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Atomic natural orbital basis sets for transition metals

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Summary. We show that atomic natural orbitals are an excellent way to contract transition-metal basis sets, even though the different low-lying electronic states may have very different basis set requirements.

Key words: Natural orbitals – Atomic NOs – Transition-metal basis sets

1 Introduction

Natural spin orbitals, the eigenfunctions of the one-electron density operator, and the corresponding natural orbitals (NOs), obtained from the spin-averaged density, were introduced by Löwdin in 1955 [1]. Since the determination of NOs from configuration interaction (CI) wave functions requires very little time, it is common to obtain the NOs to help interpret the nature of the bonding in molecules. In addition, as addressed by Löwdin, the NOs provide a more rapidly convergent CI expansion, under certain circumstances, than other sets of orbitals. That is, truncation of the NO set used to expand the CI wave function leads to smaller errors than truncation of other molecular orbital (MO) sets, such as self-consistent field (SCF) MOs, for example [2]. While this observation is most pertinent to the two-electron case, many-electron systems show the same advantageous convergence of NO-based expansions in practice. We note that associated with each NO is an *occupation number* that is a direct measure of its importance in the density. The natural orbital occupation numbers thus supply a guide to the contribution of a given NO to the CI wave function, providing a convenient truncation mechanism: eliminating NOs with the smallest occupation numbers. This approach converges much better than, say, truncating an SCF MO space by eliminating orbitals on the basis of their orbital energy, and is simply a result of the NOs being determined for the correlation problem that is being solved, while the SCF orbitals are optimized for a different problem.

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NO expansions were commonly used for truncating the orbital space in conventional CI calculations. For example, NOs could be obtained for a CI calculation using all the SCF MOs, but with a limited set of reference configurations. Then a CI calculation with a larger set of reference configurations, but using a truncated set of the NOs, was performed [2]. While this approach works well, it still requires the SCF and initial CI calculations to be performed in the full basis set. If accurate results were desired, large atomic basis sets would be necessary, and hence the SCF and initial CI calculations would be rather expensive. However, the convergence properties of the NOs can provide a solution to this problem as well. If the NOs from an atomic calculation, *atomic natural orbitals* (ANOs), are used to contract a set of primitive Gaussian functions, instead of the more conventional atomic SCF-based schemes, a compact contracted basis can be generated for each atom [3]. Using these ANOs in the molecular calculation results in less computational effort, since the basis sets are optimized with the correlation problem in mind. Hence the requirement of performing an initial CI calculation, to determine the optimal basis set for the accurate CI calculation, can be avoided. In addition, since the contraction is performed as the first step, very large, nearly complete, primitive basis sets can be used. Experience has shown that this is indeed an excellent way to contract basis sets [4, 5].

One limitation of the ANO approach is that the contraction is based only on the correlation energy. Some one-electron properties require additional flexibility in the outer regions of the wave function and therefore it is often desirable to uncontract the outermost primitive functions [6–8]. Another problem arises where several atomic or ionic states of different character make similar contributions to the molecular wave function. If basis set contraction is performed for a single state of the atom, the ANO basis set may be biased towards that state. One way of reducing this bias is to obtain the ANOs from an average over several states. For example, in ionic halide compounds the halogen basis could be obtained by averaging over the neutral and negative ion ground states [9]. This approach has been generalized by Widmark and co-workers to include averaging over atomic states perturbed by an applied electric field as well as various neutral, cationic and anionic states [10, 11]. Perhaps the most challenging application of techniques of this sort is to the determination of transition metal ANO basis sets, since here different electronic states have very different orbital character [12].

In the next section we discuss some general aspects of our computational methodology, including the density matrix averaging procedure. In Sect. 3 we present results for the nickel atom, and in Sect. 4 results for titanium and the molecule TiH. Our conclusions are given in Sect. 5.

2 Methods

In this section we describe only those methodological considerations that are common to all the calculations presented in this work. Specific details of primitive basis sets and electronic structure methods are given in later sections.

