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Theoretical studies of core-excited states of two- and three-electron atoms

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We have carried out configuration-interaction calculations for $^4F^{e,o}$ states of Li and Be$^+$ and for the lowest $^4D^{e,o}$ states of Be$^+$ in an effort to test the accuracy that can be achieved in transition-energy calculations by assuming transferability of relativistic, radiative, and mass-polarization corrections among similar electron cores. He and Li$^+$ $2p4f\ ^{1,3}F$ states have also been considered. The nonrelativistic result for the Li $1s2p4f\ ^4F \rightarrow 1s2s4f\ ^4F^o$ transition is $\lambda_{\rm air} = 5474.3 \pm 0.4$ Å. Including relativistic, radiative, and mass-polarization corrections for the $1s2p\ ^3P$ and $1s2s\ ^3S$ Li$^+$ cores we get $\lambda = 5471.7 \pm 0.4$ Å, in excellent agreement with a $\lambda = 5471.9 \pm 1.4$ Å recently observed in the beam-foil source. Stronger support for our basic assumption comes from three calculated (experimental) wavelengths $\lambda = 3406.0 \pm 0.3(3405.6 \pm 0.6)$, $4330.1 \pm 0.5(4330.2 \pm 0.5)$, and $3510.8 \pm 0.5(3510.8 \pm 0.5)$ Å in the Be II** spectrum. Furthermore, three lines (the first two above and $\lambda = 981$ Å) have been reassigned and three new wavelengths are predicted for this spectrum. The $1s2s4f \pm 1s2p3d$ nature of the $^4F^o(1)$ and $^4F^o(2)$ states in Be$^+$ is responsible for the uncommon situation that $^4F^o(1)$ is below $1s2s4d\ ^4D^o(2)$, thus explaining the failure of some of the earlier assignments. The lowest Be$^+$ $1s2s2p\ ^4P^o$ state is found 115.845 ± 0.016 eV above the Be$^+$ $1s^22s$ ground state, in fair agreement with a recent experimental value of 115.7 ± 0.1 eV. The He and Li$^+$ $2p4f\ ^{1,3}F$ states decay to $1s4f\ ^{1,3}F$ states with wavelengths too close to the resonance transition $2p \rightarrow 1s$ of the corresponding one-electron system to be observed in beam-foil experiments. The Li$^+$ $2p4f\ ^{1,3}F$ states, however, decay to $2p3d\ ^{1,3}D$ states with $\lambda = 3825.4 \pm 0.1$ and 4352.2 ± 0.1 Å, respectively, and they should be susceptible of experimental observation.

I. INTRODUCTION

In this paper we consider several two- and three-electron core-excited levels[1] of high orbital angular momentum (D and F states) with the highest possible multiplicity, namely, two-electron triplets and three-electron quartets. These states are amenable of very precise treatment by means of configuration interaction (CI) calculations. Our purpose is twofold: (i) to explore the accuracy that can be achieved by assuming transferability of the relativistic, radiative, and mass-polarization energy corrections $E_{\rm rrmp}$ among similar electron cores ($2p$, $1s2s\ ^3S$, $1s2p\ ^3P$, and $1s2s\ ^3S \pm 1s2p\ ^3P$) neglecting the corresponding outer-electron effects, and (ii) to identify and predict new lines in the core-excited spectra of He, Li$^+$, Li , and Be$^+$.

Let us consider two levels separated by an energy ΔE. Since $E_{\rm rrmp}$ is a small fraction of the nonrelativistic energy $E_{\rm nr}$, one may write[2]

$$E = E_{\rm nr} + E_{\rm rrmp}\ , \tag{1}$$

$$\Delta E = \Delta E_{\rm nr} + \Delta E_{\rm rrmp}\ , \tag{2}$$

where the $E_{\rm rrmp}$ contribution is calculated with a zeroth-order nonrelativistic wave function. In the following we will assume $\Delta E_{\rm rrmp} \simeq \Delta E_{\rm rrmp}$ (core electrons) which leads to

$$\Delta E \simeq \Delta E_{\rm nr} + \Delta E_{\rm rrmp}(\text{core}). \tag{3}$$

When the cores of the two levels are equal, like in the Li $1s2s4f\ ^4F^o \rightarrow$ Li $1s2s3d\ ^4D$ transition, $\Delta E_{\rm rrmp}$(core) = 0. However, in transitions such as Li $1s2p4f\ ^4F \rightarrow$ Li $1s2s4f\ ^4F^o$ there is a change from a Li$^+$ $1s2p\ ^3P$ to a Li$^+$ $1s2s\ ^3S$ core[3,4] involving a $\Delta E_{\rm rrmp} = 8.58$ cm^{-1} yielding a noticeable effect both in the experimental wavelength and in the theoretical calculation which in this particular case has been carried out here with an uncertainty of ±1.2 cm^{-1}.

