

Atomic Hyperfine-Coupling Parameters for the Transition Metals

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Dipolar hyperfine-coupling parameters for transition-metal nd and $(n + 1)p$ orbitals and isotropic hyperfine-coupling parameters for $(n + 1)s$ orbitals are computed from SCF–Hartree–Fock–Slater atomic orbitals. The parameters depend strongly on electronic configuration, particularly on the number of d electrons, and empirical equations are presented to allow computation of the parameters, given an assumed configuration. © 1997 Academic Press

INTRODUCTION

There have been several compilations of atomic parameters for use in the interpretation of nuclear hyperfine couplings observed in electron paramagnetic resonance spectra ($I-4$). The compilation of Morton and Preston (3), which was based on SCF–Hartree–Fock–Slater atomic orbitals, computed and tabulated by Herman and Skillman (5), has been most widely used and has generally given results which are at least consistent with electron conservation and expectations based on semiquantitative MO theory considerations. This compilation has several shortcomings, however, which are particularly serious for the transition metals. Since parameters are given only for the ground-state configurations of neutral atoms, e.g., $[\text{Ar}]3d^54s^1$ for Cr and $[\text{Ar}]3d^54s^2$ for Mn, significant errors may result when applied to transition-metal complexes or organo-transition-metal radicals in which the effective configuration is different. Several EPR spectra have been reported which exhibit metal hyperfine structure which can be understood only by postulating a significant contribution of an $(n + 1)p$ orbital to the singly occupied molecular orbital (SOMO) (6, 7). Again since only ground-state configurations were considered by Herman and Skillman, there is no way to evaluate the magnitude of this contribution. For these reasons, the computations of Herman and Skillman have been extended, using a slightly modified version of the original FORTRAN program.

COMPUTATIONS

The original SCF–Hartree–Fock–Slater program of Herman and Skillman (5) was modified to include computation of $\langle r^{-3} \rangle$ for p and d orbitals by numerical integration using

all 521 computed points (the tabulated wavefunctions published by Herman and Skillman included every fourth point). The modifications also included extrapolation of s -orbital wavefunctions to $r = 0$, using a quadratic fit to the first 20 points. Computations were carried out for each of the 24 elements of groups 4–11 (IVA–IB) for the 14 configurations listed in Table 1 (the SCF program failed to converge for the $3d^94s^1$ and $3d^{10}4s^1$ configurations of Ni and Cu, respectively; thus for these two elements, only 13 configurations were used).

RESULTS AND DISCUSSION

On inspection of the computed results, it became apparent that all three parameters— $\langle r^{-3} \rangle_{nd}$, $\langle r^{-3} \rangle_{(n+1)p}$, and $\psi(0)_{(n+1)s}^2$ —depend strongly on the number of nd electrons and less strongly on the number of $(n + 1)s$ and $(n + 1)p$ electrons.

TABLE 1
Electronic Configurations Used in Computations

Charge	nd^a	Δn_d	$(n + 1)s$	$(n + 1)p$
0^b	$g - 1$	+1	1	0
0	$g - 1$	+1	0	1
0^c	$g - 2$	0	2	0
0	$g - 2$	0	1	1
0	$g - 3$	-1	2	1
1	$g - 1$	+1	0	0
1	$g - 2$	0	1	0
1	$g - 2$	0	0	1
1	$g - 3$	-1	2	0
1	$g - 3$	-1	1	1
2^d	$g - 2$	0	0	0
2	$g - 3$	-1	1	0
2	$g - 3$	-1	0	1
3	$g - 3$	-1	0	0

^a g , group number.

^b Ground-state configuration for Cr, Cu, Nb, Mo, Tc, Ru, Rh, Ag, Pt, and Au.

^c Ground-state configuration for Ti, V, Mn, Fe, Co, Ni, Zr, Hf, Ta, W, Re, Os, and Ir.

^d Reference configuration in this work.