Several different types of density matrix averaging are performed in this work, and we will distinguish between the approaches here. First, for degenerate states of atoms and molecules we apply an averaging procedure to all individual density matrices to ensure that the orbitals, at every stage of the calculation, display full symmetry and equivalence restrictions [13]. This corresponds to projecting out the totally symmetric component of the density matrix [14]. We will henceforth assume that this symmetrization is always performed, and will not discuss it further. More important here is the averaging of several density matrices, to obtain averaged natural orbitals as the eigenvectors of the resulting matrix. Since the primitive atomic basis is not orthonormal, it is necessary to express the matrices to be averaged in some common orthonormal basis. If a single SCF or complete-active-space SCF (CASSCF) calculation is performed initially and followed by different CI calculations on different electronic states, the CI density matrices can simply be expressed in the SCF or CASSCF orbital basis. By performing state-averaged SCF or CASSCF calculations a suitable common orbital set can be determined. However, in some cases it is necessary or desirable to perform independent SCF/CASSCF/CI calculations on the different states. In such cases we express the density matrices in the symmetrically orthonormalized atomic basis before averaging and diagonalizing. While it would be possible to weight the various density matrices used in the averaging differently, we have used equal weights throughout this work.

For systems as heavy as the first transition row, relativistic effects on energies and state separations are far from negligible. In this work we estimate these effects using first-order perturbation theory [15], identifying such results throughout as "corrected for relativity" and denoting the correction by +R.

All calculations reported here were performed with the MOLECULE-SWEDEN program system [16] on the CRAY Y-MP/864 at the NASA Ames Central Computing Facility.

3 Separations in Ni atom

The $^3F(3d^84s^2)$ and $^3D(3d^94s^1)$ states of Ni are very close (0.03 eV) in energy [17], and experience has shown that both can contribute to the bonding in the ground and low-lying states of molecules containing Ni. One example is NiH [18], where the bonding arises from a mixture of both atomic asymptotes. The experimental determination of the dipole moment of the ground state can be viewed as confirmation of this mixed character of the bonding – see the discussion in Ref. [18]. Even the $^1S(3d^{10})$ state, which lies 1.70 eV above the ground state, has been shown to contribute strongly to the bonding of Ni-containing compounds, especially those with dative bonding such as $Ni(CO)_4$ [19]. With differing numbers of $3d$ electrons, it is not surprising to find that the $3d$ orbitals in these states have different $\langle r \rangle$ values: 0.965, 1.050, and 1.169 a_0 for the ^3F, ^3D, and ^1S states, respectively. This difference in radial extent will naturally require different basis functions to describe the different states to equal accuracy [20]; treating these three states equivalently is important, because the bonding can arise from any of these three atomic states, or a combination of them. Also while a flexible basis set is required, it must still be compact enough for use in molecular calculations. In this work we focus on achieving the goal of treating the three states equivalently using a compact basis set. We compare the results in the contracted basis sets with those in the uncontracted basis set, not with experiment, because while our correlation treatments are expected to supply stringent tests of the basis set contraction, they are not sufficiently accurate to compare with experiment.

All of the contracted basis sets in this section are derived from the same $(20s\ 15p\ 10d\ 6f)$ primitive set [21], obtained as follows. To the $(20s\ 12p\ 9d)$ set optimized for the $^3F(3d^84s^2)$ state of Ni, three even-tempered p functions (extended outward from the outermost original p function with a ratio of 2.5) are added to describe the $4p$ orbital and for correlation of the $4s$ orbital. A diffuse even-tempered $3d$ function, obtained again by dividing the outermost original d exponent by 2.5, is added to improve the description of the $^3D(3d^94s^1)$ and $^1S(3d^{10})$ states. Six even-tempered f polarization functions, with exponents of the form 0.2024×2.5^n, for $n = 0$ to 5, are also added. The uncontracted basis set yields $^3D - {}^3F$ and $^1S - {}^3F$ separations that agree with numerical Hartree–Fock [22] to within 0.02 eV.

