.05) field	2.663
INO-ACPF($4p$)(0.05)	2.41
MRCI($4p$)(0.025)	1.802
ACPF($4p$)(0.025)	2.453
MRCI($4p$)(0.01)	2.045
ACPF($4p$)(0.01)	2.431
CAS($3d - 3d'$)	3.110
MRCI($3d - 3d'$)(0.05)	2.999
MRCI($3d - 3d'$)(0.05) field	2.836
MRCI($3d - 3d'$)(0.05) + Q field	2.678
ACPF($3d - 3d'$)(0.05)	2.337
ACPF($3d - 3d'$)(0.05) field	2.583
MRCI($3d - 3d'$)(0.025)	2.900
ACPF($3d - 3d'$)(0.025)	2.471

value. Adding the +Q correction reduces the dipole moment only slightly. The finite-field results are not in much better agreement with experiment than the expectation values. The poor response in the field is probably a consequence of the fact that the MRCI method does not correctly balance the $3d^84s^2$ and $3d^94s^1$ components to the bonding. This is consistent with our observation that the finite-field approach becomes better when the bonding description is improved by including $3d - 3d'$ correlation. The MRCI($3d - 3d'$) finite-field value is in better agreement with experiment than the expectation value, and the +Q correction improves the dipole moment even further, yielding a value in good agreement with the INO value based on the MRCI($4p$) treatment. The ACPF($4p$) finite-field value is 0.2 D larger than the ACPF expectation value. Even the ACPF finite-field value is improved when based on the CAS($3d - 3d'$) active space, and is in better agreement with the ACPF expectation values. At the ACPF level, μ computed as an expectation value, with finite-field methods, and with NO iterations varies by only 0.25 D.

In Table 5 we compare the original and Siegbahn's modification of the ACPF method using the CAS($4p$) zeroth-order reference wave function. Using a 0.05 threshold the original ACPF method yields a dipole moment that is too large, and has three important valence occupations in the final wave function. The modified ACPF

Table 5. Comparison of the modified and original ACPF(4*p*) treatments for the $X^2\Delta$ state dipole moment (D) of NiH at $r = 2.7\ a_0$

	MRCI	ACPF (original)	ACPF (modified)
0.05 from CASSCF	1.827	2.992	2.130
0.05 plus 3 ref from ACPF (original)	2.037	2.485	2.457
0.025 from CASSCF	1.802	2.757	2.098
0.025 plus 2 ref from ACPF (original)	1.989	2.453	2.423
0.01 from CASSCF	2.045	2.431	2.524

μ value is better than the MRCI value, but is still smaller than experiment. However, the modified ACPF and MRCI approaches have no important CSFs in the final wave function that are outside the reference space. If the three additional occupations from the original ACPF wave function are added to the reference space, both formulations yield essentially the same dipole moment, but the MRCI value is still too small. If the reference selection threshold is reduced to 0.025, the original ACPF result is improved, but the modified ACPF and MRCI values are essentially unchanged. Again adding the additional references changes the dipole moment in both ACPF formulations, bringing them into agreement. At a threshold of 0.01, there are no important CSFs in the ACPF wave function outside the reference space, and the two ACPF formulations are in good agreement. Thus, although the modified ACPF approach is superior to the MRCI, it does not identify missing correlation effects as does the original ACPF formulation. Since it is less expensive to perform the original ACPF(0.05) calculation including the additional references, than to converge the modified ACPF with respect to selection threshold, the original formulation would appear to be superior for the calculation of properties.

In summary, for NiH we find that while the INO-MRCI method performs relatively well, the MRCI finite-field approach yields a μ value for NiH that is significantly too large unless an extended CASSCF active space is employed. The ACPF method is capable of identifying additional important configurations that must be added to the reference space. When these are added to the reference space, the ACPF method yields essentially the same result for the four different choices of the CASSCF active space, regardless of whether μ is evaluated as an expectation value or using finite-field methods. In addition, natural-orbital iterations do not significantly change the expectation value. As all of these ACPF results are in good agreement with experiment, this method is preferred, since the cost of the calculation, even with the larger expansion, is less expensive than the INO-MRCI procedure.

