Calculation of hyperfine coupling constants of the CN and CP ground state radicals

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By carrying out a systematic basis set and electron correlation investigation, we have determined accurately the hyperfine coupling constants of the ground states of CN and CP. The basis set studies began with Dunning's correlation consistent bases, after which systematic uncontractions and extensions with diffuse and tight functions were introduced until saturation was achieved. The basis set self-consistent-field (SCF) wave function results compare favorably with numerical Hartree–Fock (HF) results. The electron correlation study was based on extending systematically the active space of a complete valence orbital spin-restricted multiconfiguration self-consistent-field (MCSCF) wave function and using the MCSCF restricted–unrestricted response function approach to obtain the hyperfine coupling constants.

I. INTRODUCTION

The evalutation of hyperfine coupling constants has proven to be a great challenge to *ab initio* computational quantum chemistry. *Ab initio* programs almost exclusively use conventional Gaussian atomic orbital basis sets even though these functions are known to be incapable of reproducing the cusp of the electronic wave function near the nuclear centers. Because the isotropic hyperfine coupling constant A_{iso} depends on the amplitude of the wave function at the nucleus, it is important to investigate whether Gaussian-orbital-based methods can be trusted.

The issues surrounding the choice of an adequate atomic orbital basis set have also made it difficult to decide what level of electron correlation is needed to properly describe hyperfine coupling constants. This question is further complicated because the electronic configurations that are important for obtaining an accurate total electronic energy are not necessarily those that are important for describing the hyperfine coupling constant.

In this paper we carry out a detailed and thorough study of the hyperfine coupling constants of the $X\,^2\Sigma^+$ ground states of CN and CP. These radicals have recently been studied both experimentally and using *ab initio* methods. For CN, recent calculations by Momose, Yamaguchi, and Shida[1] using the symmetry adapted cluster expansion-configuration interaction method (SAC-CI) gave results that compared very favorably with earlier experimental results.[2,3] However, a closer examination, in particular of the basis set used in Ref. 1 (see later in Sec. III) shows that this agreement is fortuitous and a result of cancellation of basis set and correlation errors. In fact, the statement made in Ref. 1 that a Dunning double zeta basis[4] without polarization functions is capable of giving accurate hyperfine constants for molecules containing first row atoms is incorrect as demonstrated later by our data.

The hyperfine coupling constant of CP has recently been determined experimentally by Knight *et al.*[5] who also carried out careful *ab initio* studies of this molecule. These calculations revealed that it is extremely difficult to calculate the hyperfine coupling constants correctly even when using very sophisticated electronic structure methods. Reference 5 used large multireference single- and double-excitation configuration interaction (MRSD) calculations and obtained very accurate coupling constants (i.e., excellent agreement with Knight's experimental data) for the carbon atom. However, the isotropic A_{iso} coupling constant on phosphorous proved very difficult to obtain even to within the proper sign. In their largest MRSD calculation, the sign of A_{iso} was correct but the calculated A_{iso} value was only ~55% of the experimental value. It is thus very timely for us to undertake a detailed investigation of the hyperfine coupling constants of CN and CP.

We begin our investigation with a careful basis set study using a complete active space (CAS) multiconfiguration self-consisted-field (MCSCF) wave function where all valence electrons are distributed among all eight valence orbitals. We denote this MCSCF CAS valence space as CASV. Our goal in this part of the study is to determine a basis set for which the CASV correlated results are stable to within 2 MHz. At the same time, we also examined the basis set dependence of the self-consistent-field (SCF) wave function results. Comparison with the numerical Hartree–Fock results of Richman, Shi, and McCullough[6] could be used to evaluate our basis choice. The SCF results for the optimized CASV bases and the numerical Hartree–Fock results[6] gave hyperfine coupling constants consistent with the 2 MHz limit. Our bases were formed by starting with Dunning's correlation consistent basis sets,[7] performing systematic uncontractions, and extending the bases with diffuse and tight functions until saturation is achieved (see Sec. II for details).

Electron correlation was included in our calculations using the restricted–unrestricted (RU) approach of

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Fernandez *et al.*[8] In this approach, we describe the molecular system in the absence of the Fermi contact (FC) or spin dipole (SD) operators[9] with a conventional spin-restricted MCSCF wave function. In the presence of the FC or the SD operator, the wave function spin relaxes and 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. This RU approach (see Sec. II for details) has previously been successfully benchmarked against full configuration interaction (FCI) results for BH_2 and N,[8] and has produced accurate hyperfine coupling constants for B_3.[10] In the present work, we demonstrate that by systematically extending the configuration space of the MCSCF calculation beyond the starting CASV space we can obtain accurate results for CN and CP using the RU method.

In the next section, we briefly summarize our calculational procedure, including basis and configuration choices and the RU approach. Section III describes the results of our calculations, and in the last section we give our concluding remarks.

