Calculation of hyperfine coupling constants of the ground state $X\ ^3\Sigma^-$ of NH and B_2

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Following a systematic examination of basis set and electron correlation effects, accurate hyperfine coupling constants have been determined for the $X\ ^3\Sigma^-$ states of NH and B_2 using the multiconfiguration self-consistent-field (MCSCF) restricted–unrestricted (RU) response function approach. These species were chosen for study because their unpaired electrons reside in π orbitals; so at the single configuration self-consistent-field (SCF) approach, they display zero hyperfine coupling constants. The approach advocated here has been tested successfully on σ-radical species with unpaired electrons occupying σ orbitals; this work represents the extension to π-radical species which are expected to be more difficult cases. In designing the atomic orbital basis sets, effects of uncontraction of the orbitals (to permit maximal flexibility especially in describing electron density near nuclei) and of addition of diffuse and tight functions were taken into account. Our final bases give hyperfine coupling constants that agree with numerical Hartree–Fock (HF) and with numerical complete active space valence (CASV) MCSCF results, which indicates that our basis sets are accurate enough to be used in further studies that treat electron correlation more accurately. For dealing with electron correlation in a manner that, based on our past experience, could provide the requisite over all accuracy in the final coupling constants, the CASV configuration spaces were systematically extended to larger CAS (complete active space) spaces using natural orbital occupation numbers to determine which orbitals to include in active spaces for each symmetry. Our final results compare favorably with the available experimental data. The results show that the hyperfine coupling constant for B in B_2 and N in NH results from a near cancellation of large and opposite signed core and valence contributions.

I. INTRODUCTION

The hyperfine coupling constant tensor (**A**) is related to the energy of interaction between the electron and nuclear spins, and can be written as the sum of an isotropic Fermi-contact (FC contribution) and an anisotropic spin-dipole term (SD contribution).[1] Its theoretical evaluation within conventional *ab initio* methods has proven to be quite difficult primarily because it depends on the unpaired electron density near nuclear centers. In either the restricted Hartree–Fock (RHF) or conventional multiconfiguration self-consistent-field (MCSCF) methods, the spin polarization of the electrons in the doubly occupied orbitals is ignored and reliable coupling constants are difficult to obtain because inner shell "core" orbitals are kept doubly occupied.[2] Moreover, methods as unrestricted Hartree–Fock (UHF) and single excitation configuration interaction CI (SECI) are known to overestimate the spin polarization of inner-shell orbitals, thus, producing hyperfine coupling constants that are unrealistically large.[3] The evaluation of hyperfine coupling constants is therefore very challenging for computational quantum chemistry, especially when the effect vanishes when treated at the single-configuration SCF level as for the ground electronic states of the π-orbital based radicals: $NH(^3\Sigma^-)$ and $B_2(^3\Sigma^-)$, we treat in this paper.

Experimentally, the NH has been studied, using laser magnetic resonance[4] and high-resolution–molecular beam-laser induced fluorescence spectroscopies.[5] Theoretical studies have been done by Chipman,[6] Bender and Davidson,[7] Engels and Peyerimhoff,[8] and Kristiansen and Veseth.[9] In general, the agreement between the calculated and the experimental results are good having errors in the computed values of, at most, a few percent.

The B_2 radical's hyperfine tensor is known to be highly anisotropic. When trapped in Ne and Ar matrices at 5 K, its hyperfine coupling constant has been determined by the Knight and Davidson groups who also carried out careful *ab initio* studies of this molecule.[10(a)] When judged against the experimental data, their calculations revealed that it is extremely difficult to calculate the hyperfine coupling constant correctly even when using large multireference single and double excitation configuration interaction (MR-SDCI) methods preceded by second-order perturbation

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theory screening of the energetically most important double excitations. These authors obtained qualitatively correct results for the anisotropic contribution, but the isotropic term proved very difficult to obtain even to within the proper sign. In their largest MR-SDCI calculation, the sign of the isotropic contribution was wrong and its magnitude only ca. 18% of the experimental value. Subsequent theoretical work by Feller and Davidson[10(b)] used larger MR-CI wave functions and improved the calculated isotropic term somewhat. However, even these calculations did not demonstrate convergence as functions of reference space size or configuration selection threshold [see Fig. 3 of Ref. 10(b)] and their best isotropic constant result was a factor of 3 smaller than the experimental result. Thus, the proper and efficient treatment of electron correlation as pertaining to hyperfine coupling constant calculation remains a difficult fundamental problem and one addressed here.

As our earlier work demonstrated,[11,12] the selection of a flexible atomic orbital basis set is decisive in performing reliable calculations of hyperfine coupling constants. Therefore, we began our investigation with a careful basis set study using SCF and complete active space (CAS) MCSCF wave function where all valence electrons are distributed among all valence orbitals in any manner consistent with overall spatial and spin symmetry. We denote this MCSCF CAS valence space as CASV. Our goal in this part of the study was to determine a basis set for which the SCF and CASV correlated results (i) compare well to the corresponding numerical-basis results and (ii) are stable to within a few MHz with respect to further improvement of the basis. Our bases were formed by starting with Dunning's correlation consistent basis sets,[13] performing systematic uncontractions of the contracted *s* and *p* orbitals, and augmenting the bases with diffuse and tight functions until saturation was achieved (see Sec. II for details).