Up to this point we have neglected relativistic effects. While the ANO basis set used should yield an accurate description of correlation effects, it is over-contracted for including relativistic effects by perturbation theory. Furthermore, relativistic effects tend to increase the bias towards the $3d^84s^2$ occupation. Marian et al. obtained good agreement for the relativistic contributions from a variational (no pair) and perturbation theory approach. Their results indicated that relativistic effects reduced r_e by 0.03 a_0, increased ω_e by 60 cm^{-1} and reduced μ by 0.3 D. Our best values, taken as the ACPF($3d-3d'$), differ from experiment in absolute magnitude by 0.01 a_0, 54 cm^{-1} and 0.1 D. Thus, to within the accuracy of the calculations, we agree with the relativistic contributions deduced by Marian et al. However, the relativistic contribution to the dipole moment of 0.3 D may be too large, because of the increased bias that relativistic effects introduce towards the $3d^84s^2$ occupation.

3.2. TiO

In this section we consider the dipole moment of the $X^3\Delta$ state of TiO, since an accurate experimental value of 2.96 ± 0.05 has recently been determined using the technique of intermodulated fluorescence spectroscopy in conjunction with the Stark effect [9]. For our multireference treatments of TiO we determine the molecular orbitals using a CASSCF active space consisting of the Ti 4*s* and 3*d* orbitals and the O 2*p* orbital. Note, unlike NiH, addition of the $4p\sigma$ orbital is not required as there are three σ electrons and three σ orbitals with this choice of the active space. The Ti 4*s* and 3*d* electrons and O 2*p* electrons are always correlated. The O 2*s* orbital is rather atomic-like and the electron affinity of O is better described when the 2*s* electrons are not correlated, except when very high levels of correlation treatment are employed [27]. Therefore calculations have been performed both with and without O 2*s* correlation. When we include O 2*s* correlation, we have a 10-electron treatment, which we denote as MRCI(2*s*). With a reference selection threshold of 0.05, there are seven reference occupations. For the ACPF and ACPF(2*s*) treatments, four additional occupations must be added to the reference space to have all valence configurations with coefficients greater than 0.05 in the final wave function included in the reference space. Note, like NiH, there is one non-valence configuration with a coefficient greater than 0.05 in the final ACPF wave function that is not included in the reference space.

The spectroscopic constants, dipole moments, and dipole derivatives for the $X^3\Delta$ state of TiO at various levels of correlation treatment are summarized in Table 6. All methods give r_e and ω_e values in good agreement with experiment [28], in contrast to NiH. This is due to the fact that there are no qualitative changes in the bonding between the CASSCF and MRCI approaches: the CASSCF, MRCI, and ACPF 3*d* populations and net charges on Ti agree to within 0.04 electrons. The dipole moment and dipole derivative of TiO also vary less than for NiH. At the MRCI level

Table 6. Summary of the spectroscopic constants and dipole moments for the $X^3\Delta$ state of TiO

Calculation	r_e (a_0)	ω_e (cm^{-1})	μ_e^a (D)	$d\mu_e/dr^a$ (D/a_0)
CASSCF	3.069	1028	2.724	3.742
MRCI	3.082	1004	3.072	3.455
MRCI + Q	3.096	979		
ACPF	3.092	986	3.412	3.468
MRCI(2*s*)	3.085	1008	2.931	3.484
MRCI + Q(2*s*)	3.104	976		
ACPF(2*s*)	3.102	977	3.486	3.419
CPF(2*s*)	3.083	998	2.690	2.585
MCPF(2*s*)	3.083	1003	2.623	2.583
Basis set for 3*s*3*p* correlation				
CPF(2*s*)	3.077	998	2.793	2.599
MCPF(2*s*)	3.077	1003	2.728	2.574
CPF(3*s*3*p*)	3.098	922	2.863	2.015
MCPF(3*s*3*p*)	3.085	963	2.665	1.882
Expt.	3.062[b]	1009[b]	2.96 ± 0.05[c]	

[a] Evaluated at the computed r_e value for each method

[b] Huber and Herzberg [28]

[c] Steimle et al. [9]

correlating the O 2*s* reduces the dipole moment slightly, but the opposite is true at the ACPF level. The CPF(2*s*) and MCPF(2*s*) methods yield a smaller dipole moment, in fact smaller than the CASSCF; the CPF(2*s*) and MCPF(2*s*) results are about as much smaller than experiment as the MRCI and ACPF methods are larger. All of the treatments yield a large dipole derivative as expected for this ionic system.

