Autoionization of Triply Excited Rydberg Series

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The Auger rates of triply excited Rydberg series are shown to behave rather differently from doubly excited series. It is shown that in hollow atoms the Auger decay rates for Rydberg series of the type $2l2l'nl''$ with $n \geq 2$ are expected to be nearly independent of n, while for doubly excited series of the type $2lnl'$ the decay rate in general decreases with increasing n. In addition the ratio between the rates for $2l2l'nl''$ Rydberg series with different l'' values will be fixed and often the ratio will be equal to one.

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The study of Auger spectra of multiply excited atoms and ions has been a very active area of research during the last 20 to 30 years. This observation applies particularly to doubly excited states while more systematic studies of triply excited states is of fairly recent origin [1–5]. Studies of nonradiative decays of triply excited states are still often limited to the lowest states, although recently the first observation of the Rydberg series associated with such states has been reported [6]. Most calculations have also been limited to the lowest states although this situation is beginning to change too [7,8]. In this Letter, we point out that the decay properties of such states can be expected to be different from the familiar behavior of doubly excited series. This is important, for example, in trying to untangle the competition between radiative and nonradiative decay for such states [9,10].

We begin with a short review of the theory of Auger decay of doubly excited states in two-electron systems. Auger decay usually means filling a single vacancy in the core. Here we consider systems without a core and we use the term Auger decay to mean the filling of one of the (possibly many) inner vacancies. We will restrict ourselves to decay via the Coulomb interaction since this is the important decay mechanism in light systems. The following will also apply to doubly excited states outside closed shells in many-electron systems. Consider the doubly excited $2lnl'$ Rydberg series in He which lie between the $n = 1$ and $n = 2$ limits. These states can decay only to the $1s$ limit in He II with the emission of a continuum electron with energy ϵ and angular momentum ℓ where the latter is determined by parity and angular momentum coupling selection rules. The decay rate depends on a Coulomb factor $I(2lnl', 1s\epsilon\ell)$ where I stands for both direct and exchange integrals and usually comprises several R^k integrals. In addition I contains an angular factor (in practice one angular factor associated with each R^k integral) determined by the coupling conditions in the Rydberg series, but if the Rydberg series is unperturbed this factor is the same for all n values and the radial integrals in I determine the decay rate as a function of n. Since the overlap between $2l$ and nl' will decrease with increasing n we expect that the decay rates will decrease with n (roughly as n^{-3} [11]). In practice this behavior can fairly easily be obscured, for example, if Rydberg series perturb each other. Nevertheless, the gradual decrease in the Auger decay rate with increasing n is a well-known property of the doubly excited Rydberg series [12]. Note that possible nonorthogonalities between initial and final state orbitals automatically are taken into account for these states in the calculation of the I factor.

Nonorthogonalities are not automatically included when we consider triply excited states and since orthogonality simplifies the analysis we will initially assume that initial and final state orbitals are orthogonal. In practice, as we will see, this will often be a rather bad approximation. Surprisingly, the assumption does not, it turns out, seriously invalidate the analysis presented below, at least not for $2l2l'nl''$ series.

Consider a Rydberg series of the type $2s2p\,^3P\,nl\,^4L$ in a three-electron system such as Li I. This series can be considered to be built on the $2s2p\,^3P$ term in Li II, and it lies above the ionization limit of Li II. This means that there are an infinity of limits of the form $1sn'l'\,^3L$ available for the Auger decay. However, the main conclusions of this Letter rely on that most of the limits are inaccessible in the approximation we have chosen. This follows from the explicit expression for the decay rate which has three parts of which

$$I(2s2p, 1s\epsilon\ell)\,\langle nl|n'l'\rangle \tag{1}$$

usually will be the largest and the essential point is that Eq. (1) is zero unless $n = n'$ and $l = l'$. Therefore in the orthogonal approximation, the Rydberg electron is a spectator electron and the decay rate is approximately the same for all values of n, being determined by the same $I(2s2p, 1s\epsilon\ell)$ factor since ϵ is roughly independent of n. The two other contributions are decays in which one of the $2l$ electrons is the spectator and the only limits that can be reached in these decays are therefore $1s2s\,^3S$ and $1s2p\,^3P$. The I factors associated with these two decay routes, for example $I(2pnl, 1s\epsilon\ell)$ and $I(2snl, 1s\epsilon\ell)$ for the decay of $2s2pnl$, *do* contain the Rydberg electron. Therefore these two contributions can be expected to be smaller than Eq. (1) when $n > 2$. We note that one of these two

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is the only contribution present for the more well-known (doubly excited) $1s2lnl'\,^4L$ series, consistent with the analysis of the difference between doubly and triply excited series. Thus if $n > 2$, we assume in the following that the decay rate is determined primarily by Eq. (1). One practical consequence of this result is that, if the total decay rate of the lowest member of a Rydberg series has been determined, this value can serve as a first estimate for the decay rates of the higher members.