Electron correlation was included in our calculations using the restricted–unrestricted (RU) approach of Fernández *et al.*[2] In this approach, we describe the molecular system in the absence of the Fermi-contact (FC) or spin-dipole (SD) operators with a conventional spin-restricted MCSCF wave function (either the CASV function or an extension to higher levels). In the presence of the FC or the SD operator, the wave function spin relaxes as a result of which the expressions of all first-order molecular properties acquire, in addition to the conventional average-value term, a so called relaxation term that includes the first-order response of the wave function to the FC or SD perturbations. The latter term does not vanish because the spin-restricted MCSCF wave function is not optimized with respect to the orbital spin relaxation parameters (see Sec. II for details).

In addition to computing the hyperfine tensor for NH and B_2 for bases and CAS spaces we judge adequate, we have once again tested the accuracy of the RU approach by carrying out FCI calculations on NH and using the resultant wave function to compute the hyperfine tensor. This allows us to demonstrate that by systematically extending the configuration space of the MCSCF calculation beyond the starting CASV space, we can obtain accurate results for NH and B_2 using this method.

The MCSCF RU method has previously been successfully benchmarked against full configuration interaction (FCI) results for BH_2 and the N atom,[2] and used to achieve accurate hyperfine coupling constants for $^2A_1$ B_3, (Ref. 11) $^2\Sigma^+$ CN and $^2\Sigma^+$ CP,[12] each of which had presented interesting challenges to experimentalists and theoreticians in this area.

In the following section, we briefly summarize our calculational procedure, including the RU approach, as well as, the methods for basis set construction and for configuration space choices. Section III describes the results of our calculations, and in Sec. IV, we give our concluding remarks.

II. CALCULATIONAL PROCEDURES

The hyperfine coupling tensors of the NH and B_2 radicals were evaluated subsequent to the systematic basis set and electron correlation study whose details are given later in this section. Denoting the isotropic part of the **A** tensor by a_{iso} times the unit tensor **I**, and the anisotropic by $\mathbf{A}^d$, we have

$$\mathbf{A}=a_{\text{iso}}\mathbf{I}+\mathbf{A}^d. \tag{1}$$

The principal values of the 3×3 **A** tensor are denoted A_x, A_y, and A_z. We chose to use local coordinate systems where the *z* axes pass through the two atoms pointing away from the center of mass. Given the equivalence in the perpendicular *x* and *y* directions and the fact that $\mathbf{A}^d$ is traceless, it follows that the principal-axis components of $\mathbf{A}^d$ obey: $A_z^d=-2A_x^d=-2A_y^d$. Hence, in specifying the computed results, it is usual to give values for a_{iso} and for $a_{\text{dip}}=-A_x^d$; the two remaining components of $\mathbf{A}^d$ are then determined by the above identities.

A. The restricted–unrestricted response function method

The RU approach[2] may be viewed as follows. In the absence of the FC or SD terms[1] in the electronic Hamiltonian, we assume that the system can be described with a spin-restricted MCSCF wave function denoted $|0^{(0)}\rangle$. In the presence of the FC and SD Hamiltonian terms, which are triplet tensor operators in spin space, the wave function spin relaxes which, thus, necessitates using a spin-unrestricted description. The total energy of the system in the presence of the FC and SD couplings is then expressed in terms of the spin-relaxed wave function denoted $|\tilde{0}\rangle$.

$$E(\alpha)=\langle\tilde{0}|H+\alpha V|\tilde{0}\rangle. \tag{2}$$

Here, *H* is the Born–Oppenheimer electronic Hamiltonian in the absence of the FC and SD terms, and the perturbation *V* denotes either the FC or SD Hamiltonian. The spin relaxation of $|\tilde{0}\rangle$ is achieved by introducing triplet operators in both the orbital and configuration spaces as described in Ref. 2.

Expanding $|\tilde{0}\rangle$ in powers of the perturbation gives

$$|\tilde{0}\rangle=|0^{(0)}\rangle+\alpha|0^{(1)}\rangle+1/2\alpha^2|0^{(2)}\rangle+\cdots; \tag{3}$$

and, the first-order contributions to the energy, which relate to the molecular property of interest, are evaluated as

$$E^{(1)} = \langle 0^{(0)} | V | 0^{(0)} \rangle + \langle 0^{(1)} | H | 0^{(0)} \rangle + \langle 0^{(0)} | H | 0^{(1)} \rangle. \quad (4)$$

The first term in Eq. (4) is the standard *average value* expression (denoted ave. in the tables), whereas the last two terms are the *response terms* (denoted res. in the tables) because they involve modification of the wave function induced by the perturbation. The latter terms appear because the zeroth order wave function $|0^{(0)}\rangle$ is not optimized with respect to the triplet operators in the orbital space. In Ref. 2, details are given concerning evaluation of the response terms for such MCSCF wave functions.

B. Atomic basis sets

In our calculations, we used as our primary basis sets for NH and B_2 the spherical components of Dunning's correlation-consistent polarized valence double zeta (VDZ) ($9s4p1d/3s2p1d$), and Dunning's valence triple zeta (VTZ) ($10s5p2d1f/4s3p2d1f$) bases.[13] For both NH and B_2, starting from the VTZ bases, basis set effects were systematically examined by first uncontracting all of the *s* functions, and then uncontracting both the *s* and the *p* functions. The resultant bases are denoted by the *subscripts u and up*, respectively, when our results are reported and discussed later.

Calculations were also performed to examine saturation towards diffuse (*subscript d*) and tight basis functions (*subscript t*). In this way, a series of bases was built for each radical by (i) sequentially adding diffuse functions to the uncontracted-level basis until saturation was achieved, and (ii) then adding tight functions to the basis again until reaching saturation. In successively augmenting the basis, the exponents for the tight functions were obtained by multiplying the most tight primitive exponent of the preceding basis by a factor of 3, and the exponents for the diffuse functions were obtained by multiplying its most diffuse primitive orbital's exponent by 1/3.

