PHYSICAL REVIEW A VOLUME 26, NUMBER 4 OCTOBER 1982

Spin-orbit interval in the ground state of F-like ions

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(Received 19 April 1982)

Recommended spin-orbit intervals in the ground state, $2p^5\,{}^2P_{3/2}-{}^2P_{1/2}$, of fluorinelike ions are presented for ions of high nuclear charge ($Z \leq 56$). The recommended values are based on the relativistic Hartree-Fock calculations with corrections deduced from known experimental values in the low-Z side of the sequence.

I. INTRODUCTION

Magnetic-dipole transitions between levels separated by spin-orbit interaction, such as the $2p^5\,{}^2P_{3/2}-{}^2P_{1/2}$ transition in fluorinelike ions, have become an important tool for the diagnostics of high-temperature plasmas.[1] Theoretical transition probabilities and wavelengths for magnetic-dipole and electric-quadrupole transitions for ions isoelectronic to the first-row atoms have been calculated from relativistic Hartree-Fock wave functions and published elsewhere.[2] In Ref. 2, all relativistic configurations of same parity and total angular momentum J that can be constructed within the principal quantum number $n=2$ complex are allowed to mix. This is known as the multiconfiguration Dirac-Fock (MCDF) wave functions. For the fluorinelike ions, only one relativistic configuration for each level is possible, i.e., $2s^2 2p_{1/2}^2 2p_{3/2}^3$ for the ${}^2P_{3/2}$ level and $2s^2 2p_{1/2} 2p_{3/2}^4$ for the ${}^2P_{1/2}$ level. Hence, in reality, the wave functions used for the F-like ions in Ref. 2 as well as in the present work were single-configuration wave functions. Although the transition probabilities in Ref. 2 are sufficiently reliable for most purposes, the wavelengths need further improvement to be of practical value to spectroscopists.

The primary source of uncertainties in the transition wavelengths derived from *ab initio* calculations is the nonrelativistic electron correlation energy. However, for levels separated by the spin-orbit interaction, the nonrelativistic correlation contribution should be the same in both levels so that its effect can be canceled by forcing the two levels to have the same nonrelativistic total energy.[3] For instance, one can start from the nonrelativistic Hartree-Fock (or multiconfiguration Hartree-Fock) energy, and then calculate the spin-orbit splitting as perturbation. Another approach is to perform relativistic calculations, e.g., compute the total energies for the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ levels in separate MCDF calculations, but require that the two levels converge to the same nonrelativistic limit. In principle, these two approaches should lead to comparable results for ions of low nuclear charge. For ions with intermediate or high nuclear charge Z, however, the MCDF method offers an advantage by allowing correlation contributions from levels that will mix only relativistically. For instance, the $2p^3\,{}^4S_{3/2}$ level can mix with the $2s^2 2p^2 P_{3/2}$ level in relativistic coupling but not in nonrelativistic coupling.

On the other hand, the MCDF method[4,5] has its own pitfall: The relativistic $2p_{3/2}$ and $2p_{1/2}$ radial functions do not necessarily reduce to the same radial function in the nonrelativistic limit when the fine-structure constant α is set to zero in the MCDF program. As was pointed out by Wood and Pyper,[6] this inherent difficulty occurs whenever the parent core of the state being calculated (e.g., $2p^4$ core for F-like ions) has more than one LS term. In such cases, a singly excited configuration (e.g., $2p^4$ $3p$ for F-like ions) has a nonvanishing Hamiltonian matrix element with the ground state,[7] and consequently the two relativistic radial functions $2p_{3/2}$ and $2p_{1/2}$ simulate two nonrelativistic orbitals $2p$ and $3p$ resulting in different nonrelativistic limits. This problem, however, can be corrected simply by subtracting the spurious nonrelativistic contribution from the relativistic transition energy if the two levels are separated by the spin-orbit interaction.[3] In practice, we calculate the transition energies twice, first with the correct value of α, and next with $\alpha=0$. Then, the latter value is subtracted from the first result. This simple procedure dramatically improves the agreement between theory and experiment for low-Z ions.[3]

II. SYSTEMATICS OF TRANSITION WAVELENGTHS

The transition wavelengths for high-Z ions can be improved further by studying the Z dependence of the difference $\Delta\omega$ between the theoretical Dirac-Fock value $\omega(DF)$ and known experimental one $\omega(\exp)$. To obtain a reliable Z dependence of $\Delta\omega$, we must ensure that the theoretical transition energies exhibit as systematic a Z dependence as possible. For instance, Edlén[8] used the values from Ref. 2 *without* the Lamb-shift contribution which occasionally introduced irregular Z dependence.