TABLE 2
EPR Hyperfine Coupling Parameters

Isotope	I	μ^a	Abund. ^a	F^b		A^c	B^c	C^c	D^c
⁴⁷ Ti	5/2	-0.7885	7.3	-30.13	$\langle r^{-3} \rangle_{3d}$	2.554(7)	-0.444(5)	-0.057(5)	-0.009(8)
⁴⁹ Ti	7/2	-1.1042	5.5	-30.14	$[\psi^2(0)]_{4s}$	37.1(6)	-12.8(3)	-5.5(4)	-2.7(4)
					$\langle r^{-3} \rangle_{4p}$	2.15(3)	-1.37(4)	-0.76(4)	—
⁵⁰ V	6	3.3457	0.25	53.26	$\langle r^{-3} \rangle_{3d}$	3.229(6)	-0.479(5)	-0.060(5)	-0.013(7)
⁵¹ V	7/2	5.1487	99.75	140.52	$[\psi^2(0)]_{4s}$	42.6(6)	-14.3(3)	-6.1(4)	-2.9(4)
					$\langle r^{-3} \rangle_{4p}$	2.42(4)	-1.53(4)	-0.86(4)	—
⁵³ Cr	3/2	-0.4745	9.50	-30.22	$\langle r^{-3} \rangle_{3d}$	3.990(6)	-0.517(4)	-0.062(4)	-0.017(7)
					$[\psi^2(0)]_{4s}$	47.8(6)	-16.0(3)	-6.9(4)	-3.2(4)
					$\langle r^{-3} \rangle_{4p}$	2.69(4)	-1.70(5)	-0.97(5)	—
⁵⁵ Mn	5/2	3.4687	100.0	132.53	$\langle r^{-3} \rangle_{3d}$	4.841(5)	-0.559(4)	-0.064(4)	-0.020(6)
					$[\psi^2(0)]_{4s}$	53.6(7)	-17.8(3)	-7.6(5)	-3.4(5)
					$\langle r^{-3} \rangle_{4p}$	2.96(4)	-1.88(5)	-1.08(5)	—
⁵⁷ Fe	1/2	0.0906	2.1	17.31	$\langle r^{-3} \rangle_{3d}$	5.789(6)	-0.604(4)	-0.066(4)	-0.021(6)
					$[\psi^2(0)]_{4s}$	59.8(8)	-19.7(4)	-8.5(5)	-3.7(5)
					$\langle r^{-3} \rangle_{4p}$	3.23(5)	-2.07(5)	-1.19(5)	—
⁵⁹ Co	7/2	4.63	100.0	126.4	$\langle r^{-3} \rangle_{3d}$	6.840(5)	-0.650(4)	-0.067(4)	-0.024(6)
					$[\psi^2(0)]_{4s}$	66.2(9)	-21.7(4)	-9.4(6)	-4.0(6)
					$\langle r^{-3} \rangle_{4p}$	3.50(5)	-2.26(6)	-1.32(6)	—
⁶¹ Ni	3/2	-0.7500	1.14	-47.76	$\langle r^{-3} \rangle_{3d}$	7.997(6)	-0.700(5)	-0.070(4)	-0.024(7)
					$[\psi^2(0)]_{4s}$	73.1(12)	-23.7(8)	-10.3(8)	-4.3(8)
					$\langle r^{-3} \rangle_{4p}$	3.77(5)	-2.45(6)	-1.44(6)	—
⁶³ Cu	3/2	2.2233	69.17	141.58	$\langle r^{-3} \rangle_{3d}$	9.270(6)	-0.750(5)	-0.072(5)	-0.025(7)
⁶⁵ Cu	3/2	2.3817	30.83	151.67	$[\psi^2(0)]_{4s}$	80.3(14)	-25.8(9)	-11.3(9)	-4.6(9)
					$\langle r^{-3} \rangle_{4p}$	4.05(6)	-2.65(7)	-1.57(7)	—

^a From Ref. (8)

^b Factor defined by Eq. [4].

^c Parameters A , B , C , and D refer to Eqs. [1]–[3]; number in parentheses is uncertainty in last digit(s).