C. Configuration space choices

In all of the calculations whose results are reported here, we used reference states $|0^{(0)}\rangle$ of the conventional spin-restricted single configuration SCF, CAS MCSCF, and FCI forms. All calculations were carried out using the RESPONSE program that is attached to the SIRIUS MCSCF program.[14] As initial CAS active orbital spaces, we used the CASV spaces that contain molecular orbitals derived from the 1*s* orbital of the H atom and the 2*s* and 2*p* orbitals for the N and B atoms; this gives five active orbitals for NH and eight for B_2.

To examine the adequacy of this CASV space and to obtain a systematic means of extending this CAS space while retaining a balanced description of the molecular systems among orbitals of all point group symmetries, we carried out a CI natural orbital (CINO) occupation analysis using VTZ$ud't4$ basis for the NH and VTZu for the B_2.

To keep the number of configurations in the CINO calculation manageable, we used the restricted active space (RAS) CI expansion strategy,[15] which divides the active orbital set into three subsets (denoted RAS1, RAS2, and RAS3) in each of which the number of electrons is restricted. The occupancies of the RAS1 orbitals are allowed to vary from two to four in NH and from zero to two in B_2, and those of the RAS3 space orbitals vary from zero to two; orbitals of the RAS2 space can then take on any

TABLE I. Orbital occupation numbers for the CINO and various CAS space calculations for NH (see text). In the CINO calculation, numbers that are smaller than 0.000 01 are not given.

	σ	π	δ	ϕ
CINO	2.000 00	0.992 78	0.004 79	0.000 18
	1.969 92	0.007 34	0.000 34	
	1.959 11	0.004 60	0.000 13	
	0.026 91	0.000 82	0.000 04	
	0.011 07	0.000 44		
	0.005 67	0.000 26		
	0.001 34	0.000 10		
	0.000 99	0.000 05		
	0.000 52	0.000 02		
	0.000 31	0.000 01		
	0.000 14			
	0.000 09			
	0.000 06			
	0.000 03			
	0.000 02			
	0.000 01			
RASC	2.000 00	0.991 67	0.005 21	0.000 19
	1.966 20	0.008 70	0.000 35	
	1.952 50	0.005 13	0.000 14	
	0.032 31	0.000 86		
	0.012 98	0.000 49		
	0.006 11	0.000 28		
	0.001 45	0.000 10		
	0.001 16			
	0.000 54			
	0.000 31			
	0.000 14			
	0.000 09			
CASB	2.000 00	0.991 91	0.005 12	
	1.966 51	0.008 70	0.000 35	
	1.953 26	0.005 06		
	0.032 58	0.000 85		
	0.012 89	0.000 48		
	0.006 41			
	0.001 50			
	0.001 06			
	0.000 56			
	0.000 30			
CASA	2.000 00	0.992 57	0.005 03	
	1.970 87	0.007 90		
	1.960 26	0.004 62		
	0.031 01			
	0.011 96			
	0.005 65			
CASV	2.000 00	1.000 00		
	1.996 82			
	1.974 79			
	0.028 39			

TABLE II. Orbital occupation numbers for the CINO and various CAS and RAS space calculations for B_2 (see text).

	σ_g	π_u	δ_g	ϕ_u	σ_u	π_g	δ_u	ϕ_g
CINO	2.000 00	0.960 36	0.006 35	0.000 16	2.000 00	0.055 79	0.001 60	0.000 06
	1.937 83	0.006 03	0.000 25		1.701 79	0.001 65	0.000 06	
	0.255 26	0.003 25	0.000 09		0.014 14	0.000 32	0.000 02	
	0.008 09	0.000 31			0.004 84	0.000 09		
	0.002 62	0.000 20			0.000 92	0.000 03		
	0.000 48	0.000 03			0.000 15	0.000 00		
	0.000 23				0.000 06			
	0.000 13				0.000 04			
	0.000 07				0.000 01			
	0.000 01				0.000 00			
	0.000 00				0.000 00			
	0.000 00				0.000 00			
	0.000 00				0.000 00			
	0.000 00				0.000 00			
	0.000 00				0.000 00			
	0.000 00				0.000 00			
RASC	2.000 00	0.958 57	0.006 90		2.000 00	0.058 73	0.001 78	
	1.935 10	0.006 04	0.000 32		1.664 80	0.001 65		
	0.289 59	0.002 90			0.018 27	0.000 27		
	0.008 53	0.000 27			0.003 92			
	0.002 60	0.000 24			0.001 23			
	0.000 51							
	0.000 22							
CASB	2.000 00	0.958 14	0.007 08		2.000 00	0.058 85	0.001 78	
	1.934 29	0.006 30			1.664 44	0.001 72		
	0.290 35	0.002 97			0.018 33	0.000 29		
	0.008 94	0.000 26			0.004 29			
	0.002 78				0.001 28			
	0.000 51							
CASA	2.000 00	0.962 53	0.006 82		2.000 00	0.055 47		
	1.938 35	0.005 97			1.665 31			
	0.296 83	0.002 84			0.016 49			
	0.008 83				0.004 26			
	0.002 64							
CASV	2.000 00	0.969 22			2.000 00	0.055 88		
	1.963 50				1.665 74			
	0.302 88				0.017 66			

occupancies that accommodate the remaining electrons. In this way, a CI wave function is specified by giving the number of orbitals of each symmetry that are included in each space. The functions used in our CINO calculations are specified as follows: RAS1 (2,0,0,0); RAS2 (0,1,0,0) and RAS3 (33,10,4.1) for NH and RAS1 (1,0,0,0,0,0,0,0); RAS2 (1,1,0,0,1,1,0,0) and RAS3 (2,1,0,0,3,1,0,0) for B_2. Here, the numbers in parentheses refer to the number of orbitals of symmetries (σ,π,δ,ϕ) for the NH and $(\sigma_g,\pi_u,\delta_g,\phi_u,\sigma_u,\pi_g,\delta_u,\phi_g)$ for the B_2 in the respective spaces. For NH, we had one inactive orbital of symmetry (1,0,0,0) and for B_2 there were two inactive orbitals whose symmetries are specified (1,0,0,0,1,0,0,0).