II. CALCULATIONAL PROCEDURE

A. The restricted–unrestricted response function method

The RU approach[8] employed for the CN and CP hyperfine coupling calculation may be viewed as follows. In the absence of the FC or SD terms[9] in the electronic Hamiltonian, we describe the molecular system with a spin-restricted MCSCF wave function denoted $|0^{(0)}\rangle$. The FC and SD Hamiltonian terms are triplet tensor operators in spin space, and when these operators are applied the wave function spin relaxes thereby necessitating a spin-unrestricted description. The total energy of the molecular system in the presence of the FC and SD couplings is then expressed in terms of the spin-relaxed wave function denoted $|\tilde{0}\rangle$

$$E(\alpha)=\langle\tilde{0}|H+\alpha V|\tilde{0}\rangle. \tag{1}$$

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 the 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. 8.

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

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

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

$$E^{(1)}=\langle 0^{(0)}|V|0^{(0)}\rangle+\langle 0^{(1)}|H|0^{(0)}\rangle+\langle 0^{(0)}|H|0^{(1)}\rangle. \tag{3}$$

The first term in Eq. (3) is the standard *average value* expression (denoted aver. in the tables), whereas the last two terms are the *response terms* (denoted resp. in the tables) because they involve modification of the wave function induced by the perturbation. The latter terms do not vanish because the zeroth order spin-restricted MCSCF wave function $|0^{(0)}\rangle$ is not optimized with respect to the triplet operators in the orbital space. In carrying out this derivation, it is proper to use a nondegenerate approach because the strong external magnetic field produces the Zeeman splitting that lifts the degeneracy of the M_s substates. In Ref. 8, 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 the spherical components of Dunning's correlation-consistent polarized valence double zeta (VDZ) [(9*s*4*p*1*d*/3*s*2*p*1*d*) and (12*s*8*p*1*d*/4*s*3*p*1*d*) for the first and second row atoms, respectively] and valence triple zeta (VTZ) [(10*s*5*p*2*d*1*f*/4*s*3*p*2*d*1*f*) and (15*s*9*p*2*d*1*f*/5*s*4*p*2*d*1*f*) for first and second row atoms, respectively] bases.[7] Basis set effects were systematically examined by uncontracting all of the *s*, and then both the *s* and the *p* functions. The resultant bases are denoted by the subscript *u* and *up*, respectively. 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 by sequentially adding first diffuse functions to the VTZ basis[7] until saturation was achieved, and then adding tight functions to this final basis again until 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.

In Ref. 1 it was claimed that, for molecules containing first-row atoms such as CN, Dunning's double zeta basis without polarization functions (DZ) (Ref. 4) could be used to describe hyperfine coupling constants with reasonable accuracy. For that reason, we also computed SCF and correlated coupling constants using both the DZ basis and the DZ basis with polarization functions (DZP).

C. Configuration space choices

In our calculations, we used reference states $|0^{(0)}\rangle$ of the conventional spin restricted single configuration SCF and CAS MCSCF forms. The MCSCF calculations were carried out using the SIRIUS program.[11] As an initial active space, we used the valence space containing the 2*s* and 2*p* orbitals for the first-row atoms (C and N) and the 3*s* and 3*p* orbitals for the second-row atom (P). We denote these active space calculations as CASV calculations.

To examine the adequacy of this CAS and to obtain a systematic mean of extending the CAS for achieving balanced descriptions of the molecular systems, we carried out a CI natural orbital (CINO) occupation analysis using the

TABLE I. Natural orbital occupation numbers for CN using various wave functions.

	σ	π	δ
CINO[a]	2.000 00	1.801 37	0.004 72
	2.000 00	0.193 13	0.002 71
	1.967 32	0.007 34	
	1.899 29	0.005 16	
	1.021 18	0.002 61	
	0.051 04	0.001 27	
	0.008 56		
	0.006 27		
	0.005 46		
	0.002 32		
	0.001 75		
	0.000 16		
CASV[b]	2.000 00	1.922 47	
	2.000 00	0.083 20	
	1.990 77		
	1.957 52		
	1.022 16		
	0.018 21		
CASA[b]	2.000 00	1.909 35	0.006 81
	2.000 00	0.084 63	
	1.979 09	0.007 20	
	1.931 94	0.004 69	
	1.020 20		
	0.019 02		
	0.011 94		
	0.007 69		
	0.004 75		

[a] VDZ basis set.
[b] VTZ_{udt4} basis set.

TABLE II. Natural orbital occupation numbers for CP using various wave functions.

