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HYPERFINE INTERACTIONS: TABLES OF ISOTROPIC AND ANISOTROPIC PARAMETERS FOR THE ATOMS HYDROGEN TO BISMUTH

by

J. A. McMillan and T. Halpern

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by

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March 1971

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HYPERFINE INTERACTIONS: TABLES OF ISOTROPIC AND ANISOTROPIC PARAMETERS FOR THE ATOMS HYDROGEN TO BISMUTH

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ABSTRACT

This report discusses the hyperfine-interaction paramagnetic Hamiltonian. Tables of expectation values for the atoms hydrogen to bismuth are given for the contact term and for the principal values of the dipole-dipole interaction, reduced to g = 2. An empirical relation is given that permits one to evaluate the change in $\langle r^{-3} \rangle$ with charge in transition metal ions.

INTRODUCTION

The hyperfine term of the paramagnetic Hamiltonian is

$$\mathcal{H}_{hf} = K\hat{S} \cdot \hat{I} + \Omega\left(3\,\frac{\hat{S} \cdot \bar{r}\bar{r} \cdot \hat{I}}{r^5} - \frac{(\hat{S} - \hat{L}) \cdot \hat{I}}{r^3}\right), \tag{1}$$

where K is a scalar, $\hat{S}$ and $\hat{I}$ are the electron and nuclear spin operators, $\bar{r}$ is the electron radius vector with origin at the nucleus, $\hat{L}$ is the orbital angular momentum operator, and

$$\Omega = g_e \mu_B (g_N \mu_N / h), \tag{2}$$

with

g_e = free-electron g value,

μ_B = Bohr magneton,

and

$g_N \mu_N / h$ = nuclear Larmor precession frequency.

When the orbital angular momentum is completely quenched by the crystal field, the term in $\hat{L}$ vanishes and Eq. 1 reduces to

$$\mathscr{H}_{hf} = K\hat{S} \cdot \hat{I} + \Omega\left(3\,\frac{\hat{S} \cdot \bar{r}\bar{r} \cdot \hat{I}}{r^5} - \frac{\hat{S} \cdot \hat{I}}{r^3}\right), \tag{3}$$

which is then valid for spin-only paramagnetism.

In order to treat an incompletely quenched angular momentum, Eq. 1 is rewritten as

$$\mathscr{H}_{hf} = \hat{S} \cdot \hat{A} \cdot \hat{I}, \tag{4}$$

where $\hat{A}$ is a symmetric, second-rank tensor and $\hat{S}$ is now the effective-spin operator, for which no different symbol is used. The effective-spin operator operates on the perturbed wavefunction of the electron state including orbital effects, and not on the spin variables only.

When the ground state is an orbital singlet, for example, first-order perturbation leads to an electron wavefunction, $|0^*\rangle$, which is composed of the unperturbed ground state $|0\rangle$ and admixture of excited states $|n\rangle$; i.e.,

$$|0^*\rangle = |0\rangle - \lambda \sum_n \frac{\langle n|\hat{L} \cdot \hat{S}|0\rangle}{E_n - E_0}\,|n\rangle, \tag{5}$$

where $E_n - E_0$ is the crystal-field splitting of the electron energy levels and λ is the expectation value of the spin-orbit coupling operator which is a function of the radius alone; i.e.,

$$\hat{\lambda} = \frac{e\hbar^2}{2m^2c^2}\left[\frac{1}{r}\frac{\partial}{\partial r}\,V(r)\right]. \tag{6}$$

Equation 5 is valid if

(a) $|n\rangle$ belongs to the $|0\rangle$ manifold,

and

(b) $\lambda \ll E_n - E_0$.

The wavefunction of Eq. 5 is an eigenfunction of the effective-spin operator $\hat{S}_z$ with the eigenvalue m_S; i.e.,

$$\hat{S}_z|0^*,m_S\rangle = m_S|0^*,m_S\rangle. \tag{7}$$

Raising and lowering operators S_+ and S_- are defined in the usual manner.

Second-order perturbation leads to an effective-spin hyperfine term in which the orbital effect makes the electron-nucleus dipole-dipole interaction tensor no longer traceless. Each case has to be worked out after a

knowledge of the crystal-field splittings and leads to the hyperfine parameters that would have been observed, had the orbital angular momentum been completely quenched. These are the parameters discussed and tabulated in the present report.