A related so-called spectator model is well known for the decay of innershell resonances [13,14] which have similarities to the triply excited states we are considering here. It has been found that the spectator model is in good accord with the observations unless the Rydberg electron interacts noticeably with the inner electrons [15] and the same can be expected here.

Thus while it usually is possible in an Auger decay to reach several final bound states of either parity, in this case only *one* $1snl$ final state is possible in which both n and l are fixed (in addition to $1s2s$ and $1s2p$). That only one state is available is linked to the fact that only one state, $1s$, is available for the decay of $2l2l'$. Generalizing this result we see, for example, that for the $3l3l'nl''$ Rydberg series more limits will be available, the number being determined by the number of final state limits ($1s$, $2s$, and $2p$) that can be reached from the doubly excited $3l3l'$ state plus the final states which become available when one of the $3l$ electrons is the spectator.

Another consequence of Eq. (1) can be exemplified by considering the $2s2p(^3P)ns\,^4P^o$ and $2s2p(^3P)nd\,^4P^o$ series assuming, as above, that the nl electron is the spectator. Since the radial part of the I factor is the same for these two decays, a possible difference in decay rate must be due to the angular factor involved. Computation shows that the angular factor is the same for the two series so that we predict that the decay rate should be independent of l in this case. We note that the same angular (and radial) factors are involved in the decay of the $2s2pnd\,^4D^o$ and $^4F^o$ series, for example.

These predictions are based on a number of approximations which cannot be expected to be fulfilled very often in real atoms. Nevertheless, we have found that at least for $2l2l'nl''$ series some of the predictions can be expected to be independent of the approximations and some examples have, in fact, recently been established of Rydberg series in Li I which do show fairly constant Auger rates. The results, which will be described in more detail elsewhere [16], are obtained using a B-spline-based configuration interaction (CI) approach [17–19]. The calculations are nonrelativistic, which is a good approximation for excited states in Li. We emphasize that these calculations include a very considerable amount of correlation. Therefore it is not *a priori* obvious that a single-particle analysis is at all relevant.

In Tables I and II we show decay rates for $2s2p\,^3P\,nl\,^4P^o$ series members where l can be s and d. There is considerable mixing between the two series but the total widths of both series are found to be nearly equal as well as roughly independent of n in agreement with Eq. (1). Purities as well as total widths are shown in Table I.

TABLE I. Total Auger decay rates (in meV) for the lowest members of the triply excited $2s2pnl\,^4P^o$ series in Li I ($l = s$ and d). Also the sum of the eigenvector components belonging to the $2s2pnl$ series giving name to the term is shown (in %) in the column "purity." The column headed BN refers to values published by Berrington and Nakazaki [8] obtained by including only $1snl$ limits with $n \leq 3$, see text.

		Decay rate	
$2s2p(^3P)nl\,^4P^o$	Purity	Present	BN
$nl = 3s$	93.3	9.95	8.6
$3d$	85.8	9.58	4.7
$4s$	87.0	9.62	1.0
$4d$	85.4	9.44	1.1
$5s$	86.2	9.44	0.4
$5d$	84.2	9.45	0.4
$6s$	84.8	9.44	0.3

Table I includes also total widths from the recent paper by Berrington and Nakazaki [8]. It is seen that there is agreement with our results only for the lowest, $3s$, term. The reason is that Berrington and Nakazaki included only $1snl$ limits up to $n = 3$ and thus missed the contribution from Eq. (1) except for $3s$. It could be expected that their result for $3d$ should be the same as ours too but we will see shortly why this is not the case.

In Table II we show decay rates to $1sns\,^3S$ and to $1snd\,^3D$ limits with $n \leq 6$. We omit the term labels in the following. The order of the entries in the tables is determined by the energy of the series members, i.e., the two series are intermixed. Also results for the decay to the $1s2p$ limit are included in Table II. This decay is due to one of the two contributions we are neglecting in Eq. (1), namely the contribution corresponding to the $2p$ electron being a spectator. The neglect is seen to be fully justified in this case. The decay to the $1s2s$ limit, in which $2s$ is a spectator, is seen to be somewhat more probable but still only about 10% of the contribution from Eq. (1) in the most favorable case, if we assume that the decay rate for $2s2p3s$ to $1s2s$ is due to this effect. The decay rate decreases quickly with n as expected (Table II). Thus the contribution to the total decay rate from this channel is much smaller than 10% for higher n states.