The molecular orbitals used in these CINO calculations were obtained as converged MCSCF orbitals from the CASV-level MCSCF calculation, which has one inactive orbital (1,0,0,0) for NH and two inactive orbitals denoted (1,0,0,0,1,0,0,0) for B_2, with five (3,1,0,0) active orbitals for NH in which six active valence electrons are distributed (this results in 15 determinants), and with eight (2,1,0,0,2,1,0,0) active orbitals for B_2 containing six active electrons (this gives 252 determinants).

The diagonalization of the one electron density matrix for the resultant CI wave function gives the CI natural orbital (CINO) occupancies reported in Tables I and II for NH and B_2, respectively. These natural orbital occupancies show that the B_2 is a highly correlated system with orbital occupancies as low as 1.70 for orbitals that are doubly occupied in the SCF-level description and occupancies as large as 0.25 for orbitals that are empty in the SCF description. The significant gap in the CINO occupancies around 0.02 for NH and 0.01 for B_2 in all symmetries (below which a total of six orbitals for NH and eight orbitals for B_2 appear) shows that the orbital spaces that we denoted CASV do, indeed, provide a balanced configuration space within all orbital symmetries.

Improved descriptions of electron correlation can be obtained by including active orbitals that possess CINO occupation numbers that are smaller than the values that characterize the CASV space. In particular, lowering the limit till ca. 0.002 results in a 13 orbital active space (5,3,1,0) containing six electrons and 14 007 determinants for NH, and in a 12 orbital active space (4,3,1,0,3,1,0,0) containing six electrons and 40 580 determinants for B_2 (we denote these spaces CASA). Further lowering the cutoff to 0.0003 results in a 23 orbital active space (9,5,2,0) containing six electrons and 561 575 determinants for NH, and in an 18 orbital active space (5,4,1,0,4,3,1,0) containing six electrons and 771 066 determinants for B_2 (these spaces are denoted CASB). Finally, lowering the limit to ca. 0.0002 for B_2 produces a 25 orbital active space (6,5,2,0,4,3,1,0) with six electrons and 2 230 910 determinants and till ca. 0.0001 for NH gives a 33 orbital active space (11,7,3,1) with six electrons and 5 405 800 determinants, these largest spaces are called CASC.

In Tables I and II, we also report the natural orbital (NO) occupancies obtained for the CASV, CASA, CASB, and CASC MCSCF calculations using the atomic orbital bases VTZ*ud*′*t*4 for NH and VTZ*ut*4 for the B_2, which were determined to be stable to within a few MHz with respect to further improvement (see Sec. III). For both NH and B_2 close agreement is observed between the corresponding NO occupancies of the CASC, CASB, CASA, CASV, and the original CINO wave functions, showing that each of these active spaces are able to give a balanced description (i.e., treating orbitals of all symmetries on equal footing) of the ground state of these radicals.

Because the NH system and its VDZ basis are small enough to permit a FCI calculation (2 820 424 determinants) to be carried out on it, we were able to evaluate its hyperfine coupling constants for this full CI case, thereby gaining further evidence about the performance of the RU method as it applies to systems in which the SCF-level treatment gives a vanishing result. The hyperfine coupling tensors obtained with the FCI wave function are compared, in the following section, to those obtained from a FCI calculation with the 1*sN* orbital frozen [CI(1*s*)] (117 700 determinants), those of a CAS calculation with all the orbitals but the 1*s* active [CAS(1*s*)], and those at the SCF-SDCI (3008 det), CASA (14 007 det), CASV (15 det) and SCF levels.

Unfortunately, the B_2 molecular size does not permit such FCI calculations to be performed on it. In fact, even the MCSCF calculations, denoted CASC above, were too large to be carried out for the atomic orbital bases used in our best calculations both on NH and B_2. Therefore, we approximated the results of the desired CASC calculations by using the RAS1, RAS2, and RAS3 notation to place orbital occupation restrictions on the orbitals of the CASC spaces. In particular, we placed into the RAS3 spaces orbitals of (7,5,3,1) and (4,4,2,0,2,2,1,0) symmetries and allowed from zero to two electrons, while keeping orbitals of (4,2,0,0) and (2,1,0,0,2,1,0,0) symmetries in a RAS2 space, and retaining (1,0,0,0) and (1,0,0,0,1,0,0,0) inactive orbitals in all cases for NH and B_2, respectively. The MCSCF calculations resulting from applying these constraints to the original CASC orbital spaces (148 340 and 68 618 determinants for NH and B_2, respectively) were used to approximate the results of the desired CASC calculations. To calibrate this approach, we also carried out such calculations designed to simulate the results of the CASB calculations (which we were able to perform without approximation). In these approximate calculations, we retained (1,0,0,0) and (1,0,0,0,1,0,0,0) inactive orbitals and placed orbitals of (5,3,2,0) and (3,3,1,0,2,2,1,0) symmetries into the RAS3 spaces, as well as, orbitals of (4,2,0,0) and (2,1,0,0,2,1,0,0) into the RAS2 spaces for NH and B_2, respectively. Comparing the results of our correct CASB and approximate CASB (denoted RASB) calculations, we were able to estimate the reliability of our approximate CASC (denoted RASC) data.