Relativistic and mass-polarization corrections for Li$^+$ and Be^{++} $1s2s\ ^3S$ and $1s2p\ ^3P$ have been calculated very accurately by Accad *et al.*[3] Radiative corrections for Li$^+$ have also been calculated,[4] showing good agreement with experiment. For Be^{++} one can deduce $\Delta E_{\rm rad}$ corrections by resort to experiment, assuming the correctness of all the intermediate experimental and theoretical data.

The term $\Delta E_{\rm rrmp}$(core) can also be calculated by resort to the experimental transition core energies ΔE(core):

$$\Delta E_{\rm rrmp}(\text{core}) = \Delta E(\text{core}) - \Delta E_{\rm nr}(\text{core}). \tag{4}$$

Experimental ΔE(core) energies are available[5-7] and $\Delta E_{\rm nr}$(core) values are known very accurately.[3]

The CI calculations[8] have been carried out as in previous work,[9-11] with LS eigenfunctions and energy optimized Slater-type orbitals (STO's), and by approximating $E_{\rm nr}$ as

$$E_{\rm nr} = E_{\rm u} + \Delta E_{\rm CI} + \Delta E_{\rm STO}\ , \tag{5}$$

where $E_{\rm u}$ is a rigorous energy upper bound and the other two terms are small corrections for truncations in the CI expansion and in the STO set,

TABLE I. STO parameters for the $^4F^o(1)$ and $^4F(1)$ states of Li and STO truncation errors ΔE_{STO}, in μhartree.

State	STO's	ΔE_{STO}
$^4F^o(1)$	$1s=3.00$; $2s=1.50$; $3s=1.495$; $4s=5.90$; $5s=2.35$; $6s=1.46$ $2p=2.25$; $3p=2.11$; $4p=2.38$; $5p=4.60$; $6p=6.40$; $2p=1.03$; $3p=1.60$ $3d=0.36$; $4d=1.20$; $3d=3.10$; $4d=3.10$; $5d=3.45$; $6d=5.20$ $4f=0.25$; $5f=0.284$; $4f=3.90$; $5f=3.80$; $5g=0.39$; $6g=0.80$	41 ± 3
$^4F(1)$	$1s=3.00$; $2s=1.96$; $3s=2.44$; $4s=2.83$; $5s=8.20$ $2p=1.05$; $3p=1.41$; $4p=1.85$; $5p=3.15$; $6p=1.66$; $7p=1.51$ $3d=0.33$; $3d=0.88$; $3d=3.45$; $4d=2.28$; $5d=4.45$ $4f=0.253$; $5f=0.293$; $4f=3.22$; $5f=3.50$; $5g=0.475$; $5g=4.10$	20 ±3

respectively. Although Eq. (5) has been used for some time,[12] and spectroscopic accuracy for three- and four-electron systems has been achieved,[10,13] it is only recently that more powerful STO optimization computer programs have been constructed[11] thus reducing the human effort to acceptable levels.

II. $^4F^{e,o}$ STATES OF Li

In a recent beam-foil study of the lithium core-excited spectrum,[14] it was suggested that a weak line $\lambda = 5471.9 \pm 1.4$ Å might be due to the $E1$ decay of $1s2p4f\,^4F$ into $1s2s4f\,^4F^o$. A previous estimate[15] for this transition was around $\lambda = 5486$ Å. Because in the earlier calculations most STO parameters were optimized with respect to *other* quartet states, we decided to answer a request by Mannervik,[16] by repeating the calculations with carefully optimized STO bases and tighter error bounds.

In Table I we give the STO parameters and truncation energy errors carrying uncertainties 30 times smaller than in the previous work. Surprisingly, the leading outer-shell correlation effect in $1s2s4f$ is due to configuration $1s2p5g$ with the $5g$ orbital localized far out, in the same region as the major $4f$ orbital. This configuration contributes almost 60 cm^{-1} to the energy of the $^4F^o$ state, and it accounts for most of the discrepancy with the earlier work.

In Table II we collect the data needed to calculate the nonrelativistic energies by Eq. (5). Absolute term values are calculated by Eq. (3) using ΔE_{rrmp} (core) from calculations[3,4] and from experiment.[5] Both values of ΔE_{rrmp} (core) agree well with each other, showing the detailed consistency of the theoretical results[3,4] with experiment. Our theoretical $\lambda_{\mathrm{air}} = 5471.7 \pm 0.4$ Å agrees well with the line $\lambda = 5471.9 \pm 1.4$ Å found by Bromander *et al.*[14] thus confirming their identification.