In other words, the parameters are influenced by shielding effects rather than net charge. The results can be summarized accurately by the empirical equations

$$\langle r^{-3} \rangle_{nd} = A + B\Delta n_d + Cn_s + Dn_p \quad [1]$$

$$\frac{8\pi}{3} [\psi^2(0)]_{(n+1)s} = A + B\Delta n_d + Cn_s + Dn_p \quad [2]$$

$$\langle r^{-3} \rangle_{(n+1)p} = A + B\Delta n_d + Cn_s, \quad [3]$$

where $\Delta n_d = n_d - g + 2$, g is the group number, n_s is the number of $(n + 1)s$ electrons, and n_p is the number of $(n + 1)p$ electrons. The results for the 14 configurations were fitted by least-squares analysis to Eqs. [1]–[3] to give the parameters A – D shown in Table 2; the uncertainties quoted are from the least-squares-fitting procedure. The parameters

TABLE 2—Continued

Isotope	I	μ^a	Abund. ^a	F^b		A^c	B^c	C^c	D^c
⁹¹ Zr	5/2	-1.3036	11.22	-49.81	$\langle r^{-3} \rangle_{4d}$	3.407(11)	-0.542(9)	-0.144(9)	-0.036(13)
					$[\psi^2(0)]_{5s}$	75.7(9)	-21.3(4)	-10.3(6)	-4.8(6)
					$\langle r^{-3} \rangle_{5p}$	3.70(3)	-2.03(4)	-1.20(4)	—
⁹³ Nb	9/2	6.1705	100.0	130.98	$\langle r^{-3} \rangle_{4d}$	4.197(9)	-0.565(7)	-0.142(7)	-0.045(11)
					$[\psi^2(0)]_{5s}$	86.1(10)	-24.2(5)	-11.5(6)	-5.4(6)
					$\langle r^{-3} \rangle_{5p}$	4.14(3)	-2.27(4)	-1.35(4)	—
⁹⁵ Mo	5/2	-0.9142	15.92	-34.93	$\langle r^{-3} \rangle_{4d}$	5.043(8)	-0.591(7)	-0.140(7)	-0.050(10)
⁹⁷ Mo	5/2	-0.9335	9.55	-35.67	$[\psi^2(0)]_{5s}$	96.0(12)	-27.0(6)	-12.5(7)	-5.6(7)
					$\langle r^{-3} \rangle_{5p}$	4.55(4)	-2.51(4)	-1.49(4)	—
⁹⁹ Tc	9/2	5.6847	—	120.67	$\langle r^{-3} \rangle_{4d}$	5.951(8)	-0.619(6)	-0.137(6)	-0.053(10)
					$[\psi^2(0)]_{5s}$	106.9(15)	-30.4(7)	-14.2(9)	-6.5(9)
					$\langle r^{-3} \rangle_{5p}$	4.93(4)	-2.76(4)	-1.64(4)	—
⁹⁹ Ru	5/2	-0.7188	12.7	-24.50	$\langle r^{-3} \rangle_{4d}$	6.929(8)	-0.648(6)	-0.134(6)	-0.054(10)
¹⁰¹ Ru	5/2	-0.6413	17.1	-27.46	$[\psi^2(0)]_{5s}$	117.6(17)	-33.7(8)	-15.6(11)	-7.0(11)
					$\langle r^{-3} \rangle_{5p}$	5.29(4)	-3.00(5)	-1.78(5)	—
¹⁰³ Rh	1/2	-0.0884	100.0	-16.89	$\langle r^{-3} \rangle_{4d}$	7.980(8)	-0.678(6)	-0.132(6)	-0.055(10)
					$[\psi^2(0)]_{5s}$	128.5(20)	-37.2(9)	-17.0(12)	-7.6(12)
					$\langle r^{-3} \rangle_{5p}$	5.64(4)	-3.24(5)	-1.93(5)	—
¹⁰⁵ Pd	5/2	-0.642	22.33	-24.53	$\langle r^{-3} \rangle_{4d}$	9.107(8)	-0.710(7)	-0.129(7)	-0.055(10)
					$[\psi^2(0)]_{5s}$	139.7(23)	-40.9(11)	-18.6(14)	-8.1(14)
					$\langle r^{-3} \rangle_{5p}$	5.98(5)	-3.49(5)	-2.08(5)	—
¹⁰⁷ Ag	1/2	-0.1136	51.84	-21.70	$\langle r^{-3} \rangle_{4d}$	10.314(8)	-0.744(7)	-0.127(7)	-0.054(10)
¹⁰⁹ Ag	1/2	-0.1306	48.16	-24.95	$[\psi^2(0)]_{5s}$	151.2(26)	-44.8(12)	-20.2(16)	-8.7(16)
					$\langle r^{-3} \rangle_{5p}$	6.30(5)	-3.73(6)	-2.22(6)	—

(and uncertainties) for the Eq. [2] parameters include the semiempirical relativistic correction determined by Morton and Preston, $[1 + (3.9 \pm 0.1) \times 10^{-6} Z^3]$. The overall errors in the fits to Eqs. [1], [2], and [3] were less than about 0.5, 1.5, and 2.5%, respectively.

