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Effect of interchannel coupling on the partial and total autoionization widths: Application to the $1s3s3p\ ^4P^o$ and $1s3p^2\ ^4P$ states for $Z=2-5$, 10

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We have computed the partial and total widths with interchannel coupling for the $1s3s3p\ ^4P^o$ and $1s3p^2\,^4P$ states for $Z=2$–5 and 10, by solving the corresponding complex matrix equations constructed from square-integrable N-electron functions with numerical and analytic real and complex orbitals. The correlated wave functions are computed by the state-specific method. Oscillator strengths for one- and two-electron transitions from the metastable $1s2s2p\ ^4P^o$ state suggest that the states are reachable in He and in Li directly $(1s3p^2\,^4P)$, or via the $1s2p^2\,^4P$ state $(1s3s3p\ ^4P^o)$. The effect of interchannel coupling on the partial widths in the case of the $^4P^o$ state is considerable. On the contrary, interchannel coupling has no significant effect on the total widths. This computational result is discussed formally.

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I. INTRODUCTION

Autoionizing states decay, in general, into many continua and the resulting partial decay widths γ_i are experimentally observable since the exit channels are distinguishable by energy and symmetry considerations. For such a situation, the total width Γ of the decaying state is the sum of the partial widths:

$$\Gamma=\sum_i \gamma_i \ . \tag{1}$$

These partial widths carry information about the details of interelectronic interactions in the initial as well as in the final states, and their knowledge allows valuable understanding of the quantitative characteristics of highly excited states and of the dynamics involving the multichannel continuum.

A recent publication [1] has dealt with the problem of computing the energies and widths of the $1s3s3p\ ^4P^o$ and $1s3p^2\,^4P$ autoionizing states for the isoelectronic sequence $Z=2$–6. The method used was called the "saddle-point complex rotation," a method whose basic features and background were discussed in a recent debate [2,3].

Our attention to this work was drawn by the fact that Davis and Chung [1] claimed to have predicted the width of the $1s3s3p\ ^4P^o$ state by adding the partial widths

$$1s3s3p\ ^4P^o \rightarrow \begin{cases} 1s2s(^3S)\varepsilon p \\ 1s2p(^3P^o)\varepsilon s \ . \end{cases} \tag{2}$$

These partial widths were computed independently, without interchannel coupling (see their Table II and Sec. V). By employing large wave-function expansions, the authors put emphasis on the accuracy of their results. Yet, there are two serious limitations in their calculations, of a fundamental nature. First, if high accuracy is set as a goal, there is no *a priori* justification for neglecting interchannel coupling when computing partial widths, especially where the final core states are energetically close. Second, the interacting open channels contributing to the width are three in number and not just the two computed by Davis and Chung [see Eq. (2) above]. The third channel is the $1s2p(^3P^o)\varepsilon d\ ^4P^o$. Obviously, such an omission casts an additional doubt on the reliability of the predictions of Ref. [1] for the $^4P^o$ state. For the $1s3p^2\,^4P$ state, there is no fundamental problem since it decays to only one channel, the $1s2p(^3P^o)\varepsilon p$.

The present work has produced formal and numerical results which add to our understanding of interchannel coupling while correcting the aforementioned inadequacies of the published data on the partial and total widths of the $1s3s3p\ ^4P^o$ states. It has also produced the widths of the $1s3p^2\,^4P$ states (single-channel case), which agree well with those of Ref. [1]. In addition, we have calculated oscillator strengths and radiative transition probabilities in connection with the possible mechanisms of formation and of observation of these states as the degree of ionization increases.

Apart from the work of Davis and Chung [1], there have been a few additional theoretical investigations of these states by different methods, where the total energies and total widths have been computed. The first prediction of the position and the width ($\Gamma=0.05$ eV) of the He^- $1s3s3p\ ^4P^o$ resonance was made by Oberoi and Nesbet [4] from scattering calculations. Hazi and Reed [5] predicted the position of the He^- $1s3p^2\,^4P$ resonance. Finally, Bylicki [6] recently published results from large calculations of the energies of the He^- ^4P resonance and of the He^-, Li, and Be^+ $^4P^o$ resonances. In all cases, the results for the total energies, including our own, are in essential agreement, where the small discrepancies have no physical significance.