In Fig. 1 we illustrate this result from three perspectives. First we give the nonrelativistic result $\lambda = 5474.3 \pm 0.4$ Å lying outside the experimental value. Secondly we add $\Delta E_{\mathrm{rrmp}}(\mathrm{core}) = 8.58$ cm^{-1} obtained by combining the relativistic and mass-polarization results of Accad *et al.*[3] with the Lamb shift corrections of Ermolaev,[4] getting $\lambda = 5471.7 \pm 0.4$ Å, in good agreement with experi-

TABLE II. Nonrelativistic energies E_{nr} for the $1s\,2s4f$ and $1s2p4f$ states of Li, in a.u., and estimates of their absolute term values T, in cm^{-1}. 1 a.u. (^{7}Li) = 219 457.48 cm^{-1}.

	$1s2s4f\,^4F^o$	$1s2p4f\,^4F$
E_{u}	−5.142 798	−5.059 561
ΔE_{CI}	0	0
ΔE_{STO}, from Table I	−0.000 020(3)	−0.000 041(3)
E_{nr}, Eq. (5)	−5.142 818(3)	−5.059 602(3)
	−5.142 710(105)[a]	−5.059 690(105)[a]
E_{nr}, Li$^+$ $1s2s\,^3S$[b]	−5.110 727	
T Li$^+$ $1s2s\,^3S$	519 522.6[c]	
E_{nr}, Li$^+$ $1s2p\,^3P$[b]		−5.027 716
T Li$^+$ $1s2p\,^3P$		537 748.6[c]
ΔE_{rrmp}	0	0
ΔE_{nr}	7 042.6(0.7)	6 697.6(0.7)
T	512 480.0(0.7)	530 751.0(0.7)

[a] Rough estimate from Ref. 15.

[b] Taken from Ref. 3.

[c] Taken from Ref. 17.

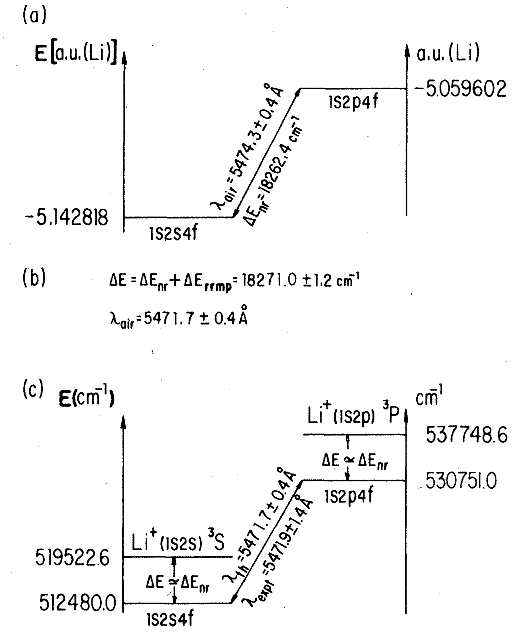

FIG. 1. The Li $1s2p4f$ $^4F\rightarrow 1s2s4f$ $^4F^o$ transition: (a) nonrelativistic results, (b) ΔE calculated from Eq. (3) and ΔE_{rrmp} taken from theoretical calculations, (c) same as (b) but ΔE_{rrmp} taken from experiment through Eq. (4).

ment. Finally, we get ΔE_{rrmp}(core) from experiment,[5] or, which is equivalent, we place the $1s2p4f$ and $1s2s4f$ levels with respect to their respective Li^+ cores by comparing nonrelativistic calculations, and then use experimental term values for the cores.[17]

III. $^4F^{e,o}$ AND $^4D^{e,o}$ STATES OF Be^+

Nonrelativistic calculations for several ^4S and $^4P^o$ states of Be^+ have been published.[18] We will present below the first calculations for $^4F^{e,o}$ and $^4D^{e,o}$ states. The experimental energy difference between Be^{++} $1s2p$ $^3P_1$ and $1s2s$ $^3S_1$ is 26 856.3±0.7 cm^{-1} (Ref. 7). Using $\Delta E_{\text{nr}}=26\,816.7$ cm^{-1} (Ref. 3) and Eq. (4) we get

$$\Delta E_{\text{rrmp}}=+39.6\text{ cm}^{-1}. \tag{6}$$

Thus a more stringent test for the transferability of E_{rrmp} corrections is possible in Be^+ (compare with $\Delta E_{\text{rrmp}}=8.58$ cm^{-1} in Li). Also, we will see that $^4F^o(1)$, for example, instead of being represented by a leading configuration $1s2s4f$ is more properly described by