DISCUSSION OF TABLES

The hyperfine-interaction tensor $\hat{A}$, reduced to spin-only paramagnetism, is composed of an isotropic part K and a traceless tensor $\hat{T}$ such that

$$\hat{A} = K + \hat{T}. \tag{8}$$

Since $\hat{T}$ is traceless, K is given by one-third the trace of $\hat{A}$; i.e.,

$$K = \frac{1}{3} \mathrm{Tr}\hat{A}. \tag{9}$$

In the orthogonal reference frame that diagonalizes $\hat{T}$ (and hence $\hat{A}$), the principal values of both tensors are related by

$$A_{ii} = K + T_{ii}, \tag{10}$$

where the subscripts stand for the coordinates; i.e., i = x, y, z.

In s states, the isotropic term, also called Fermi or contact term, is given by

$$K = \frac{8\pi}{3} \Omega |\psi_{ns}(0)|^2. \tag{11}$$

The values of K in MHz and in gauss are given in Table I.

For core polarization, K is given by

$$K = \frac{8\pi}{3} \Omega \sum_{ns} \left[|\psi_{ns}(0)\uparrow|^2 - |\psi_{ns}(0)\downarrow|^2 \right] \tag{12}$$

where the arrow pointing up identifies the orientation of the total spin S of the ion. Spin-polarized Hartree-Fock calculations have been performed for several ion series.[1-3] These calculations indicate that the polarization is opposed to that of the ion total spin S, being of -125, -375, and -700 kG at the nucleus for $m_S = \frac{1}{2}$, approximately, for the first (3d), second (4d), and third (5d) transition series, respectively. Values have also been calculated for some of the rare earths and several typical elements.[1,2]

TABLE I. Parameters of Hyperfine Interaction

Nucleus	% Abundance	Nuclear Spin I	$g_N\mu_N/h$, MHz/kG	Isotropic Splitting: Orbital	$A^2 = 4\pi\psi^2_{ns}(0)$, a.u.	K: MHz	K: Gauss	Anisotropic Splitting: Orbital	$\langle r^{-3}\rangle$, a.u.	$2\mu_B g_N \mu_N \langle r^{-3}\rangle$: MHz	$2\mu_B g_N \mu_N \langle r^{-3}\rangle$: Gauss
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
^{1}H	99.9844	1/2	4.25759	1s		1,420	508				
^{2}H	1.56×10^{-2}	1	0.65357			218	78				
^{3}H*[a]	-	1/2	4.5414			1,515	542				
^{3}He	$10^{-7} - 10^{-5}$	1/2	-3.2435		22.6	-6,125	-2,192				
^{6}Li	7.43	1	0.6265	2s	2.09	109	39				