Since 3*s*3*p* correlation affects the separations of the Ti atomic states [29], we have considered the effect of this correlation on the dipole moment. To study the effect of 3*s*3*p* correlation, we used the larger ANO basis developed specifically to account for inner-shell correlation. Since the MRCI expansions are prohibitively large when 18 electrons are correlated, we have considered the effect of inner-shell correlation using the CPF and MCPF approaches. Repeating the CPF(2*s*) and MCPF(2*s*) treatments in the second ANO basis set results in about a 0.1 D increase in the dipole moment. Since there is more correlation in the eight 3*s* and 3*p* electrons than in the four 3*d* and 4*s* electrons, the larger ANO basis set appears to be slightly biased in favor of 3*s* and 3*p* correlation, even though it contains more contracted functions. However, the 0.1 D difference between basis sets is sufficiently small, and the agreement between the CPF and MRCI methods is sufficiently good, that the CPF approach should accurately reflect the importance of inner-shell correlation, which reduces the dipole moment by only 0.06 D at both the CPF and MCPF levels of treatment. Thus we conclude that inner-shell correlation does not contribute significantly to the dipole moment of TiO.

In Table 7 we show the effect of NO iterations on the dipole moment of TiO. Given the small difference between the CASSCF and MRCI results, it is not surprising that NO iterations have only a small effect on the dipole moment. However, NO iterations increase μ, thereby increasing the disagreement with experiment.

In Table 8 we summarize the dipole moment at 3.1 a_0 at the various levels of theory used. The MRCI, MRCI + Q and ACPF results computed using the finite-field method are similar to the ACPF and INO-MRCI approaches. TiO thus differs from NiH in this respect. We also note that the SCF value is much too large as expected, whereas the CPF and MCPF μ values are both too small.

Also summarized in Table 8 are the results of expanding the one-particle basis. Uncontracting the outermost *s*, *p*, *d*, and *f* primitive functions on Ti or the outermost *s*, *p*, and *d* primitive functions on oxygen changes μ only slightly. Finally, reducing the selection threshold in the CASSCF-based calculation also has little effect on μ.

Table 7. TiO NO iterations

Iteration	Without oxygen 2*s* correlation			With oxygen 2*s* correlation		
	Energy (E_h)[a]	Ref%[b]	Dipole (D)	Energy (E_h)[a]	Ref%[b]	Dipole (D)
0	−0.582712	94.5	3.134	−0.670696	93.1	2.983
1	−0.583035	94.6	3.250	−0.670992	93.2	3.073
2	−0.583034	94.6	3.316	−0.670995	93.1	3.145
3	−0.583029	94.6	3.352	−0.670996	93.1	3.196
4	−0.583024	94.6	3.369	−0.670995	93.1	3.232
5	−0.583022	94.6	3.379	−0.670992	93.1	3.255
6	−0.583021	94.6	3.384	−0.670986	93.1	3.282
7				−0.670985	93.1	3.289

