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Childs, W.J.; Fred, M.; Schrödl, E.; van Kleef, T.A.

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Composition of the Ir I atomic ground state, and nuclear electric-quadrupole moments of ^{191}Ir and ^{193}Ir†

W. J. Childs and M. Fred
Argonne National Laboratory, Argonne, Illinois 60439

E. Schrödl
Institut für Angewandte Physik der Universität Bonn, Bonn, Germany

Th. A. M. van Kleef
Zeeman Laboratorium, Amsterdam, Netherlands

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In order to evaluate more accurately the nuclear electric-quadrupole moments of ^{191}Ir and ^{193}Ir from recent atomic-beam hyperfine-structure (hfs) studies, the eigenvector of the atomic ground state is obtained from a three-configuration least-squares fit to all known low-lying even-parity atomic levels. Relativistic Dirac-Slater $\langle r^{-3}\rangle$ values are used in interpreting the hfs. The nuclear dipole moments deduced in this way from the dipole hfs are within 3% of the known values. The resulting quadrupole moments are 0.67(13) b and 0.61(12) b for ^{191}Ir and ^{193}Ir, respectively. Most of the quoted uncertainty arises from uncertainty in the Sternheimer shielding correction applied.

I. INTRODUCTION

In a recent atomic-beam magnetic-resonance study[1] of the hyperfine structure (hfs) of ^{191}Ir and ^{193}Ir, the electric-quadrupole hfs interaction constants B were measured for the atomic ground state. The nuclear electric-quadrupole moments Q were then evaluated under the assumption that the ground state is pure $5d^7 6s^2\,{}^4F_{9/2}$, as listed by Moore.[2] The calculated Q values are very sensitive, however, to small ground-state components with different angular or radial properties which become admixed from other states through intermediate coupling or configuration interaction. We have therefore derived the composition of the iridium ground state by least-squares fitting of the energy levels to Slater parameters for all configurations likely to contribute, and obtain a purity of 84% $^4F_{9/2}$; the remainder is mostly $^2G_{9/2}$. Based on this composition, the quadrupole moment values were reevaluated. The use of theoretical relativistic Dirac-Slater $\langle r^{-3}\rangle$ values, and new estimates of the Sternheimer shielding also affect the results. The final quadrupole moment values are 16% smaller than those reported[1] previously. We also list the calculated composition of other low-lying levels in anticipation of further atomic-beam measurements.

II. ENERGY-LEVEL FITTING

The analysis of the Ir I spectrum is due mostly to van Kleef[3] who gave LS designations to the levels on the basis of Zeeman data; these are reproduced in Ref. 2. The ground configuration $5d^7 6s^2$ extends from 0 to 45 000 cm^{-1} and consists of eight LS terms (Table I) which are further split by spin-orbit interaction into 19 levels. The next even configuration $5d^8 6s$ starts at 2834 cm^{-1} and extends almost as far, with seven terms and 16 levels. There is a third even configuration $5d^9$ at 25 000 cm^{-1} consisting of only a ^2D term and two levels. The six highest levels have not been observed experimentally. The levels listed in Ref. 2, together with their nominal designations, are shown in Fig. 1.

There is strong spin-orbit interaction and clearly there is also strong configuration interaction, so that the sequence of J values is quite irregular and the levels are mixtures. A more exact description of the levels expresses them as expansions of the pure LS states, and is provided by the eigenvectors which diagonalize the energy matrix. Each element of this matrix is a linear combination of products of parameters and appropriate coefficients. The parameters correspond to the Slater radial integrals F^k, G^k, etc., but are treated as empirical quantities to be adjusted by least-squares fitting of the eigenvalues to the experimental level energies. The coefficients are angular integrals and can be calculated exactly by Racah tensor algebra.

The parameters are listed in Table I: the F^k and G^k are the direct and exchange integrals, ζ_{5d} the spin-orbit integrals, R^k the configuration-interaction integrals, and α and β are two-body effective-interaction parameters which describe the perturbation from higher configurations. There is thus a total of 18 parameters to account for 37 levels, or rather 31 known levels. This statement is, however, misleading because all J levels of a

TABLE I. Least-squares values found for the Slater parameters for Ir I. The values of $R^2(dd,ds)$, which are designated with an asterisk, were constrained to be equal. The value of $R^2(dd,ss)$ designated with a double asterisk was held equal to $G^2(5d,6s)$. Experimentally unknown terms are in parentheses. The two ^2D terms of $5d^76s^2$ are distinguished as in C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* MIT Press, Cambridge, Mass., 1963).

