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QUARTET SPECTRA IN THREE-ELECTRON ATOMS

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UDC 539.184.01

Routine calculations have been performed on the quartet terms of configurations $1s2sn\bar{l}$ and $1s2pn\bar{l}$, $n = 2, 3, 4, 5$; $\bar{l} = 0, 1, 2, 3$ for the isoelectronic series Li-Ne^{+7} in the one-configuration approximation by direct minimization. The conditions for orthogonality between wave functions identical in symmetry are provided by the frozen excited core approximation. The errors of this approximation are examined, and it is shown that the results are quite satisfactory for qualitative analysis of quartet spectra in the z sequence. A study is made of the changes in relative position of the levels as the nuclear charge alters; the intersection of terms identical in symmetry as functions of z is discussed. The z dependence of the allowed transitions is examined.

It is extremely important to study the spectra of highly excited states in atoms and ions involving the excitation of two or more electrons in outer shells for the transfer of internal electrons to higher orbitals, particularly for the physics of electron-atom and ion-atom collisions, plasma physics, astrophysics, etc.

Here we examine the general picture of the quartet spectrum of $1s2\bar{l}n\bar{l}'$ configurations in the isoelectronic series for the Li atom ($z = 3-10$, where z is the nuclear charge). These states lie along an isoelectronic series at distances from some tens to some hundreds of electron-volts above the $1s^2$ state and fall mainly in the region of the $1s^2\epsilon\bar{l}$ doublet continuum. As the discrete levels and the continuum states are different in multiplet order, Coulomb autoionization of the quartet states is forbidden, and they have sufficiently long lifetimes (about 10^{-8} sec) [1]. The quartet levels decay because of non-Coulomb interactions, and these levels may be considered as metastable in the nonrelativistic approximation, so the methods of stationary quantum mechanics can be used to calculate them. This approach to calculating quartet terms in three-electron atoms was first used by Holþien and Geltman [2].

The literature contains fairly many calculations on quartet spectra for individual atoms [3-17], including some very careful ones [6-9, 11, 12]. The fullest theoretical and experimental studies relate to the structure of the quartet terms in the atoms Li [6-8, 11, 12, 17], Be^+ [9, 18], O^{+5} [3, 10, 19], F^{+6} [3, 19], and in part N^{+7} [10, 21]. In [13, 15, 16], Hartree-Fock calculations were used to examine some features in the quartet-term pattern dependent on the nuclear charge.

To establish the absolute energy-level positions requires one to incorporate electron correlation in the excited states as well as relativistic corrections. Such methods are of precision character and involve either large configuration expansions [6, 9] or the inclusion of correlation factors in the wave function [11, 12], which, because of the effort involved, makes them unsuitable for routine calculations.

On this basis we have performed unified calculations on quartet terms for the isoelectronic series within the framework of the one-configuration approximation by direct minimization of the energy functional. The following assumptions were made:

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TABLE 1. Energies (atomic units) and Sequence N of Quarter Terms for Li-Ne⁺