The first calculations use the uncontracted basis set, but orbitals determined from four different zero-order calculations. We optimize the orbitals for the ^3F state using the SCF and CASSCF approaches. The CASSCF has the $4s$ and $4p$ orbitals in the active space to account for the well-known near-degeneracy. The orbitals are optimized for the ^3D and ^1S states using only the SCF approach. Using these four sets of orbitals a CI calculation is performed; a single reference SDCI calculation for the ^3D and ^1S states and an MRCI calculation for the ^3F state. The four references in the MRCI correspond to the $3d^84s^2$ and three components of the $3d^84p^2$ occupations. These calculations are summarized in Table 1. The first set is for the case where each state is treated using the orbitals optimized for that state; these are clearly the best results for this level of theory. The second set of entries uses the orbitals from the SCF treatment of the ^3F state. The orbital bias is evident in the results. The separations are a factor of two too large. This is expected since the $\langle r \rangle$ values for the ^3F state is significantly

Table 1. Ni calculations using the full basis set. The MRCI treatment is used for the ^3F state, while the ^3D and ^1S states are treated using the SDCI approach – see the text

State	Energy (E_h)	Separation (eV)
Each state described with its own orbitals[a]		
$^3F(3d^84s^2)$	−1507.189 319	
$^3D(3d^94s^1)$	−1507.176 406	0.351
$^1S(3d^{10})$	−1507.091 797	2.654
The orbitals are taken from the SCF calculation for $^3F(3d^84s^2)$		
$^3F(3d^84s^2)$	−1507.179 012	
$^3D(3d^94s^1)$	−1507.151 211	0.757
$^1S(3d^{10})$	−1506.983 626	5.317
The orbitals are taken from the CASSCF calculation for $^3F(3d^84s^2)$		
$^3F(3d^84s^2)$	−1507.189 319	
$^3D(3d^94s^1)$	−1507.151 452	1.030
$^1S(3d^{10})$	−1506.982 743	5.621
The orbitals are taken from the SCF calculation for $^3D(3d^94s^1)$		
$^3F(3d^84s^2)$	−1507.142 122	
$^3D(3d^94s^1)$	−1507.176 406	−0.933
$^1S(3d^{10})$	−1507.057 381	2.306
The orbitals are taken from the SCF calculation for $^1S(3d^{10})$		
$^3F(3d^84s^2)$	−1507.012 871	
$^3D(3d^94s^1)$	−1507.101 495	−2.412
$^1S(3d^{10})$	−1507.091 797	−2.148

[a] The CASSCF orbitals are used for the ^3F state

smaller than for the other states. The ^1S state with the largest $\langle r \rangle$ value has a much larger error than the ^3D state. Using the CASSCF orbitals from the ^3F state does not significantly affect the results; as can be seen from the total energies, the biggest effect is to improve the description of ^3F state, rather than further degrade the ^3D or ^1S state. That is the CASSCF orbitals describe the $4s^2$ to $4p^2$ excitation better and hence lower the energy of the ^3F state rather than affecting the size of the $3d$ orbitals. Using the SCF orbitals from the ^3D state yields a $^3F - {}^1S$ separation in very good agreement with separate state optimizations, because it degrades the description of the ^3F and ^1S states equally. However, it results in a ^3D state that is significantly too low relative to the ^3F and ^1S states. Using the ^1S SCF orbitals is also clearly unacceptable; the ^3F state is the highest in energy rather than the lowest.

This series of calculations using the uncontracted basis set shows how the very different radial extents of the $3d$ orbitals can result in a strong bias against the other states. Because the uncontracted primitive basis is used, in the limit of a full CI the correlation treatment must eliminate the effects of this bias. However, a contraction scheme must not introduce any orbital bias into the contraction, because no level of correlation treatment will subsequently be able to overcome this bias.

The calculation of the polarizability of the ^3F state is summarized in Table 2. It is important to obtain an accurate polarizability to be able to describe the distortion that occurs in molecules. We consider only the ^3F state, but similar effects are expected for the ^3D state. We use only the SCF/SDCI treatment. The first entry in the table is for the uncontracted basis set. The first contraction is based on the NOs of the MRCI treatment of the ^3F state; the natural orbital occupation numbers are used to identify a $[6s\ 5p\ 3d\ 2f]$ set. The contracted basis set recovers 93.4% of the correlation energy from the full basis set, but only 71.5% and 75.3% of the polarizability at the SCF and CI levels, respectively. Uncontracting the outermost s and p primitives – denoted $(6+1)s$ and $(5+1)p$ – yields a significant improvement in the results. Adding an additional

Table 2. Calculation of the polarizability of the $^3F(3d^8 4s^2)$ state of Ni[a]

