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LETTER TO THE EDITOR

The importance of the ATR effect for radiative stabilization in double-electron capture

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Abstract. We discuss a mechanism which Bachau *et al* suggested would increase the probability for retaining both electrons on the projectile after double-electron capture (TDC). The mechanism, called 'auto transfer to Rydberg states' (ATR), relies on the Stark effect of the receding target on the energy levels of the projectile in cases where there is overlap between a $n\ell n'\ell'$ configuration with $n \approx n'$ and a Rydberg series. The consequence was predicted to be an increase in the radiative decay rate relative to the probability for autoionization for the initially populated $n\ell n'\ell'$ states. We show here for the specific case of the $4\ell 4\ell'$ configurations in N^{3+} , which overlap the $3\ell n\ell'$ Rydberg series, that, if the interaction with the Rydberg series is strong, the ATR mechanism can lead to a decrease in the radiative branching ratio. This explains why, in the cases studied so far, the increase in the TDC probability, when averaged over a number of states, has been significantly smaller than anticipated when the ATR mechanism was introduced.

Since Roncin *et al* (1991) observed large probabilities for retaining both electrons on the projectile in particular double-capture processes this has been a lively area of research in slow ion–atom collisions. The process goes under the name of true double capture (TDC) and previously it was believed that autoionizing double capture (ADC), in which one of the two electrons leaves the projectile again, would become the dominant process with increasing charge of the projectile. The reason for this belief was the success of the extended classical over-barrier model (ECBM) (Bárány *et al* 1985, Niehaus 1986) in describing electron-transfer processes in ion–atom collisions. The ECBM assumes that the two electrons are picked up independently of each other and thus in configurations with nearly equivalent n values. Such configurations were expected to preferentially autoionize (Hansen 1989, Luc-Koenig and Bauche 1990), thus favouring ADC. The situation following the experiments by Roncin *et al* (1991), in which large TDC probabilities were obtained using projectiles such as N^{7+} , was summed up by Barat and Roncin (1992) who commented that the ECBM has been very successful in describing the stripping of the electrons from the target but less successful in predicting how many of the electrons will be retained by the projectile. This is of course not too surprising since the model has no dynamic component and after the initial pick-up a considerable amount of 'dynamic relaxation' of the ion can be expected before a final state is reached. Nevertheless the observation of large TDC probabilities has stimulated a lively activity as exemplified by a large number of contributions on this subject to the recent ICPEAC conference (Andersen *et al* 1993).

Roncin *et al* (1991) noticed that the cases with large TDC probabilities, which have been observed so far, coincide with atomic structures where the $n\ell n'\ell'$ configurations, which are expected to be populated, overlap Rydberg series in the free atom and Bachau *et al* (1992)

exploited this when proposing the 'auto transfer to Rydberg states' (ATR) mechanism. They realized that the receding (ionized) target would influence the $n\ell n\ell'$ levels and the Rydberg series in a different way. A possible consequence is that the $n\ell n\ell'$ energy levels traverse the Rydberg series on the way out of the collision and during each level crossing some of the original $n\ell n\ell'$ population can be transferred to the Rydberg levels that were supposed to decay radiatively. The effect was thus expected to favour 'radiative stabilization' of the two electrons on the ion and we will use the term '(radiative) stabilization' as synonymous with TDC. In the following the overlap between the $4\ell 4\ell'$ states and the $3\ell n\ell'$ Rydberg states in N^{5+} is used as a concrete example of the ATR mechanism.

It was assumed that although the coupling at each crossing might be weak this could be compensated by the large number of crossings and this assumption meant that the ATR mechanism would be particularly effective for those $4\ell 4\ell'$ states that in the free atom are located above the $N = 3$ threshold. These states would after all, in general, sweep through the largest number of Rydberg states on the way out of the collision. Subsequently, Vaeck and Hansen (1993) pointed out that autoionization can compete with radiative decay even for fairly high members of the $3\ell n\ell'$ Rydberg series and Roncin *et al* (1993) incorporated this feature into quantitative time-dependent close-coupling calculations for the $4\ell 4\ell'$ singlet terms in N^{5+} crossing the $3\ell n\ell'$ Rydberg series. The result of the calculations was a fairly small increase in the stabilization when averaged over all $4\ell 4\ell'$ states although for particular terms the increase could be very large. The disappointment has led Roncin and collaborators to emphasize the effect of the receding ion on the angular momentum of the electrons being picked up (Kazansky 1992) as a means of increasing the radiative decay probability versus the autoionization rate.