^{7}Li	92.57	3/2	1.6547			288	103				
^{9}Be	100	3/2	-0.5983		7.15	-358	-128				
^{10}B	18.83	3	0.4575		17.7	677	242	2p	0.7756	44.5	15.9
^{11}B	81.17	3/2	1.3660			2,022	723			133	47.6
^{13}C	1.108	1/2	1.0705		35.0	3,128	1,119		1.6618	223	79.8
^{14}N	99.635	1	0.3076		60.5	1,557	557		3.0205	117	41.9
^{15}N	0.365	1/2	-0.4315			-2,184	-781			-163	-58.3
^{17}O	3.7×10^{-2}	5/2	-0.5772		96.1	-4,637	-1,659		4.9490	-358	-128
^{19}F	100	1/2	4.0055		143	47,959	17,160		7.5451	3,790	1,356
^{21}Ne	0.257	3/2	0.3363		204	27,630	9,886		10.906	460	165
^{22}Na*	-	3	0.4434	3s	6.66	247	88.4		17.004	945	338
^{23}Na	100	3/2	1.1262			627	224			2,401	859
^{24}Na*	-	4	0.322			174	62.3		17.004	687	246
^{25}Mg	10.05	5/2	-0.2606		15.3	-333	-119		24.919	-814	-291
^{27}Al	100	5/2	1.1094		29.6	2,748	983	3p	1.088	151	54.0
^{29}Si	4.70	1/2	-0.8458		48.1	-3,403	-1,218		2.027	-215	-76.9
^{31}P	100	1/2	1.7236		71.3	10,275	3,676		3.266	706	253
^{33}S	0.74	3/2	0.3266		99.8	2,724	975		4.8364	198	70.8
^{35}S*	-	3/2	0.508			4,236	1,516			308	110
^{35}Cl	75.4	3/2	0.4172		134	4,673	1,672		6.7688	354	127
^{36}Cl	-	2	0.4893			5,480	1,961			415	148
^{37}Cl	24.6	3/2	0.3472			3,889	1,391			295	106
^{39}K	93.08	3/2	0.1987	4s	8.73	145	51.9		8.9747	224	80.1
^{40}K*	1.19×10^{-2}	4	-0.2470			-180	-64.4			-278	-99.5
^{41}K	6.91	3/2	0.1092			80	28.6			123	44.0
^{42}K*	-	2	-0.434			-317	-113			-488	-175
^{43}Ca	0.13	7/2	-0.2865		17.4	-418	-150		17.7403	-637	-228
^{45}Sc	100	7/2	1.0344		21.2	1,836	657	3d	1.4294	185	66.2
^{47}Ti	7.75	5/2	-0.2400		24.8	-498	-178		1.9751	-59	-21.1
^{49}Ti	2.401	7/2	-0.2401			-498	-178			-59	-21.1
^{49}V*	-	7/2	1.02		28.4	2,424	867		2.5888	331	118
^{50}V	0.24	6	0.4245			1,008	361			138	49.4
^{51}V	99.76	7/2	1.1193			2,658	951			363	130
^{53}Cr	9.54	3/2	-0.2406		32.1	-645	-231		3.2812	-49	-17.5
^{53}Mn*	-	7/2	1.100		35.9	3,297	1,180		4.0597	560	200
^{55}Mn	100	5/2	1.0553			3,163	1,132			537	192
^{57}Fe	2.245	1/2	0.138		39.8	459	164		4.9306	85	30.4
^{56}Co*	-	4	0.7347		43.8	2,692	963		5.8997	544	195
^{57}Co*	-	7/2	1.01			3,701	1,324			747	267
^{58}Co*	-	2	1.544			5,661	2,026			1,142	409