II. COMPUTATION OF PARTIAL WIDTHS WITH INTERCHANNEL COUPLING

The problems with calculating reliably partial widths of multichannel autoionizing states are related to the choice of formalism and its implementability for the computation of wave functions accounting for the important interelectronic interactions in the localized and the scattering parts. A formal and computational simplification is the independent channel approximation (ICA), where the width of each channel is computed separately. However, because of the limited experience with rigorous calculations of multichannel autoionization widths, the reliability of the ICA cannot be evaluated *a priori*, especially for states such as the $1s3s3p\ {}^4P^o$.

For many years, the available formalism allowing in principle the calculation of partial widths with interchannel coupling was of the scattering type (e.g., see the review by Åberg and Howat [7]). Only a few applications to the problem of multichannel decay of autoionizing states have been published, where the coupling has been computed to all orders [e.g., 8–10]. In fact, the formalism and methods of [8] allow the systematic computation of both electron correlation and multichannel interactions for any type of atomic state.

An alternative coupled-channel theory has been developed and implemented [2,11,12], which uses simple configuration-interaction (CI) notions and square-integrable functions. It is state specific, allowing the systematic incorporation of electron correlation with due respect to the electronic structure of the states involved, and is not limited in practice by the number of open channels. For example, it has been applied to the Ne^+ $1s2s^22p^6\,{}^2S$ nine-electron Auger state [11] and to the He^- $1s(nl)^2\,{}^2S$ two-electron ionization ladder states [12]. It is this approach which we have implemented in this work. Its basic features and computational steps are the following.

We aim at the nonperturbative solution of the complex eigenvalue Schrödinger equation (CESE):

$$(H-z_0)\Psi=0\ , \tag{3}$$

where

$$z_0=E_0+\sum_i\left[\delta_i-\frac{i}{2}\gamma_i\right]\equiv E_0+\Delta-\frac{i}{2}\Gamma\ , \tag{4}$$

$$\Psi=\alpha\Psi_0+\sum_i b_i X_{as}^i\ , \tag{5}$$

$$X_{as}^i=\sum_i\left[\Psi_{\mathrm{core}}^i\otimes g^i\right]\ , \tag{6}$$

$$g^i=\sum_n c_n\varphi_n(\rho^*)\ ,\quad \rho^*=re^{-i\theta} \tag{7}$$

$$\varphi_n=\text{complex Slater orbitals}$$

$$\text{with a nonlinear parameter }\beta\ , \tag{8}$$

$$\delta_i-\frac{i}{2}\gamma_i=\frac{b_i}{\alpha}\langle\Psi_0|H|X_{as}^i\rangle\ , \tag{9}$$

$$E_0=\langle\Psi_0|H|\Psi_0\rangle\ , \tag{10}$$

$$\Psi_0=\Phi_{\mathrm{MCHF}}+X_{\mathrm{loc}}\ . \tag{11}$$

Φ_{MCHF} is the state-specific numerical multiconfigurational Hartree-Fock solution. We chose the simplest expansions: For the ${}^4P^o$ state the $1s(3s3p+3p3d)$ configurations and for the ${}^4P$ state the $1s(3p^2+3d^2)$ configurations. X_{loc} represents the remaining localized correlation, obtained variationally by minimizing E_0 of Eq. (10), where the optimized analytic virtual orbitals in the singly and doubly excited configurations are kept orthogonal to core orbitals and to the MCHF orbitals. The number of symmetry-adapted correlation configurations were 26 for the ${}^4P^o$ state (9 virtual orbitals) and 30 for the ${}^4P$ state (12 virtual orbitals). As regards the Gamow orbitals g^i, [Eq. (7)], they were expanded in terms of ten complex Slater functions per symmetry.