	σ	π	δ
CINO[a]	2.000 00	2.000 00	0.010 27
	2.000 00	1.870 18	0.002 96
	2.000 00	0.121 46	
	2.000 00	0.009 33	
	1.971 40	0.005 81	
	1.922 79	0.002 31	
	1.007 87	0.001 09	
	0.027 88		
	0.008 26		
	0.006 26		
	0.004 91		
	0.002 83		
	0.000 82		
	0.000 14		
CASV[b]	2.000 00	2.000 00	
	2.000 00	1.894 15	
	2.000 00	0.112 23	
	2.000 00		
	1.990 21		
	1.960 77		
	1.010 74		
	0.025 52		
CASA[b]	2.000 00	2.000 00	0.014 57
	2.000 00	1.878 55	
	2.000 00	0.112 78	
	2.000 00	0.011 81	
	1.971 94	0.006 14	
	1.919 03		
	1.006 98		
	0.032 93		
	0.009 80		
	0.007 42		
	0.004 21		

[a] VDZ basis set.
[b] VTZ_{u^*dt4} basis set.

VDZ basis. To keep the number of configurations in the CINO calculation manageable, we used the restricted active space (RAS) CI expansion,[12] based on dividing the active orbital set into three subsets (RAS1, RAS2, and RAS3) in each of which the number of electrons is restricted. In this way, a CI wave function is specified by giving the number of orbitals in each space.

The functions used in our CINO calculations are specified as follows: RAS1 (1,0,0), RAS2 (3,2,0), and RAS3 (6,4,2) for CN and RAS1 (1,0,0), RAS2 (2,2,0), and RAS3 (7,4,2) for CP. Here the numbers in parentheses refer to the number of orbitals of symmetries (σ, π, δ) in the respective spaces. The occupancies of the RAS1 and RAS3 spaces were both allowed to vary from 0 to 2 electrons, with the RAS2 space then accommodating the remaining electrons. For CN we had (2,0,0) inactive orbitals and for CP (4,1,0) inactive orbitals (i.e., orbitals that are doubly occupied in all configurations).

The molecular orbitals used in the CI function were obtained as converged MCSCF orbitals from the CASV-level MCSCF calculation, which has a total of two (2,0,0) inactive orbitals for CN, six (4,1,0) for CP, and eight (4,2,0) active orbitals that contain the nine active valence electrons (this results in 1000 determinants).

The diagonalization of the one electron density matrix for the resultant CI wave function gives the CINO occupancies reported in Tables I and II for CN and CP, respectively. These natural orbital occupancies show that both CN and CP are correlated systems with orbital occupancies as low as 1.80 in orbitals that are doubly occupied in the SCF-level description and occupancies as large as 0.19 in orbitals that are empty in the SCF description. The significant gap in the CINO occupancies around 0.02 shows that the orbital space denoted CASV earlier provides a balanced configuration space for all orbital symmetries.

An improved description of electron correlation can be obtained by defining active orbitals that possess CINO occupation numbers larger than ~0.005, which for both CN and CP results in an active space (7,4,1) containing nine active electrons. We denote the electronic functions obtained from this improved CAS CASA (which contains 3 648 576 determinants).

In Tables I and II we also report the natural orbital (NO) occupancies obtained for the CASV and CASA MCSCF calculations using the bases which have been determined to reproduce SCF and CASV results with ~2 MHz accuracy (VTZ_{udt4} for CN and VTZ_{u^*dt4} for CP, see Sec. III). A significant change is observed for CN between the CINO occupation numbers of the most correlating orbitals and the corresponding CASV and CASA numbers.

TABLE III. CASV energies (a.u.), Fermi contact (A_{iso})[a] and spin dipole (A_{dip})[b] contributions (MHz) for CN at the experimental equilibrium geometry (2.214 a.u.) (Ref. 14).

		C atom				N atom			
		A_{iso}		A_{dip}		A_{iso}		A_{dip}	
Basis	Energy	resp.	aver.	resp.	aver.	resp.	aver.	resp.	aver.
DZ	−92.226 515	90.0	400.9	−3.3	37.8	9.5	−4.8	0.5	22.2
DZ$_u$	−92.229 447	64.2	385.8	−2.8	37.7	5.5	−4.6	0.7	22.3
DZP	−92.241 276	87.9	389.3	−3.5	39.1	7.2	−8.2	1.9	22.1
DZP$_u$	−92.243 497	63.4	371.8	−3.0	39.2	3.5	−7.3	1.9	22.3
VDZ	−92.233 586	53.3	355.0	−3.2	39.3	6.7	−4.6	1.8	21.7
VDZ$_u$	−92.233 754	62.8	357.6	−3.2	39.3	3.7	−6.5	1.8	21.7
VTZ	−92.369 303	25.9	384.4	0.2	50.0	4.1	−18.6	1.2	17.8
VTZ$_u$	−92.369 953	45.5	606.3	0.3	50.0	3.1	−19.3	1.2	17.8
VTZ$_{up}$	−92.370 152	47.1	607.0	0.2	49.8	3.3	−19.3	1.2	17.7
VTZ$_{ud1}$	−92.370 381	45.9	611.5	0.2	49.9	2.9	−19.1	1.2	17.7
VTZ$_{ud2}$	−92.370 445	45.9	611.6	0.1	49.9	2.9	−19.1	1.2	17.7
VTZ$_{udt1}$	−92.370 681	46.3	618.1	0.2	49.9	2.9	−19.3	1.2	17.7
VTZ$_{udt2}$	−92.371 014	47.1	627.4	0.2	49.9	3.0	−19.6	1.2	17.7
VTZ$_{udt3}$	−92.371 020	47.1	629.1	0.2	49.9	3.0	−19.7	1.2	17.7
VTZ$_{udt4}$	−92.371 035	47.4	632.5	0.2	49.9	3.0	−19.8	1.2	17.7
VTZ$_{udt5}$	−92.371 035	47.4	632.9	0.2	49.9	3.0	−19.8	1.2	17.7