[a]Radioactive element.

TABLE I (Contd.)

Nucleus	% Abundance	Nuclear Spin I	$g_N\mu_N/h$, MHz/kG	Isotropic Splitting: Orbital	$A^2 = 4\pi\psi^2_{ns}(0)$, a.u.	K: MHz	K: Gauss	Anisotropic Splitting: Orbital	$\langle r^{-3}\rangle$, a.u.	$2\mu_B g_N \mu_N \langle r^{-3}\rangle$: MHz	Gauss
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
^{59}Co	100	7/2	1.0103	4s	43.8	3,702	1,325	3d	5.8997	747	267
^{60}Co*	-	5	0.46			1,686	603			340	122
^{61}Ni	1.25	3/2	0.379		48.1	1,523	545		6.9724	331	118
^{63}Cu	69.09	3/2	1.1285		52.4	4,947	1,770		8.1540	1,154	413
^{64}Cu*	-	1	0.30			1,315	471			307	110
^{65}Cu	30.91	3/2	1.2090			5,300	1,896			1,236	442
^{67}Zn	4.12	5/2	0.2664		57.0	1,269	454		9.450	316	113
^{69}Ga	60.2	3/2	1.0219		87.3	7,454	2,667	4p	2.8908	370	132
^{71}Ga	39.8	3/2	1.2984			9,471	3,389			471	169
^{73}Ge	7.61	9/2	-0.1485		120	-1,494	-535		4.7334	-88	-31.5
^{75}As	100	3/2	0.7292		157	9,590	3,431		6.8542	627	224
^{77}Se	7.50	1/2	0.8131		198	13,461	4,816		9.2715	945	338
^{79}Se*	-	7/2	-0.2211			-3,660	-1,310			-257	-92.0
^{79}Br	50.57	3/2	1.0667		243	21,700	7,764		11.9994	1,605	574
^{81}Br	49.43	3/2	1.1499			23,394	8,370			1,730	619
^{83}Kr	11.55	9/2	-0.164		293	-4,022	-1,439		14.8867	-306	-109
^{85}Kr*	-	9/2	0.170			4,169	1,492			317	113
^{81}Rb*	-	3/2	1.02	5s	16.3	1,388	497		20.097	2,571	920
^{85}Rb	72.8	5/2	0.4111			559	200			1,036	371
^{86}Rb*	-	2	(-)0.65			(-)884	(-)316			(-)1,638	(-)586
^{87}Rb	27.2	3/2	1.3932			1,896	678			3,511	1,256
^{87}Sr	7.02	9/2	-0.1845		30.0	-4,628	-1,656		25.8947	-5,991	-2,144
^{89}Y	100	1/2	-0.2086		37.6	-656	-235	4d	1.7117	-44.8	-16.0
^{91}Zr	11.23	5/2	-0.3958		44.1	-1,458	-522		2.3974	-119	-42.6
^{93}Nb	100	9/2	1.0407		50.0	4,349	1,556		3.1220	407	146
^{95}Mo	15.78	5/2	-0.2774		55.6	-1,290	-462		3.9001	-136	-48.7
^{97}Mo	9.60	5/2	-0.2833			-1,317	-471			-139	-49.7
^{99}Tc*	-	9/2	0.9583		61.0	4,887	1,749		4.7390	569	204
^{99}Ru	12.81	5/2	-0.19		66.2	-1,052	-376		5.6438	-134	-47.9
^{101}Ru	16.98	5/2	-0.21			-1,163	-416			-149	-53.3
^{103}Rh	100	1/2	-0.1340		71.3	-799	-286		6.6185	-111	-39.7
^{105}Pd	22.23	5/2	-0.174		76.3	-1,110	-397		7.6666	-167	-59.8
^{107}Ag	51.35	1/2	-0.1723		81.3	-1,170	-419		8.7911	-190	-68.0
^{109}Ag	48.65	1/2	-0.1981			-1,346	-482			-218	-78.0
^{111}Ag*	-	1/2	-0.221			-1,501	-537			-244	-87.3
^{111}Cd	12.86	1/2	-0.9028		86.1	-6,500	-2,326		9.9041	-1,121	-401
^{113}Cd	12.34	1/2	-0.9444			-6,800	-2,433			-1,173	-420
^{113}In	4.16	9/2	0.9310		123	9,551	3,417	5p	4.4572	520	186
^{115}In*	95.84	9/2	0.9329			9,571	3,425			521	186
^{115}Sn	0.35	1/2	-1.392		160	-18,640	-6,669		6.7468	-1,178	-421
^{117}Sn	7.67	1/2	-1.517			-20,313	-7,268			-1,283	-459
^{119}Sn	8.68	1/2	-1.587			-21,250	-7,603			-1,343	-481
^{121}Sb	57.25	5/2	1.019		200	17,019	6,089		9.2313	1,180	422
^{123}Sb	42.75	7/2	0.5518			9,216	3,297			639	229
^{123}Te	0.89	1/2	-1.116		242	-22,584	-8,081		11.9366	-1,671	-598
^{125}Te	7.03	1/2	-1.345			-27,217	-9,738			-2,013	-720
^{127}I	100	5/2	0.8519		287	20,459	7,320		14.8724	1,589	569
^{129}I*	-	7/2	0.5669			13,614	4,871			1,057	378
^{129}Xe	26.24	1/2	-1.178		336	-33,055	-11,827		17.8266	-2,633	-942
^{131}Xe	21.24	3/2	0.3490			9,793	3,504			780	279
^{127}Cs*	-	1/2	2.15	6s	21.0	3,771	1,349		23.2545	6,270	2,243
^{129}Cs*	-	1/2	2.24			3,929	1,406			6,532	2,337

TABLE I (Contd.)