	Configuration		
	$5d^76s^2$	$5d^86s$	$5d^9$
LS terms	$^4P, ^4F$ $(^2P), (^2D1), ^2D2$ $(^2F), ^2G, ^2H$	$^4P, ^4F$ $^2S, ^2P, ^2D$ $^2F, ^2G$	^2D
Parameters			
F^0	19455±99	15488±1940	23067±335
$F^2(5d,5d)$	47514±645	42688±950	
$F^4(5d,5d)$	33723±723	30954±1764	
$G^2(5d,6s)$		12636±638	
α	33±18	63±27	
β	−195±339	102±635	
ζ_{5d}	3585±54	3537±70	3131±234
$R^2(dd,ds)5d^76s^2$		−18970±280*	
$R^2(dd,ds)5d^86s$			−18970±280*
$R^2(dd,ss)^{**}5d^9$	12636±638		
Number of levels	19	16	2
Number of LS terms	8	7	1
Number of electrostatic parameters (excluding configuration interaction)	5	6	1

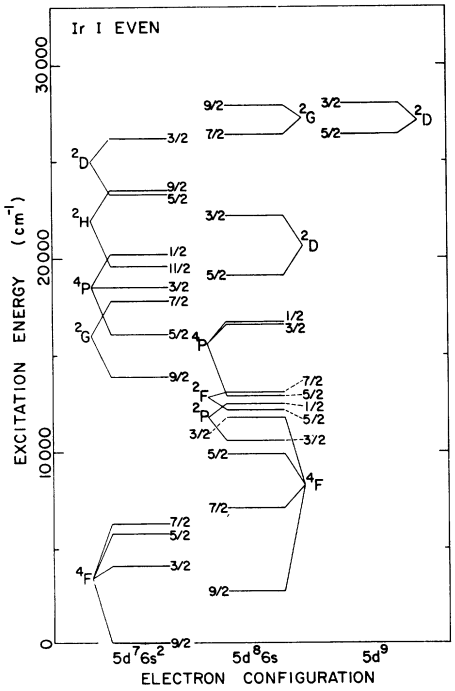

FIG. 1. The low-lying, even-parity levels of Ir I. The designations are those of Ref. 2, and are limited by the very strong mixing of the levels. A three-configuration least-squares fit to all the levels shown plus one new one at 31476 cm^{-1} is described in the text.

given LS term have the same dependence on the electrostatic parameters, i.e., all parameters except ζ_{5d}; hence the 15 electrostatic parameters describe only 13 known terms. The number of free parameters could be reduced to 13 by reasonable constraints on the configuration interaction as indicated in Table I, and in practice reduced further by an iterative procedure in which some of the less well determined parameters are frozen sequentially. Because the coupling in Ir is intermediate, the large ζ_{5d} produces large off-diagonal matrix elements which mix different LS terms in a way which varies with J, so that the number of degrees of freedom is more nearly 15 (31 levels −16 total parameters), rather than zero (13 terms −13 electrostatic parameters).

The final fitted values are given in Table I with the statistical uncertainties. It will be seen that α is not well determined and β is meaningless and could have been omitted without much effect on the fit. The other parameters are fairly well determined although the uncertainties are a bit large, especially for $5d^86s$ which is least favorable for fitting. It was very valuable to have a new level at 31476 cm^{-1}, supplied by one of the authors (Th. A. M. v. K.).

Table II compares the energy eigenvalues calculated from the parameter values of Table I with the known[2] excitation energies. The order of agree-

TABLE II. Comparison between observed and calculated energies and g values. The two largest amplitudes in the eigenvector are also given for each state. The complete eigenvectors are given in Table III for the states below 10 000 cm^{-1}.