The quantities δ_i (partial energy shift to all orders) and γ_i (partial width to all orders) are obtained from Eq. (9) after the diagonalization of H in the total function space defined by Ψ of Eq. (5). For problems requiring the diagonalization of many bound wave functions Ψ_0^n with many continua X_{as}^i (e.g., see [13]), the total complex Hamiltonian matrix has the general form

$$\underset{\sim}{H}(\theta)=\begin{bmatrix} H_{QQ} & H_{QP}(\theta) \\ H_{PQ}(\theta) & H_{PP}(\theta)\end{bmatrix}\ , \tag{12}$$

where Q and P represent the function spaces of Ψ_0^n and X_{as}^i, respectively. The nonorthonormality among the orbitals representing function spaces which are optimized separately is computed explicitly. The diagonalization produces the coefficients α and b_i of Eq. (5) and a stabilized complex eigenvalue z_0 $(\beta_{\mathrm{opt}},\theta_{\mathrm{opt}})$ for the solution $\tilde{\Psi}$, satisfying

$$\langle\tilde{\Psi},\Psi_0\rangle=(\text{maximum})\ , \tag{13}$$

where Ψ_0 is the correlated wave function of the localized part of the state of interest.

III. RESULTS

Our results for the partial and total widths are shown in Table I, together with those of Davis and Chung [1]. For the $1s3p^2\,{}^4P$ single-channel case, the agreement between the two calculations, which employed the same method [2] but different wave functions, is very good. For the $1s3s3p\ {}^4P^o$ three-channel case, the intrinsic inaccuracies of the previous work have been corrected. The present theory has produced partial widths with interchannel coupling (WIC). The effect of the coupling is significant. For example, in Li it reduces the partial width of the $1s2s\varepsilon p$ channel by a factor of 6 and in Be^+ by a factor of 9. It is noteworthy that the WIC partial width of the $1s2p\varepsilon d$ channel is larger than that of the $1s2s\varepsilon p$ channel in He^-, in B^{2+}, and in Ne^{+7}. In all cases, the $1s2p\varepsilon s$ channel is dominant. The effect of coupling on the total width is very small. This result is discussed formally in Sec. IV.

We now comment on the possibility of creating and observing these states. In general, high-spin multiply excited states can be created in ion-atom or ion-foil collisions and this is expected to hold in the present case as well. Electron scattering from the $n=2$ channels is another mechanism. In addition, if one considers the metastable $1s2s2p\ {}^4P^o$ state, the following single or multiphoton ab-

TABLE I. Theoretical results from Ref. [1] and from this work for the partial autoionization widths and their sum of the $1s3s3p\,^4P^o$ and $1s3p^2\,^4P$ states (in meV). ICA, independent channel approximation; WIC, with interchannel coupling to all orders. The ^4P state has only one open channel. For the $^4P^o$ state, the independent width for the $1s2p\varepsilon d$ channel was not discussed and was not computed in Ref. [1]. Interchannel coupling changed the partial widths considerably, while their sum remains essentially the same. The decay of the $^4P^o$ state is dominated by the $1s2p\varepsilon s$ channel, whose probability increases slowly as a function of Z.

(a) $1s3s3p\,^4P^o$

	Channel	ICA		WIC
		Ref. [1]	This work	This work
He^-	$1s2s\varepsilon p$	7	9	2
	$1s2p\varepsilon s$	35	46	47
	$1s2p\varepsilon d$		12	14
	Total	42	67	63
Li	$1s2s\varepsilon p$	27	29	5
	$1s2p\varepsilon s$	40	45	66
	$1s2p\varepsilon d$		2	3
	Total	67	76	74
Be^+	$1s2s\varepsilon p$	34	36	4
	$1s2p\varepsilon s$	41	43	73
	$1s2p\varepsilon d$		3	3
	Total	75	82	80
Be^{2+}	$1s2s\varepsilon p$	36	39	2
	$1s2p\varepsilon s$	42	43	77
	$1s2p\varepsilon d$		4	4
	Total	78	86	83
Ne^{7+}	$1s2s\varepsilon p$		42	1
	$1s2p\varepsilon s$		45	84
	$1s2p\varepsilon d$		7	7
	Total		94	92