$$^4F^o(1)=(53.2\%)\,1s2s4f+(46.5\%)\,1s2p3d+\ldots\,. \tag{7}$$

Therefore, when computing ΔE_{rrmp} between Be^{++} $1s2s$ ^3S and Be^+ $^4F^o(1)$ instead of getting $\Delta E_{\text{rrmp}}=0$ we obtain

$$\Delta E_{\text{rrmp}}=0.465(-39.6)=-18.4\text{ cm}^{-1}. \tag{8}$$

In Table III we give the STO parameters together with the corresponding STO truncation errors. Except for obvious details, the outer-shell STO sets do not change much from one state to another. These small changes, however, do influence sin-

TABLE III. STO parameters for several Be II** states and STO truncation errors ΔE_{STO}, in μhartree.

State	STO's	ΔE_{STO}
$^4D(1)$	$1s=4.00$; $2s=1.00$; $3s=2.175$; $3s=0.99$; $4s=1.13$; $5s=6.70$; $6s=7.926$; $7s=9.259$ $2p=1.54$; $3p=0.848$; $4p=2.56$; $5p=1.17$; $6p=3.52$; $2p=2.90$; $3p=2.90$; $4p=6.45$ $3d=0.715$; $4d=0.878$; $5d=1.04$; $6d=0.77$; $3d=4.098$; $4d=4.098$ $4f=1.03$; $5f=1.237$; $6f=1.25$; $4f=5.00$; $5f=5.00$; $5g=1.70$; $6h=2.00$	62 ± 5
$^4F^o(1)$	$1s=4.00$; $2s=1.305$; $3s=2.035$; $4s=9.455$; $5s=6.589$; $6s=7.926$; $7s=9.259$ $2p=1.455$; $2p=2.60$; $4p=1.93$; $5p=1.73$; $5p=0.90$; $5p=5.40$; $7p=6.38$ $3d=0.726$; $4d=1.96$; $5d=5.81$; $3d=4.098$; $4d=4.098$; $5d=7.00$; $6d=10.50$ $4f=0.559$; $5f=1.36$; $6f=2.58$; $7f=3.80$; $4f=5.00$; $5f=5.00$; $5g=0.772$; $5g=6.00$	62 ± 8
$^4F^o(2)$	$1s=4.00$; $2s=1.46$; $2s=2.17$; $3s=2.31$; $4s=1.875$; $4s=9.455$; $5s=6.589$ $2p=1.65$; $2p=1.00$; $3p=2.65$; $3p=1.70$; $4p=6.45$; $5p=6.40$ $3d=0.72$; $3d=1.36$; $4d=0.60$; $3d=4.098$; $4d=4.098$; $5d=7.00$ $4f=0.40$; $4f=0.97$; $5f=0.53$; $5f=1.12$; $4f=5.00$; $5f=5.00$; $5g=0.66$; $5g=1.40$	88 ± 13
$^4D^o(1)$	$1s=4.00$; $3s=3.36$; $4s=5.98$; $2s=2.72$ $2p=1.58$; $3p=2.28$; $4p=5.30$; $5p=2.40$; $6p=1.04$; $6p=6.38$; $7p=4.16$ $3d=0.693$; $4d=0.859$; $5d=1.018$; $6d=0.71$; $3d=4.87$; $4d=3.25$; $5d=6.70$; $6d=7.20$ $4f=1.16$; $4f=1.90$; $4f=4.40$; $5f=4.93$; $5g=1.72$; $5g=5.73$; $6h=2.00$	82 ± 3
$^4F(1)$	$1s=4.00$; $3s=3.36$; $4s=5.98$; $2s=2.72$ $2p=1.55$; $3p=2.34$; $4p=5.40$; $5p=2.09$; $6p=6.38$; $7p=4.16$ $3d=0.635$; $4d=1.836$; $5d=2.30$; $3d=4.87$; $4d=3.25$; $5d=6.70$; $6d=7.20$ $4f=0.51$; $5f=0.597$; $6f=1.30$; $4f=4.40$; $5f=4.93$; $5g=5.73$; $5g=0.826$; $6g=1.81$; $6h=1.27$	30 ± 2

nificantly the energy and its convergence thus justifying a separate STO optimization for each state. In Table IV we calculate absolute term values analogously as we did for Li states in Table II.