z	3		4		5		6		7		8		9		10		
	Configu- tion	N	-E	N	-E	N	-E	N	-E	N	-E	N	-E	N	-E		
${}^4S^e$	$1s2s3s$	1	5,20431	1	9,60603	1	15,37077	1	22,49738	1	30,98442	1	40,83410	1	52,04469	1	64,61663
	$1s2s4s$	2	5,125470	2	9,45286	3	15,06391	3	21,99010	3	30,22827	3	39,77945	3	50,64319	3	62,81968
	$1s2s5s$	3	5,13502	4	9,38949	4	14,93571	4	21,77179	5	29,89907	5	39,31766	5	50,02379	5	62,02103
	$1s2p3p$	4	5,09473	3	9,43131	2	15,13262	2	22,19955	2	30,62202	2	40,40926	2	51,55789	2	64,07159
	$1s2p4p$	5	5,06036	5	9,30880	5	14,87225	5	21,74968	4	29,93889	4	39,44158	4	50,25695	4	62,38631
	$1s2p5p$	6	5,04581	6	9,25610	6	14,75820	6	21,55135	6	29,63451	6	39,00807	6	49,67202	6	61,62590
${}^4P^o$	$1s2s2p$	1	5,35571	1	10,05259	1	16,25251	1	23,94577	1	33,15575	1	43,85814	1	56,06081	1	69,76366
	$1s2s3p$	2	5,17548	2	9,55409	2	15,29659	2	22,39741	2	30,86790	2	40,69589	2	51,88520	2	64,43578
	$1s2s4p$	3	5,13924	4	9,42847	5	15,03237	5	21,94700	5	30,17931	5	39,72181	5	50,57700	5	62,74543
	$1s2s5p$	4	5,12459	6	9,37577	6	14,91720	7	21,74712	8	29,87143	8	39,28448	8	49,98758	8	61,97985
	$1s2p3s$	5	5,11159	3	9,46705	3	15,18466	3	22,26687	3	30,70778	3	40,51269	3	51,67983	3	64,20529
	$1s2p4s$	7	5,06401	7	9,31924	7	14,88941	6	21,77411	6	29,97185	6	39,48552	6	50,30503	6	62,44153
	$1s2p5s$	9	5,04820	9	9,26220	9	14,76827	9	21,55541	9	29,65342	9	39,03122	9	49,69782	9	61,65760
	$1s2p3d$	6	5,07750	5	9,39111	4	15,06941	4	22,11053	4	30,51367	4	40,27845	4	51,40467	4	63,89224
	$1s2p4d$	8	5,05414	8	9,29517	8	14,85084	8	21,71991	7	29,90195	7	39,39676	7	50,20421	7	62,32424
	$1s2p5d$	10	5,04310	10	9,24997	10	14,74854	10	21,53787	10	29,61760	10	38,98755	10	49,64767	10	61,59787

${}^4P^e$	$1s2p^2$	1	5,23222	1	9,84522	1	15,97281	1	23,60297	1	32,73451	1	43,36683	1	55,49972	1	69,13294
	$1s2p3p$	2	5,07796	2	9,40988	2	15,10534	2	22,16303	2	30,58243	2	40,36331	2	51,50554	2	64,00904
	$1s2p4p$	3	5,04414	3	9,29194	3	14,85434	3	21,73026	3	29,91799	3	39,42056	3	50,23557	3	62,36182
	$1s2p5p$	4	5,02993	4	9,24024	4	14,74211	4	21,53483	4	29,61877	4	38,99138	4	49,65528	4	61,60949
${}^4D^e$	$1s2s3d$	1	5,16627	1	9,52717	1	15,25320	1	22,34200	1	30,79270	1	40,60496	1	51,77861		64,31355
	$1s2s4d$	2	5,14128	3	9,42487	3	15,02239	3	21,93298	3	30,15637	3	39,69243	3	50,54110	3	62,70234
	$1s2s5d$	3	5,12962	4	9,37748	4	14,91624	5	21,74544	5	29,86485	5	39,27437	5	49,97393	5	61,96350
	$1s2p3p$	5	5,09844	2	9,44184	2	15,14848	2	22,22042	2	30,65157	2	40,44423	2	51,56155	2	64,07159
	$1s2p4p$	6	5,06168	6	9,31269	5	14,87902	4	21,75794	4	29,94848	4	39,45478	4	50,27259	4	62,40076
	$1s2p5p$	7	5,04636	7	9,25813	7	14,76133	7	21,55593	7	29,64021	7	39,01477	6	49,67927	6	61,63482
${}^4D^o$	$1s2p3d$	1	5,08122	1	9,39897	1	15,07991	1	22,12299	1	30,52777	1	40,29403	1	51,42163	1	63,91051
	$1s2p4d$	2	5,05541	2	9,29737	2	14,85362	2	21,72327	2	29,90591	2	39,40137	2	50,20942	2	62,33024
	$1s2p5d$	3	5,04368	3	9,25097	3	14,74981	3	21,53943	3	29,61947	3	38,98967	3	49,65024	3	61,60080
${}^4F^o$	$1s2s4f$	1	5,14047	1	9,42058	2	15,01379	2	21,91983	2	30,13856	2	39,66993	2	50,51388	2	62,67040
	$1s2s5f$	2	5,12921	3	9,37554	3	14,91239	3	21,73952	4	29,85680	4	39,26419	4	49,96165	4	61,94611
	$1s2p3d$	4	5,08104	2	9,40593	1	15,09692	1	22,15077	1	30,56657	1	40,34396	1	51,48275	1	63,98285
	$1s2p4d$	5	5,05574	5	9,30090	4	14,86127	4	21,73390	3	29,92001	3	39,41889	3	50,23043	3	62,35423
	$1s2p5d$	6	5,04389	6	9,25283	6	14,75311	6	21,54473	6	29,62611	6	38,99813	5	49,65996	5	61,61228
${}^3S^e$	$1s2s^*$		5,11073		9,29717		14,73390		21,42075		29,55768		38,54465		48,98164		60,66864
${}^3P^o$	$1s2p^*$		5,02772		9,17497		14,57314		21,22171		29,12050		38,26942		48,66842		60,31748