[a] The FC values given represent one third of the trace of the hyperfine tensor (A).

[b] The SD values given are $(A_{\parallel} - A_{\perp})/3$, where $A_{\parallel}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ one of the other two elements.

For example, the two most correlated π orbitals have CINO occupancies of 1.80 and 0.19, and for CASA the corresponding numbers are 1.91 and 0.08. This large difference is due to constraints in the VDZ basis to properly describe the CN molecule. For the less correlated orbitals, close agreement is observed between the CINO, the CASV, and the CASA occupations, indicating that our chosen active spaces really are able to give a balanced description of the ground state of the CN radical. For CP close agreement is observed between the corresponding NO occupancies of the CASA, CASV, and CINO wave functions, showing that we also have obtained balanced descriptions with the above CAS configuration spaces for this system.

III. RESULTS

A. Basis set dependence

Following the procedure given in Sec. II B, optimized basis sets were determined for CN and CP to give CASV hyperfine constants that are unchanged (i.e., saturated) to ~2 MHz accuracy. The corresponding results for CN and CP are given in Tables III and IV, respectively. Since the

TABLE IV. CASV energies (a.u.), Fermi contact (A_{iso})[a] and spin dipole (A_{dip})[b] contributions (MHz) for CP at the experimental equilibrium geometry (2.952 a.u.) (Ref. 14).

		C atom				P atom			
		A_{iso}		A_{dip}		A_{iso}		A_{dip}	
Basis	Energy	resp.	aver.	resp.	aver.	resp.	aver.	resp.	aver.
VDZ	−378.580 408	31.5	536.5	−0.4	44.8	37.9	−163.5	11.5	121.7
VDZ$_u$	−378.580 611	35.3	536.9	−0.4	44.9	−5.4	−151.9	12.2	121.2
VTZ	−378.599 947	−24.8	531.5	1.0	47.0	0.9	−160.7	21.0	124.2
VTZ$_u$	−378.600 131	22.3	545.1	1.0	47.1	−17.2	−148.5	21.5	123.7
VTZ$_{up}$	−378.600 274	23.3	545.7	1.0	46.9	−16.7	−147.8	28.0	122.3
VTZ$_{u*}$	−378.600 181	22.3	545.2	1.0	47.0	−16.2	−148.4	29.9	122.2
VTZ$_{u*d1}$	−378.600 491	22.8	546.7	0.9	47.0	−21.3	−147.2	29.8	121.9
VTZ$_{u*d2}$	−378.600 507	22.8	546.7	0.9	47.0	−21.3	−147.2	29.8	121.9
VTZ$_{u*dt1}$	−378.600 678	22.9	552.6	0.9	47.0	−21.4	−147.9	29.8	121.9
VTZ$_{u*dt2}$	−378.600 885	23.4	560.9	0.9	47.0	−21.5	−148.7	29.8	121.9
VTZ$_{u*dt3}$	−378.600 889	23.4	562.5	0.9	47.0	−21.6	−148.9	29.8	121.9
VTZ$_{u*dt4}$	−378.600 899	23.5	565.5	0.9	47.0	−21.6	−149.2	29.8	121.9
VTZ$_{u*dt5'}$	−378.600 895	23.5	565.8	0.9	47.0	−21.5	−148.7	29.8	121.9

[a] The FC values given represent one third of the trace of the hyperfine tensor (A).

[b] The SD values given are $(A_{\parallel} - A_{\perp})/3$, where $A_{\parallel}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ one of the other two elements.

TABLE V. SCF energies (a.u.), Fermi contact (A_{iso})[a] and spin dipole (A_{dip})[b] contributions (MHz) for CN at the experimental equilibrium geometry (2.214 a.u.) (Ref. 14).