Transition probabilities and wavelengths are collected in Table V. It is seen that there are three lines λ = 3406, 3511, and 4330 Å associated with fair transition probabilities showing good agreement with experiment.[19] Our basic assumption, Eq. (3), is confirmed to within ±2 cm^{-1} , which for Be II** is five percent of $\Delta E_{\rm rmp}$, or

$$\Delta E_{\rm rmp} = \Delta E_{\rm rmp}(\text{core}) \pm 0.05 \Delta E_{\rm rmp}\,. \qquad (9)$$

Future experiments and calculations of improved accuracy may prove that Eq. (3) holds still better than reflected by Eq. (9). The present results also prompt a reinterpretation of some features of Be II** spectrum which we discuss in the following.

A. Emission spectrum of Be II**

The first detailed study of the Be beam-foil spectrum[19] showed fourteen lines that could be assigned to the Be II** spectrum. Another line λ = 804 Å has since been incorporated.[20]

One closed loop[19] involving the $^4P^o(1)$, $^4S(1)$, $^4P^o(3)$, and $^4P(1)$ states and lines at λ = 1020, 3181, 1156, and 2325 Å seems to be well established, having received recent support from calculations.[18] The occurrence of this loop in the beam-foil spectrum is also expected on account of its prominence in the Li I** spectrum.[14]

Another closed loop[19] involving the $^4P^o(1)$, $^4D(1)$, $^4D^o(1)$, and $^4P(1)$ states and lines at λ = 865, 3406, 981, and 2325 Å fits extremely well with the experimental data, but the present calculations show that it is a spurious one. Indeed, the $^4D^o(1) \rightarrow {}^4D(1)$ transition occurs with λ = 3381 Å (see Table V) while the λ = 3406 Å line corresponds to the $^4F(1) \rightarrow {}^4F^o(1)$ transition. It is interesting to notice that Hontzeas *et al.*[19] were expecting a more intense $^4D^o(1) \rightarrow {}^4D(1)$ transition. The transition probabilities in Table V predict a branching ratio of 40 for $[{}^4D^o(1) \rightarrow {}^4P(1)]/[{}^4D^o(1) \rightarrow {}^4D(1)]$. If one compares this result with the branching ratio of 11 in the similar Li I** transitions,[14] the relative weakness of the still unobserved $^4D^o(1) \rightarrow {}^4D(1)$ transition at λ = 3381 Å is understood. Also, the Li $^4D^o(1)$ state is known to autoionize significantly,[15] through the spin-orbit interaction.[21] A higher autoionization rate is expected for higher members of the isoelectronic sequence, such as Be⁺, reducing still further the relative intensity of the λ = 3381 Å line.

If the λ = 3406 Å line falls out of the closed loop, the classification of the remaining lines must be reconsidered. The λ = 2325 Å line is safely assigned[22] to the $^4P(1) \rightarrow {}^4P^o(1)$ transition from intensity

TABLE IV. Nonrelativistic energies E_{nr}, in a.u., and absolute term values for several Be II** states, in cm^{-1}. 1 a.u.(^{9}Be) = 219 461.36 cm^{-1}.

	$^4D(1)$	$^4F^o(1)$	$^4F^o(2)$	$^4D^o(1)$	$^4F(1)$
E_u	−9.540 861	−9.435 724	−9.411 135	−9.406 258	−9.302 112
$\Delta E_{\rm CI}$	0	−0.000 003	−0.000 012(3)	0	0
$\Delta E_{\rm STO}$	−0.000 062(5)	−0.000 062(8)	−0.000 088(13)	−0.000 082(3)	−0.000 030(2)
$E_{\rm nr}$, Eq. (5)	−9.540 923(5)	−9.435 789(8)	−9.411 235(16)	−9.406 340(3)	−9.302 142(2)
$E_{\rm nr}({\rm Be}^{++})$	−9.297 167 [a]	−9.297 167 [a]	−9.297 167 [a]	−9.174 973 [b]	−9.174 973 [b]
$T({\rm Be}^{++})$	1 103 398.0	1 103 398.0	1 103 398.0	1 130 254.3	1 130 254.3
$\Delta E_{\rm nr}$, in cm^{-1}	53 495.0(1.1)	30 422.2(1.8)	25 033.5(3.5)	50 776.1(0.7)	27 908.7(0.5)
$\Delta E_{\rm rmp}$, Eq. (4), in cm^{-1}	−3.7 [c]	−18.4 [d]	−18.0 [c]	0	0
$T(\text{Be II}^{**})$	1 049 906.7(1.1)	1 072 994.2(1.8)	1 078 382.5(3.5)	1 079 478.2(0.7)	1 102 345.6(0.5)

[a] For the $1s2s\ {}^3S$ state, Ref. 3.
[b] For the $1s2p\ {}^3P$ state, Ref. 3.
[c] Analogously as in Eq. (8).
[d] Equation (8).