	Energy (cm^{-1})			g Value			Eigenvector components			
J	Obs.	Calc.	Obs. − Calc.	Obs.	Calc.	Obs. − Calc.	Largest		Next largest	
$\frac{1}{2}$	12 503	12 448	58	1.22	1.13	0.09	$d^7s^2\,^2P$	−0.69	$d^8s\,^2P$	−0.53
	16 681	16 693	−12	2.61	2.61	0.00	$d^8s\,^4P$	0.95	$d^8s\,^2S$	−0.29
	20 237	20 176	61	2.08	2.15	−0.07	$d^7s^2\,^4P$	0.85	$d^8s\,^2P$	−0.46
		33 273			0.94		$d^7s^2\,^2P$	0.66	$d^8s\,^2P$	−0.62
		43 764			1.85		$d^8s\,^2S$	0.88	$d^8s\,^2P$	−0.35
$\frac{3}{2}$	4079	4397	−319	1.12	1.14	−0.02	$d^7s^2\,^2P$	−0.59	$d^8s\,^2P$	−0.42
	10 579	10 612	−34	0.97	0.95	0.02	$d^8s\,^4F$	−0.54	$d^8s\,^2D$	0.51
	11 831	12 089	−258	0.54	0.53	0.01	$d^7s^2\,^4F$	0.84	$d^8s\,^4F$	−0.30
	16 565	16 585	−20	1.39	1.38	0.01	$d^8s\,^4P$	0.79	$d^8s\,^4F$	0.49
	18 547	18 618	−71	1.39	1.44	−0.05	$d^7s^2\,^4P$	0.60	$d^8s\,^4P$	0.54
	22 110	21 880	230	1.00	0.95	0.05	$d^8s\,^2D$	−0.51	$d^8s\,^4F$	−0.46
	26 230	25 898	331	0.94	0.90	0.04	$d^7s^2\,^2D2$	−0.75	$d^8s\,^2P$	0.44
	27 970	28 107	−137	0.85	0.93	−0.08	$d^9\,^2D$	0.70	$d^8s\,^2D$	−0.37
		35 641			1.05		$d^7s^2\,^2P$	−0.48	$d^7s^2\,^2D2$	0.47
		44 835			0.84		$d^7s^2\,^2D1$	0.89	$d^7s^2\,^2P$	0.24
$\frac{5}{2}$	5785	5765	19	1.20	1.20	0.00	$d^8s\,^2D$	−0.52	$d^7s^2\,^4F$	0.45
	9878	9766	111	1.17	1.18	−0.01	$d^7s^2\,^4F$	−0.63	$d^8s\,^4F$	0.44
	12 219	12 321	−103	1.13	1.09	0.04	$d^8s\,^4F$	0.79	$d^8s\,^4P$	0.37
	12 952	13 167	−216	1.49	1.49	0.00	$d^7s^2\,^4P$	−0.86	$d^7s^2\,^4F$	0.40
	16 103	16 047	56	1.34	1.36	−0.02	$d^8s\,^4P$	−0.67	$d^9\,^2D$	0.42
	19 061	19 241	−181	1.00	1.00	0.00	$d^8s\,^2F$	−0.67	$d^9\,^2D$	0.56
	23 310	23 169	141	1.20	1.18	0.02	$d^7s^2\,^2D2$	−0.65	$d^9\,^2D$	0.59
	26 404	26 325	79	1.16	1.12	0.04	$d^8s\,^2D$	0.55	$d^7s^2\,^2F$	0.53
	31 477	31 570	−94		0.97		$d^7s^2\,^2F$	0.65	$d^8s\,^2F$	0.51
		46 467			1.18		$d^7s^2\,^2D1$	−0.81	$d^7s^2\,^2D2$	−0.46
$\frac{7}{2}$	6324	6103	221	1.21	1.20	0.01	$d^8s\,^4F$	−0.72	$d^8s\,^2F$	−0.52
	7107	6960	146	1.23	1.22	0.01	$d^7s^2\,^4F$	0.90	$d^8s\,^4F$	0.35
	13 088	13 132	−45	1.17	1.17	0.00	$d^8s\,^2F$	0.77	$d^8s\,^4F$	−0.58
	17 779	17 755	24	0.92	0.92	0.00	$d^7s^2\,^2G$	0.78	$d^8s\,^2G$	−0.54
	26 365	26 295	71	0.92	0.91	0.01	$d^8s\,^2G$	−0.81	$d^7s^2\,^2G$	−0.50
		33 232			1.12		$d^7s^2\,^2F$	0.92	$d^7s^2\,^2G$	0.30
$\frac{9}{2}$	0	−138	138	1.30	1.30	0.00	$d^7s^2\,^4F$	0.92	$d^7s^2\,^2G$	0.37
	2835	2825	9	1.33	1.33	0.00	$d^8s\,^4F$	−0.98	$d^8s\,^2G$	−0.17
	13 940	13 863	76	1.10	1.10	0.00	$d^7s^2\,^2G$	−0.76	$d^7s^2\,^2H$	−0.45
	23 506	23 577	−72	1.04	1.06	−0.02	$d^8s\,^2G$	0.83	$d^7s^2\,^2H$	0.54
	27 914	28 060	−147	1.03	1.02	0.01	$d^7s^2\,^2H$	0.70	$d^7s^2\,^2G$	−0.54
$\frac{11}{2}$	19 593	19 654	−61	1.09	1.09	0.00	$d^7s^2\,^2H$	1.00		