		C atom				N atom			
		A_{iso}		A_{dip}		A_{iso}		A_{dip}	
Basis	Energy	resp.	aver.	resp.	aver.	resp.	aver.	resp.	aver.
DZ	−91.992 442	−265.8	72.7	6.5	45.1	−97.2	61.6	2.4	24.3
DZ$_u$	−91.995 583	−264.0	71.9	6.7	45.2	−97.8	59.5	2.5	24.1
DZP	−92.015 495	−259.6	58.2	8.6	44.8	−94.9	52.2	3.6	24.5
DZP$_u$	−92.017 722	−259.1	57.5	8.5	45.4	−95.3	50.5	3.6	24.6
VDZ	−92.008 651	−196.2	52.3	8.1	44.6	−82.1	48.3	3.5	24.0
VDZ$_u$	−92.008 873	−259.7	54.6	8.2	44.5	−95.7	50.1	3.5	24.0
VTZ	−92.217 512	850.8	913.7	−178.4	61.1	−93.4	12.3	69.2	7.9
VTZ$_u$	−92.218 138	1030.6	942.7	−178.5	61.2	−157.6	11.5	69.2	7.8
VTZ$_{up}$	−92.218 261	940.0	942.9	−170.7	60.8	−155.5	11.5	67.4	7.8
VTZ$_{ud1}$	−92.218 775	1021.9	946.3	−177.0	61.1	−160.7	11.7	68.5	7.8
VTZ$_{ud2}$	−92.218 832	1025.3	946.3	−177.9	61.1	−161.2	11.7	68.8	7.8
VTZ$_{udt1}$	−92.219 074	1032.1	956.4	−177.0	61.1	−162.1	11.8	68.5	7.8
VTZ$_{udt2}$	−92.219 407	1048.3	970.9	−177.0	61.1	−164.7	12.0	68.5	7.8
VTZ$_{udt3}$	−92.219 414	1050.8	973.5	−177.0	61.1	−165.1	12.0	68.5	7.8
VTZ$_{udt4}$	−92.219 429	1056.6	978.8	−177.0	61.1	−166.0	12.1	68.5	7.8
VTZ$_{udt5}$	−92.219 429	1057.0	979.3	−177.0	61.1	−166.0	12.1	68.5	7.8
HF[c]			975.6		62.4		11.9		8.0

[a] The FC values given represent one third of the trace of the hyperfine tensor (A).

[b] The SD values given are $(A_{\parallel} - A_{\perp})/3$, where $A_{\parallel}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ one of the other two elements.

[c] Numerical Hartree–Fock results of Ref. 6.

VDZ and VDZ$_u$ basis sets cannot realiably describe the hyperfine coupling constants, we used the VTZ bases as starting points in our optimizations. It is seen that uncontraction of the VTZ basis (as in VTZ$_u$) is important especially for A_{iso} on C. Uncontraction of the p functions has little effect for CN, and for CP, A_{dip} for the P atom changed from 145.2 to 150.3 MHz. Most of this change was recovered in the VTZ$_{u*}$ basis where only the outer primitive p function of the VTZ$_u$ basis was uncontracted.

Saturation towards diffuseness was obtained after adding one set of diffuse functions to the VTZ$_u$ basis for CN and the VTZ$_{u*}$ basis for CP. The symbols VTZ$_{ud1}$ (VTZ$_{u*d1}$) and VTZ$_{ud2}$ (VTZ$_{u*d2}$) denote bases formed by adding one and two sets of diffuse s, p, and d functions,

TABLE VI. SCF energies (a.u.), Fermi contact (A_{iso})[a] and spin dipole (A_{dip})[b] contributions (MHz) for CP at the experimental equilibrium geometry (2.952 a.u.) (Ref. 14).

		C atom				P atom			
		A_{iso}		A_{dip}		A_{iso}		A_{dip}	
Basis	Energy	resp.	aver.	resp.	aver.	resp.	aver.	resp.	aver.
VDZ	−378.455 499	−216.0	573.3	33.8	63.3	32.4	97.7	−71.9	73.3
VDZ$_u$	−378.455 573	−192.0	591.3	33.7	63.3	−69.1	93.8	−71.8	73.1
VTZ	−378.476 148	−189.0	579.9	35.8	66.6	−8.5	101.1	−68.7	76.0
VTZ$_u$	−378.476 302	−192.3	594.5	35.8	66.6	−75.5	100.5	−69.0	75.7
VTZ$_{up}$	−378.476 417	−189.2	594.6	36.0	66.4	−65.4	100.6	−70.7	74.2
VTZ$_{a*}$	−378.476 354	−192.1	594.5	35.7	66.6	−73.3	100.6	−70.6	74.0
VTZ$_{u*d1}$	−378.476 872	−190.5	596.4	36.2	66.5	−71.1	101.7	−72.7	73.9
VTZ$_{u*d2}$	−378.476 882	−192.8	596.4	36.1	66.5	−73.5	101.7	−72.1	73.9
VTZ$_{u*dt1}$	−378.477 059	−195.0	602.8	36.1	66.5	−73.8	102.2	−72.1	73.9
VTZ$_{u*dt2}$	−378.477 267	−200.6	611.9	36.1	66.5	−77.0	102.8	−71.5	73.9
VTZ$_{u*dt3}$	−378.477 271	−198.4	613.6	36.1	66.5	−74.4	102.9	−72.1	73.9
VTZ$_{u*dt4}$	−378.477 280	−199.5	616.9	36.1	66.5	−74.5	103.1	−72.1	73.9
VTZ$_{u*dt5'}$	−378.477 276	−199.6	617.2	36.1	66.5	−74.2	102.8	−72.1	73.9
HF[c]			618.3		67.9		104.7		73.9

