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Probabilities for transition processes crucial to Li lasers

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We present results of electron corrrelation calculations in the Briet-Pauli approximation for radiative allowed and forbidden transition probabilities of highly excited Li states, contained in recent schemes for short-wavelength lasers. This is the first quantitative prediction for the phenomenon of relativistic radiative autoionization (RRA). RA has already been singled out as a fundamental deexcitation mechanism which might lead to efficient lasing systems.

In recent Letters, Willison *et al.*[1,2] reported results of measurements on the Li $1s2p^2\,{}^2P$ state, which has been singled out as the lasing state in a recently proposed[3] x-ray laser scheme via the discrete transition Li $1s2p^2\,{}^2P \rightarrow 1s^22p\,{}^2P^o$.

As Harris has stated,[3] key to his proposal is the transition probability for the intercombination line Li $1s2s2p\,{}^4P^o \rightarrow 1s2p^2\,{}^2P$, via which the population of the ${}^2P$ state is achieved. The detection of this transition using an intense laser at 2952 Å was reported two years ago.[1]

The optimum design of this laser system depends on, among other things, the accurate knowledge of the radiative excitation and decay dynamics of the two states involved, the ${}^4P^o$ and ${}^2P$. Furthermore, such data are essential to feasibility studies for the construction of Li lasers using the phenomenon of radiative autoionization (RA).[4,5]

Finally, these two states and the one adjacent to the ${}^4P^o$ continuum form the basis of a recently proposed model of "photon-catalyzed autoionization."[6]

As regards the Li $1s2s2p\,{}^4P^o \rightarrow 1s2p^2\,{}^2P$ transition, the only *ab initio* value for its oscillator strength is the one published by Nussbaumer[7] immediately after Harris's proposal. Based on his results, a value of $f=2\times10^{-8}$ for the ${}^4P^o_{5/2} \rightarrow {}^2P_{3/2}$ transition was employed in the work reported in Ref. 1. These results were obtained using radial functions from adjustable Thomas-Fermi and hydrogenic potentials and a limited configuration-interaction calculation. Harris[3] originally used a reasonable extrapolation from the He intercombination line calculations of Drake and Dalgarno,[8] which yield an average $f=2.83\times10^{-8}$. Later on, Rothenberg and Harris[9] used a value of $f=2.5\times10^{-8}$ for the ${}^4P^o_{5/2} \rightarrow {}^2P_{3/2}$ transition, based again on Ref. 7.

Given the approximations involved in Nussbaumer's calculation and the fact that high accuracies of spectroscopic data are essential to the optimum operation of lasers, we have looked at this transition from a different computational point of view, aiming at increasing the reliability of the theory.

Important considerations can also be based on the radiative properties of the $1s2s2p\,{}^4P^o$ and $1s2p^2\,{}^2P$ states, apart from their connecting transition. It was recently pointed out[4,5] that all metastable atomic and molecular states embedded in the electronic continuum of opposite parity, of which the Li ${}^4P^o$ and ${}^2P$ states are samples, have, in many cases, a non-negligible probability of a one-photon two-electron spontaneous transition into the adjacent continuum.

TABLE I. Allowed transition probabilities, in 10^8 sec^{-1}, from the $1s2p^2\,{}^4P$ and ${}^2P$ states. We give only the geometric mean of length and velocity formulations of our correlated results. In spite of the new value for RA (due to electron correlation and the Hartree-Fock scattering function) there is still a small difference between the recent experimental value for the lifetime of ${}^2P$ (Ref. 23) and our theory.

Transition	Theory				Experiment
	This work	Ref. 24	Ref. 4	Ref. 25	Ref. 23
$1s2p^2\,{}^4P-1s2s2p\,{}^4P^o$	1.70	1.7			
$1s2p^2\,{}^2P-1s2s2p\,{}^2P^o$	0.93		1.2		
$1s2p^2\,{}^2P-1s^22p\,{}^2P^o$			198	197	
$1s2p^2\,{}^2P-1s^23p\,{}^2P^o$			13.7	13	
$1s2p^2\,{}^2P-1s^24P\,{}^2P^o$			3.9	4	
$1s2p^2\,{}^2P-1s^2(5p,6p,\ldots){}^2P^o$			4.8		
$\int_0 d\epsilon p$	12.4		22.4		
Lifetime of $1s2p^2\,{}^2P$ (sec)	0.43×10^{-10}		0.41×10^{-10}		$(0.49\pm0.05)\times10^{-10}$