The results confirm that Eq. (1) provides the main contribution to the decay rate in this case, which means that the nl series should decay preferentially to the $1snl$ limits and Table II shows that this is followed quite well. With regard to decay to the $1sns$ limits, Table II shows that the decay rates for the nd series members are small except for the decay of $2s2p3d$, which is large to the $1s4s$ limit, while the $2s2p4d$ decay is large to the $1s5s$ limit. This can be explained by mixing between $2s2pnd$ and $2s2p(n+1)s$. In both cases the decay rate for the term called $2s2pnd$ is

TABLE II. Auger decay rates (in meV) for the lowest members of the triply excited $2s2pnl\,^4P^o$ series in Li I to the limits $1snl$ with $n \leq 6$ and $l = s$ and d as well as to the $1s2p$ limit in Li II. The notation a-b means $a \times 10^b$.

$2s2p(^3P)nl\,^4P^o$	Limit	Decay rate	Limit	Decay rate
$nl = 3s$	$1s2s\,^3S$	1.170	$1s2p\,^3P$	0.044
$3d$		0.002		0.015
$4s$		0.301		0.013
$4d$		2.9−4		0.008
$5s$		0.125		0.009
$5d$		1.3−4		0.004
$3s$	$1s3s\,^3S$	7.98	$1s3d\,^3D$	0.180
$3d$		0.074		4.64
$4s$		0.208		0.188
$4d$		0.031		1.01
$5s$		0.037		0.077
$5d$		0.016		0.358
$3s$	$1s4s\,^3S$	0.549	$1s4d\,^3D$	0.004
$3d$		0.902		3.76
$4s$		5.33		0.834
$4d$		0.021		0.675
$5s$		0.871		0.009
$5d$		0.002		0.477
$3s$	$1s5s\,^3S$	0.011	$1s5d\,^3D$	2.1−5
$3d$		0.098		0.086
$4s$		2.63		0.105
$4d$		0.768		5.73
$5s$		1.98		0.734
$5d$		0.156		0.098
$3s$	$1s6s\,^3S$	0.003	$1s6d\,^3D$	2.4−5
$3d$		6.6−5		1.7−5
$4s$		2.4−4		7.5−5
$4d$		0.363		0.836
$5s$		4.98		0.415
$5d$		0.352		4.55

smaller than for the $2s2p(n + 1)s$ partner. The opposite behavior is found for the decay of the $2s2pnd$ series to the $1snd$ limits. For the decay of the s series we expect according to Eq. (1) a maximum for the limit with an n value corresponding to the n value for the series member. It can be seen that this prediction is valid up to $n = 4$ while $2s2p5s$ has its largest decay rate to the $1s6s$ limit. Larger deviations are shown by the $2s2pnd$ series where the n value of the initial state even for $3d$ does not unambiguously define the main final state. The reason is another effect we have neglected so far namely the lack of orthogonality between the orbitals in the initial and final states.

It has been known for some time [15,20−23] that the existence of an inner hole can have profound influence on the orthogonality between initial and final state orbitals. This is easily understood when it is considered that the $2s'$ electron in the $1s2s'$ limit (we use a prime to distinguish final from initial state orbitals) sees the nuclear charge screened by the $1s$ electron while the $2s$ electron in the $2s2pnl$ states sees a basically unscreened nuclear charge. The screening depends on the particular case and for the cases shown in Table II the orthogonality between the initial $2s$ and the final $1s$ function is rather good. First for the initial $4s$ orbital is there a large mixing, while the initial $5s$ has the expansion 11:21:64:3 in terms of the final $4s'$:$5s'$:$6s'$:$7s'$ orbitals. The expansion coefficients correspond very closely to the decay rates. For example, $2s2p5s$ decays to the limits $4s'$:$5s'$:$6s'$:$7s'$ in the proportions 11:25:63:2 according to Table II.