ment is considered fair. Higher-lying configurations would have to be included explicitly to improve the over-all agreement significantly, and this would have little influence on the composition of the ground state. It can be seen that the energy fit is relatively successful for the levels with $J=\frac{1}{2}$, $\frac{7}{2}$, $\frac{9}{2}$, and $\frac{11}{2}$, and poorest for those with $J=\frac{3}{2}$ and $\frac{5}{2}$. Indeed, for the intermediate J values even relatively low-lying levels are difficult to fit. The calculated and experimental[1,2] g_J values are also compared in Table II. It is seen that the agreement is rather good for $J=\frac{11}{2}$, $\frac{9}{2}$, and $\frac{7}{2}$, but deteriorates for states with smaller J values. For the ground state the agreement between the measured value[1] 1.29694(3) and the calculated value 1.29855 is excellent. The very slight difference between theory and experiment is of the right sign and approximate magnitude expected from our failure to take account of relativistic and diamagnetic corrections[4] to the theoretical value.

The eigenvectors found for the seven states below 10 000 cm^{-1} (i.e., those that could be populated thermally for an atomic-beam experiment) are given in Table III. The signs of the components are for LS basis states (not SL) and for hole states rather than particle states. It can be seen that the degree of mixing is substantial even for the lowest states. In most cases, it is not possi-

TABLE III. Eigenvector components, listed vertically, for each of the levels below 10 000 cm^{-1}.

Eigenvector component	J value and energy of state: $\frac{9}{2}$ 0.0	$\frac{9}{2}$ 2835.0	$\frac{7}{2}$ 6324.0	$\frac{7}{2}$ 7106.6	$\frac{5}{2}$ 5784.6	$\frac{5}{2}$ 9877.6	$\frac{3}{2}$ 4097.0
$5d^8 6s\,^4F$	−0.0716	−0.9800	−0.7243	0.3541	0.2112	0.4409	0.1836
^4P					−0.3150	−0.4223	−0.1069
^2G	−0.0727	−0.1744	−0.1912	0.0346			
^2F			−0.5180	0.1881	−0.1448	0.0195	
^2D					−0.5163	−0.3625	−0.3833
^2P							−0.4233
$5d^7 6s^2\,^4F$	0.9181	−0.0950	0.3809	0.8995	0.4507	−0.6327	0.2368
^4P					0.2104	−0.1881	−0.3063
^2H	0.0913	0.0031					
^2G	0.3720	0.0112	0.0922	0.1693			
^2F			0.1299	0.0178	0.1291	−0.1048	
$^2D1$					0.3204	−0.1510	0.1047
$^2D2$					−0.3519	0.1363	−0.3347
^2P							−0.5887
$5d^9\,^2D$					−0.2794	−0.0864	−0.0970

ble to assign meaningful L and S labels. The eigenvector of the ground state, (g.s.) which is used below in analyzing the hyperfine structure, is given explicitly in Eq. (1):

$$|\,\text{g.s.}, J=\tfrac{9}{2}\rangle = 0.9181\,|\,5d^7 6s^2\,^4F\rangle + 0.3720\,|\,5d^7 6s^2\,^2G\rangle + 0.0913\,|\,5d^7 6s^2\,^2H\rangle - 0.0727\,|\,5d^8 6s^2\,G\rangle - 0.0716\,|\,5d^8 6s\,^4F\rangle\,. \quad (1)$$