In the case of Li $1s2p^{2}\,{}^{2}P$, this mechanism of radiative autoionization[4] was later verified by the Stanford group.[2]

The existence of RA as a natural phenomenon and the recent demonstration[5,10] that, in certain negative-ion spectra, conditions for RA and relativistic RA (RRA) are optimum has led one of us (C.A.N) to a proposal of constructing efficient lasers, which can be summarized as follows: *Excitation to radiatively autoionizing quantized states provides a natural scheme for population inversion and conditions of lasing from the optical to the x-ray regions.*[5] (This realization should be contrasted to the intrinsic difficulties of the thus far widely researched free electron laser.[11])

The previous statement applies to both ${}^{4}P^{o}$ and ${}^{2}P$ states. For the Li $1s2P^{2}\,{}^{2}P$ state, automatic population inversion exists with respect to the $\text{Li}^{+}\,1s^{2}\epsilon p\,{}^{2}P^{o}$ continuum and, should one wish to enhance it, a laser tuned to the Li $1s^{2}2s\,{}^{2}S-1s^{2}2p\,{}^{2}P^{o}$ line could be applied (see footnote in Ref. 5). Similarly, automatic population inversion exists between a populated Li $1s2s2p\,{}^{4}P^{o}$ level and the $1s^{2}\epsilon s\,{}^{2}S$ and $1s^{2}\epsilon d\,{}^{2}D$ continua, into which it can decay via RRA (see below).

In this Communication we present results of many-electron calculations on the cross sections of the processes discussed above. For RRA, these results constitute the first data for this unusual phenomenon whose magnitude has up to now been *terra incognita*. For RA, cross-section information has been published only for negative ions,[5,12,13] where the emission spectrum starts from zero and peaks very quickly. For neutrals, such as the Li ${}^{2}P$ state studied here, the shape of the cross section is different, starting from a maximum and quickly decaying.

The calculations of such transition probabilities constitute a challenging theoretical problem: They require the consistent consideration of *electron correlation, relativistic,* and *continuum* effects. Such a theory has been developed and programmed[14] within a configuration-interaction scheme with the Coulomb and Pauli Hamiltonians and Hartree-Fock bound and scattering orbitals and variationally optimized virtual bound orbitals. The relativistic algebra is based on the work of Beck.[15,16] In this short paper, we outline only the main theoretical points and present the results.

Theoretical analysis and results. In the nonrelativistic approximation, the Li $1s2s2p\,{}^{4}P^{o}$ and $1s2p^{2}\,{}^{2}P$ states are discrete and no transition is allowed between them. Inclusion of one- and two-electron relativistic perturbations into the Hamiltonian alters the discrete spectrum and makes it continuous. The new and more accurate representation of these states is now energy dependent. In terms of the main *LS*-coupled configurations, the *JM*-coupled, energy-dependent vectors are linear combinations of the type (e.g., for the $J=\frac{3}{2}$ even state)

$$E_{3/2}=a(E)|1s2p^{2}\,{}^{2}P_{3/2}\rangle+b(E)|1s2p^{2}\,{}^{2}D_{3/2}\rangle+d(E)|1s2p^{2}\,{}^{4}P_{3/2}\rangle+\int c_{E}(\epsilon)|1s^{2}\epsilon d\,{}^{2}D_{3/2}\rangle\,d\epsilon\ . \quad (1)$$

Similar expressions characterize the $E^{0}_{5/2}$, $E^{0}_{3/2}$, $E^{0}_{1/2}$, and $E_{1/2}$ states.

The relativistic representation allows the recognition of a variety of possible one-photon, electric dipole induced radiative continuum processes in the Li spectrum, which include (a) the ordinary, allowed emission "lines" (the ${}^{2}P^{o}$ is Coulomb autoionizing) ${}^{2}P$-${}^{2}P^{o}$ and ${}^{4}P$-${}^{4}P^{o}$; (b) the intercombination lines ${}^{4}P^{o}-1s2p^{2}\,{}^{2}P$, $1s^{2}ns\,{}^{2}S$, $1s^{2}nd\,{}^{2}D$; and (c) the RA (Ref. 4) and RRA (Refs. 5 and 10) processes: ${}^{2}P\rightarrow 1s^{2}\epsilon p\,{}^{2}P^{o}$, ${}^{4}P^{o}\rightarrow 1s^{2}\epsilon s\,{}^{2}S$, $1s^{2}\epsilon d\,{}^{2}D$. The RA decay of

TABLE II. Fine-structure and total transition probabilities, in sec^{-1}, for the intercombination line used in the laser system of Refs. 1-3.