Contraction[b]	Basis[c]	Energy (E_h)		α (a_0^3)	
		SCF	CI	SCF	CI
uncontracted	$(20s\ 15p\ 10d\ 6f)$	−1506.873 290	−1507.180 768	64.62	52.08
^3F MRCI NOs	$[6s\ 5p\ 3d\ 2f]$	−1506.872 939	−1507.166 789	46.23	39.24
^3F MRCI NOs	$[(6+1)s\ (5+1)p\ 4d\ 2f]$	−1506.873 260	−1507.170 094	63.79	49.80
^3F MRCI NOs	$[(6+1)s\ (5+1)p\ 4d\ 3f]$	−1506.873 269	−1507.175 874	63.79	49.92
^3F MRCI NOs	$[(6+2)s\ (5+2)p\ 4d\ 2f]$	−1506.873 260	−1507.170 537	64.56	50.66
^3F MRCI NOs	$[(6+2)s\ (5+2)p\ (3+1)d\ 2f]$	−1506.873 216	−1507.168 024	64.50	51.48
^3F MRCI NOs	$[(6+2)s\ (5+2)p\ (4+1)d\ 2f]$	−1506.873 264	−1507.170 758	64.58	51.64
^3F MRCI NOs	$[(6+2)s\ (5+2)p\ (4+1)d\ 3f]$	−1506.873 273	−1507.176 658	64.59	51.74
Average NOs	$[6s\ 5p\ 4d\ 2f]$	−1506.873 128	−1507.168 320	41.27	36.75
Average NOs	$[(6+1)s\ (5+1)p\ 4d\ 2f]$	−1506.873 147	−1507.168 776	63.06	50.03

[a] The polarizability is computed for the $^3A_1[3d(\sigma)^1 3d(x^2-y^2)^1]$ component of the ^3F state using an SCF/SDCI approach

[b] Origin of the contraction coefficients

[c] All basis sets use the $(20s\ 15p\ 10d\ 6f)$ primitive set

contracted *f* function lowers the CI energy, but has only a small effect on α. Uncontracting a second *s* and *p* primitive makes only a small improvement.

Replacing the four $3d$ ANOs by the $(3+1)d$ set, in which the outermost *d* primitive is uncontracted, improves α, but the total energy at the CI level is significantly degraded. Uncontracting the outermost *d* primitive from the $4d$ set, i.e., forming the $(4+1)d$ set, improves the polarizability by somewhat more than the $(3+1)d$ set, and does so without the loss of correlation energy. Adding the third *f* ANO has the same small effect that was observed for the smaller contracted set.

Table 3. Comparison of total energies and separation for the ^3F, ^3D, and ^1S states for Ni as a function of method of contracting the basis set[a]

	Energy (E_h)		Separation (eV)[b]	
	SCF	CI	SCF	CI
Uncontracted basis set				
$^3F(3d^84s^2)$	−1506.908 118	−1507.189 319		
$^3D(3d^94s^1)$	−1506.823 313	−1507.176 406	2.308	0.351 (0.397)
$^1S(3d^{10})$	−1506.669 000	−1507.091 797	6.507	2.654 (0.597)
$[(6+1)s\ (5+1)p\ 4d\ 2f]$ from the CASSCF/MRCI $^3F(3d^84s^2)$ calculation				
$^3F(3d^84s^2)$	−1506.908 111	−1507.178 670		
$^3D(3d^94s^1)$	−1506.822 917	−1507.164 870	2.318	0.376
$^1S(3d^{10})$	−1506.661 504	−1507.071 546	6.711	0.915
$[(6+1)s\ (5+1)p\ 4d\ 2f]$ from the SCF/SDCI $^3F(3d^84s^2)$ calculation				
$^3F(3d^84s^2)$	−1506.908 088	−1507.178 363		
$^3D(3d^94s^1)$	−1506.823 058	−1507.164 937	2.314	0.365
$^1S(3d^{10})$	−1506.663 581	−1507.074 082	6.653	2.838
$[(6+1)s\ (5+1)p\ 4d\ 2f]$ from the SCF/SDCI $^3D(3d^94s^1)$ calculation				
$^3F(3d^84s^2)$	−1506.907 539	−1507.177 747		
$^3D(3d^94s^1)$	−1506.823 279	−1507.165 592	2.293	0.331
$^1S(3d^{10})$	−1506.666 630	−1507.078 036	6.556	2.713
$[(6+1)s\ (5+1)p\ 4d\ 2f]$ from the SCF/SDCI $^1S(3d^{10})$ calculation				
$^3F(3d^84s^2)$	−1506.885 045	−1507.156 254		
$^3D(3d^94s^1)$	−1506.815 160	−1507.157 142	1.902	−0.024
$^1S(3d^{10})$	−1506.668 877	−1507.082 629	5.882	2.003
$[(6+1)s\ (5+1)p\ 4d\ 2f]$ from the average of ^3F, ^3D and ^1S				
$^3F(3d^84s^2)$	−1506.907 896	−1507.177 175		
$^3D(3d^94s^1)$	−1506.823 226	−1507.164 583	2.304	0.343 (0.602)
$^1S(3d^{10})$	−1506.668 959	−1507.081 033	6.502	2.616 (1.044)
$[(6+2)s\ (5+2)p\ (4+1)d\ 2f]$ from the average of ^3F, ^3D and ^1S				
$^3F(3d^84s^2)$	−1506.908 048	−1507.178 510		
$^3D(3d^94s^1)$	−1506.823 285	−1507.165 665	2.307	0.350 (0.525)
$^1S(3d^{10})$	−1506.668 980	−1507.081 973	6.505	2.627 (0.903)
$[(4+3)s\ (2+4)p\ (1+4)d\ 3f]$ from the SCF for ^3D				
$^3F(3d^84s^2)$	−1506.908 057	−1507.174 933		
$^3D(3d^94s^1)$	−1506.823 231	−1507.162 227	2.308	0.346 (0.454)
$^1S(3d^{10})$	−1506.668 867	−1507.078 226	6.509	2.632 (0.713)