TABLE III. SCF energies (a.u.), Fermi-contact (a_{iso}), and spin-dipole (a_{dip}) contributions (MHz) for NH at the experimental geometry (1.9595 au).

		H atom				N atom			
		a_{iso}		a_{dip}		a_{iso}		a_{dip}	
Basis	Energy	res.	ave.	res.	ave.	res.	ave.	res.	ave.
VDZ	−54.959 569	−90.2	0.0	6.0	28.7	51.4	0.0	1.2	−21.6
VTZ	−54.973 537	−95.4	0.0	5.0	28.2	14.5	0.0	0.8	−22.3
VTZ*u*	−54.973 586	−89.8	0.0	5.0	28.2	34.5	0.0	0.9	−22.3
VTZ*up*	−54.973 611	−89.8	0.0	5.0	28.2	34.5	0.0	0.8	−22.3
VTZ*ud*	−54.974 742	−89.5	0.0	5.0	28.1	36.4	0.0	0.9	−22.2
VTZ*ud*′	−54.974 610	−89.7	0.0	5.1	28.1	36.4	0.0	0.9	−22.2
VTZ*ud*′2	−54.974 641	−89.6	0.0	5.1	28.1	36.4	0.0	0.9	−22.2
VTZ*ud*′*t*1	−54.974 826	−91.8	0.0	5.1	28.1	36.7	0.0	0.9	−22.2
VTZ*ud*′*t*2	−54.975 074	−95.9	0.0	5.1	28.1	37.4	0.0	0.9	−22.2
VTZ*ud*′*t*3	−54.975 079	−96.4	0.0	5.1	28.1	37.4	0.0	0.9	−22.2
VTZ*ud*′*t*4	−54.975 090	−97.9	0.0	5.1	28.1	37.6	0.0	0.9	−22.2
VTZ*ud*′*t*5	−54.975 090	−97.9	0.0	5.1	28.1	37.6	0.0	0.9	−22.2
Numerical	−54.978 45		0.0		28.17		0.0		−22.6

III. RESULTS

A. Basis set dependence

Following the procedure outlined in Sec. II B, optimized basis sets were generated for NH and B_2 that give SCF and CASV hyperfine constants that converged to the specified a few MHz precision and that agreed with the numerical results. The corresponding results for NH and B_2 are given in Tables III, IV, V, and VI, respectively. Since the VDZ basis sets cannot reliably describe the hyperfine coupling constants, we used the VTZ bases as starting points in our optimizations.

For the NH molecule uncontraction of the *p* functions has no effect on the hyperfine coupling constants, but addition of one set of diffuse *s*, *p*, and *d* functions (subscript *d* in the tables), changes significantly the a_{iso} value on the *N* atom. This change is completely due to the diffuse *s* and *p* functions (subscript *d*′), as can be seen in Table IV by comparing the VTZ*ud* and VTZ*ud*′ results. With calculations with two sets of diffuse *s* and *p* functions (subscript *ud*′2), it is seen that the values remain unchanged. Addition of four *s* tight functions on both atoms to the VTZ*ud*′

TABLE IV. CASV energies (a.u.), Fermi-contact (a_{iso}), and spin-dipole (a_{dip}) contributions (MHz) for NH at the experimental geometry (1.9595 a.u.).

		H atom				N atom			
		a_{iso}		a_{dip}		a_{iso}		a_{dip}	
Basis	Energy	res.	ave.	res.	ave.	res.	ave.	res.	ave.
VDZ	−54.985 581	8.0	−76.9	−0.5	33.9	15.6	30.2	0.0	−20.6
VTZ	−54.999 579	12.0	−86.2	−1.6	33.5	−26.8	34.5	−0.4	−21.2
VTZ*u*	−54.999 724	11.9	−80.8	−1.5	33.5	−8.7	36.0	−0.4	−21.2
VTZ*up*	−54.999 769	11.9	−80.8	−1.5	33.5	−8.6	36.0	−0.4	−21.3
VTZ*ud*	−55.000 814	12.1	−80.7	−1.6	33.4	−6.7	36.0	−0.3	−21.2
VTZ*ud'*	−55.000 670	12.1	−80.7	−1.5	33.4	−6.7	36.0	−0.3	−21.2
VTZ*ud'*2	−55.000 702	12.1	−80.7	−1.5	33.4	−6.7	36.0	−0.3	−21.2
VTZ*ud't*1	−55.000 889	12.6	−82.9	−1.5	33.4	−6.8	36.4	−0.3	−21.2
VTZ*ud't*2	−55.001 139	13.0	−86.4	−1.5	33.4	−6.8	36.9	−0.3	−21.2
VTZ*ud't*3	−55.001 143	13.2	−87.0	−1.5	33.4	−6.9	37.0	−0.3	−21.2
VTZ*ud't*4	−55.001 155	13.3	−88.2	−1.5	33.4	−6.9	37.2	−0.3	−21.2
VTZ*ud't*5	−55.001 155	13.4	−88.3	−1.5	33.4	−6.9	37.2	−0.3	−21.2
Numerical	−55.004 577		−89.1		33.4		40.3		−21.7

basis is necessary to achieve saturation within the present limit (the subscript *ti* means that *i* tight functions have been added).