Note that the parameters A represent values of $\langle r^{-3} \rangle_{nd}$, $(8\pi/3)[\psi^2(0)]_{(n+1)s}$, and $\langle r^{-3} \rangle_{(n+1)p}$ for the usual ground-state configuration of the $2+$ ions, or for a transition-metal atom in a molecule with $g - 2$ nd electrons and traces of $(n + 1)s$ and $(n + 1)p$ electrons contributing to the filled molecular orbitals.

The EPR parameters P_{nd} , $P_{(n+1)p}$, and $A_{(n+1)s}$ are obtained

from the least-squares parameters $A-D$ by multiplication by the factor F given by

$$F = \frac{g_e g_N \mu_0 \mu_B \mu_N}{4\pi h} \times (6.74834 \times 10^{30} \text{ au}^3 \text{ m}^{-3})(10^{-6} \text{ MHz s}^{-1}), \quad [4]$$

where $g_N = \mu/I$. The F factors are given for each of the transition-metal isotopes listed in Table 2 with μ taken from the *Handbook of Chemistry and Physics* (8). Thus, for example, the dipolar coupling parameters P_{3d} and P_{4p} and $4s$ iso-

TABLE 2—Continued

Isotope	I	μ^a	Abund. ^a	F^b		A^c	B^c	C^c	D^c
177Hf	7/2	0.7935	18.61	21.66	$\langle r^{-3} \rangle_{5d}$	6.34(2)	-0.99(2)	-0.30(2)	-0.07(2)
179Hf	9/2	-0.6409	13.63	-13.60	$[\psi^2(0)]_{6s}$	274(5)	-73(2)	-36(2)	-16(2)
					$\langle r^{-3} \rangle_{6p}$	6.80(5)	-3.61(6)	-2.21(6)	—
181Ta	7/2	2.370	100.0	64.68	$\langle r^{-3} \rangle_{5d}$	7.51(2)	-0.99(1)	-0.29(1)	-0.09(2)
					$[\psi^2(0)]_{6s}$	310(6)	-81(2)	-40(2)	-18(2)
					$\langle r^{-3} \rangle_{6p}$	7.51(6)	-3.96(7)	-2.42(7)	—
183W	1/2	0.1178	14.28	22.50	$\langle r^{-3} \rangle_{5d}$	8.72(1)	-1.00(1)	-0.28(1)	-0.10(2)
					$[\psi^2(0)]_{6s}$	345(7)	-90(2)	-44(3)	-20(3)
					$\langle r^{-3} \rangle_{6p}$	8.16(6)	-4.30(7)	-2.63(7)	—
185Re	5/2	3.1871	37.40	121.77	$\langle r^{-3} \rangle_{5d}$	9.98(1)	-1.02(1)	-0.27(1)	-0.11(2)
187Re	5/2	3.2197	62.60	123.02	$[\psi^2(0)]_{6s}$	387(8)	-103(3)	-52(4)	-25(4)
					$\langle r^{-3} \rangle_{6p}$	8.77(6)	-4.65(7)	-2.84(7)	—
187Os	1/2	0.0646	1.6	12.34	$\langle r^{-3} \rangle_{5d}$	11.30(1)	-1.03(1)	-0.26(1)	-0.11(2)
189Os	3/2	0.6599	16.1	42.02	$[\psi^2(0)]_{6s}$	417(9)	-110(3)	-53(4)	-24(4)
					$\langle r^{-3} \rangle_{6p}$	9.33(7)	-4.98(8)	-3.05(8)	—
191Ir	3/2	0.151	37.3	9.62	$\langle r^{-3} \rangle_{5d}$	12.68(1)	-1.05(1)	-0.26(1)	-0.11(2)
193Ir	3/2	0.164	62.7	10.44	$[\psi^2(0)]_{6s}$	454(10)	-120(4)	-58(4)	-26(4)
					$\langle r^{-3} \rangle_{6p}$	9.85(7)	-5.32(8)	-3.26(8)	—
195Pt	1/2	0.6095	33.8	116.44	$\langle r^{-3} \rangle_{5d}$	14.12(1)	-1.08(1)	-0.25(1)	-0.11(2)
					$[\psi^2(0)]_{6s}$	491(11)	-131(4)	-63(5)	-27(5)
					$\langle r^{-3} \rangle_{6p}$	10.34(7)	-5.64(9)	-3.45(9)	—
197Au	3/2	0.1458	100.0	9.285	$\langle r^{-3} \rangle_{5d}$	15.64(1)	-1.10(1)	-0.24(1)	-0.10(2)
					$[\psi^2(0)]_{6s}$	530(12)	-143(5)	-68(6)	-29(6)
					$\langle r^{-3} \rangle_{6p}$	10.80(8)	-5.97(9)	-3.66(9)	—