[a] The FC values given represent one third of the trace of the hyperfine tensor (A).

[b] The SD values given are $(A_{\parallel} - A_{\perp})/3$, where $A_{\parallel}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ one of the other two elements.

[c] Numerical Hartree–Fock results of Ref. 6.

TABLE VII. Fermi contact (A_{iso})[a] and spin dipole (A_{dip})[b] contributions (MHz) for CN at the experimental equilibrium geometry (2.214 a.u.) (Ref. 14) using the VTZ$_{udt4}$ basis.

		C atom						N atom					
		A_{iso}			A_{dip}			A_{iso}			A_{dip}		
	Energy (a.u.)	resp.	aver.	tot.	resp.	aver.	tot.	resp.	aver.	tot.	resp.	aver.	tot.
SCF	−92.219 429	1056.6	978.8	2035.4	−177.0	61.1	−115.9	−166.0	12.1	−153.9	68.5	7.8	76.3
CASV	−92.371 035	47.4	632.5	680.0	0.2	49.9	50.1	3.0	−19.8	−16.8	1.2	17.7	18.8
CASA	−92.491 984	−49.8	639.0	589.1	2.6	49.2	51.8	−16.6	−6.0	−22.6	0.3	18.7	19.0
V.Co.[c]				−4.9			−0.2			0.2			0.1
Exp.[d]				588.1			45.0			−12.6			15.4
Exp.[e]										−13.9			20.1

[a] The FC values given represent one third of the trace of the hyperfine tensor (A).

[b] The SD values given are $(A_{\|} - A_{\perp})/3$, where $A_{\|}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ one of the other two elements.

[c] Vibrational corrections evaluated at the CASV level.

[d] Rare gas isolation technique, Ref. 3.

[e] Microwave results, Ref. 2.

respectively. VTZ$_{udti}$ (VTZ$_{u*dti}$) means that i tight functions have been added to the VTZ$_{ud1}$ (VTZ$_{u*d1}$) basis on every atom. The prime in VTZ$_{udt5'}$ indicates that the fifth tight function was added only to C. The results in Tables III and IV show that saturation towards tight functions within the 2 MHz accuracy was obtained after adding four tight functions. From Tables III and IV it is seen that basis set saturation is obtained at about the same level for the average value and for the response term. Our *final choice of bases,* which give saturation to an accuracy of 2 MHz in the CASV calculations, is the VTZ$_{udt4}$ basis for CN and the VTZ$_{u*dt4}$ basis for CP.

For all the basis sets where CASV calculations were carried out, we also performed SCF calculations. These SCF results are given in Tables V and VI for CN and CP, respectively. The basis set saturation observed at the SCF level is very similar to what was observed for CASV wave functions. It is interesting to compare our optimized basis set SCF results with numerical Hartree–Fock results, as the latter give the complete-basis result. Both for the CN and CP it is seen that our optimized bases give SCF results that agree with the numerical Hartree–Fock results to approximately the prespecified accuracy of 2 MHz. It thus appears that only small basis set errors will be encountered if we use the optimized bases for our larger correlated calculations.

Momose *et al.*[1] recently carried out calculations of hyperfine coupling constants for a variety of radicals containing first row atoms. They claimed that Dunning's DZ basis[4] could give accurate hyperfine coupling constants. To examine this, we report in Tables III and V results of DZ, DZ$_u$, DZP, and DZP$_u$ calculations for CN.[4] The results clearly demonstrate that these bases produce very large basis set errors both for the SCF and the CASV wave functions. Good agreement between calculated and experimental hyperfine coupling constants using the DZ basis set can thus only be caused by cancellation of basis set and correlation contributions. The DZ basis set should therefore not be used in hyperfine coupling constant calculations.