*The nonrelativistic values from [28] were taken for the boundary energies of the ${}^3S^e$ and ${}^3P^o$ terms.

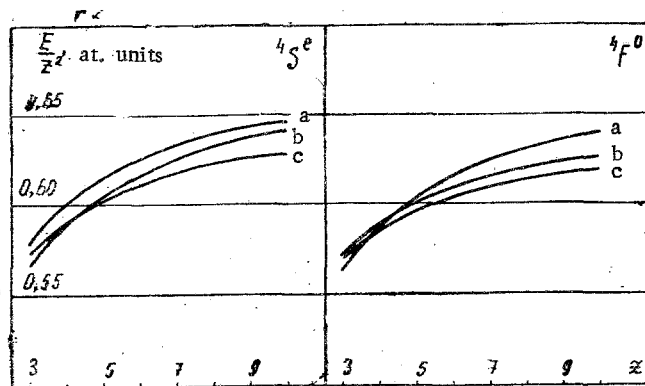


Fig. 1. Intersections in the $4S^e$ and $4F^o$ term systems: $4S^e$: a) $1s2s3s$, b) $1s2p3p$, c) $1s2s4s$; $4F^o$: a) $1s2p3d$, b) $1s2s4f$, c) $1s2s5f$.

- 1) The correlation corrections to the energies of the quartet terms are small, and they do not influence the relative disposition of the energy levels;
- 2) the relativistic corrections are approximately the same for all terms; and
- 3) the LS coupling scheme is used in state classification. The wave functions for terms of a given symmetry should form an orthonormalized set.

Assumption 1 has been tested previously [22] on the $1s2pns$ and $1s2snp$ $4P^o$ terms as well as the $1s2sns$ $4S^e$ ones, and it was shown that when the orthogonality conditions for the complete wave functions are suitably incorporated, the positions of these terms calculated in the one-configuration approximation agree completely with the observed ones [1]. In [7], an estimate was made of the relativistic corrections to the excited levels in the Li atom, which confirmed assumption 2. If, following [7], we compare the relativistic corrections for the $1s2s$ $3S$ and $1s2p$ $3P$ terms in the isoelectronic series, we see that they are also approximately identical in magnitude for a given nuclear charge. The main difficulty arises in meeting the orthogonality conditions for wave functions of a given symmetry. In the calculations on a series of terms of given symmetry, for example $1s2sns$ $4S^e$, it was impossible to satisfy all the conditions even by using nonorthogonal orbitals without resorting to freezing the core functions. In [17], the one-configuration functions were found in the frozen field of a one-electron ion. We used the frozen excited core approximation [22], i.e., for all terms in the $1s2l$ sequence the $3L$ core was identical. Apart from meeting the necessary orthogonality conditions, that approach enables one to use orthogonal one-electron functions, although it leads to certain additional errors related to core relaxation on going from one excited state to another.

These assumptions were used in calculating the quartet terms of configurations $1s2snl$ and $1s2pnl$, $l = 0, 1, 2, 3$, $n = 2, 3, 4, 5$. The one-electron radial orbitals were taken in the hydrogen form with variable parameters [23].