In the present work, we took additional precautions to ensure systematic Z dependence of theoretical transition energies: (a) We subtracted the spurious nonrelativistic correlation contribution mentioned above; (b) we included the estimate of the Lamb shift for all K- and L-shell electrons in the field of the bare nuclear charge; and (c) we used the Fermi distribution for the nucleus to assure the continuity of both amplitude and slope of radial functions at the nuclear boundary. These improvements lead both to better numerical values of the theoretical transition energies and to more systematic and reliable Z dependence of $\Delta\omega$ as is shown in Fig. 1.

For F-like ions up to Ge^{23+} ($Z=32$), it is a simple task to determine most likely values of the spin-orbit interval based on smooth Z dependence of $\Delta\omega$. A few values of $\Delta\omega$ plotted in Fig. 1 deviate from the rest, clearly indicating experimental aberrations. Since it is clear from Fig. 1 that the uncertainties in $\Delta\omega$ can be determined an order of magnitude better than the values of $\Delta\omega$ themselves, we can bracket the most likely values, or recommended values of $\omega=\omega(\mathrm{DF})-\Delta\omega$ to an accuracy unattainable by *ab initio* calculations alone.

The extrapolation of $\Delta\omega$ to higher Z is less reliable because experimental values are either nonexistent or bear large uncertainties. Furthermore, no clear theoretical guidelines are available for extrapolating $\Delta\omega$ to higher Z because the Z dependence of ω is very complicated.[9] Numerically, the Z dependence of $\Delta\omega$ for $20<Z<40$ in Fig. 1 is approximately $\Delta\omega \propto Z^5$. For $Z>40$, we extrapolated $\Delta\omega$ in Fig. 1 by making it proportional to Z^5. We assigned uncertainties of $\sim 25\%$ in $\Delta\omega$ for ions beyond Kr^{27+}.

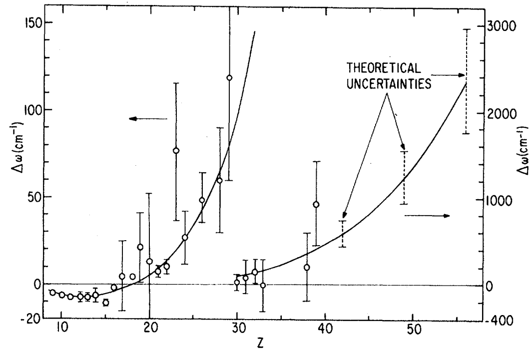

FIG. 1. Correction $\Delta\omega$ to the theoretical spin-orbit splitting as a function of the nuclear charge Z of F-like ions. Note that the left half of the figure ($Z \leq 32$) uses the left scale and the right half of the figure ($Z \geq 30$) uses the right scale. Circles are the differences between the Dirac-Fock values ω(DF) and experimental values quoted in Table I. Solid curves are the corrections $\Delta\omega$(DF) to obtain recommended transition energies from ω(DF). Theoretical uncertainties are roughly 25% of $\Delta\omega$(DF).

III. RESULTS

Our recommended values are presented in Table I and compared with experimental data and semiempirical values recommended by Edlén.[8] The close agreement with Edlén's recommended values is expected because our procedure and Edlén's are similar. We quoted only representative experimental values in Table I. The experimental value for

TABLE I. Energies for the $2p^5\,{}^2P_{3/2}-{}^2P_{1/2}$ transition of the fluorine isoelectronic sequence (in cm^{-1}).

		Theory		Recommended	Recommended by Edlén		
Z	Ion	ω(DF)	$\Delta\omega$(DF)	[ω(DF)$-\Delta\omega$(DF)]	(Ref. 8)	Experiment	References
9	F	399	-5	404 ± 2		404.1 ± 0.3	Lidén[a]
10	Ne^{+}	774	-6	780 ± 2	779	780.34 ± 0.14	Persson[b]
11	Na^{2+}	1359	-7	1366 ± 2	1367	1366.3 ± 1	Martin[c]
12	Mg^{3+}	2221	-7	2228 ± 3	2230	2228 ± 2	Martin[d]
13	Al^{4+}	3435	-7	3442 ± 5	3445	3442 ± 2	Martin[e]
14	Si^{5+}	5084	-6	5090 ± 5	5094	5090 ± 4	Artru[f]
15	P^{6+}	7264	-5	7269 ± 5	7272	7275 ± 2	Eidelsberg[g]
16	S^{7+}	10078	-3	10081 ± 5	10084	10080	Robinson[h]
17	Cl^{8+}	13636	-2	13638 ± 5	13641	13631 ± 40	Kaufman[i]
18	Ar^{9+}	18063	0	18063 ± 5	18065	18059	Moore[j]
19	K^{10+}	23488	2	23486 ± 5	23485	23467 ± 20	Corliss[k]