TABLE V. Calculated wavelengths, f values, and transition probabilities for some lines in the Be II** spectrum.

Transition	Wavelength (in Å)	Wavelength (experimental)[a]	f	A_{ki} (in 10^8 sec^{-1})	$S(i,k)$
${}^4F(1)\to{}^4D^o(1)$	4371.8(0.3)		0.863	2.15	249
$\to{}^4F^o(1)$	3406.0(0.3)	3405.6(0.6)	0.15	0.86	46
$\to{}^4F^o(2)$	4171.9(0.6)		0.0005	0.002	0.19
${}^4D^o(1)\to{}^4P(1)$	979.1[b]		0.617	24.9	24.3
$\to{}^4D(1)$	3380.6(0.3)		0.11	0.64	24
${}^4F^o(2)\to{}^4D(1)$	3510.8(0.5)	3510.8(0.5)	0.44	1.7	102
${}^4F^o(1)\to$	4330.1(0.5)	4330.2(0.5)	0.41	1.0	117

[a] Reference 19.

[b] The position of the ${}^4P(1)$ state is calculated by combining our absolute term value for the ${}^4D(1)$ state with the experimental wavelengths for the ${}^4D(1)\to{}^4P^o(1)$ and ${}^4P(1)\to{}^4P^o(1)$ transitions in Ref. 19.

considerations. By combining an approximate energy[18] for Be$^+$ ${}^4P^o(1)$ with our result for ${}^4D(1)$ we get $\lambda = 867$ Å, which should get closer to $\lambda = 865.3 \pm 1.0$ as better wave functions lower the nonrelativistic energy of the ${}^4P^o(1)$ state, and also by considering relativistic corrections for the $2p$ orbital in ${}^4P^o(1)$. Since the ${}^4D(1)$ state of Li is known not to autoionize to any significant degree[15] and ${}^4D(1)\to{}^4P^o(1)$ should be the preferred path for the $E1$ decay of ${}^4D(1)$, we conclude that $\lambda = 865.3$ has been correctly assigned.[19] We thus find that the ${}^4D^o(1)\to{}^4P(1)$ transition must be at $\lambda = 979.1$ Å, blended with the $\lambda = 981.4$ line, which we now reassign to the Be$^+$ $[1s2p\ {}^3P\ 3d]\,{}^2D^o\to 1s2p^2\ {}^2D$ transition, on account of similarities with the Li I** spectrum.[23]

Figure 2 shows the main features of the Be II** spectrum. The $\lambda = 3406$ Å line corresponds to the ${}^4F(1)\to{}^4F^o(1)$ transition. Furthermore, the transition probabilities in Table V indicate that the ${}^4F(1)$ state should decay preferentially to ${}^4D^o(1)$ with $\lambda = 4372$ Å. This line has not been reported so far.[19,20]

The $\lambda = 3511$ Å line had been assigned correctly.[20] Not so the $\lambda = 4330$ Å line which clearly correponds to ${}^4F^o(1)\to{}^4D(1)$ and not to ${}^4F(1)\to{}^4F^o(2)$ as proposed recently.[20] In this connection it is interesting to notice that Hontzeas *et al.*[19] had already thought about our present classification but dis-

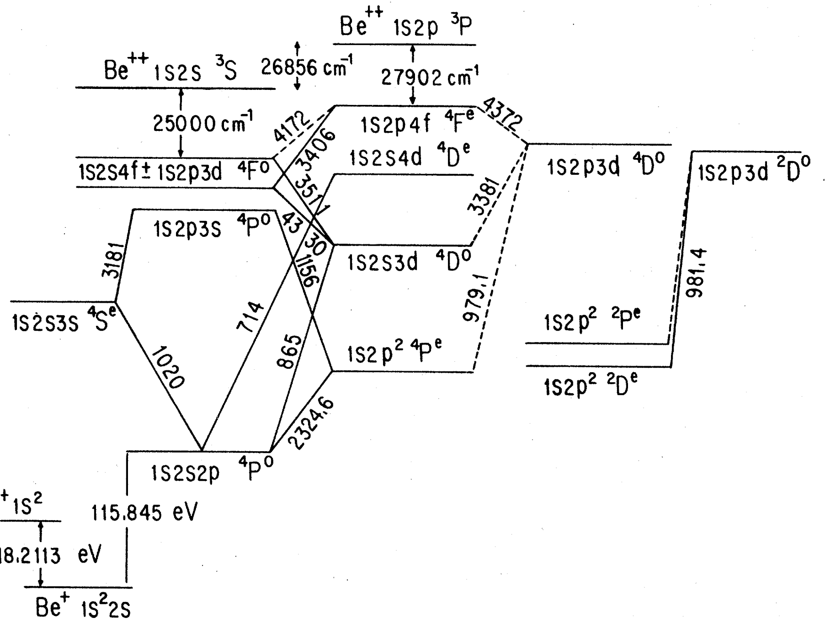

FIG. 2. Emission spectrum of Be II** showing observed (——) and unobserved (---) transitions. Some of the observed lines have been reassigned.