[a] For all basis sets, the CASSCF/MRCI treatment is used for the ^3F state, while the SCF/SDCI is used for the ^3D and ^1S states

[b] The values in parentheses are the relativistic contributions to the separation

Using the occupation numbers as a guide gives a [6*s* 5*p* 4*d* 2*f*] contracted set when an average of the ^3F, ^3D and ^1S states is used. It is probably not surprising that to account for the different size of the 3*d* orbitals, the average set has one more contracted *d* function than the NOs from the ^3F state. The polarizability using these average NOs is even worse than with those from the ^3F state. However, if the outermost *s* and *p* primitive functions are uncontracted, the polarizability is as accurate as that for the same sized set contracted based only on the ^3F state. Thus averaging has not adversely affected the flexibility of the basis set. Uncontracting additional diffuse functions for the average NOs will have a very similar effect to that found for the orbitals derived from the ^3F state.

In Table 3 we consider the separation between the three states using different sets of contracted orbitals. In all cases we uncontract at least one *s* and one *p* function, based on the results for α. The first set of entries is for the uncontracted basis set where each state is described in terms of its own orbitals. The next four sets use the MRCI and SDCI NOs from the ^3F state and the SDCI NOs from the ^3D and ^1S states for the contraction. As expected, using the NOs from one state degrades the description of the others; this is evident even at the SCF level. The average NOs result in separations that are in very good agreement with the uncontracted basis set. Uncontracting a second *s* and *p* primitive as well as one *d* primitive makes only a small change in the results. The last entry is a general contraction based on the SCF wave function for the ^3D state. While this basis set is larger than those using the average NOs, it yields less correlation energy. It does, however, produce separations that are in good agreement with the uncontracted results. Given that the SCF-based contraction results in a larger basis set, with results that are not superior to the average NOs, the average NOs appear to be a better approach here.

One additional aspect of basis set contraction that we consider is the relativistic contribution to the separation. This is also given in Table 3. The results in the [(6 + 1)*s* (5 + 1)*p* 4*d* 2*f*] average set are in poor agreement with the uncontracted basis set. Uncontracting an additional *s*, *p*, and *d* function improves the calculation of the relativistic contribution to the separation, but the agreement is still not acceptable. The SCF-based contraction is superior to either set of average NOs, but it still has an error of more than 0.1 eV for the $^3F - {}^1S$ separation. It is clear that an even more flexible contraction is required to compute this quantity accurately [23]. Unfortunately this results in basis sets that may be too large for molecular calculations. It is clear that more study is required on the contraction required to accurately compute the relativistic contribution, and caution will be necessary when estimating the +R correction.