tropic coupling for the $3d^54s^2$ and $3d^64s^1$ configurations of Mn are

$$P_{3d} = F\langle r^{-3} \rangle_{3d} \\ = 132.53(4.841 - 0.064 \times 2) = 625 \text{ MHz}$$

$$P_{3d} = F\langle r^{-3} \rangle_{3d} \\ = 132.53(4.841 - 0.559 - 0.064) = 559 \text{ MHz}$$

$$P_{4p} = F\langle r^{-3} \rangle_{4p} \\ = 132.53(2.96 - 2 \times 1.08) = 106 \text{ MHz}$$

$$P_{4p} = F\langle r^{-3} \rangle_{4p} \\ = 132.53(2.96 - 1.88 - 1.08) = 0 \text{ MHz}$$

$$A_{4s} = F\psi(0)_{4s}^2 \\ = 132.53(53.6 - 2 \times 7.6) = 5089 \text{ MHz}$$

$$A_{4s} = F\psi(0)_{4s}^2 \\ = 132.53(53.6 - 17.8 - 7.6) = 3737 \text{ MHz.}$$

These results demonstrate the sensitivity of the hyperfine-coupling parameters to the d -electron count, particularly for

TABLE 3
Parameters for Inner-Shell s Orbitals for the nd^2 Configurations

	nd		1s			2s		3s		4s		5s	
	E	E	$\frac{8\pi\psi^2(0)}{300}$	E	$\frac{8\pi\psi^2(0)}{30}$	E	$\frac{8\pi\psi^2(0)}{3}$	E	$\frac{8\pi\psi^2(0)}{3}$	E	$\frac{8\pi\psi^2(0)}{3}$	E	$\frac{8\pi\psi^2(0)}{3}$
Ti	-1.89	-362	273	-41.6	239	-6.26	334	—	—	—	—	—	—
V	-2.03	-398	312	-46.6	278	-6.86	393	—	—	—	—	—	—
Cr	-2.16	-436	355	-51.7	320	-7.48	459	—	—	—	—	—	—
Mn	-2.29	-476	402	-56.9	367	-8.10	530	—	—	—	—	—	—
Fe	-2.42	-517	452	-62.4	417	-8.74	608	—	—	—	—	—	—
Co	-2.54	-560	507	-68.2	472	-9.39	692	—	—	—	—	—	—
Ni	-2.66	-605	566	-74.1	532	-10.1	783	—	—	—	—	—	—
Cu	-2.78	-652	629	-80.3	596	-10.7	881	—	—	—	—	—	—
Zr	-1.62	1292	1657	-179	1676	-31.0	2918	-5.37	475	—	—	—	—
Nb	-1.77	-1361	1784	-190	1813	-33.6	3199	-5.86	539	—	—	—	—
Mo	-1.92	-1433	1918	-202	1957	-36.2	3497	-6.34	607	—	—	—	—
Tc	-2.06	-1506	2059	-214	2109	-39.0	3814	-6.81	679	—	—	—	—
Ru	-2.20	-1581	2206	-227	2268	-41.8	4149	-7.28	755	—	—	—	—
Rh	-2.35	-1658	2360	-239	2435	-44.7	4503	-7.76	835	—	—	—	—
Pd	-2.49	-1736	2520	-252	2610	-47.7	4877	-8.23	920	—	—	—	—
Ag	-2.63	-1817	2688	-266	2793	-50.7	5271	-8.71	1010	—	—	—	—
Hf	-1.59	-4445	9617	-730	10606	-167	23298	-34.0	5577	-5.63	929	—	—
Ta	-1.72	-4575	10020	-754	11067	-173	24398	-35.8	5873	-6.02	1010	—	—
W	-1.85	-4707	10434	-778	11543	-180	25531	-37.6	6181	-6.42	1094	—	—
Re	-1.98	-4841	10860	-803	12032	-186	26698	-39.4	6502	-6.81	1193	—	—
Os	-2.12	-4976	11296	-828	12534	-193	27902	-41.3	6836	-7.20	1275	—	—
Ir	-2.24	-5114	11744	-854	13050	-200	29140	-43.3	7183	-7.59	1371	—	—
Pt	-2.37	-5253	12203	-879	13580	-207	30413	-45.2	7543	-7.98	1471	—	—
Au	-2.50	-5394	12674	-906	14123	-214	31722	-47.3	7916	-8.37	1575	—	—