TABLE I. (*Continued.*)

Z	Ion	Theory ω(DF)	$\Delta\omega$(DF)	Recommended [ω(DF) $-$ $\Delta\omega$(DF)]	Recommended by Edlén (Ref. 8)	Experiment	References
20	Ca^{11+}	30 055	5	30 050 ± 5	30 048	30 041 ± 40	Kaufman[i]
21	Sc^{12+}	37 915	8	37 907 ± 5	37 905	37 908 ± 3	Suckewer (Ref. 1)
22	Ti^{13+}	47 229	13	47 216 ± 5	47 215	47 219 ± 4	Hinnov[l]
23	V^{14+}	58 170	19	58 151 ± 5	58 150	58 093 ± 40	Kaufman[i]
24	Cr^{15+}	70 919	26	70 893 ± 10	70 895	70 892 ± 15	Suckewer (Ref. 1)
25	Mn^{16+}	85 671	34	85 637 ± 10	85 640	85 505	Fawcett[m]
26	Fe^{17+}	102 629	43	102 586 ± 10	102 590	102 580 ± 15	Suckewer (Ref. 1)
27	Co^{18+}	122 010	53	121 957 ± 10	121 960		
28	Ni^{19+}	144 038	64	143 974 ± 20	143 975	143 978 ± 30	Suckewer (Ref. 1)
29	Cu^{20+}	168 953	80	168 873 ± 20	168 874	168 833 ± 60	Hinnov[n]
30	Zn^{21+}	197 006	97	196 909 ± 20	196 908	196 980 ± 90	Kononov[o]
31	Ga^{22+}	228 457	120	228 337 ± 30	228 337	228 379 ± 200	Kononov[o]
32	Ge^{23+}	263 583	145	263 438 ± 30	263 435	263 435 ± 140	Hinnov[n]
33	As^{24+}	302 671	175	302 496 ± 30	302 491	302 678 ± 300	Kononov[o]
34	Se^{25+}	346 022	205	345 817 ± 40	345 806		
35	Br^{26+}	393 949	234	393 715 ± 40	393 693		
36	Kr^{27+}	446 783	272	446 511 ± 60	446 479		
37	Rb^{28+}	504 863	313	504 550 ± 80			
38	Sr^{29+}	568 547	360	568 187 ± 100		568 343 ± 390	Reader[p]
39	Y^{30+}	638 207	415	637 792 ± 100		637 267 ± 490	Reader[p]
40	Zr^{31+}	714 231	464	713 767 ± 100			
41	Nb^{32+}	797 023	526	796 497 ± 150			
42	Mo^{33+}	887 003	590	886 413 ± 150			
43	Tc^{34+}	984 608	660	983 948 ± 150			
44	Ru^{35+}	1 090 292	730	1 089 562 ± 200			
45	Rh^{36+}	1 204 529	810	1 203 719 ± 200			
46	Pd^{37+}	1 327 816	900	1 326 916 ± 250			
47	Ag^{38+}	1 460 655	1000	1 459 655 ± 250			
48	Cd^{39+}	1 603 582	1110	1 602 472 ± 250			
49	In^{40+}	1 757 149	1230	1 755 919 ± 300			
50	Sn^{41+}	1 921 931	1360	1 920 571 ± 300			
51	Sb^{42+}	2 098 525	1500	2 097 025 ± 400			
52	Te^{43+}	2 282 551	1650	2 280 901 ± 400			
53	I^{44+}	2 489 656	1810	2 487 846 ± 450			
54	Xe^{45+}	2 705 507	1980	2 703 527 ± 500			
55	Cs^{46+}	2 935 801	2160	2 933 641 ± 500			
56	Ba^{47+}	3 181 278	2350	3 178 928 ± 600			

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Mn^{16+} is clearly out of step with the rest of the data. The difference (166 cm^{-1}) between ω(DF) and the experimental value is too large to be included in Fig. 1. For ions with $Z > 25$, the magnitudes $\Delta\omega$(DF) and accompanying uncertainties are very small fractions of ω(DF), comparable to the uncertainties in the experimental values quoted in Table I.

We hope that the publication of our predicted values will stimulate enough interest among spectroscopists to provide additional experimental values and improve our "recommended" values. Similar determination of spin-orbit intervals of other ions isoelectronic to the first-row atoms is in progress.

ACKNOWLEDGMENTS

The authors would like to thank Dr. W. C. Martin, Dr. J. Reader, Dr. J. Sugar, and Dr. E. Hinnov for providing us with experimental values quoted in Table I, and Professor B. Edlén for sending us his recommended term values prior to publication. This work was supported by the U. S. Department of Energy under Contract No. W-31-109-ENG-38.

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