TABLE VI. STO parameters for the $2p4f\,^{1,3}F$ states of He and Li, and STO truncation energy errors ΔE_{STO}, in μhartree.

State	STO's (inner shell)	STO's (outer shell)	ΔE_{STO}
$^{1,3}F$(He)	$2p=1.0$; $3p=1.0$; $4p=1.0$ $3d=0.87$; $4d=1.1$; $5g=1.3$	$3d=0.33$; $4f=0.26$; $5f=0.25$; $4f=0.72$; $6f=0.62$ $5g=0.47$; $6h=0.75$	2 ± 1
$^{1,3}F$(Li)	$2p=1.5$; $3p=1.5$; $4p=1.5$ $3d=1.32$; $4d=1.78$; $5g=2.1$	$3d=0.64$; $4f=0.52$; $5f=0.52$; $4f=1.41$; $6f=1.22$ $5g=0.89$; $6h=1.45$	3 ± 1

carded it because, they argued, this would imply for $^4F^o(1)$ a lower excitation energy than for $^4D(2)$. Indeed this is the case, as it may be seen from Fig. 2. The anomalous position of $^4F^o(1)$ is caused by its $1s2s4f+1s2p3d$ nature, see Eq. (8). The $^4F^o(2)$ state is $1s2s4f$-$1s2p3d$. As one moves to B III** and higher isoelectronic series members, $^4F^o(1)$ becomes $1s2p3d$ while $^4F^o(2)$ and $^4F^o(3)$ are represented by various degrees of admixture between $1s2s4f$ and $1s2p3d$. From Table V we see that the $^4F(1)\rightarrow{}^4F^o(2)$ transition at $\lambda=4172$ Å is too weak to be observed.

Core-excited quintet states of negative lithium[11] have recently been identified in beam-foil spectra.[24-26] The role of the corresponding isoelectronic quintets is beginning to be considered.[26-29] Brooks *et al.*[26] have identified the $1s2p^3\,^5S\rightarrow1s2s2p^2\,^5P$ from Be I through F VI. In Be I they assign this transition to the rather intense $\lambda=1909$ Å line. Andersen[27] has also suggested this classification, and rough preliminary calculations[28] yield $\lambda=1915\pm20$ Å confirming the assignment. (We also get[28] the less intense $1s2s2p3s\,^5P^o\rightarrow1s2s2p^2\,^5P$ transition at about the same wavelength.) Other transitions between Be I quintets are now being investigated[28] in the hope of further clarifying the Be II** spectrum.

IV. He AND Li$^+$ $2p4f\,^{1,3}F$ STATES

In Table VI we give the STO parameters and corresponding STO truncation errors. The inner-shell STO parameters for Li$^+$ are approximately 1.5 times the ones for He, while the outer-shell orbital exponents are twice as large. This behavior is expected from a coulomb model for each electron. The strict application of this model, e.g., the use of Li$^+$ basis functions obtained according to a hydrogenic criteria, yields an energy only 4 μhartree above the one obtained with optimized basis sets. Thus one can extend these calculations along the isoelectronic series in a straightforward way. In Table VII we deduce absolute term values by combing the available experimental data with the present results. Also in Table VII, we compare our results with recent theoretical calculations.[30]

A. He

The most complete compilation[31] of energy levels of neutral He does not include core-excited F states. Transitions between $2p4f\,F$ and $2pnd\,D$ states are in the infrared and they have not been studied experimentally. Transitions between core-excited and singly-excited states have been observed[32] in the far uv between 286 and 345 Å. We find that He $2p4f\,^{1,3}F$ decays to $1s4f\,^{1,3}F$ with $\lambda=303.932$ Å and $\tau=0.10$ nsec, assuming negligible autoionization of the upper level. Thus, in the beam-foil spectra, this line is irremediably blended with the resonance $2p\rightarrow1s$ transition in He$^+$ at 303.8 Å. A similar fate probably awaits transitions from higher excited $2pnf$, $2png$, etc., He levels,

TABLE VII. Nonrelativistic energies E_{nr} for the $2p4f\,^{1,3}F$ states of He and Li$^+$ in a.u. (atom), and estimates of their absolute term values T, in cm^{-1}. 1 a.u.(^{4}He) = 219 444.53 cm^{-1}; 1 a.u.(^{7}Li) = 219 457.48 cm^{-1}.