P_{4p} , and underscore the understanding that spin densities obtained from EPR dipolar couplings alone should be treated as order-of-magnitude estimates at best.

The parameter $P_{3d} = 625$ MHz for the $3d^54s^2$ configuration of Mn can be compared with the value given by Morton and Preston, 622.1 MHz, based on the same configuration (3). Most of the present values are similarly slightly different

from those in the Morton/Preston tabulation; there are several reasons for these differences: (i) Because four times as many points were used, the numerical integrations are slightly more accurate in the present work than those based on the Herman-Skillman-tabulated wavefunctions; thus, for Mn, Morton and Preston found $\langle r^{-3} \rangle_{3d} = 4.721$ compared with 4.7177 for the same configuration but with 521 points.

(ii) The least-squares parameters are subject to fitting error; in the case of Mn, the least-squares parameters give $\langle r^{-3} \rangle_{3d} = 4.713$, 0.1% smaller than the actual computed value. (iii) The magnetic moments used in the present tabulations are from a more modern tabulation and differ slightly from those used by Morton and Preston; thus, the factor F used for Mn in the Morton/Preston tabulation was 131.8 MHz, 0.6% smaller than the present value.

The parameters P_{nd} and $P_{(n+1)p}$ are used in practice with an angular factor to compute the electron-nuclear dipolar coupling. The components of the hyperfine matrices for the SOMO of Eq. [5] are given by Eqs. [6] (9):

$$|\text{SOMO}\rangle = a_z^2|z^2\rangle + a_{x^2-y^2}|x^2 - y^2\rangle + a_{xy}|xy\rangle \\ + a_{xz}|xz\rangle + a_{yz}|yz\rangle + \dots \quad [5]$$

$$A_{xx} = \frac{2}{7}P_{nd}(-a_z^2 + a_{x^2-y^2}^2 + a_{xy}^2 + a_{xz}^2 \\ - 2a_{yz}^2 - 2\sqrt{3}a_{x^2-y^2}a_z^2) \quad [6a]$$

$$A_{yy} = \frac{2}{7}P_{nd}(-a_z^2 + a_{x^2-y^2}^2 + a_{xy}^2 - 2a_{xz}^2 \\ + a_{yz}^2 + 2\sqrt{3}a_{x^2-y^2}a_z^2) \quad [6b]$$

$$A_{zz} = \frac{2}{7}P_{nd}(2a_z^2 - 2a_{x^2-y^2}^2 - 2a_{xy}^2 + a_{xz}^2 + a_{yz}^2) \quad [6c]$$

$$A_{xy} = \frac{2}{7}P_{nd}(-2\sqrt{3}a_z^2a_{xy} + 3a_{xz}a_{yz}) \quad [6d]$$

$$A_{xz} = \frac{2}{7}P_{nd}(\sqrt{3}a_z^2a_{xz} + 3a_{xz}a_{x^2-y^2} + 3a_{yz}a_{xy}) \quad [6e]$$

$$A_{yz} = \frac{2}{7}P_{nd}(\sqrt{3}a_z^2a_{yz} - 3a_{yz}a_{x^2-y^2} + 3a_{xz}a_{xy}). \quad [6f]$$