Nucleus	% Abundance	Nuclear Spin I	$g_N\mu_N/h$, MHz/kG	Isotropic Splitting: Orbital	$A^2 = 4\pi\psi_{ns}^2(0)$, a.u.	K: MHz	K: Gauss	Anisotropic Splitting: Orbital	$\langle r^{-3}\rangle$, a.u.	$2\mu_B g_N \mu_N \langle r^{-3}\rangle$: MHz	Gauss
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
^{131}Cs*	-	5/2	1.06	6s	21.0	1,859	665	5p	23.2545	3,091	1,106
^{133}Cs	100	7/2	0.5585			980	351			1,629	583
^{134}Cs*	-	4	0.564			989	354			1,645	589
^{135}Cs*	-	7/2	0.594			1,042	373			1,732	620
^{137}Cs*	-	7/2	0.618			1,084	388			1,802	645
^{135}Ba	6.59	3/2	0.4230		37.3	1,318	472		29.0659	1,542	552
^{137}Ba	11.32	3/2	0.4732			1,474	527			1,725	617
^{138}La	0.089	5	0.5617		38.9	1,824	653	4f	3.694	260	93.0
^{139}La	99.911	7/2	0.6014			1,953	699			279	99.8
^{141}Ce*	-	7/2	0.035		40.3	118	42.2		4.3005	18.9	6.76
^{141}Pr	100	5/2	1.195		41.8	4,177	1,495		4.9127	736	263
^{143}Nd	12.20	7/2	-0.272		43.3	-984	-352		5.5410	-189	-67.6
^{145}Nd	8.30	7/2	0.17			615	220			118	42.2
^{147}Nd*	-	9/2	0.037			134	47.9			25.7	9.20
^{147}Sm	15.07	7/2	-0.15		46.2	-579	-207		6.8637	-129	-46.2
^{149}Sm	13.84	7/2	-0.12			-463	-166			-103	-36.9
^{151}Eu	47.77	5/2	1.049		47.7	4,179	1,495		7.5645	995	356
^{153}Eu	52.23	5/2	0.4638			1,848	661			440	157
^{154}Eu	-	3	0.51			2,032	727			484	173
^{155}Gd	14.68	3/2	-0.12		49.1	-493	-176		8.2938	-125	-44.7
^{157}Gd	15.64	3/2	-0.17			-698	-250			-177	-63.3
^{159}Tb	100	3/2	0.772		50.6	3,268	1,169		9.0537	876	313
^{161}Dy	18.73	5/2	0.12		52.1	523	187		9.8451	148	53.0
^{163}Dy	24.97	5/2	0.16			698	250			198	70.8
^{165}Ho	100	7/2	0.722		53.7	3,240	1,159		10.6693	966	346
^{167}Er	22.82	7/2	0.104		55.2	480	172		11.5275	150	53.7
^{169}Tm	100	1/2	0.349		56.8	1,657	5,929		12.4204	544	195
^{171}Yb	14.27	1/2	0.751		58.4	3,664	1,311		13.3495	1,257	450
^{173}Yb	16.08	5/2	-0.21			-1,024	-366			-352	-126
^{175}Lu	97.40	7/2	0.486		71.8	2,918	1,044	5d	3.3816	206	73.7
^{176}Lu*	2.60	6	0.53			3,182	1,139			225	80.5
^{177}Hf	18.39	7/2	0.13		82.9	901	322		4.4934	73	26.1
^{179}Hf	13.78	9/2	-0.080			-555	-199			-45	-16.1
^{181}Ta	100	7/2	0.509		93.0	3,957	1,416		5.6057	358	128
^{183}W	14.28	1/2	0.175		102.4	1,498	536		6.7504	148	53.0
^{185}Re	37.07	5/2	0.9586		111	8,911	3,188		7.9414	955	342
^{187}Re	62.93	5/2	0.9684			9,002	3,221			964	345
^{187}Os	-	1/2	0.18		120	1,800	644		9.1859	207	74.1
^{189}Os	16.1	3/2	0.3307			3,307	1,183			381	136
^{191}Ir	38.5	3/2	0.0813		128	1,107	396		10.4886	107	38.3
^{193}Ir	61.5	3/2	0.086			1,171	419			113	40.4
^{195}Pt	33.7	1/2	0.9153		135	10,366	3,709		11.8527	1,360	487
^{197}Au	100	3/2	0.0731		143	874	313		13.2809	122	43.7
^{198}Au*	-	2	0.19			2,271	813			316	113
^{199}Au*	-	3/2	0.12			1,434	513			200	71.6
^{197}Hg*	-	1/2	0.79		150	9,923	3,550		14.6560	1,452	520
^{199}Hg	16.86	1/2	0.760			9,547	3,416			1,397	500
^{201}Hg	13.24	3/2	-0.280			-3,517	-1,258			-515	-184
^{203}Tl	29.52	1/2	2.433		205	41,625	14,893	6p	7.5553	2,305	825
^{205}Tl	70.48	1/2	2.457			42,035	15,040			2,328	833
^{207}Pb	21.11	1/2	0.8899		258	19,195	6,868		10.9883	1,226	439
^{209}Bi	100	9/2	0.6842		312	17,869	6,394		14.5706	1,250	447