Meanwhile Vaeck *et al* (1993) and van der Hart *et al* (1994) carried out calculations of branching ratios for radiative decay, R^r , for the $4\ell 4\ell'$ terms in the free O^{6+} ion and in this 'static' approach found a somewhat higher branching ratio for the singlets than obtained by Roncin *et al* (1993) for N^{5+} by including the ATR effect. The fact that N^{5+} was expected to be a more favourable case for the ATR mechanism than O^{6+} , since seven singlet terms are located above the $N = 3$ limit compared to four in O^{6+} , compelled us to have a closer look at the two approaches and in this letter we compare static results for the singlets in N^{5+} with results including the ATR effect. Again we find that the static results for the branching ratios often are larger than the dynamic ones and we ascribe this to the fact that the ATR is too successful: transferring the $4\ell 4\ell'$ population already at the beginning of the traverse and therefore into Rydberg states which lie so low that they autoionize while in the static calculation the interaction is with higher Rydberg levels.

Figure 1 shows the position of the singlet terms in $4\ell 4\ell'$ relative to the $N = 3$ threshold and also the average energy of a $3\ell 18\ell'$ state in the free N^{5+} ion. The interaction with the Rydberg series has not been taken into account and for the $^1I^e$ term, for example, this interaction leads to extensive mixing which means that the actual 'position' of $^1I^e$ is less well defined than the figure suggests. Keeping this in mind, the figure shows that seven terms are located above the $N = 3$ limit while four are found between $3\ell 18\ell'$ and the limit, where the density of Rydberg levels is so high that the Rydberg series behaves as a quasi-continuum (Bachau *et al* 1992). This is also roughly the region where radiative decay of the Rydberg series is the dominating decay mode (Roncin *et al* 1993, van der Hart *et al* 1994). Twelve terms are located below $3\ell 18\ell'$ where autoionization generally will be the dominating decay mode for the Rydberg states.

Figure 2 shows examples of the mixing between a $4\ell 4\ell'$ term and the Rydberg series for two terms located at approximately the same energy. The figure shows that the $^1D^o$ term, which has a weak interaction with the series, is mixed into only a few nearby states, while

Figure 1. The position of the singlet $4\ell 4\ell'$ terms relative to the $N = 3$ limit in N^{6+} . Also the average energy of the $3\ell 18\ell'$ Rydberg states is indicated. The interaction with the Rydberg series is not taken into account in the calculation of the $4\ell 4\ell'$ terms. The natural parity ($\Pi = (-1)^L$) terms are indicated by fully drawn lines, the unnatural parity ($\Pi = (-1)^{L+1}$) terms with broken lines. The unnatural parity terms have in general a weaker interaction with both Rydberg series and continua.

Figure 2. Examples of weak, $^1D^\circ$, and strong, $^1P^\circ$, interactions between a $4\ell 4\ell'$ term and the $3\ell n\ell'$ Rydberg series. Note that the terms are located in the same energy region so that the density of Rydberg states is similar in the two cases. There are three Rydberg series with $^1D^\circ$ symmetry and five with $^1P^\circ$ symmetry but the particular $4\ell 4\ell'$ $^1P^\circ$ term interacts primarily with just one series.

the $^1P^\circ$ term, which has a strong interaction with the series, is 'dissolved' in the series with less than 11% $4\ell 4\ell'$ character in any state.

Table 1 compares our results for the free ion to results obtained taking the ATR effect into account (Roncin *et al* 1993). We show 'static' R^f ratios calculated as $R_s^f = A^f / (A^f + A^a)$

Table 1. Stabilization ratios for the $4\ell 4\ell'$ singlet terms in N^{5+} calculated including the interaction with the $3\ell n\ell'$ Rydberg series. The branching ratios are averaged over all states with the given LS symmetry. The number of $4\ell 4\ell'$ states in each LS symmetry and (in parenthesis) the number of states above threshold in N^{5+} are given as well. The present results, R_s^r , for the free ion are based on large scale configuration interaction calculations while the results due to Roncin *et al* (1993) are time-dependent close-coupling calculations which takes the interaction with the Rydberg series into account in two different ways. The 'static' results, R_s^r , should be comparable to our results, while the 'dynamic' results, R_d^r , include the ATR effect. The data in parentheses correspond to cases where one or more of the individual close-coupling calculations have not converged. These values should be considered as lower limits to the correct values. The average values, Av, are weighted with $(2L + 1)$.

LS	Number of states	Present work	Roncin <i>et al</i> (1993)	
		R_s^r (%)	R_s^r (%)	R_d^r (%)
$^1S^e$	4(2)	10.1	(8.5)	(14.3)
$^1P^o$	3(1)	10.9	2.6	(10.2)
$^1D^e$	5(1)	16.6	17.4	(12.9)
$^1D^o$	2	66.0	39.	61.5
$^1F^o$	3(1)	9.8	2.3	8
$^1F^e$	1	41.5	16	75
$^1G^e$	3(1)	13.8	(13.5)	(10.9)
$^1G^o$	1	18.0	3.5	28
$^1H^o$	1(1)	24.8	(15)	2.1
$^1I^e$	1	36.3	(29)	4
Av		22.0	14.6	17.7