B. SCF versus CAS results

In Table VII we report hyperfine tensor values for CN obtained using the VTZ$_{udt4}$ basis and, in Table VIII, the corresponding numbers are reported for CP with the

TABLE VIII. Fermi contact (A_{iso})[a] and spin dipole (A_{dip})[b] contributions (MHz) for CP at the experimental equilibrium geometry (2.952 a.u.) (Ref. 14) using the VTZ$_{udt4}$ basis.

		C atom						P atom					
		A_{iso}			A_{dip}			A_{iso}			A_{dip}		
	Energy (a.u.)	resp.	aver.	tot.	resp.	aver.	tot.	resp.	aver.	tot.	resp.	aver.	tot.
SCF	−378.477 280	−199.5	616.9	417.4	36.1	66.5	102.7	−74.5	103.1	28.6	−72.1	73.9	1.7
CASV	−378.600 899	23.5	565.5	589.0	0.9	47.0	47.9	−21.6	−149.2	−170.8	29.8	121.9	151.7
CASA	−378.712 342	−52.5	557.8	505.3	−0.9	49.3	48.5	−155.1	−39.4	−194.5	24.5	131.6	156.1
V.Co.[c]				−1.5			−0.2			−0.1			0.7
Exp.[d]				474.7			52.7			−131.0			138.0

[a] The A_{iso} values given represent one third of the trace of the hyperfine tensor (A).

[b] The A_{dip} values given are equal to $(A_{\|} - A_{\perp})/3$, where $A_{\|}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ one of the other two elements.

[c] Vibrational corrections evaluated at the CASV level.

[d] Reference 5.

TABLE IX. CASV energies (a.u.), Fermi contact (A_{iso})^a and spin dipole (A_{dip})^b contributions (MHz) at several geometries (R,a.u.), and spectroscopic constants^c for CN.

		C atom		N atom	
R	Energy	A_{iso}	A_{dip}	A_{iso}	A_{dip}
2.974	−92.246 640	433.5	36.9	−5.0	24.8
2.774	−92.289 618	490.7	39.8	−8.0	23.5
2.574	−92.330 761	553.7	43.1	−12.0	22.1
2.374	−92.362 417	622.6	46.8	−15.8	20.4
2.334	−92.366 432	636.8	47.6	−16.4	20.0
2.294	−92.369 332	651.2	48.4	−16.7	19.7
2.254	−92.370 957	665.9	49.2	−16.9	19.2
2.214	−92.371 035	680.0	50.1	−16.8	18.8
2.174	−92.369 402	680.3	50.9	−16.8	18.4
2.134	−92.365 776	708.4	51.8	−15.6	18.0
2.094	−92.359 867	722.3	52.7	−14.3	17.5
2.054	−92.351 349	735.9	53.6	−12.5	17.0
1.854	−92.255 051	792.8	58.0	7.0	14.5
1.654	−92.013 931	808.4	62.4	50.6	12.0
1.454	−91.504 291	725.6	68.4	120.9	10.5
Spectroscopic constants^c		Calc.		Expt.^{d}	
R_e		2.232 0		2.214 4	
ω_e		2 001.1		2 068.59	
$\omega_e x_e$		14.02		13.087	
B_e		1.79		1.899 7	
α_e		0.015 6		0.017 36	

[a] The A_{iso} values given represent one third of the hyperfine tensor (A).

[b] The A_{dip} values given are $(A_{\parallel} - A_{\perp})/3$, where $A_{\parallel}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ the other two elements.

[c] R_e are given in a.u. and the other constants in cm^{-1}.

[d] Experimental values for ^{12}C^{14}N (Ref. 14).

TABLE X. CASV energies (a.u.), Fermi contact (A_{iso})^a and spin dipole (A_{dip})^b contributions (MHz) at several geometries (R,a.u.), and spectroscopic constants^c for CP.

		C atom		P atom	
R	Energy	A_{iso}	A_{dip}	A_{iso}	A_{dip}
3.711 7	−378.536 230	523.6	26.4	−252.5	216.9
3.511 7	−378.560 759	538.1	33.0	−248.6	190.9
3.311 7	−378.582 763	560.7	38.4	−237.7	173.5
3.111 7	−378.598 015	580.9	43.7	−210.6	160.2
3.071 7	−378.599 756	583.9	44.7	−202.2	157.9
3.031 7	−378.600 824	586.2	45.8	−193.2	155.8
2.991 7	−378.601 247	588.0	46.8	−182.7	153.7
2.951 7	−378.600 899	589.0	47.9	−170.8	151.7
2.911 7	−378.599 700	589.3	49.0	−157.8	149.9
2.871 7	−378.597 533	588.7	50.1	−143.3	148.1
2.831 7	−378.594 195	587.1	51.3	−126.7	146.5
2.791 7	−378.589 848	584.6	52.4	−109.4	145.1
2.591 7	−378.544 082	553.9	58.7	9.3	140.6
2.391 7	−378.442 321	488.4	65.8	192.0	142.9
2.191 7	−378.248 398	384.0	74.6	482.6	157.0
Spectroscopic constants^c		Calc.		Expt.^{d}	
R_e		2.988 6		2.951 7	
ω_e		1 178.5		1 239.67	
$\omega_e x_e$		3.535		6.86	
B_e		0.735		0.798 6	
α_e		0.004 8		0.005 97	

[a] The A_{iso} values given represent one third of the hyperfine tensor (A).