[a] Energy relative to −923

[b] Percent of reference in final wave function

Table 8. Summary of TiO dipole moment (D) at $r = 3.10\ a_0$

CASSCF	2.839
MRCI	3.134
MRCI + Ti(*spdf*)	3.118
MRCI + Ti(*spdf*)(0.02)	3.122
MRCI + Ti(*spdf*) + O(*spd*)	3.119
INO-MRCI	3.38
ACPF	3.440
MRCI-field	3.360
MRCI + Q-field	3.360
ACPF-field	3.389
MRCI(2*s*)	3.134
INO-MRCI(2*s*)	3.29
ACPF(2*s*)	3.479
CAS($3d - 3d'$)	2.780
MRCI($3d - 3d'$)(0.025)	3.118
ACPF($3d - 3d'$)(0.025)	3.430
MRCI($3d - 3d'$)(0.025)(2*s*)	3.000
ACPF($3d - 3d'$)(0.025)(2*s*)	3.510
MRCI($3d - 3d'$)(0.01)	3.401
SCF	4.441
CPF(2*s*)	2.733
MCPF(2*s*)	2.667
Basis set for 3*s*3*p* correlation	
SCF	4.566
CPF(2*s*)	2.851
MCPF(2*s*)	2.787
CPF(3*s*3*p*)	2.867
MCPF(3*s*3*p*)	2.692

Since the inclusion of $3d - 3d'$ correlation into the CASSCF significantly improved the zeroth-order description of the dipole moment of NiH, we considered its inclusion for TiO as well. However, as can be seen from Table 8, it has a much smaller effect in this case, probably because of the much smaller number of 3*d* electrons. Our best ACPF dipole moment is about 3.48 D, obtained by subtracting 0.03 D from the ACPF($3d - 3d'$)(0.025)(2*s*) value to correct for improving the reference selection from 0.025 to 0.01. As the current CI expansions are approaching three million CSFs, larger ACPF calculations are not possible with the present implementation of the codes and existing hardware. Thus our best ACPF dipole moment is slightly larger than all of the MRCI calculations, even those including NO iterations.

As the INO-MRCI, ACPF and MRCI finite-field methods all yield similar dipole moments, our best estimate including only valence correlation is 3.4 D. Since 3*s*3*p* correlation should reduce this value by up to 0.1 D, our best theoretical estimate for μ is about 0.3–0.4 D larger than the experimental value [9] of 2.96 ± 0.05 D. Although this discrepancy is difficult to rationalize in terms of limitations of the theoretical calculations, if the experimental value is correct to within the stated error bars, then it may be that the effect of core-valence correlation is underestimated in the present study.

3.3. FeO

The μ value for the $X^5\Delta_2$ state of FeO has been measured as 4.7 ± 0.2 D from an analysis of the Stark shift in the orange band system ($(2)^5\Delta - X^5\Delta$) [11]. None of the previous theoretical values [30–33], which range from 2.5 to 7.4 D, agree well with this experimental value. Thus we have studied this system using the single reference SCF/MCPF method as well as the multireference INO-MRCI and ACPF methods.

For the multireference treatments, two CASSCF active spaces were used. The first active space contains three σ, three π, and one δ orbital (denoted as CAS11, since there are eleven active orbitals). This active space is derived from the Fe $3d$ and $4s$ orbitals, the oxygen $2p$ orbital and a third π orbital, which is primarily a correlating orbital for the oxygen $2p\pi$ orbital with some Fe $4p\pi$ character mixed in. Thus this active space allows for a good description of the FeO bond, but does not include any of the $d \rightarrow d'$ Fe atomic correlation. The reference list for the MRCI calculation included eight occupations, most of which involve promotion of one or two electrons from the σ bonding to antibonding orbital. The twelve electrons in the Fe $3d$ and $4s$ orbitals and the O $2p$ orbitals were correlated, resulting in an expansion of 1.92 million CSFs. The oxygen $2s$ electrons are essentially atomic like and therefore correlation of these electrons is not expected to significantly change μ. Also, in analogy with TiO, inner-shell correlation is expected to have little effect, and thus was not considered for FeO.