III. ANALYSIS OF GROUND-STATE HYPERFINE STRUCTURE

A. Magnetic-dipole hfs and the nuclear dipole moments of ^{191}Ir and ^{193}Ir

The appropriate effective-operator Hamiltonian for the magnetic-dipole hfs interaction has been given by Sandars and Beck.[5] It may be expressed as

$$\mathcal{H}_{\text{hfs}}(M1) = h\vec{I}\cdot\sum_i [a^{01}\vec{l}_i - (10)^{1/2}a^{12}\{\vec{s}\times\vec{C}^{(2)}\}_i^{(1)} + a^{10}\vec{s}_i\,], \quad (2)$$

where the a's are radial parameters proportional to the dipole moment of the nucleus and to effective values of $\langle r^{-3}\rangle$ for the relevant electrons. The quantity $\vec{I}$ is the nuclear spin, $\vec{l}_i$ and $\vec{s}_i$ are the respective orbital and spin angular momenta of the i^{th} electron, and $\vec{C}^{(2)}$ is the rank-two spherical tensor operator proportional to Y^2. The sum is extended over all electrons in incomplete shells. General expressions for the matrix elements and dipole A factors that arise from such operators have been published[6,7] for configurations of the types l^N and $l^N l'$. When the matrix elements are evaluated between (or within) basis states of $5d^7 6s^2$, only the $5d$ electrons are involved and the contribution to the A factor may be expressed as a linear combination of the quantities $a^{01}(5d^7 6s^2)$, $a^{12}(5d^7 6s^2)$, and $a^{10}(5d^7 6s^2)$. When an element is evaluated between states of $5d^8 6s$, we obtain contributions from all three terms of Eq. (2) for the $5d$ electrons, and find in addition that the final term of the Hamiltonian can contribute for the $6s$ electron. In addition, we recognize that the radial parameters for the $5d$ electrons could differ slightly between the configurations $5d^7 6s^2$ and $5d^8 6s$. Thus, in this case the contribution to the A factor is a linear combination of the four quantities $a^{01}(d^8 s)$, $a^{12}(d^8 s)$, $a^{10}(d^8 s)$, and $a_{6s}(d^8 s)$. Finally, for the ground-state eigenvector of Eq. (1), we can obtain contributions to the A factor from matrix elements between states of $5d^7 6s^2$ and those of $5d^8 6s$. Of these, all vanish except those involving the operator $\{\vec{s}\times\vec{C}^{(2)}\}^{(1)}$. The parameters a^{01} and a^{12} are proportional to the expectation values of r^{-3}, and if one evaluates $\langle 5d\,|\,r^{-3}\,|\,6s\rangle$ one finds it is about 20 times smaller than $\langle 5d\,|\,r^{-3}\,|\,5d\rangle$. For this reason, it is reasonable to ignore contributions to A (and also to the electric-quadrupole hyperfine-interaction constant B) that arise from matrix elements *between* the configurations $5d^7 6s^2$ and $5d^8 6s$. From the eigenvector [Eq. (1)] for the Ir I atomic ground state, we therefore obtain for the A factor the expression

$$A(\text{g.s.}) = 0.6940a^{01}(d^7s^2) - 0.0423a^{12}(d^7s^2) + 0.2956a^{10}(d^7s^2) + 0.0081a^{01}(d^8s) - 0.0012a^{12}(d^8s) + 0.0011a^{10}(d^8s) + 0.0012a_{6s}(d^8s), \quad (3)$$

in which all the parameters except $a_{6s}(d^8s)$ refer to the d electrons.

This expression is not immediately useful since it depends on so many parameters. Lewis[8] has used the relativistic Dirac-Slater technique to calculate for the $5d$ electrons of Ir I the three relativistic radial integrals $F_{jj'}$ that occur in the magnetic-dipole hfs interaction; these all have the nonrelativistic limit $\langle r^{-3}\rangle_{nl}$. Lewis's results for the $5d$ electrons of the $5d^76s^2$ configuration of Ir I are $9.6790a_0^{-3}$, $11.3287a_0^{-3}$, and $10.1294a_0^{-3}$ for $\langle r^{-3}\rangle_{5d}^{++}$, $\langle r^{-3}\rangle_{5d}^{--}$, and $\langle r^{-3}\rangle_{5d}^{+-}$, respectively. From Eqs. (58), (59), and (62) of Ref. 6 we obtain from these values

$$\langle r^{-3}\rangle_{5d}^{01} = 10.4889\, a_0^{-3},$$
$$\langle r^{-3}\rangle_{5d}^{12} = 13.2482\, a_0^{-3}, \quad (4)$$
$$\langle r^{-3}\rangle_{5d}^{10} = -1.1999\, a_0^{-3}.$$