4 Ti atom and TiH

Good performance of a basis set for atomic calculations is a necessary, but not sufficient, condition for good performance in molecular calculations. The spectroscopic constants and properties of the lowest $^4\Phi$ and $^2\Delta$ states of TiH provide a simple but comprehensive example of contraction for molecular calculations. It is convenient to illustrate some points using contraction results for Ti atom, and these are displayed in Table 4.

All calculations were performed using the same primitive atomic basis set. This is Partridge's (21*s* 13*p* 8*d*) set [21], augmented with three diffuse *p* functions, two diffuse *d* functions, and six *f* functions. The diffuse function exponents

Table 4. Ti atom MRCI calculations. Each state is individually optimized at the CASSCF/MRCI level

State	MRCI Energy (E_h)	MRCI + R Energy (E_h)	MRCI Separation (cm^{-1})	MRCI + R Separation (cm^{-1})
Uncontracted basis				
$^3F(3d^24s^2)$	−848.462 123	−852.760 480		
$^5F(3d^34s^1)$	−848.427 318	−852.720 303	7639	8818
$^5D(3d^4)$	−848.323 807	−852.613 838	30 357	32 184
[7*s* 6*p* 4*d* 2*f*] basis from the average of ^3F, ^5F, and ^5D				
$^3F(3d^24s^2)$	−848.461 550	−852.749 315		
$^5F(3d^34s^1)$	−848.426 135	−852.713 485	7773	7864
$^5D(3d^4)$	−848.316 285	−852.590 784	31 882	34 793
[(6 + 1)*s* (5 + 1)*p* (3 + 1)*d* 2*f*] basis from the average of ^3F and ^5F				
$^3F(3d^24s^2)$	−848.460 676	−852.748 152		
$^5F(3d^34s^1)$	−848.425 972	−852.706 987	7617	9035
$^5D(3d^4)$	−848.322 528	−852.597 188	30 320	33 133
[(5 + 1)*s* (4 + 1)*p* (2 + 1)*d* 1*f*] basis from the average of ^3F and ^5F				
$^3F(3d^24s^2)$	−848.455 492	−852.742 706		
$^5F(3d^34s^1)$	−848.418 503	−852.699 576	8118	9466
$^5D(3d^4)$	−848.316 553	−852.591 049	30 494	33 285

were obtained as an even-tempered extension from the smallest original exponent, with a successive ratio of 2.5. The f functions form an even-tempered sequence of the form 0.056×2.5^n, for $n = 0$ to 5. By extension from the Ni case, one contraction strategy would be to obtain averaged natural orbitals for the lowest states of the three occupations $3d^24s^2$, $3d^34s^1$, and $3d^4$, namely, ^3F, ^5F, and ^5D, respectively. The contraction errors for a [7*s* 6*p* 4*d* 2*f*] ANO set obtained this way are shown in Table 4. The wave functions are obtained from separate CASSCF and MRCI calculations on each electronic state. Four electrons are active in the CASSCF, and all CASSCF configurations are used as references in a four-electron MRCI calculation.

Clearly, the contraction procedure yields a very good description of the $3d^24s^2$ and $3d^34s^1$ occupations: the contraction errors in the total energy of the ^3F and ^5F states are around 1 mE_h. However, the contraction error in the ^5D state energy is almost an order of magnitude larger. This error is very evident in the MRCI energy differences given in the table. The $^3F - {}^5D$ separation is in error by more than 1000 cm^{-1}. While this error could be reduced by including more ANOs in the basis set, the resulting basis would become too large for convenient use in molecules. The problem is again that the d NOs for the $3d^4$ occupation are much more diffuse than for the other occupations, and the averaged orbitals are simply not diffuse enough. Further, the major correlation effect in the ^5D state is $3d - 3d'$ radial correlation, and hence the correlating d NOs for this state also need to be more diffuse. Diffuse p functions also contribute because of $3d^2 - 4p^2$ excitations.

Given the need to provide more flexibility for the diffuse part of the ^5D wave function, an alternative is again to uncontract the outermost primitive functions. When this is done there is no need to include the $3d^4$ occupation in the averaging, and the contraction coefficients can be obtained from an average over the ^3F and ^5F states only. Results are given for a $[(6+1)s\ (5+1)p\ (3+1)d\ 2f]$ basis obtained in this way. Inspection of the results of Table 4 reveals that this set provides a much more balanced description of the three occupations. The contraction errors in the total energy are somewhat larger than previously obtained for the ^3F and ^5F states, but much smaller for the ^5D state. The state separations are now in very good agreement with the uncontracted results. We can in fact delete the most weakly occupied ANO of each symmetry and still obtain fairly good energies from the resulting $[(5+1)s\ (4+1)p\ (2+1)d\ 1f]$ contracted basis.

