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Orbital configuration assignment of $^4S^e$ doubly excited states of lithium isoelectronic sequence

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Results of Hartree-Fock and multiconfiguration Hartree-Fock calculations using only two configurations (degenerate in zero order within the context of the nuclear-charge-expansion perturbation method) for $^4S^e$ doubly excited states of lithium isoelectronic sequence are used to propose an orbital configuration classification of these states, extending the similar classification by Holoien and Geltman for $^4S^e$ states of lithium only.

I. INTRODUCTION

Line radiation due to dipole transitions from a large number of doubly excited quartet states of the lithium isoelectronic sequence has been identified with the advent of beam-foil spectroscopy.[1] These line radiations, along with others arising from dipole transitions between metastable states of other multiply charged ions, have been detected in plasma discharges[2] and are believed to arise in the solar corona due to dielectronic recombination of heliumlike ions by electron-impact and/or inner-shell excitation of excited lithiumlike ions by electron impact.[3-6] The identification and assignment of such narrow-line radiations and the indirect inference of relative positions of metastable states in the energy scale have evoked considerable theoretical interest. In a pioneering study, Garcia and Mack[7] used the central-field model to give an orbital configuration designation of quartet states of lithium, and proposed assignment of some lines by calculating energies of such states on the basis of screening theory within the context of the nuclear-charge-expansion perturbation method (NCEPT).[8]

Holoien and Geltman[9] (HG) used explicitly correlated basis functions to calculate energies of low-lying $^4P^o$, $^4P^e$, and $^4S^e$ states of lithium isoelectronic sequence from Li to Ne^{+7}, and proposed an orbital configuration assignment for states of lithium only. Recently, Junker and Bardsley[10] used a limited-configuration-interaction approach to calculate variationally the energies of a large number of metastable states of 3, 4, and 5 electron atomic systems. They proposed an orbital configuration classification of $^4P^o$, $^4P^e$, $^4S^e$, and $^2P^e$ states of lithiumlike oxygen and fluorine atoms on the basis of the dominating weight of a configuration in their configuration-interaction wave function. Specifically, they assign the orbital configurations $1s2s3s$, $1s2p3p$, and $1s2s4s$ to the three lowest $^4S^e$ states, respectively, in the order of increasing energy for O^{5+} and F^{6+} as compared to Holoien and Geltman's[9] orbital configuration assignment $1s2s3s$, $1s2s4s$, and $1s2s5s$ to the three lowest $^4S^e$ states, respectively, in the order of increasing energy in lithium. Very recently, Lunell[11] has studied the orbital configuration classification of $^4P^o$ and $^4P^e$ states of lithium and some members of the isoelectronic sequence by using the natural-orbital analysis and the Hartree-Fock method. He has questioned Holoien and Geltman's orbital configuration assignment of higher $^4P^o$ states in lithium, and suggested possible crossing of configurations with increasing atomic number. In the present paper, we study the problem of the assignment of orbital configurations to $^4S^e$ states of the lithium isoelectronic sequence as a function of nuclear charge by using the Hartree-Fock method.

Both $1s2sns$ and $1s2pnp$ orbital configurations, based on the independent-particle central-field model, give rise to $^4S^e$ states, and in the limit of infinite nuclear charge are degenerate in zero order within the context of NCEPM.[8] But the degeneracy is lifted in the first order, predicting an asymptotic ordering of such states belonging to the same "complex"[8] that is valid in the limit $Z\rightarrow\infty$. However, it is not clear at which value of Z the asymptotic ordering is expected to be achieved. Further, this gives no clue as to the relative energy ordering of $1s2pnp$ $^4S^e$ and $1s2sms$ $^4S^e$, $n\neq m$ for finite Z, particularly for Z near the neutral end of the isoelectronic sequence. Of course, an exact and complete NCEPM calculation of the energy of $^4S^e$ states—an impossible task—could, in principle, answer all these questions for finite nuclear charge. However, since in these quartet states three electrons move in three different radial orbitals localized on different regions of space (radially speaking), and move with "parallel spins," correlation of electronic motion due to the antisymmetry of the wave function for electron

TABLE I. HF and MCHF energies (a.u.) for $1s2s3s\,^4S^e$ and $1s2p3p\,^4S^e$.

Nuclear	$1s2s3s\,^4S^e$			$1s2p3p\,^4S^e$	
charge Z	HF	MCHF	HG[a]	HF	MCHF
3	−5.2044	−5.2112	−5.2110	−5.09753	−5.06818
4	−9.6061	−9.6179	−9.6177	−9.4356	−9.3996
5	−15.3709	−15.3874	−15.3869	−15.1375	−15.0961
6	−22.4976	−22.5186	−22.5176	−22.2017	−22.1554
7	−30.9857	−31.0112	−31.0097	−30.6277	−30.5767
8	−40.8352	−40.8651	−40.8627 (−40.782)[b]	−40.4151	−40.3595
9	−52.0459	−52.0803	−52.0769 (−51.973)[b]	−51.5639	−51.5037
10	−64.6178	−64.6566	−64.6520	−64.0740	−64.0092

[a] HG, Holoien and Geltman, Ref. 9.