where A^a and A^r are the decay rates for autoionization and radiative decay in the free ion, respectively. The values are based on the assumption that only the $4\ell 4\ell'$ part of the wavefunction is populated initially and the method of calculation is described by van der Hart *et al* (1994). The main difficulty is how to treat the very high Rydberg states in a reliable way. We use B -spline basis sets which allow us to describe accurately very high ($n \sim 50$) Rydberg states (van der Hart *et al* 1994). In N^{5+} several terms are located very close to the $N = 3$ limit (figure 1) which makes severe demands on the computations. We have checked the quality of these calculations by using several box sizes (B -splines are L^2 -integrable functions defined in a box) but it is clear that the results for such terms as $^1I^e$ are less reliable than for other terms. For the symmetries for which more than one term exist we show average values. In our calculations, those terms, that are located well above the $N = 3$ limit and thus do not mix with the bound part of the Rydberg series, decay by autoionization to this limit and do not contribute to the radiative stabilization. This applies to the terms above, and including, the highest $^1G^e$ term (figure 1) except that the highest $^1S^e$ term has a small (8%) radiative branching ratio. In contrast, the ATR mechanism was expected to be particularly effective for these terms which consequently would make a significant contribution to the overall radiative stabilization of the $4\ell 4\ell'$ states.

In table 1 are also shown R^r results from Roncin *et al* (1993). These are based on time-dependent close-coupling calculations assuming that a $4\ell 4\ell'$ term is populated initially and followed as it crosses the Rydberg series with a constant speed of $v = 0.2$ au. In one calculation, R_d^r , the distance between the $4\ell 4\ell'$ term and the series is varied to simulate the ATR effect. In the other, R_s^r , this distance is fixed at the value in the free atom and does not vary with time. This static calculation could be expected to give a result similar to ours since stabilization in both approaches is due to mixing with Rydberg states that lie so high that they decay by radiation. However, in our approach stabilization for these

states is strongly influenced by destructive interference between the autoionization rates for the $4\ell 4\ell'$ and $3\ell n\ell'$ components, an effect which is not taken into account in the close-coupling calculation. Also the assumptions about the radiative decay rates are different in the two calculations. Nevertheless, the results are not too different. The branching ratio averaged over all singlets assuming a statistical population distribution is 14.6% in the static calculation due to Roncin *et al* (1993) compared to 22.0% with our approach. The more interesting point is that including the ATR effect raises the average to only 17.7%.

Table 1 shows the reason for this surprising result which can be understood particularly easily by considering the symmetries for which only one $4\ell 4\ell'$ term exists. We notice that the $^1H^o$ and $^1I^o$ terms, which are located close to the $N = 3$ threshold, have much larger radiative branching ratios both in our calculation and in the static calculation due to Roncin *et al* (1993) than in the calculations including the ATR effects. (The same applies to the $^1P^o$ term in figure 2.) Both terms have a strong interaction with the Rydberg series and the interaction is apparently so strong that the main part of the $4\ell 4\ell'$ population is transferred at the beginning of the traverse of the Rydberg series, i.e. into $3\ell n\ell'$ states that autoionize. Therefore $R_d^r < R_s^r$ and $R_d^i < R_s^i$, but if the speed of the collision is increased we expect the radiative branching ratio to increase. Roncin has kindly carried out calculations at $v = 0.4$ au and found an increase in R_d^r by roughly a factor of two for these terms in agreement with this expectation.

Conversely, the $^1F^o$ and $^1G^o$ terms are so called 'unnatural parity' terms (another example is the $^1D^o$ term in figure 2), which have a much weaker interaction not only with the $3\ell n\ell'$ Rydberg series but also with the $2\ell\ell\ell'$ continua. For these terms our branching ratios are large but the dynamic R_d^r values are much larger, particularly for the $^1F^o$ term which has a very weak interaction with the Rydberg series (see table 1 in Roncin *et al* (1993)). Because the interaction is so weak, $4\ell 4\ell'$ population is transferred also to the highest Rydberg levels and thus a high degree of stabilization is obtained. However, we note that the position of these two terms in the free atom is below $n = 18$ and other factors are probably also important. It points in the same direction that a speed up of the collision by a factor of two had a negligible influence on R_d^r for these terms (Roncin 1993).

The mixture of terms with strong and weak interactions within one configuration explains why the net effect of the ATR effect on the average branching ratio is small while the effect can be large for individual terms. The same reason lies behind the fact that generally there is little difference between the R_s^r and R_d^r values for those symmetries for which several terms exist, since there usually is a variety of different interaction strengths within each symmetry.

Thus we conclude that although the ATR mechanism can increase the radiative branching ratio for particular terms by large amounts, the effect averaged over a number of terms generally will be much smaller. Secondly we notice that the mechanism does not necessarily have a maximum at low collision energies and it would be interesting to study the velocity dependence in more detail. For a more definitive evaluation of the importance of the effect it seems necessary to incorporate into the time-dependent approach not only the 'Kazansky effect' but also the interference between the $4\ell 4\ell'$ and the $3\ell n\ell'$ autoionization amplitudes, which has been found to be very important in the static case.

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