[b] The A_{dip} values given are $(A_{\parallel} - A_{\perp})/3$, where $A_{\parallel}$ represents the diagonal element of this contribution to the tensor in the direction of the molecular axis and $A_{\perp}$ the other two elements.

[c] R_e are given in a.u. and the other constants in cm^{-1}.

[d] Experimental values for ^{12}C^{31}P (Ref. 14).

VTZ_{u^*dt4} basis. The results of Tables VII and VIII show that a SCF description is inadequate for both CN and CP. In the worse case, A_{iso} on P, the SCF calculations give a numerical value of the wrong sign. At the CASV level, all hyperfine coupling constants have the right sign and their numerical values are at most 20% different from the experimental results.

At the CASA level the agreement with the experimental results improves. A large change has been found in the individual contributions to A_{iso} comparing the CASV and CASA results. For the C atom, the response contribution changes sign and for N and P both the response and the average value contributions change significantly. To understand this we must recognize that the active orbital space used in the CASV calculations gives a poor description of the dynamical valence correlation. The spin polarization resulting from the dynamical valence correlation is therefore described by the response term in CASV. In contrast, within the CASA calculation, the active orbital space is enlarged significantly to give a much better description of the dynamical valence correlation. The spin polarization contribution from the dynamical valence correlation is therefore contained in the correlated description of the valence space and is part of the average value contribution.

Experimental results have been reported for the CN radical using a rare gas matrix isolation technique[3] and for A_{iso} and A_{dip} of the N atom also using microwave spectroscopy.[2] For the CP molecule Knight *et al.* have previously carried out large scale MRCI calculations of the hyperfine coupling constants,[5] obtaining for A_{iso} and A_{dip} on the P atom an accuracy similar to ours. They had difficuties determining even the correct sign for A_{iso} on P, probably caused by the fact that the SCF description is quite inadequate and that a pure multiconfigurational treatment is therefore required. From our CASA results it is seen that whereas for the C atoms the spin polarization of the core orbitals contributes to the A_{iso} values in only about an 8%, for the N and P atoms it represents the main contribution (∼80%). This is one of the reasons for the difficulties in determining these constants.

The vibrational corrections were evaluated for both systems at the CASV level using the Vibrot program in MOLCAS,[13] and are shown to be insignificant and below the experimental uncertainties. The vibrational averages were carried out based on the calculations whose results are reported in Tables IX and X, which give reasonable spectroscopic constants. These results show that the internuclear distance dependence of the hyperfine constants is small except for the P atom in CP. This hyperfine coupling constant gave the largest difference between the theoretical and the experimental values; for this reason, it is interesting to observe that a small compression in the internuclear equilibrium distance, as may, for example, be due to matrix isolation, gives close agreement between theory and experiment.

IV. OVERVIEW AND DISCUSSION

We used the MCSCF RU approach to evaluate the hyperfine coupling constants for the ground electronic states of CN and CP. In this 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 spin of the system is allowed to relax. As a result, any first order molecular property becomes evaluated as a sum of an average term and a term containing the first order response of the wave function to the perturbation. This last term does not vanish here because the spin restricted MCSCF wave function is not optimized with respect to the 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 term; the spin polarizations of the core orbitals are taken care of by the response term. Our results show that for the C atoms the size of the response term describing the core polarization effects is small, most of the spin polarization is actually caused by the valence orbitals; but for the N and P atoms, the opposite trend holds.

Our calculations show that a SCF wave function is inadequate for describing the hyperfine coupling constants. In contrast, using a CAS valence wave function gives a qualitatively correct treatment of the hyperfine coupling constants, with the correct sign and with numerical values differing in general $<20\%$ from the experimental values. Extending the active space of the MCSCF calculation to include the next layer of correlating orbitals giving a balanced description of the molecular system increases significantly the accuracy of the hyperfine coupling constants.

Determination of accurate hyperfine coupling constants requires very good basis sets to be used. We therefore initiated all of our calculations with a careful basis set analysis and found that triple zeta basis sets with uncontracted *s* functions, one set of diffuse *s*, *p*, and *d* functions and a few additional tight *s* functions are appropiate for hyperfine coupling calculations. Recently Momose *et al.*[1] stated that it suffices to use double zeta basis sets to obtain accurate hyperfine coupling constants; our basis set investigations clearly demonstrate this statement to be incorrect.

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