Relativistic contributions to the total energies and state separations are also given in Table 4. As in the Ni case, the contraction error in this contribution is large for all of the contracted sets. The error is especially large for the orbitals obtained by averaging all three states, but none of the contracted sets produce a satisfactory result. It is again clear that more work is needed in how to generate contracted sets that satisfy our criteria for the nonrelativistic contraction errors and also yield acceptable relativistic corrections.

One other aspect of the Ti atom calculations may be of interest. In Table 5 we list results obtained by performing a state-averaged CASSCF calculation on the three electronic states of interest, and then MRCI calculations on these states. That is, all three states are expanded in the same set of CASSCF orbitals. This is generally a cheaper and simpler option than state-specific optimizations. As the table shows, the error in the CI state separations from the state-averaging varies somewhat from basis to basis: in effect, the contraction error observed is somewhat different when state-averaged CASSCF orbitals are used in the MRCI calculations. In general, the contraction errors are somewhat smaller, when comparing the state-averaged CASSCF-based calculations among themselves, than in the state-specific case. However, the differences in both total energies and state separations between these treatments are small.

Table 5. Ti atom MRCI calculations. Except as noted, a state-averaged CASSCF calculation is used to define orbitals for the MRCI calculations

State	MRCI Energy (E_h)	MRCI + R Energy (E_h)	MRCI Separation (cm^{-1})	MRCI + R Separation (cm^{-1})
Uncontracted basis, state-specific orbitals				
$^3F(3d^24s^2)$	−848.462 123	−852.760 480		
$^5F(3d^34s^1)$	−848.427 318	−852.720 303	7639	8818
$^5D(3d^4)$	−848.323 807	−852.613 838	30 357	32 184
Uncontracted basis				
$^3F(3d^24s^2)$	−848.457 180	−852.753 815		
$^5F(3d^34s^1)$	−848.425 888	−852.719 767	6868	7473
$^5D(3d^4)$	−848.322 904	−852.614 614	29 470	30 551
$[(6+1)s\ (5+1)p\ (3+1)d\ 2f]$ basis from the average of ^3F and ^5F				
$^3F(3d^24s^2)$	−848.455 787	−852.741 222		
$^5F(3d^34s^1)$	−848.424 571	−852.705 880	6851	7757
$^5D(3d^4)$	−848.321 740	−852.597 222	29 420	31 604
$[(5+1)s\ (4+1)p\ (2+1)d\ 1f]$ basis from the average of ^3F and ^5F				
$^3F(3d^24s^2)$	−848.450 364	−852.735 164		
$^5F(3d^34s^1)$	−848.417 152	−852.698 507	7289	8045
$^5D(3d^4)$	−848.316 535	−852.591 851	29 372	31 453

We now consider the $^4\Phi$ and $^2\Delta$ states of the molecule TiH. The contracted basis sets for Ti are based on averaging independent calculations for the ^3F and ^5F states, and uncontracting the outermost s, p, and d primitives, as described above. The H basis sets are contracted as described in Ref. [3]. The calculations were performed at $r_{\mathrm{TiH}} = 3.380\ a_0$ ($^4\Phi$) and $r_{\mathrm{TiH}} = 3.308\ a_0$ ($^2\Delta$). Total energies and selected one-electron properties for both states are given in Table 6. The electronic wave functions are obtained from independent CASSCF/MRCI calculations on each TiH state: there are five active electrons in the CASSCF calculations and the MRCI wave functions comprise all single and double excitations out of all CASSCF occupations, correlating the five valence electrons. The active orbital space for the $^4\Phi$ state is denoted (6221), since it includes 6 a_1, 2 b_2, 2 b_1, and 1 a_2 orbitals. A (5111) active space is used for the $^2\Delta$ state. The choice of active spaces is motivated by full CI benchmark calculations on this system, as described in detail by Bauschlicher [24]. The calculations were performed in C_{2v} symmetry, although full $C_{\infty v}$ symmetry and equivalence restriction were imposed on the MOs.