Thus, a SOMO with a hybrid d -orbital contribution may have a nondiagonal hyperfine matrix in the xyz -axis system, in other words, principal axes which differ from the molecular axes. If there are p -orbital contributions to the SOMO, as in Eq. [7], the additional dipolar matrix element terms are given by Eqs. [8]:

$$|\text{SOMO}\rangle = b_x|x\rangle + b_y|y\rangle + b_z|z\rangle + \dots \quad [7]$$

$$A_{xx} = \frac{2}{5}P_{(n+1)p}(2b_x^2 - b_y^2 - b_z^2) \quad [8a]$$

$$A_{yy} = \frac{2}{5}P_{(n+1)p}(-b_x^2 + 2b_y^2 - b_z^2) \quad [8b]$$

$$A_{zz} = \frac{2}{5}P_{(n+1)p}(-b_x^2 - b_y^2 + 2b_z^2) \quad [8c]$$

$$A_{ij} = -\frac{6}{5}P_{(n+1)p}b_ib_j. \quad [8d]$$

An isotropic metal hyperfine coupling normally has at least three contributions: (i) a direct contribution from $(n+1)s$ spin density, $\langle A \rangle_i = A_{(n+1)s}\rho^s$; (ii) a small contribution from the spin-orbit coupling correction to the dipolar coupling, usually on the order of $\langle A \rangle_{ii} = P_{nd}\langle g \rangle - g_e$; and (iii) a contribution, of opposite sign to $\langle A \rangle_i$, proportional to the d -electron spin density but arising from polarization of inner-shell s orbitals, $\langle A \rangle_{iii} = Q_{nd}\rho^d$. In practice, the

TABLE 4
Spin Density Calculations for $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]^-$

Configuration	P_{5d}	P_{6p}	ρ^{5d}	ρ^{6p}	ρ_{total}
d^3s^1	1440	1866	0.211	0.087	0.596
d^4	1348	1645	0.226	0.099	0.650
d^4s^1	1315	1297	0.231	0.125	0.712
d^5	1223	1075	0.249	0.151	0.800
d^5s^1	1190	727	0.256	0.224	0.959
d^6	1098	515	0.277	0.322	1.198

third contribution usually dominates. Although at present there is no adequate theoretical way of predicting the Q parameters, they are expected to be proportional to $(8\pi/3)\psi^2(0)$ and inversely proportional to $(E_{nd} - E_s)$. These parameters, obtained from the present computations, are given in Table 3 for the standard M^{2+} configuration, $\Delta n_d = n_s = n_p = 0$. The inner-shell s parameters are relatively insensitive to Δn_d , n_s , and n_p .

An $(n+1)p$ -orbital contribution to the SOMO has been postulated in cases where, for reasons of symmetry, a nonaxial hyperfine matrix cannot be explained by nd -orbital contributions alone. For example, Kawamura and co-workers (6) obtained EPR spectra of $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_8]^-$ (D_{2h} symmetry) and found a markedly nonaxial $^{185,187}\text{Re}$ hyperfine matrix (278, 105, 393 MHz) (all assumed negative). MO arguments suggested that the SOMO is of b_{1g} symmetry with possible d_{xy} and p_y contributions, each of which gives an axial hyperfine matrix, but with different major axes, as shown by

$$\mathbf{A} = A_s + \frac{2}{7}P_{5d}\rho^{5d} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \\ + \frac{2}{5}P_{6p}\rho^{6p} \begin{bmatrix} -1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & -1 \end{bmatrix}. \quad [9]$$