For the d series the lack of orthogonality is already important for the initial $3d$ orbital which can be expressed as 57:42 in final $3d'$:$4d'$ orbitals. Berrington and Nakazaki [8] included only the $1s3d'$ limit in their calculation for $3d$ in Table I and, consequently, their calculated width is only half of the expected value. The initial $4d$ orbital has the expansion 13:8:68:10 in terms of $3d'$:$4d'$:$5d'$:$6d'$. Thus in this case the radial overlap $\langle 4d|4d'\rangle$ is ≈ 0 as previously observed in Ar I [15,23]. This nonorthogonality is also observed in the calculated branching ratios where the $2s2p4d$ decay shows the branching 13 :9:74:11 to $3d'$:$4d'$:$5d'$:$6d'$, confirming the small overlap between the $4d$ orbitals.

Chung and Gou [7] realized, for example, that "for resonances such as $2s2s7p$, the $1s7p + \epsilon\ell$ may be a very important decay channel." For this reason Chung and Gou included, in addition to $1snl$ limits up to $n = 3$, also the $1snl''$ limit in calculations of the total width for $2l2l'nl''$ terms. However, we have shown that, except for the lowest n values, the presence of nonorthogonalities means that this is not enough since the $1s(n + 1)l$ limit, for example, may be more important than the $1snl$ limit. This means that the total rates calculated by Chung and Gou [7] for the higher terms are smaller than ours and that they, consequently, could not observe the effect we are reporting here. However, Chung and Gou studied only the $^2P^o$ series for which the n independence anyway is less obvious [16].

Nonorthogonalities make additional limits possible. Consider the $2s$ electron in the $2s2pnd$ series as the spectator, then a nonzero $\langle 2s|1s\rangle$ overlap will allow decays such as $2s2pnd \rightarrow 1sn'l\epsilon\ell$ where l can be arbitrary except limited by the coupling and parity requirements in the $I(2pnd, n'l\epsilon\ell)$ factor. As mentioned already, in the present case $\langle 2s|1s\rangle \approx 0$ so such decays can be neglected. Also $\langle 2p|2p'\rangle \approx 1$ and therefore the main consequence of nonorthogonality is the behavior of the Rydberg electrons, ns and nd, which we have discussed above.

The extension of the previous arguments to multiply excited states is fairly straightforward. That the Coulomb interaction is a two-electron operator leads to the conclusion that there will be several spectator electrons and the decay rate can be approximated by a sum over decay rates corresponding to a set of doubly excited states, where the terms in the sum involving electrons with different n values will be small.

In conclusion, we have shown that in an orthogonal approximation, triply excited Rydberg series of the form

$2l2l'nl''$ will decay preferentially to one particular final state namely $1snl''$ and the decay rate will be independent of n and often also of l''. In practice a large number of effects could be expected to obscure this simple result, in particular mixing between configurations and nonorthogonalities, which, as we have seen, can be large when inner electrons are missing in the initial state. However, when total decay rates are considered the n and l'' independence may show up anyway. This follows directly from that there is only one decay route in the orthogonal approximation, since even when this amplitude is distributed over a large group of levels via the nonorthogonalities there is little possibility for interference so that the total width will remain unchanged (Table I). For series for which the l'' independence applies, also CI between the series has little effect on the total rates as also demonstrated in Table I. However, we note that this of course does not mean that interference is absent between the direct and the resonant photoionization channels in a photoionization experiment. This effect has been observed and in fact found to obscure the observation of Rydberg states in the $1snl$ channels [6].

Diehl *et al.* [5,6] have studied the decay of $^2P^o$ series members and noticed that the partial cross sections, as predicted here, are very dependent on the initial state. Unfortunately the $2s2p(^3P)nl\,^2P^o$ and $2s^2np\,^2P^o$ series are mixed together so that the $1snl$ series with $l = p$ are possible as limits, in addition to $l = s$ and d, complicating the analysis for these series. However, we notice that Diehl *et al.* [6] looked for the $2s2p(^3P)ns$ series in the partial cross section to $1s2s\,^3S$ while we predict that a more sensitive approach would be to use the $1sns\,^3S$ limits (or perhaps $n + 1$ due to the orthogonality problem).

Finally, we notice that the preceding analysis has been based essentially on a single particle picture modified in particular by the orthogonality problem. In fact, the use of the single particle picture to describe these strongly correlated states has been questioned. The observation of Rydberg states can to some extent be taken as experimental proof of the usefulness of the single particle picture. However, for $3l3l'nl''$ series the number of interacting series will increase considerably and complicate the analysis further so that the presence of Rydberg series in triply excited atoms should not be taken for granted.

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