Table 1 gives the calculated energies in atomic units and the sequence N of terms in each series for ions in the isoelectronic Li series. The published data [13-16] imply that the energies obtained by the variational method are close to those derived from solving the Hartree-Fock equations. A comparison may be made with multiconfiguration calculations [2, 5, 17], which incorporate electron correlation, and which include the most precise calculations [6-9], and these show that the maximum error of about 0.02 atomic units occurs in the calculation of $4P^e$ and the lower $4P^o$ terms (about 0.011 atomic units). There is less error in our calculations by comparison with the multiconfiguration values for other terms (of the order of thousandths of an atomic unit). It was found that the errors in determining the term energies become more systematic for the transitions between excited levels, and this enables one to obtain good results for the wavelengths. Table 2 compares the data for the level positions and transition wavelengths in the quartet spectrum of O^{+5} obtained from our results against the theoretical data and the experiments of [10]. The same agreement with experiment (within limits of 1 nm) occurs for other transitions between excited quartet terms.

Therefore, the one-configuration results obtained by the variational method with essential obedience to the orthogonality conditions are quite suitable for qualitative analysis of the quartet-spectrum pattern.

TABLE 2. Positions of Energy Levels in eV and Wavelengths in nm for Certain Transitions in the Quartet Spectrum of O^{+5}

Transition	Level position*		λ		
	our study	exp. [10]	our study	other calculation	exp. [10]
$1s2s2p\ ^4P^0$	554,31	554,25		15,15 ^a 14,95 ^b	15,23 15,16
$-1s2s3s\ ^4S^e$	636,60	636,6—637,0	15,07	15,00 ^c 14,01 ^b	14,05
$-1s2s3d\ ^4D^e$	642,83	643,4	14,01	14,03 ^c	
$-1s2p3p\ ^4S^e$	648,16	649,8	13,21	13,02 ^a 13,21 ^b	13,10
$1s2p^2\ ^4P^e$	567,68	—		16,97 ^a	16,87
$-1s2s3p\ ^4P^0$	640,36	641,7	17,06	16,85 ^b 15,74 ^a	15,78
$-1s2p3s\ ^4P^0$	645,34	646,7	15,96	15,92 ^b	
$-1s2p3d\ ^4P^0$	651,71	652,3	14,75	14,73 ^b	14,73
$1s2p3p\ ^4D^e$	647,20	647,7—648,4			
$-1s2p5d\ ^4P^0$	686,84	688,2	31,28	30,9 ^c	31,32
$-1s2p5d\ ^4D^0$	686,78		31,32		
$-1s2p5d\ ^4F^0$	686,55		31,51		

*The positions of the levels have been calculated above the $1s^22s$ state of O^{+5} : a) [2]; b) [3]; c) [10].

Table 1 shows that, in each series of terms, apart from $^4P^e$ and $^4D^0$ terms, we have two systems of levels that converge to the $1s2s\ ^3S$ and $1s2p\ ^3P$ boundaries, respectively (the values of the boundary energies are also given in the table). All the terms that converge to the $1s2p\ ^3P$ limit in the Li atom lie above the $1s2s\ ^3S$ limit, i.e., against the background of the $1s2s\ ^3L$ continuum, apart from the $1s2p3s\ ^4P^0$ limit. The $1s2s\ ^3S$ term should be considered as belonging to both sets of levels in this system. As the nuclear charge increases, the spectrum alters: the levels descend and converge to the $1s2p\ ^3P$ limit in the $1s^2e\ ^2L$ doublet continuum. Already in Be^+ , above the $1s2s\ ^3S$ limit there are only levels with large values of the principal quantum number for the outer electron $n \geq 4$. In the B^{+2} ion, all the levels lie below the 3S limit. In the heavier ions, the $1s2pn\ ^3L$ levels descend even further below the 3S limit. Levels with this symmetry type, but converging to different limits $1s2sn\ ^3L$ and $1s2pn\ ^3L$, form Rydberg-type series. On the whole, though, the picture given by the terms of a given symmetry is fairly confused, and for the $^4P^0$ terms it is further complicated by the fact that the $1s2p\ ^3P$ limit is that of convergence for levels of configurations of two types: $1s2pns\ ^4P^0$ and $1s2pnd\ ^4P^0$.

An interesting feature of the quartet terms considered in the isoelectronic sequence is the change in the level order (Table 1). Figure 1 shows the z dependence of $^4S^e$ and $^4F^0$ terms. The change in order leads to intersections between terms of the same symmetry type, which occur in all these term systems, although there are intersections only for terms that converge to different limits.