For the B_2, it is seen that whereas uncontraction of the *s* functions in the VTZ basis (VTZ_u) is important for a_{iso} on B, additional uncontraction of the *p* functions and addition of one set of diffuse *s*, *p*, and *d* functions to the VTZ_u basis have little effect. Saturation towards tight functions was obtained after adding four tight functions on every atom to the VTZ_u basis. Since Gaussian atomic orbital basis sets are known to be unable to reproduce the cusp of the wave function near the nuclear centers and because a_{iso} depends on the amplitude of the wave function at the nucleus, it is much more sensible to the basis set than a_{dip}. As a result, basis set saturation for a_{dip} is achieved faster, yet for both contributions it is obtained at about the same level for the average value and for the response term. Our final choice of bases is the $\mathrm{VTZ}_{ud't4}$ for the NH and the VTZ_{ut4} basis for B_2.

For the selected bases both the SCF and CASV results for a_{iso} and a_{dip} of H and B, and a_{dip} on N agree very well with complete-basis numerical Hartree–Fock and CASV results (see Tables III and VI), which indicates that only small basis set errors will be encountered if we use the optimized bases for our larger correlated calculations. For a_{iso} on N the difference between the numerical and CASV results is 3.1 MH, which implies that errors up to this size can appear in our larger calculations.

B. SCF, CAS, and CI results

Table VII reports the results of the calibration of the RU method for the NH system using the VDZ basis set. The adequacy of the RU approach is demonstrated by comparing the FCI and the CAS(1*s*) results. In the latter, the electrons in the "1*s* *N* orbital" remain inactive and the spin polarization of this orbital is in the RU method taken care of by the response term. The close agreement for a_{iso}

TABLE V. SCF energies (a.u.), Fermi-contact (a_{iso}), and spin-dipole (a_{dip}) contributions (MHz) for B_2 at the experimental equilibrium geometry (3.0047 a.u.) (Ref. 17).

		B atom			
		a_{iso}		a_{dip}	
Basis	Energy	res.	ave.	res.	ave.
VDZ	−49.082 907	39.2	0.0	−1.5	−9.4
VTZ	−49.088 559	17.8	0.0	−2.1	−9.5
VTZ_u	−49.088 724	0.7	0.0	−2.1	−9.5
VTZ_{up}	−49.088 748	0.5	0.0	−2.1	−9.6
VTZ_{ud}	−49.088 848	1.4	0.0	−2.1	−9.5
VTZ_{ut1}	−49.088 910	0.7	0.0	−2.1	−9.5
VTZ_{ut2}	−49.089 115	0.7	0.0	−2.1	−9.5
VTZ_{ut3}	−49.089 119	0.7	0.0	−2.1	−9.5
VTZ_{ut4}	−49.089 129	0.7	0.0	−2.1	−9.5
VTZ_{ut5}	−49.089 129	0.7	0.0	−2.1	−9.5
Numerical	−49.091 02		0.0		−9.8

TABLE VI. CASV energies (a.u.), Fermi-contact (a_{iso}), and spin-dipole (a_{dip}) contributions (MHz) for B_2 at the experimental equilibrium geometry (3.0047 a.u.) (Ref. 17).

		B atom			
		a_{iso}		a_{dip}	
Basis	Energy	res.	ave.	res.	ave.
VDZ	−49.212 179	−1.8	55.3	−0.8	−11.0
VTZ	−49.218 429	−73.3	67.9	−1.6	−11.1
VTZ_u	−49.218 711	−57.2	69.8	−1.6	−11.1
VTZ_{up}	−49.218 863	−57.3	69.7	−1.6	−11.1
VTZ_{ud}	−49.218 786	−57.2	69.8	−1.6	−11.1
VTZ_{ut1}	−49.218 895	−57.9	70.6	−1.6	−11.1
VTZ_{ut2}	−49.219 100	−58.7	71.7	−1.6	−11.1
VTZ_{ut3}	−49.219 105	−58.9	71.9	−1.6	−11.1
VTZ_{ut4}	−49.219 114	−59.2	72.3	−1.6	−11.1
VTZ_{ut5}	−49.219 114	−59.3	72.4	−1.6	−11.1
Numerical	−49.221 26		72.4		−11.3

TABLE VII. Fermi-contact (a_{iso}) and spin-dipole (a_{dip}) contributions (MHz) for NH at 1.9595 a.u. using the VDZ basis set.

		H atom						N atom					
		a_{iso}			a_{dip}			a_{iso}			a_{dip}		
	Energy	res.	ave.	tot.	res.	ave.	tot.	res.	ave.	tot.	res.	ave.	tot.
FCI	−55.093 483	0.0	−63.7	−63.7	0.0	32.6	32.6	0.0	40.8	40.8	0.0	−20.2	−20.2
CAS(1*s*)	−55.091 972	0.0	−63.8	−63.8	0.0	32.6	32.6	−4.9	45.8	40.9	0.0	−20.2	−20.2
CI(1*s*)	−55.091 972	0.0	−63.7	−63.7	0.0	32.6	32.6	0.0	45.8	45.8	0.0	−20.2	−20.2
CISD(HF)	−55.088 810	0.0	−59.4	−59.4	0.0	32.2	32.2	0.0	37.3	37.3	0.0	−20.3	−20.3
CASA	−55.072 349	−0.1	−66.7	−66.9	0.3	32.4	32.7	−3.9	45.4	41.5	0.0	−20.2	−20.1
CASV	−54.985 581	8.0	−76.9	−68.8	−0.5	33.9	33.4	15.6	30.2	45.8	0.0	−20.6	−20.6
SCF	−54.959 569	−90.2	0.0	−90.2	6.0	28.7	34.8	51.4	0.0	51.4	1.2	−21.6	−20.4

and for a_{dip} in the FCI and CAS(1*s*) calculations demonstrates that the RU method is able to properly describe the spin polarization accurately.