After approximate corrections for spin-orbit coupling, the matrix can be factored to obtain $P_{5d}\rho^d = 304$ MHz, $P_{6p}\rho^p = 162$ MHz. In order to employ the parameters obtained in the present work, we must assume an effective configuration for the Re atoms, i.e., the number of Re $5d$, $6s$, and $6p$ orbitals which are incorporated into filled MOs in the complex. In Table 4, we show the results of calculations for several assumed configurations. Clearly, the d^6 configuration is impossible and the d^5s^1 configuration unlikely since the SOMO is at least somewhat delocalized onto the equatorial CO ligands. Taking the H ligands as hydrides, the formal oxidation state of Re in the complex is +0.5. Thus, the d^3s^1 and d^4 configurations with a net charge of

TABLE 5
Spin Density Calculations for $[(C_5Ph_5)M(CO)_2]^-$ (M = Co, Rh)

Configuration	P_{3d}^{Co}	P_{4p}^{Co}	ρ^{3d}	ρ^{4p}	P_{4d}^{Rh}	P_{5p}^{Rh}	ρ^{4d}	ρ^{5p}
d^6	946	728	0.420	0.093	-146	-150	0.280	0.122
d^6s^1	938	561	0.424	0.121	-144	-117	0.284	0.155
d^7	865	442	0.460	0.154	-135	-95	0.304	0.191
d^7s^1	856	276	0.465	0.257	-133	-63	0.309	0.291
d^8	782	157	0.509	0.434	-121	-8	0.338	$\gg 1$

+3 on each Re atom seem unlikely. This leaves the d^4s^1 or d^5 configuration with a net charge of +2 and 25–30% $6p$ character in the SOMO. Because the dipolar parameter P for $(n + 1)p$ orbitals is so very sensitive to electronic configuration, it is unlikely that, from EPR evidence alone, the SOMO composition can be determined more exactly.

A very similar problem was encountered by Connelly *et al.* (7), in the interpretation of the EPR parameters for $[(C_5Ph_5)M(CO)_2]^-$, M = Co, Rh. Assuming pseudo- C_{2v} symmetry for the complexes, the SOMO presumably is primarily metal d_{yz} with other d -orbital contributions symmetry forbidden. The nonaxial hyperfine matrices were explained qualitatively by invoking admixture of metal $(n + 1)p_y$ character. Given the hyperfine matrices (-473, -50, -132) and (79, 22, 44) for Co and Rh, respectively, we obtain $P_{3d}\rho^{3d} = 398$ and $P_{4p}\rho^{4p} = 68$ MHz for Co and $P_{4d}\rho^{4d} = 41$ MHz and $P_{5p}\rho^{5p} = 18$ MHz for Rh. The results of various assumed electron configurations are shown in Table 5. Here the formal metal oxidation number is zero, but the d^9 or d^8s^1 configuration has P_p close to zero. The d^8 configuration results in too high a metal spin density; d^7s^1 , d^7 , and d^6s^1 give plausible results, although a metal charge of +2 seems too large.

Again, the parameters obtained in this work are useful primarily in verifying that $(n + 1)p$ -orbital admixture to the SOMO is indeed a plausible explanation of the departure of the metal hyperfine matrix from axial symmetry.

REFERENCES

1. B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.* **32**, 3206 (1970).
2. S. Fraga, K. M. S. Saxena, and B. W. N. Lo, *At. Data* **3**, 323 (1971); S. Fraga and K. M. S. Saxena, *At. Data* **4**, 255,269 (1972); F. Fraga, J. Kaarwowski, and K. M. S. Saxena, "Handbook of Atomic Data," Elsevier, Amsterdam, 1976.
3. J. R. Morton and K. F. Preston, *J. Magn. Reson.* **30**, 577 (1978).
4. A. K. Koh and D. J. Miller, *At. Data Nucl. Data Tables* **33**, 235 (1985).
5. F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, New Jersey, 1963.
6. T. Sowa, T. Kawamura, T. Tamabe, and T. Yonezawa, *J. Am. Chem. Soc.* **107**, 6471 (1985).
7. N. G. Connelly, W. E. Geiger, G. A. Lane, S. J. Raven, and P. H. Rieger, *J. Am. Chem. Soc.* **108**, 6219 (1986).
8. D. R. Lide (Ed.), "Handbook of Chemistry and Physics," 75th ed., CRC Press, Boca Raton, Florida, 1994.
9. P. H. Rieger, in "Organometallic Radical Processes" (W. C. Troglor, Ed.), p. 270, Elsevier, Amsterdam, 1990.