All the intersections so far found occur up to $z \leq 6$ and correspond to fractional values of the charge. The term classification in the LS coupling scheme is shown by calculations and comparison with experiment to be correct for each ion, but if we consider the energy functional as a continuous function of the nuclear charge, we get a conflict with the theorem that terms of the same symmetry do not intersect [24].

In [2], it was suggested that the quartet terms of the quasidegenerate $1s2snp$ and $1s2pns$ configurations may be classified by means of a $+$ -scheme. In this scheme, the $^4P^0(2)$ term corresponds to the state $1s23sp_+$ ($1s2s3p\ ^4P^0$ in the LS coupling scheme), while the following term $^4P^0(3)$ is $1s23sp_-$ (Table 2). This term sequence was obtained for the entire isoelectronic sequence Li-Ne $^{+7}$. However, subsequent theoretical [11, 12] and experimental [1] studies have shown that the $^4P^0(3)$ term in the Li atom corresponds to the $1s2s4p\ ^4P^0$ term, so the classification scheme of [2] is incorrect for the entire isoelectronic sequence. A similar situation occurs for other terms. In [4] it was pointed out that the $(+ -)$ classification may apply for $z \geq 6$.

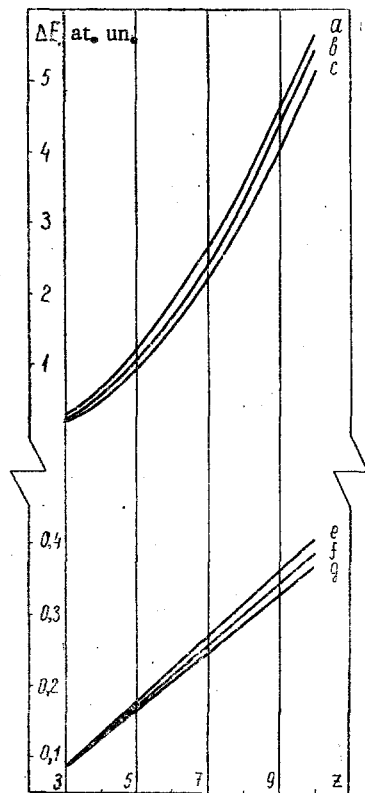


Fig. 2. Illustration of the z dependence for certain transition in the quartet-term system: a) $1s2s2p\ ^4P^o-1s2s3s\ ^4S^e$; b) $1s2s2p\ ^4P^o-1s2s3d\ ^4D^e$; c) $1s2s2p\ ^4P^o-1s2p3p\ ^4S^e$; e) $1s2p3d\ ^4D^o-1s2s3d\ ^4D^e$; f) $1s2p4d\ ^4D^o-1s2s4d\ ^4D^e$; g) $1s2p5d\ ^4D^o-1s2s5d\ ^4D^e$.

We note that configuration overlap does not alter the situation: The nondiagonal matrix elements in the Hamiltonian between the wave functions of the intersecting terms are almost linearly dependent on the nuclear charge and have small values in regions of z close to the intersections [4]. The multiplet splitting is also small by comparison with the distances between terms, so transition to other quantum numbers such as LSJ does not eliminate the intersections.

The cause evidently lies in the insufficiency of the classification schemes used to describe this term system. The quartet terms converging to different limits are different in physical nature: The $1s2sn$ configurations are formed in one-electron excitations, but from an internal shell, while the $1s2pn\ell$ configurations are doubly excited. As long ago as 1933, Beitzler [25] introduced literal indices to give an additional characterization of the terms formed by excitation of internal electrons. These literal symbols are not quantum numbers, but they are convenient in interpreting the spectra. It is possible that a nonconflicting quantum-mechanical description of this system of quartet terms requires the definition of new quantum numbers such that terms converging to different limits would have different symmetries, which would eliminate the question of term intersection in the z sequence. An example of the new approach to classifying doubly excited states in two-electron atoms has been demonstrated recently [26, 27].

In conclusion we note a further feature occurring in the z dependence of the transitions in the quartet spectrum. Figure 2 shows typical relationships for transitions involving state change in an outer electron and for transitions in which the state change is that of an internal electron with $n = 2$ for the principal quantum number. It is evident that the first ones form a hydrogen-type relationship to the nuclear charge, whereas the second have almost a linear relationship.

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