The CI(1*s*) wave function differs from the FCI one, in that, it does not describe the 1*s* spin polarization, and as expected the corresponding *a* values equal the $a_{\mathrm{ave.}}$ CAS(1*s*) ones. The CASV calculation gives differences of 8% and 12% for H and N, respectively, but at the CASA level, the values improve considerably—differences of 5% for H and 2% for N. The SCF values have the correct sign, but significantly overestimate both a_{iso} constants.

In Tables VIII and IX, respectively, we report hyperfine tensor values for NH and B_2 obtained using the optimal bases described above. These results show that an SCF description, even though it gives the correct sign for both contributions to the hyperfine coupling constant, is inadequate for both NH and B_2. The 0.0 values for the average-value SCF contributions reflect the fact that the unpaired electrons lie entirely in π orbitals within this description. Even when corrected for spin polarization, the SCF predictions for a_{iso} are grossly in error.

At the CASV level, the total a_{iso} and a_{dip} values are closer to the experimental results. It should be noted that the a_{iso} value for the B atom in B_2 and N atom in NH results from the near cancellation of large but oppositely signed core, and valence contributions that are described by the response and the average value terms, respectively.

At the CASA level, the agreement with the experimental data improves further; although for the H atom, differences of the order of 7 MHz (for a_{iso}) remain. In moving from CASB to CASC (as judged from the RASB, CASB, and RASC data of Tables VIII and IX), no significant changes occur showing that we have converged with respect to correlation level.

Vibrational corrections to a_{iso} and to a_{dip} were evaluated for both systems at the CASV level using the Vibrot program in MOLCAS.[16] We computed both hyperfine parameters at internuclear distances ranging from 1.20 a.u. to 2.72 a.u. for NH and from 2.24 au to 3.76 au for B_2, over which a_{iso} ranged smoothly from −88.1 MHz to −120.0 MHz for H, from 16.4 MHz to 25.7 MHz for N, and from −35.7 MHz to 36.7 MHz for B; and a_{dip} varied gradually from 41.3 MHz to 20.0 MHz for H, −22.1 MHz to −19.6 MHz for N, and from −14.8 MHz to −12.1 MHz for B. Even though the potential function of B_2 is rather "soft" (the experimental harmonic vibrational frequency is only $\omega_e = 1035\ \mathrm{cm}^{-1}$),[10] as shown in Tables VIII and IX, the effects of vibrational averaging for B and N are found to be insignificant and well below the experimental uncertainties, in agreement with the results obtained by Knight *et al.*[10]

TABLE VIII. Fermi-contact (a_{iso}) and spin-dipole (a_{dip}) contributions (MHz) for NH at 1.9595 a.u. using the VTZ*ud′t*4 basis.

		H atom						N atom					
		a_{iso}			a_{dip}			a_{iso}			a_{dip}		
	Energy	res.	ave.	tot.	res.	ave.	tot.	res.	ave.	tot.	res.	ave.	tot.
SCF	−54.975 090	−97.9	0.0	−97.9	5.1	28.1	33.2	37.6	0.0	37.6	0.9	−22.2	−21.2
CASV	−55.001 155	13.3	−88.2	−74.9	−1.5	33.4	31.9	−6.9	37.2	30.3	−0.3	−21.2	−21.5
CASA	−55.106 205	−8.0	−65.1	−73.1	−0.3	31.3	31.0	−50.4	68.3	17.9	−0.5	−20.6	−21.1
CASB	−55.133 023	1.0	−68.1	−67.1	−0.1	31.0	30.9	−45.7	62.2	16.5	0.0	−21.3	−21.3
RASB[a]	−55.132 147	1.2	−68.0	−66.7	−0.2	31.0	30.8	−46.0	62.6	16.6	0.0	−21.3	−21.3
RASC[b]	−55.141 291	1.2	−67.2	−66.0	−0.1	30.9	30.8	−45.4	62.4	17.0	0.0	−21.3	−21.3
V.Co.[c]				−2.0			−0.9			−0.1			0.1
Expt.[d]				−66.23			30.57			19.22			−22.64

[a] See for further details of how this approximation to the CASB calculation is performed.
[b] See for further details of how this approximation to the CASC calculation is performed.
[c] Vibrational corrections evaluated at the CASV level.
[d] Reference 5.

TABLE IX. Fermi-contact (a_{iso}) and spin-dipole (a_{dip}) contributions (MHz) for B_2 at the experimental equilibrium geometry (3.005 a.u.) (Ref. 17) using the VTZ_{ut4} Basis.

		B atom					
		a_{iso}			a_{dip}		
	Energy (a.u.)	res.	ave.	tot.	res.	ave.	tot.
SCF	−49.089 129	0.7	0.0	0.7	−2.1	−9.5	−11.7
CASV	−49.219 114	−59.2	72.3	13.1	−1.6	−11.1	−12.7
CASA	−49.273 737	−40.1	55.1	15.0	−0.4	−11.3	−11.8
CASB	−49.291 563	−39.1	51.2	12.1	−0.2	−11.6	−11.8
RASB[a]	−49.290 408	−40.0	51.8	11.8	−0.2	−11.6	−11.8
RASC[b]	−49.293 763	−40.1	51.6	11.5	−0.1	−11.7	−11.8
V.Co.[c]				0.6			0.0
Expt.[d]				15			−13

[a] See for further details of how this approximation to the CASB calculation is performed.

[b] See for further details of how this approximation to the CASC calculation is performed.

[c] Vibrational corrections evaluated at the CASV level.

[d] Reference 10.