Fine-structure lines	This work HF	This work HF plus correlation	Ref. 7
$1s2p^{2}\,{}^{2}P_{1/2}-1s2s2p\,{}^{4}P^{o}_{1/2}$	27.09	15.78	18.2
$1s2p^{2}\,{}^{2}P_{1/2}-1s2s2p\,{}^{4}P^{o}_{3/2}$	0.14	0.54	0.09
$1s2p^{2}\,{}^{2}P_{3/2}-1s2s2p\,{}^{4}P^{o}_{1/2}$	15.43	10.00	9.9
$1s2p^{2}\,{}^{2}P_{3/2}-1s2s2p\,{}^{4}P^{o}_{3/2}$	2.03	1.39	1.5
$1s2p^{2}\,{}^{2}P_{3/2}-1s2s2p\,{}^{4}P^{o}_{5/2}$	36.08	24.53	25.5
Multiplet			
	44.77	29.38	30.0

TABLE III. Fine-structure transition probabilities (in sec^{-1}) for the intercombination Rydberg lines $1s2s2p\,{}^{4}P^{o}-1s^{2}ns\,{}^{2}S$. The results for only the lowest state and the sum over all states are presented.

Transition	HF	HF plus correlation
${}^{4}P^{o}_{1/2}-2s\,{}^{2}S_{1/2}$	66	1102
${}^{4}P^{o}_{3/2}-2s\,{}^{2}S_{1/2}$	84	1779
${}^{4}P^{o}_{1/2}-(2s,3s,\ldots)^{2}S_{1/2}$	95	1106
${}^{4}P^{o}_{3/2}-(2s,3s,\ldots)^{2}S_{1/2}$	122	1803
Multiplet		
${}^{4}P^{o}-(2s,3s,\ldots)^{2}S$	56	785

TABLE IV. Fine-structure transition probabilities (in sec^{-1}) for the intercombination Rydberg lines $1s2s2p\,{}^{4}P^{o}-1s^{2}nd\,{}^{2}D$. The results for only the lowest state of the sum over all states are presented.

Transition	HF	HF plus correlation
${}^{4}P^{o}_{1/2}-3d\,{}^{2}D_{3/2}$	71	45
${}^{4}P^{o}_{3/2}-3d\,{}^{2}D_{3/2}$	9	3
${}^{4}P^{o}_{3/2}-3d\,{}^{2}D_{5/2}$	82	23
${}^{4}P^{o}_{1/2}-(3d,4d,\ldots)^{2}D_{3/2}$	119	73
${}^{4}P^{o}_{3/2}-(3d,4d,\ldots)^{2}D_{3/2}$	15	4
${}^{4}P^{o}_{3/2}-(3d,4d,\ldots)^{2}D_{5/2}$	137	36
Multiplet		
${}^{4}P^{o}-(3d,4d,\ldots)^{2}D$	71	26

TABLE V. Fine-structure and total relativistic radiative autoionization (RRA) transition probabilities, in $\sec^{-1}$. Being strongly Z dependent, RRA for such metastable states increases rapidly along isoelectronic sequences.

Fine-structure RA	HF	HF plus correlation
$1s2s2p\ ^4P^o_{1/2}-1s^2\epsilon d\ ^2D_{3/2}$	85.7	32.5
$1s2s2p\ ^4P^o_{3/2}-1s^2\epsilon d\ ^2D_{3/2}$	12.9	1.8
$1s2s2p\ ^4P^o_{5/2}-1s^2\epsilon d\ ^2D_{3/2}$	115.8	16.1
$1s2s2p\ ^4P^o_{1/2}-1s^2\epsilon s\ ^2S_{1/2}$	15.3	1.6
$1s2s2p\ ^4P^o_{3/2}-1s^2\epsilon s\ ^2S_{1/2}$	23.0	11.0
Total relativistic RA		
$^4P^o$-^2D	57.2	11.4
$^4P^o$-^2S	10.2	3.9
$^4P^o$-$(^2D+{}^2S)$	67.4	15.3

the $1s2p^2\,{}^4P$ state to the $(1s2s)^3S\epsilon p$ continuum is estimated to be very small compared to the discrete transition of case (a).