In the second treatment, we attempted to include the dominant effects of $3d - 3d'$ correlation on the orbital optimization by adding the $3d'$ shell to the CASSCF active space subject to the following restrictions:

$$(3d\sigma 3d\sigma' 4s 2p\sigma)^3 (3d\pi_x 2p\pi_x (3d\pi'_x + 2p\pi'_x))^3$$

$$(3d\pi_y 2p\pi_y (3d\pi'_y + 2p\pi'_y))^3 (3d\delta_{x^2-y^2} 3d\delta'_{x^2-y^2})^1 (3d\delta_{xy} 3d\delta'_{xy})^2.$$

We denote this as CAS($3d - 3d'$). In addition to the restrictions on the spatial distribution, some constraints are made on the spin coupling in each subset. As in the CAS11-based calculations, only twelve electrons are correlated in the MRCI and ACPF calculations. To make the ACPF calculations tractable, the eight σ, five π, four δ and two ϕ orbitals with the highest orbital energies in the average Fock operator [34] were deleted.

The spectroscopic constants at the CAS11 and MRCI11(+Q) levels for the $X^5\Delta$ state of FeO are compared with experiment in Table 9. The bond length is too long

Table 9. Spectroscopic constants for the $X^5\Delta$ state of FeO[a]

Calculation	r_e (a_0)	ω_e (cm^{-1})	μ_e (D)	$d\mu_e/dr$ (D/a_0)
CAS11	3.202	677	4.675	2.738
MRCI11	3.090	819	4.523	3.816
MRCI11 + Q	3.089	854		
Expt	3.055[b]	880.4[b]	4.7 ± 0.2[c]	

[a] Evaluated at the computed r_e value for each method

[b] [28]

[c] [11]

and ω_e is too small at the CASSCF level, because the antibonding character in the wave function is overemphasized. The spectroscopic constants are much improved at the MRCI and MRCI + Q levels. The dipole moments (at the computed r_e value) are slightly less than the experimental value. The CASSCF value is less than the MRCI value because of the large difference in r_e values and steep slope of the dipole moment function. At 3.1 a_0 the MRCI value is about 0.2 D larger than the CASSCF value (see Table 10).

One potential limitation of the MRCI calculation arises from the selection of reference occupations, since a 0.05 selection threshold gives a reference energy that is significantly above the CASSCF. We can ensure that the valence energy is equal to the CASSCF energy and that the most important external correlation effects are also included by forming the union of the CASSCF and MRCI CSFs. However, this does not significantly affect the dipole moment based on the MRCI11 or MRCI($3d-3d'$) calculations for either TiO or FeO. Therefore, it is probable that these extra CSFs will not affect properties of other systems.

At the SCF level the molecule is much too ionic, having a charge in excess of one on Fe and a dipole moment at 3.1 a_0 of about 9.1 D. The dipole moment at the MCPF level is, however, again less than the experimental value. The poorer performance of single reference-based approaches for FeO is due to the fact that the SCF is a poor zeroth-order description of the molecule.

Table 10. Summary of the FeO dipole moments at $r = 3.10\, a_0^{a}$

	Energy (E_h)	Dipole (D)	
CAS11	−1337.384192	4.357	
MRCI11(field)	···	5.525	
MRCI11 + Q (field)	···	5.857	
ACPF11[b]	−1337.605526	5.475	
CAS($3d-3d'$)	−1337.429328	5.445	
MRCI($3d-3d'$)[b]	−1337.569326	5.073	
ACPF($3d-3d'$)[b]	−1337.60399	5.04	
SCF	−1337.237068	9.088	
MCPF	−1337.665507	4.271	
MRCI NO iterations iteration	Energy	Dipole	Ref%[c]
0 (MRCI11)	−1337.640637	4.562	89.83
1	−1337.641685	4.740	90.73
2	−1337.641728	4.891	90.84
3	−1337.641685	5.003	90.84
4	−1337.641631	5.082	90.82
5	−1337.641582	5.137	90.80
6	−1337.641542	5.175	90.78
7	−1337.641511	5.201	90.77
Expt		4.7 ± 0.2[d]	

[a] Field values are ±0.002 a.u.
[b] Truncated virtual space used
[c] Percent of reference in final wave function
[d] [11]