These results include relativistic effects, but ignore any distortions due to configuration interaction. Because of the proportionality

$$a_{nl}^{k_s,k_l} = \frac{2\mu_B\mu_N}{h}\,\frac{\mu_I}{I}\,\langle r^{-3}\rangle_{nl}^{k_s,k_l} \quad (5)$$

between the a^{k_s,k_l} and the $\langle r^{-3}\rangle^{k_s,k_l}$, we may use the ratios of Eqs. (4) to express the A factor of the ground state as

$$A(\text{g.s.}) = 0.6068a^{01}(d^7s^2) + 0.0065a^{01}(d^8s) + 0.0012a_{6s}(d^8s). \quad (6)$$

Because the value of the spin-orbit constant ζ_{nl}, like $a_{nl}^{k_s,k_l}$, is approximately proportional to $\langle r^{-3}\rangle_{nl}$, we may express $a^{01}(d^8s)$ in terms of $a^{01}(d^7s^2)$ by writing

$$a^{01}(d^8s)/a^{01}(d^7s^2) \cong \zeta_{5d}(d^8s)/\zeta_{5d}(d^7s^2). \quad (7)$$

This approximation should be relatively good for the ground state, which is nearly free from configuration interaction. When the values of ζ_{5d} from Table I are used we obtain

$$A(\text{g.s.}) \cong 0.6133a^{01}(d^7s^2) + 0.0012a_{6s}(d^8s). \quad (8)$$

Even though $a_{6s}(d^8s)$ is considerably larger than $a^{01}(d^7s^2)$, the second term is expected to contribute very much less than the first because of its very small coefficient. In the first term we have from Eq. (5)

$$a^{01}(d^7s^2) = \frac{2\mu_B\mu_N}{h}\,\frac{\mu_I}{I}\,\langle r^{-3}\rangle_{5d}^{01}. \quad (9)$$

If one uses the known value[9] $\mu_I(^{191}\text{Ir}) = 0.145\mu_N$, and Lewis's[8] value $\langle r^{-3}\rangle_{5d}^{01} = 10.4889a_0^{-3}$, one finds

$$a^{01}(d^7s^2) = 96.74 \text{ MHz}, \quad (10)$$

and hence

$$A(^{191}\text{Ir}) \cong 59.3 \text{ MHz}. \quad (11)$$

The measured value[1] of $A(^{191}\text{Ir})$ is 57.521 MHz, only 3% different from the value we have calculated from the known dipole moment. The errors in our calculated value stem mostly from our incomplete treatment of configuration interaction, and to inaccuracies in Lewis's calculated radial integrals. Neglect of the second term of Eq. (8) might contribute an additional error of a few percent. For the electric-quadrupole part of the hyperfine interaction the analogous term is zero.

The basic result of comparing our calculated value of the dipole-hfs constant with the measured value is to give us confidence in using the same procedure to evaluate the quadrupole moment of the nucleus from the measured quadrupole hfs. In particular, the values calculated[8] for the required relativistic radial integrals appear to be dependable.

B. Electric-quadrupole hfs and the quadrupole moments of ^{191}Ir and ^{193}Ir

The proper effective-operator Hamiltonian for the electric-quadrupole hfs interaction has been given by Sandars and Beck.[5] It may be expressed[6] as

$$\mathcal{H}_{\text{hfs}}(E2) = e^2 r_n^{-2}\tilde{C}_n^{(2)} \cdot \sum_i r_i^{-3}\left[\left(\frac{2l(l+1)(2l+1)}{(2l-1)(2l+3)}\right)^{1/2}\frac{b^{02}}{b_{nl}}\,\tilde{U}_i^{(02)2} + \left(\frac{3}{10}\right)^{1/2}\frac{b^{13}}{b_{nl}}\,\tilde{U}_i^{(13)2} + \left(\frac{3}{10}\right)^{1/2}\frac{b^{11}}{b_{nl}}\,\tilde{U}_i^{(11)2}\right] \quad (12)$$

in which the sum extends over all electrons in incomplete shells (for the Ir I ground-state eigenvector given above, the only contribution is from the $5d$ shell). In this expression, the $\tilde{U}^{(k_s,k_l)k}$ are double tensor operators defined by Sandars and Beck,[5] and the associated parameters b^{k_s,k_l} are proportional to the electric-quadrupole moment Q of the nucleus, and to effective values of $\langle r^{-3}\rangle$. The quantity b_{nl} is the familiar $e^2Q\langle r^{-3}\rangle_{nl}$.