The radiationless transitions from the states with main configurations $1s2s2p$ and $1s2p^2$ have also been studied.[17]

Space does not permit a detailed presentation of our theoretical approach here. The basic notations and computational steps (we now deal with the Pauli Hamiltonian) can be found in previously published papers.[5,15–22]

In Table I, the important new result is that which shows that electron correlation and the Hartree-Fock scattering orbital have reduced the previous RA result by a factor of 2. However, the effect on the lifetime is small and so some discrepancy with the new, revised measurement[23] remains. Note that the $^2P-1s2s2p\ ^2P^o$ transition probability is only a small fraction of the total RA. The agreement of our results with those of Bunge[24,25] is excellent. The ^2P state can autoionize relativistically. Relativistic multiconfigurational Hartree-Fock calculations with $1s2p^2$, $1s2s^2$, $1s2s3d$, $1s^23d$, $1s^22s$ configurations yield a rate of the order of 10^6 $\sec^{-1}$.

In Table II we collect our results for the intercombination line $^4P^o$-^2P both from a Hartree-Fock (HF) as well as from a HF plus electron correlation calculation. For certain fine-structure lines, the agreement between our values and those of Nussbaumer is good. For others (e.g., $^2P_{1/2}$-$^3P^o_{5/2}$) a large discrepancy exists. Our f value for the crucial (for the Li laser) $^4P^o_{5/2}$-$^2P_{3/2}$ transition is 2.07×10^{-8}.

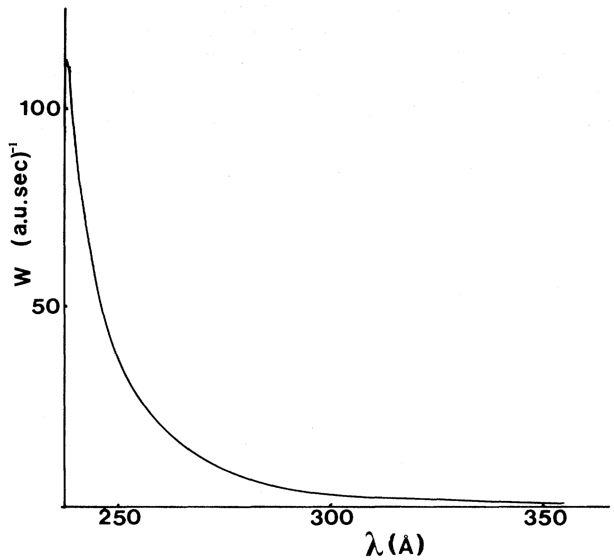

FIG. 1. Distribution of the spontaneous RRA probability for the Li $1s2s2p\ ^4P^o$ into the $\epsilon d\ ^2D$ and $\epsilon s\ ^2S$ channels, as a function of emitted photon wavelength.

In Tables III and IV, we collect the predictions of our calculations for the discrete fine-structure transition probabilities of the $1s2s2p\ ^4P^o-1s^2ns\ ^2S$ and $1s^2nd\ ^2D$ lines. In Table V, the RRA results are presented. In these calculations we first took into account the localized correlation[20,21] using the Pauli Hamiltonian and then we computed the photoemission transition probability, in the length formulation, using the HF approximation for the continuum state.

The total RRA rate, 15.3 $\sec^{-1}$, is much smaller than the relativistic autoionization rate of the Li $1s2s2p\ ^4P^o$ state, which is of the order of 10^7 for the $\frac{1}{2}$ state and 10^5 for the $\frac{5}{2}$ state.[26] The discrete $^4P^o$-^2S, ^2D transition probabilities are larger than the RRA (as is the case for the nonrelativistic transitions—Table I) but still smaller than the autoionization rates. Nevertheless, the metastability of the $^4P^o$ state and the relative ease with which it can be populated with current techniques allow optimism for the possibility of creating effective population inversions for laser activity.

Finally, in Fig. 1 we present the first result of the distribution of the RRA rate as a function of emitted photon energies. The same shape is obtained for the RA cross section of the $1s2p^2\,{}^2P$ state.

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