[b] JB, Junker and Bardsley, Ref. 10.

interchange would simulate somewhat the desired correlation of electronic motion. Thus a rather simple wave function such as the Hartree-Fock wave function might yield a satisfactory description of such states, and Hartree-Fock energies would not be too different from "exact" energies. This conjecture is seen to be correct on comparison of Hartree-Fock and exact energies for $^4P^o$ states.[11] In other words, correlation effects are small enough so as not to upset the ordering of energies of states obtained from Hartree-Fock energies of pure configurations, and the "zero-order" configuration mixing between $1s2sns\,^4S^e$ and $1s2pnp\,^4S^e$ Hartree-Fock wave functions is small.

II. RESULTS AND DISCUSSION

In Tables I and II we list Hartree-Fock energies for $1s2sms\,^4S^e$ states, $m=3$–6, and $1s2pnp\,^4S^e$ states, $n=3,4$, for Li to Ne^{+7}, which were obtained by using the well-known numerical Hartree-Fock computer code of Froese-Fischer.[12] We note that the Hartree-Fock energies of $1s2sms\,^4S^e$ states, for $m=3$–6, for Li and Be$^+$ are quite close to the values reported by HG. Further, the difference between Hartree-Fock energy and the corresponding HG energy gets smaller and smaller as m increases for lithium. This is also seen to be the case for $m=3$ and 4 for Be$^+$. But the difference between Hartree-Fock energy and HG energy for $m=4$ and 5, for $Z=5$–10 is much too large to be attributed to the neglect of correlation in the Hartree-Fock method. In fact, the HG energies are much too low compared to $1s2sms\,^4S^e$, $m=4$ and 5, for $Z=5$–10 Hartree-Fock energies. Since the HG energies are most accurate for Li and possibly Be$^+$, and the Hartree-Fock energies of $1s2sms\,^4S^e$ are quite close to the HG energies for Li and Be$^+$, the Hartree-Fock results of $1s2sms\,^4S^e$, $m=4$ and 5, must be of satisfactory accuracy. Assuming the correctness of HG energies, this must mean that the character of the orbital configuration of $^4S^e$ states changes as Z increases, leading to crossing of orbital composition: $1s2sms$ and $1s2pnp$.

Thus on the basis of Hartree-Fock energies given in Tables I and II, we suggest the orbital configuration assignment of the four lowest $^4S^e$ states for $Z=3$–10 in Table III, indicating several crossings of orbital configuration assignment as nuclear charge increases. We note that our assignment is

TABLE II. HF energies (a.u.) of $1s2sms\,^4S^e$, $m=4$–6 and $1s2p4p\,^4S^e$ states.

Nuclear charge Z	$1s2s4s\,^4S^e$ HF	$1s2s5s\,^4S^e$ HF	$1s2s6s\,^4S^e$ HF	$1s2p4p\,^4S^e$ HF
3	−5.1549	−5.13614	−5.12700	−5.06249
4	−9.4539	−9.39175	−9.36021	−9.31222
5	−15.0665	−14.9382	−14.8719	−14.8762
6	−21.9923	−21.7751	−21.6617	−21.7535
7	−30.2308	−29.9022	−29.7294	−29.9437
8	−39.7820	−39.3194	−39.0749	−39.4467
9	−50.6458	−50.0266	−49.6983	−50.2623
10	−62.8220	−62.0239	−61.5995	−62.3905

TABLE III. Orbital configuration designation and relative energy ordering of the first four $^4S^e$ states: $1s2s3s$ $^4S^e=1$; $1s2p3p$ $^4S^e=2$; $1s2s4s$ $^4S^e=3$; $1s2p4p$ $^4S^e=4$; $1s2s5s$ $^4S^e=5$; $1s2s6s$ $^4S^e=6$; $1s2s7s$ $^4S^e=7$.

Nuclear charge	Energy order of $^4S^e$ states
3	$1<3<5<6<7$
4	$1<3<2<5<6$
5, 6	$1<2<3<5$
7–10	$1<2<3<4$

in perfect harmony with that of HG for lithium and of Junker and Bardsley for O^{5+} and F^{6+}.

To test whether the effect of configuration interaction is large enough to spoil the relative energy ordering suggested in Table III on the basis of Hartree-Fock energies, we have performed a multiconfiguration Hartree-Fock calculation[12,13] (MCHF) in which we include only two configurations, $1s2s3s$ $^4S^e$ and $1s2p3p$ $^4S^e$, which are degenerate in zero order with NCEPM. These results are shown under the heading MCHF in Table I. We note with gratification that the two configuration MCHF energies for the lowest $^4S^e$ compare very well with those from elaborate calculations of HG. The change in calculated energy due to the MCHF procedure is of the order of 0.03–0.06 a.u. for $1s2s3s$-$1s2p3p$ mixing, but would be much less for $1s2sms$-$1s2pmp$, $m=4$ and 5, mixing, thus indicating that the Hartree-Fock energies may be used as valid basis for classification and designation of the orbital configuration of $^4S^e$ states.

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