It should be noted that in this Hamiltonian there

are three quadrupole operators instead of the customary single (nonrelativistic) operator. The electric-quadrupole hyperfine-interaction constant B of the Ir I ground state will be a linear combination of the quantities $b^{02}(5d^76s^2)$, $b^{13}(5d^76s^2)$, $b^{11}(5d^76s^2)$, $b^{02}(5d^86s)$, $b^{13}(5d^86s)$, and $b^{11}(5d^86s)$. (As for the dipole case, the cross-configuration contributions are small enough to ignore.) When the matrix elements of Ref. 6 are used to obtain an expression for the B factor, the result is

$$\begin{aligned} B(\text{g.s.}) = {} & 0.2082b^{02}(5d^76s^2) - 0.0287b^{13}(5d^76s^2) \\ & - 0.1019b^{11}(5d^76s^2) - 0.0075b^{02}(5d^86s) \\ & + 0.0005b^{13}(5d^86s) - 0.0003b^{11}(5d^86s). \end{aligned} \tag{13}$$

As for the dipole case, it is desirable to use Lewis's ratios between $\langle r^{-3}\rangle$ values to reduce the number of parameters in this expression. The electric-quadrupole Dirac-Slater $\langle r^{-3}\rangle$ values $R_{jj'}$ obtained relativistically by Lewis[8] for $5d$ electrons in the $5d^76s^2$ configuration of Ir I are $9.9256a_0^{-3}$, $12.7883a_0^{-3}$, and $10.5160a_0^{-3}$ for R_{++}, R_{--}, and R_{+-}, respectively. From Eqs. (63) and (66) of Ref. 6 we obtain from Lewis's results the values

$$\begin{aligned} b^{02}(d^7s^2) &= (e^2Q/h)(10.8689a_0^{-3}), \\ b^{13}(d^7s^2) &= (e^2Q/h)(6.9281a_0^{-3}), \\ b^{11}(d^7s^2) &= (e^2Q/h)(-2.2243a_0^{-3}), \end{aligned} \tag{14}$$

and we may therefore express the factor B as

$$B(\text{g.s.}) = 0.2107b^{02}(d^7s^2) - 0.0071b^{02}(d^8s).$$

Using the same argument as for the dipole case, $b^{02}(d^8s)$ may be expressed in terms of $b^{02}(d^7s^2)$ through the known values of ζ_{5d} for the two configurations

$$\frac{b^{02}(d^8s)}{b^{02}(d^7s^2)} = \frac{\zeta_{5d}(d^8s)}{\zeta_{5d}(d^7s^2)}. \tag{15}$$

We therefore obtain the result

$$B(\text{Ir I, g.s.}) = 0.2038b^{02}(d^7s^2) \tag{16}$$

$$= 0.2038(e^2Q/h)\langle r^{-3}(d^7s^2)\rangle_{5d}^{02}, \tag{17}$$

where the last result is implicit in the Hamiltonian itself. With Lewis's[8] value $\langle r^{-3}(5d^76s^2)\rangle_{5d}^{02} = 10.8689a_0^{-3}$, we find for the electric-quadrupole moment of the nuclear ground state

$$Q = \frac{hB}{(0.2038e^2)10.8689a_0^{-3}}. \tag{18}$$

The measured[1] values $B(^{191}\text{Ir}) = 471.2$ MHz and $B(^{193}\text{Ir}) = 426.2$ MHz yield the results

$$Q(^{191}\text{Ir}) = 0.906 \text{ b}, \quad Q(^{193}\text{Ir}) = 0.819 \text{ b}, \tag{19}$$

uncorrected for Sternheimer shielding.[10,11] The extent of such shielding effects in the $5d$ shell of Ir I is not accurately known, but may be closely estimated by comparison with values estimated theoretically by Sternheimer[11] for La, and measured[12] in Lu, Hf, and Ta. From these considerations it appears that the correction factor for Ir is

$$1/(1 - R_{5d}) = 0.74$$

with an uncertainty of about 15%.

We therefore obtain (with the Sternheimer correction included) the final results

$$Q(^{191}\text{Ir}) = 0.67(13) \text{ b}, \quad Q(^{193}\text{Ir}) = 0.61(12) \text{ b}.$$

where the uncertainty quoted includes a 10% uncertainty in the determination of the uncorrected values, and 15% in the shielding correction applied. The latter uncertainty could ultimately be removed if a complete calculation of the shielding could be done.

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