	He $2p4f\,^1F$	He $2p4f\,^3F$	Li$^+$ $2p4f\,^1F$	Li$^+$ $2p4f\,^3F$
E_u	−0.531 992	−0.531 988	−1.252 513	−1.252 442
ΔE_{CI}	0	0	0	0
ΔE_{STO}	−0.000 002(1)	−0.000 002(1)	−0.000 003(1)	−0.000 003(1)
E_{nr}	−0.531 994(1)	−0.531 990(1)	−1.252 516(1)	−1.252 445(1)
	(−0.531 972)[a]	(−0.531 968)[a]	(−1.252 331)[a]	(−1.252 258)[a]
$E_{nr}(2p_{1/2})$	−0.5	−0.5	−1.125	−1.125
$T(2p_{1/2})$	527 493[b]	527 493[b]	1 394 318[b]	1 394 318[b]
ΔE_{rrmp}	0	0	0	0
ΔE_{nr}, in cm^{-1}	7 020.9	7 020.0	27 984.3	27 968.8
T	520 472	520 473	1 366 333.7	1 366 349.2

[a] Reference 30.

[b] References 3 and 6; average of the multiplet.

thus explaining their absence in the beam-foil spectra.

B. Li^+

In contrast with He, little is known abut the spectrum of doubly excited Li^+. A beam-foil study[33] in the 2000-11000 Å region detected the $2p^2\ {}^3P \rightarrow 2s2p\ {}^3P^o$ transition at 5510±5 Å. The decay of Li^+ $2p^2\ {}^3P$, $2p3p\ {}^3P$, and $2p3p\ {}^3D$ to $1snp\ {}^3P^o$ states has been observed in beam-foil spectra in the 20-2000 Å range.[34] Also, the $2p3d\ {}^3D^o \rightarrow 2p^2\ {}^3P$ transition has been observed [34] at 1036 Å. The transitions expected from Li^+ $2p4f\ {}^{1,3}F$ states are given in Table VIII. The transitions to the singly-excited $1s4f\ {}^{1,3}F$ levels occur at 135.098 and 135.095 Å, respectively, and they should be completely blended with the prominent $Ly\ \alpha$ line similarly as in He.

Our results in Table VII can be combined with the very accurate eigenvalues of Doyle *et al.*[35] for $2p3d\ {}^{1,3}D^o$ states, yielding $\lambda = 3825.4$ and 4352.2 Å for the $2p4f\ {}^{1,3}F \rightarrow 2p3d\ {}^{1,3}D^o$ transitons, respectively. Because the branching ratio for decay to the singly-excited states is about 250, these transitions should be relatively very weak but still within the possibilities of observation.

TABLE VIII. Calculated wavelengths, f values, and transition probabilities for the decay of Li^+ $2p4f\ {}^{1,3}F$ levels.

	Wavelength (in Å)	f	A_{ki} (in 10^8 sec^{-1})
$2p4f\ {}^1F \rightarrow 1s4f\ {}^1F^o$	135.098	0.138	510
$\rightarrow 2p3d\ {}^1D^o$	3825.4(0.1) [a]	0.85	2.1
$2p4f\ {}^3F \rightarrow 1s4f\ {}^3F^o$	135.095	0.138	510
$\rightarrow 2p3d\ {}^3D^o$	4352.2(0.1) [a]	0.85	2.1

[a] The position of the ${}^{1,3}D^o$ states is taken from Ref. 35.

V. CONCLUSIONS

We have calculated absolute term values for several core-excited quartets of Li and Be^+, assuming exact transferability of ΔE_{rrmp} corrections between two-electron cores of the general type

$$\Psi_{core}(1,2) = a\ 1s2s\ {}^3S + b\ 1s2p\ {}^3P. \tag{10}$$

The calculated transition energies agree with experiment to within the uncertainties in both the calculations and the experimental values. These uncertainties are between 2 and 5 cm^{-1}, e.g., between 5 and 12 percent of the value of ΔE_{rrmp} for the $1s2p\ {}^3P \rightarrow 1s2s\ {}^3S$ transition in Be^{++}. Such an accuracy is achieved whenever the outer electron is outside the electron shells of the core electrons.

We do not know at present how general this result could be. But it is quite encouraging on spectroscopic grounds: Transition energies between states where the outer electrons are clearly separated from the core should be accurately given by Eq. (3). The largest source of error in Eq. (3) is expected to be in the determination of ΔE_{nr}.

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