The contraction errors for the nonrelativistic energies are small for both states. More importantly, the *differential* contraction error for the two states is very small, even in the smaller contracted set. The MRCI state separation is

Table 6. TiH energies and properties[a]

	$^4\Phi$	$^2\Delta$
Uncontracted basis		
E_{CASSCF}[b]	−849.010 445	−848.980 892
E_{MRCI}	−849.043 976	−849.031 469
$E_{\mathrm{MRCI+R}}$	−853.340 918	−853.329 965
T_e (MRCI)		2745
T_e (MRCI + R)		2404
μ (MRCI)	−0.858	−0.598
Θ (MRCI)[c]	−5.618	−2.370
$[(6+1)s\ (5+1)p\ (3+1)d\ 2f/4s\ 3p\ 2d]$ basis		
E_{CASSCF}[b]	−849.010 014	−848.980 268
E_{MRCI}	−849.042 109	−849.029 294
$E_{\mathrm{MRCI+R}}$	−853.326 746	−853.317 980
T_e (MRCI)		2813
T_e (MRCI + R)		1924
μ (MRCI)	−0.860	−0.599
Θ (MRCI)[c]	−5.472	−2.264
$[(5+1)s\ (4+1)p\ (2+1)d\ 1f/3s\ 2p\ 1d]$ basis		
E_{CASSCF}[b]	−849.008 548	−848.979 457
E_{MRCI}	−849.035 480	−849.022 680
$E_{\mathrm{MRCI+R}}$	−853.319 909	−853.311 229
T_e (MRCI)		2809
T_e (MRCI + R)		1905
μ (MRCI)	−0.881	−0.636
Θ (MRCI)[c]	−5.253	−2.313

[a] Energies in E_h, T_e in cm^{-1}, μ and Θ in a.u.

[b] CASSCF active space is (6221) for $^4\Phi$ and (5111) for $^2\Delta$ (see text)

[c] Ti at origin

affected no more than 70 cm^{-1} by contraction, or about 2.5%. This is a very significant result, because, as discussed in detail in Ref. [24], the wave functions for the two states are very different: the $^4\Phi$ state arises from a mixture of the $3d^24s^2$ and $3d^34s^1$ atomic occupations, while $^2\Delta$ arises mainly from the former. Hence the contracted basis sets appear to be capable of representing the contributions of different atomic states to the molecular wave function very well. The contraction errors in the relativistic energy contributions are again very large – not a surprising result since this quantity will be dominated by the Ti contribution. Further, there is a large differential error in the relativistic energies, which could also be expected in light of the atomic results. Thus the poor prediction of the contribution of relativistic effects to the atomic state separations is also seen in the molecule.

The dipole moments of the $^4\Phi$ and $^2\Delta$ states are rather different, and this difference is predicted rather well by the larger contracted basis. The smaller basis yields a significantly larger contraction error for the $^2\Delta$ state than for the $^4\Phi$ state, and neither the absolute value of the dipole moments nor the difference between the two states is described well by this basis. The difference between the quadrupole moments of the two states (origin at Ti) is more than a factor of two, and is fairly well described by the larger contracted basis. However, a proper description of the quadrupole moment probably requires considerably more flexibility in the outermost region of the wave function than is available in the primitive set used here (see, e.g., Ref. [8]). Overall, the results show that the averaged ANOs provide a compact and effective basis set both for transition metal atom calculations and for calculations on molecules containing transition metals. This general approach has been used widely in our group for accurate calculations on transition-metal systems [4] (see also Refs. [25] and [26] and references therein).

5 Conclusions

The use of atomic natural orbitals obtained by averaging the one-particle density matrices over different transition-metal electronic states is shown to be a convenient route to compact, accurate transition-metal basis sets. It is possible to contract very large primitive sets to a manageable size in this way. Contraction errors in total energies, state separations, and atomic and molecular properties are all small. However, significant errors can arise in calculated relativistic energy contributions. This is not directly related to the use of ANOs, since atomic SCF-based general contractions also show the same phenomenon. Since simply uncontracting more primitives to try to correct this defect leads to basis sets that would be unmanageably large for most molecular calculations, the problem of reducing contraction error in the relativistic correction warrants further attention.

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