The results of natural orbital iterations based on MRCI wave functions are given in Table 10. In the INO procedure an additional configuration occurs in the MRCI wave function with a coefficient slightly larger than 0.05. Although this configuration was not added to the reference list, the dipole moment is not expected to be significantly altered by its exclusion. The dipole moment increases monotonically with natural orbital iteration, as observed for NiH and TiO. The converged value is in excess of 5.2 D. Thus even allowing for the fact that the value at r_e should be at least 0.1 D less than at 3.1 a_0, the theoretical value is larger than experiment. The discrepancy with experiment is even larger when the MRCI μ is evaluated with finite-field methods. Also the +Q correction suggests that higher excitations further increase μ. Thus while the values of μ are smaller than experiment at the CASSCF, MCPF, and MRCI levels (evaluated as an expectation value), the values at the INO-MRCI, and MRCI (finite field) levels are larger than experiment. This is completely analogous to the results for TiO.

Considering the success of the ACPF method for the NiH and TiO molecules, we also attempted ACPF calculations for FeO. However, the reference space comprised only a very small percentage of the final ACPF wave function when based on the CAS11 reference list. The process of adding configurations outside the reference space that were important in the ACPF wave function and redoing the ACPF calculation was repeated five times until the ACPF wave function did not contain any valence configurations with coefficients larger than 0.05. The resulting 40 reference occupations generated about 2.5 million CSFs even using the truncated virtual space. This calculation yields a dipole moment of 5.48 D and the reference comprised 81% of the ACPF wave function.

Based on the configurations added to the original CASSCF list, a deficiency in the σ space was identified, as manifested by the fact that the CASSCF and ACPF natural orbitals were very different. These orbital differences were significantly reduced when four π orbitals were excluded from the correlation treatment. Thus the deficiency in the σ space appears to be amplified by a coupling between the σ and π spaces. Since the NiH wave function was substantially improved by adding $3d-3d'$ correlation, we carried out the comparable CAS($3d-3d'$) calculation for FeO. This improves the σ active space as a result of the addition of a $3d\sigma$ correlating orbital. Inclusion of $3d-3d'$ correlation substantially increases μ at the CASSCF level—see Table 10. The ACPF treatment based on this CASSCF was stable, and after several cycles no valence configurations appear in the final wave function with a coefficient greater than 0.05. At this level, the dipole moment is 5.05 D, which is in reasonable agreement with experiment. Unfortunately, even this ACPF calculation is not ideal, as the reference comprises still only 82.9% of the wave function. The most important additional configurations involve a π orbital that is predominantly of Fe $4p$ character. However, it is not computationally feasible to add this orbital to the active space.

It is disappointing that the dipole moments from the two ACPF calculations differ by 0.4 D, even though the reference percentages are similar (81% vs 83%). However, the severe problems in generating the reference list for the ACPF11 calculation, and the large changes between the CAS11 orbitals and the ACPF11 natural orbitals suggest that the CAS11 is a much poorer starting point than CAS($3d-3d'$). The FeO calculations show that the zeroth-order wave function must contain the most important correlation effects for the ACPF method to succeed. Because of the factorial growth of the CASSCF CI expansion with number of electrons and orbitals, in some cases it is difficult to generate a suitable set of molecular orbitals for the ACPF. Thus MCSCF approaches that reduce the number of CSFs and therefore include more orbitals in the active space might be a better starting point for an ACPF treatment.

4. Conclusions

We have explored the effectiveness of various *n*-particle treatments in determining accurate dipole moments for the $X^2\Delta$ state of NiH, the $X^3\Delta$ state of TiO, and the $X^5\Delta$ state of FeO. The dipole moments provide an excellent diagnostic of the wave function, since they are sensitive to the degree of mixing of the different metal-atom asymptotes. The multireference methods that appear to be most reliable are the INO-MRCI and ACPF methods. However, considering the slow convergence of the INO-MRCI procedure, the ACPF method would appear to be more cost-effective. However, the larger reference lists required with the ACPF method can lead to extremely large calculations. Since the number of references required for a stable ACPF calculation depends on the CASSCF zeroth-order reference, it may be worthwhile considering alternative forms of MCSCF as a starting point for the ACPF calculation. Our best results for NiH are in excellent agreement with experiment, but the corresponding results for TiO and FeO are about 10%–15% larger than experiment.

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