Thus, our *final predictions* are $a_{iso} = -68.0$, 16.9, 12.2 MHz and $a_{dip} = 29.9$, -21.2, -11.8 MHz for H, N, and B, respectively. Experimental results have been reported for both radicals. Laser magnetic resonance[4] and high resolution, molecular beam, laser-induced fluorescence spectroscopies[5] were used for NH, and a rare gas matrix isolation technique (Ne and Ar matrices at 5 K) was used for B_2.[10] The *experimental values* are $a_{iso} = -66.23$, 19.22, 15 MHz, and $a_{dip} = 30.57$, -22.64, -13 MHz, for H, N, and B, respectively.

IV. OVERVIEW AND DISCUSSION

We used the MCSCF RU approach[2] to evaluate the hyperfine coupling constants for the ground electronic states of NH and B_2 and obtained final optimal basis, optimal correlation, and vibrationally averaged values of $a_{iso} = -68.0$, 16.9, 12.2 MHz and $a_{dip} = 29.9$, -21.2, -11.8 MHz, for H, N, and B, respectively. The RU approach used here allows us to achieve a rather high level treatment of electron correlation while retaining a relatively compact configuration expansion length in contrast to the MR-CI approach.[10] Most important, however, is that a reasonable level of convergence is reached using the present approach. In the RU approach the molecular system is described with a spin restricted MCSCF wave function when the Fermi-contact or the spin-dipole perturbation is absent. In the presence of either of these perturbations, the system is allowed to spin polarize. As a result of combining this spin polarization with the MCSCF wave function's treatment of correlation, any first order molecular property can be evaluated as a sum of an average-value term, and a term describing the first-order response of the wave function to the perturbation. The latter term does not vanish because the spin restricted MCSCF wave function has not been optimized with respect to orbital spin relaxation parameters. In the RU approach, the spin polarizations of the valence-shell orbitals are predominantly described by the MCSCF wave function and are contained in the average value terms; the spin polarizations of the inner-shell core orbitals are taken care of by the response terms.

Our experience shows that determining accurate hyperfine coupling constants requires very good atomic orbital basis sets. We therefore initiated all of our calculations with a careful basis set analysis in which we found that triple zeta bases with uncontracted *s* functions, and a few additional diffuse and tight functions are capable of producing accurate hyperfine coupling constants.

Our results also demonstrate that an SCF wave function is inadequate for describing hyperfine coupling constants, especially for π-radical systems such as NH and B_2. In contrast, using a CAS valence wave function gives a qualitatively correct, yet still not highly accurate, treatment of the hyperfine coupling constants. Extending the active-orbital spaces of the MCSCF calculations to include more correlating orbitals, using the natural orbital occupations to retain a balanced description among orbitals of different symmetry, can increase significantly the accuracy of the hyperfine coupling constants. In the present case, this prescription leads to values of the correct sign, that remain stable to within a few MHz with respect to basis set expansion, and whose numerical values differ from experimental values by 1.8, 2.3, 2.8 MHz for a_{iso}, and 0.7, -1.4, -1.2 MHz for a_{dip} (Experimental–Theoretical) for H, N, and B, respectively.

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[1] Explicit expressions for the FC and SD operators are for example given in: O. Vahtras, H. Ågren, P. Jørgensen, H. J. Aa. Jensen, and T. Helgaker, J. Chem. Phys. **96**, 6120 (1992).

[2] B. Fernández, P. Jørgensen, J. Byberg, J. Olsen, T. Helgaker, H. J. Aa. Jensen, J. Chem. Phys. **97**, 3412 (1992).

[3] A. Hinchcliffe, *Ab Intio Determination of Molecular Properties* (Adam Hilger, Bristol, 1987).

[4] F. C. van den Heuvel, W. L. Meerts, and A. Dymanus, Chem. Phys. Lett. **92**, 215 (1982).

[5] W. Ubachs, J. J. ter Meulen, and A. Dymanus, Can. J. Phys. **62**, 1374 (1984).

[6] D. M. Chipman, J. Chem. Phys. **91**, 5455 (1989).

[7] C. F. Bender and E. R. Davidson, Phys. Rev. **183**, 23 (1969).

[8] B. Engels and S. D. Peyerimhoff, Mol. Phys. **67**, 583 (1989).

[9] P. Kristiansen and L. Veseth, J. Chem. Phys. **84**, 6336 (1986).

[10] (a) L. B. Knight, Jr., B. W. Gregory, S. T. Cobranchi, D. Feller, and E. R. Davidson, J. Am. Chem. Soc. **109**, 3521 (1987); (b) D. Feller and E. R. Davidson, J. Chem. Phys. **88**, 7580 (1988).

[11] B. Fernández, P. Jørgensen, and J. Simons, J. Chem. Phys. **98**, 3060 (1993).

[12] B. Fernández, P. Jørgensen, and J. Simons, J. Chem. Phys **98**, 7012 (1993).

[13] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).

[14] H. J. Aa. Jensen, H. Ågren, and J. Olsen, SIRIUS: A General Purpose Direct Second Order MCSCF Program. In Modern Techniques in Computational Chemistry: MOTECC-90, edited by E. Clementi, Leiden, 1990.

[15] J. Olsen, B. O. Roos, P. Jørgensen, and H. J. Aa. Jensen, J. Chem. Phys. **89**, 2185 (1988).

[16] Vibrot, a program from MOLCAS version 2, K. Andersson, M. P. Fülscher, R. Lindh, P.-A. Malmquist, J. Olsen, B. O. Roos, and A. J. Sadlej, University of Lund, Sweden; and P.-O. Widmark, IBM Sweden, 1991.

[17] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Constants of Diatomic Molecules, Vol. 4 (Van Nostrand Reinhold, New York, 1977).