(b) $1s3p^2\,^4P$

	Ref. [1]	This work
He^-	33	35
Li	125	104
Be^+	146	133
B^{2+}	155	146
Ne^{7+}		166

sorption processes are possible:

$$1s2s2p\,^4P^o \rightarrow 1s2p^2\,^4P \rightarrow 1s3s3p\,^4P^o \quad (14a)$$

$$\rightarrow 1s3p^2\,^4P\ . \quad (14b)$$

Energy differences for these processes can be obtained from Ref. [1] and references therein. In order to acquire knowledge about the probabilities of these transitions by one-photon absorption, we computed the corresponding oscillator strengths and spontaneous emission probabilities using state-specific correlated wave functions. They are presented in Table II. Considering the energy

TABLE II. Oscillator strengths for the transitions of processes 14 and for the determination of the radiative lifetime of $1s3p^2\,^4P$ in B^{2+} and Ne^{7+}.

Transition	He^-	Li	B^{2+}	Ne^{7+}
$1s2s2p\,^4P^o - 1s2p^2\,^4P$	0.484	0.356		
$1s2p^2\,^4P - 1s3s3p\,^4P^o$	0.040	0.0045	Very small	Very small
$1s2s2p\,^4P^o - 1s3p^2\,^4P$	0.0072	0.0038	0.0013	2.9×10^{-4}
$1s2s3p\,^4P^o - 1s3p^2\,^4P$			0.177	0.240

differences and the f values for the two-electron transitions, only He^- and Li offer realistic possibilities for reaching these states. As Z increases, orthogonality between the Hartree-Fock orbitals of the two states becomes almost exact, and thus the two-electron transitions occur only because of electron correlation [14]. We note that in He^-, the $1s2p^2\,{}^4P$ state is an observable shape resonance just above the He $1s2p\,{}^3P^o$ threshold [5,15]. We also note that the Li spectrum offers a nice opportunity for the multiphoton population and study of the ${}^4P^o$ state. There, four photons of about 3.34 eV are needed to reach the $1s3s3p\,{}^4P^o$ state, where the first step is exactly on resonance with the $1s2p^2\,{}^4P$ state, while the second reaches the dense Rydberg continuum (Fig. 1).

Finally, as regards observation of these autoionizing states, it is important to know the radiative lifetime as a function of Z. Take, for example, the $1s3p^2\,{}^4P$ state. It can decay radiatively to a number of lower bound and scattering states. We chose two, the $1s2s2p\,{}^4P^o$ and the $1s2s3p\,{}^4P^o$ as the most probable. Our calculations for B^{2+} and Ne^{7+} give (Tables I and II),

$$\tau(\mathrm{rad})=1.2\times10^{-10}\ \mathrm{s}$$

and

$$\tau(\mathrm{aut})=4.5\times10^{-15}\ \mathrm{s}$$

for B^{2+} and

$$\tau(\mathrm{rad})=3.7\times10^{-12}\ \mathrm{s}$$

and

$$\tau(\mathrm{aut})=4.0\times10^{-15}\ \mathrm{s}$$

for Ne^{7+}. Hence, these states decay overwhelmingly by electron emission. This conclusion verifies that of Davis and Chung [1] who assumed $f=1$ to estimate lower bounds for the radiative lifetimes of the $1s3p^2\,{}^4P$ and $1s3s3p\,{}^4P^o$ states.