The evaluation of the principal values of the $\hat{T}$ tensor reduces to finding the expectation values of the second term of the right-hand side of Eq. 3, as provided by the ground-state wavefunction. In crystal-field configurations, the variables are separable and the evaluation of $\hat{T}$ reduces to

$$\langle T_{ii}\rangle = \langle n,\ell|\hat{T}_{ii}(r)|n,\ell\rangle\langle\ell,m|\hat{T}_{ii}(\theta,\varphi)|\ell,m\rangle, \tag{13}$$

where $|n,\ell\rangle$ and $|\ell,m\rangle$ are the radial and angular wavefunctions, respectively. The radial part of Eq. 13 reduces to

$$\langle n,\ell|\hat{T}_{ii}(r)|n,\ell\rangle = \Omega\langle r^{-3}\rangle \tag{14}$$

for all principal values and is listed in Table I in MHz and in gauss. The angular parts of Eq. 13 take the form

$$T_{xx}(\theta,\varphi) = \langle\ell,m|3\sin^2\theta\cos^2\varphi - 1|\ell,m\rangle, \tag{15}$$

$$T_{yy}(\theta,\varphi) = \langle\ell,m|3\sin^2\theta\sin^2\varphi - 1|\ell,m\rangle, \tag{16}$$

and

$$T_{zz}(\theta,\varphi) = \langle\ell,m|3\cos^2\theta - 1|\ell,m\rangle \tag{17}$$

and are listed in Table II, averaged over the real wavefunctions

$$\psi^c(\theta,\varphi) = \frac{1}{\sqrt{2}}\left(Y_{\ell,-m} + Y^*_{\ell,-m}\right) \tag{18}$$

and

$$\psi^s(\theta,\varphi) = \frac{i}{\sqrt{2}}\left(Y_{\ell,-m} - Y^*_{\ell,-m}\right), \tag{19}$$

TABLE II. Average Angular Parameters of p and d Orbitals

	p_x	p_y	p_z	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
$T_{xx}(\theta,\varphi)$	$\frac{4}{5}$	$-\frac{2}{5}$	$-\frac{2}{5}$	$-\frac{2}{7}$	$\frac{2}{7}$	$\frac{2}{7}$	$\frac{2}{7}$	$-\frac{4}{7}$
$T_{yy}(\theta,\varphi)$	$-\frac{2}{5}$	$\frac{4}{5}$	$-\frac{2}{5}$	$-\frac{2}{7}$	$\frac{2}{7}$	$\frac{2}{7}$	$-\frac{4}{7}$	$\frac{2}{7}$
$T_{zz}(\theta,\varphi)$	$-\frac{2}{5}$	$-\frac{2}{5}$	$\frac{4}{5}$	$\frac{4}{7}$	$-\frac{4}{7}$	$-\frac{4}{7}$	$\frac{2}{7}$	$\frac{2}{7}$

where the spherical harmonics $Y_{\ell,m}$ have the general expression

$$Y_{\ell,m} = (-1)^{\frac{m+|m|}{2}} \left[\frac{2\ell + 1}{4\pi} \cdot \frac{(\ell - |m|)!}{(\ell + |m|)!} \right]^{1/2} P_{\ell,|m|}(\cos\theta) \cdot e^{im\varphi}. \quad (20)$$

$P_{\ell,|m|}(\cos\theta)$ is a Legendre polynomial[4] listed in Table III for values of ℓ up to 4. The coefficient $(-1)^{\frac{m+|m|}{2}}$ accounts for the phases as prescribed by Condon and Shortley.[5] The real wavefunctions of Eqs. 18 and 19, where the superscripts c and s stand for cosine and sine, are the well-known p_x, p_y, ..., $d_{x^2-y^2}$, ..., real wavefunctions.