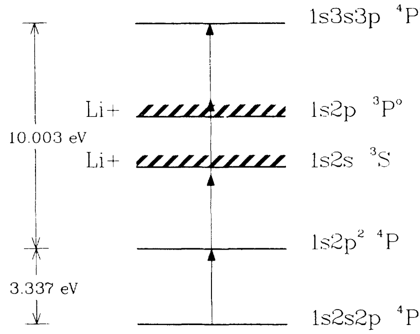

FIG. 1. A four-photon transition for the population of the Li $1s3s3p\,{}^4P^o$ doubly excited autoionizing state.

IV. THE TOTAL AUTOIONIZATION WIDTH WITHOUT AND WITH INTERCHANNEL COUPLING

From the numerical results it is seen that the effect of interchannel coupling on the total width is very small, even though it is considerable for the partial widths. It is interesting to see under what formal conditions this situation occurs in general.

Consider the case of an isolated resonance Ψ_0 decaying into two interacting channels Φ_1 and Φ_2. The present formalism allows the treatment of this problem in terms of the coupled equations with complex coefficients, c_0, c_1, c_2:

$$(E_0-z)c_0+H_0c_1+H_{02}c_2=0\ , \tag{15a}$$

$$H_{10}c_0+(H_{11}-z)c_1+H_{12}c_2=0\ , \tag{15b}$$

$$H_{20}c_0+H_{21}c_1+(H_{22}-z)c_2=0\ . \tag{15c}$$

By elimination, we obtain the complex self-energy $A(z)$ as a sum of partial self-energies to all orders:

$$A(z)=c_0^{-1}H_{01}c_1+c_0^{-1}H_{02}c_2 \tag{16}$$

$$\begin{aligned}&=H_{01}\{1-(H_{11}-z)^{-1}H_{12}(H_{22}-z)^{-1}H_{21}\}^{-1}\{(H_{11}-z)^{-1}H_{12}(H_{22}-z)^{-1}H_{20}-(H_{11}-z)^{-1}H_{10}\}\\&\quad+H_{02}\{1-(H_{22}-z)^{-1}H_{21}(H_{11}-z)^{-1}H_{12}\}^{-1}\{(H_{22}-z)^{-1}H_{21}(H_{11}-z)^{-1}H_{10}-(H_{22}-z)^{-1}H_{20}\}\ ,\end{aligned} \tag{17}$$

where the matrices $(H_{ii}-z)$, $i=1,2$, are nonsingular and z is complex.

If we neglect interchannel coupling, $H_{12}=H_{21}=0$ and

$$A^{\mathrm{ICA}}(z')=-H_{01}(H_{11}-z')^{-1}H_{10}-H_{02}(H_{22}-z')^{-1}H_{20}\ . \tag{18}$$

Then, the partial self-energies are given by

$$a_i^{\mathrm{ICA}}(z')=-H_{0i}(H_{ii}-z')^{-1}H_{i0}\ . \tag{19}$$

When interchannel coupling is accounted for, a series expansion of the inverted matrices gives

$$\begin{aligned}A(z)=&-H_{01}(H_{11}-z)^{-1}H_{10}-H_{02}(H_{22}-z)^{-1}H_{20}+2H_{01}(H_{11}-z)^{-1}H_{12}(H_{22}-z)^{-1}H_{20}\\&-H_{01}(H_{11}-z)^{-1}H_{12}(H_{22}-z)^{-1}H_{21}(H_{11}-z)^{-1}H_{10}\\&-H_{02}(H_{22}-z)^{-1}H_{21}(H_{11}-z)^{-1}H_{12}(H_{22}-z)^{-1}H_{20}+\cdots\ .\end{aligned} \tag{20}$$

Thus, if one assumes that $z'=z$, (both being very close to E_0), the first two terms are equal to $A^{\mathrm{ICA}}(z')$ of Eq. 18. Therefore, although the partial widths corresponding to Eqs. 16 and 19 may be different, the total widths may not change very much if the sum of the higher order terms of Eq. 20 happens to be very small. Obviously, this situation cannot be foreseen in the general case.

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