TABLE III. Associated Legendre Polynomials from $\ell = 0$ to $\ell = 4$

$z = \cos\theta$	
$P_{0,0}(z) = 1$	$P_{3,0}(z) = \frac{1}{2}z(5z^2 - 3)$
$P_{1,0}(z) = z$	$P_{3,1}(z) = (3/2)(1 - z^2)^{\frac{1}{2}}(5z^2 - 1)$
$P_{1,1}(z) = (1 - z^2)^{\frac{1}{2}}$	$P_{3,2}(z) = 15z(1 - z^2)$
$P_{2,0}(z) = \frac{1}{2}(3z^2 - 1)$	$P_{3,3}(z) = 15(1 - z^2)^{3/2}$
$P_{2,1}(z) = 3z(1 - z^2)^{\frac{1}{2}}$	$P_{4,0}(z) = (1/8)(35z^4 - 30z^2 + 3)$
$P_{2,2}(z) = 3(1 - z^2)$	$P_{4,1}(z) = (5/2)z(1 - z^2)^{\frac{1}{2}}(7z^2 - 3)$
	$P_{4,2}(z) = (15/2)(1 - z^2)(7z^2 - 1)$
	$P_{4,3}(z) = 105z(1 - z^2)^{3/2}$
	$P_{4,4}(z) = 105(1 - z^2)^2$

The Hartree-Fock parameters have been taken from Froese Fischer tables.[6] The nuclear Larmor precession frequencies are those listed in Varian's tables,[7] with the sign of the nuclear magnetic moment.

HARTREE-FOCK $\langle r^{-3} \rangle$ PARAMETERS OF TRANSITION METAL IONS

The parameters of Table I are those calculated by Froese Fischer for neutral atoms.[6] Freeman and Watson's results[2] for $\langle r^{-3} \rangle$ differ from Froese Fischer's in that the former are systematically lower. The advantage of Freeman and Watson's calculations lies in that the values of $\langle r^{-3} \rangle$ for different charges of the ion have been estimated. As a rule of thumb, Froese Fischer's $\langle r^{-3} \rangle$ for the neutral atom are closer to Freeman and Watson's values for the divalent ion. If Freeman and Watson's values are preferred, the values in columns XI and XII of Table I should be multiplied by the ratio of their values to the value of $\langle r^{-3} \rangle$ listed in column X of Table I.

An approximate empirical relation holds for the values of $<r^{-3}>$ of ions of the same element and charges p and p+q, namely:

$$<r^{-3}>_{p+q} = <r^{-3}>_p + q\left(0.45 + 0.1\sqrt{<r^{-3}>_p}\right)$$

in atomic units, where Froese Fischer's value for the free atom may safely be taken for Freeman and Watson's value for p = 2.

Example 1

$$<r^{-3}>(Cu^{4+}) = <r^{-3}>(Cu^{2+}) + 2\left(0.45 + 0.1\sqrt{<r^{-3}>(Cu^{2+})}\right)$$

Taking for Cu^{2+} the value for Cu^0 from Table I, which is 8.15 a.u. (Freeman and Watson's value for Cu^{2+} is 8.25 a.u.), one gets

$$<r^{-3}>(Cu^{4+}) = 9.63 \text{ a.u.}$$

in 2% agreement with Freeman and Watson's value of 9.81 a.u. for Cu^{4+}.

Example 2

$$<r^{-3}>(Ag^{+}) = <r^{-3}>(Ag^{2+}) - \left(0.45 + 0.1\sqrt{<r^{-3}>(Ag^{2+})}\right)$$

Taking for Ag^{2+} the value for Ag^0 from Table I, which is 8.80 a.u. (Freeman and Watson's value for Ag^{2+} is 8.91 a.u.), one gets

$$<r^{-3}>(Ag^{+}) = 8.05 \text{ a.u.}$$

in 2% agreement with Freeman and Watson's value of 8.22 a.u. for Ag^{+}.

In other cases, the agreement is not so good, but the discrepancies are never larger than 10%.

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