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Auger decay of hollow nitrogen atoms

Nathalie Vaeck†§ and Jørgen E Hansen‡

† Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CP160/09, 50 av. F-D Roosevelt, B-1050 Bruxelles, Belgium

‡ Van der Waals–Zeeman Institute, University of Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands

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Abstract. We present calculations of autoionization lifetimes for ‘hollow’ nitrogen atoms with and without a core of one or two 1s electrons. We have observed a very similar pattern in the N dependence of the lifetimes for all $1s^M np^N$ configurations with $M = 0, 1$ and 2 , $n = 2, 3, 4, 5, 6, 7$ and 10 and $N = 2, 3, 4, 5$ and 6 . Also some $1s n \ell^N$ configurations with $\ell \neq 1$ have been considered as well as configurations with mixed values of n . For configurations with all the electrons in the same n shell we have found that the average lifetime in *neutral* systems is very short, typically of the order of $3\text{--}5 \times 10^{-16}$ s for $n = 3$ to 7 . The same applies to configurations with mixed values of n (of the order of $1\text{--}6 \times 10^{-15}$ s for $n = 3$ to 7). We find that the importance of electron correlation increases dramatically with n and N but that the average autoionization decay rates do not change. The configurations studied are of interest, for example, in the study of processes that occur during neutralization of highly charged nitrogen ions at surfaces.

1. Introduction

During the last few years the study of atoms with a large number of inner holes have attracted considerable attention, one reason being the realization that such atoms are formed when slow highly-charged ions are neutralized at surfaces (see, for example, Das and Morgenstern 1993 and references therein). In this process it is believed that if an ion approaches a surface it attracts electrons from the conduction band even before it reaches the surface. Since this initial pick-up is expected to occur resonantly, the electrons are attracted into high-lying atomic states and it has become accepted wisdom that it is possible to pick up a large number of electrons in such states, and in fact to completely neutralize the ion before impact with initially all the electrons in high-lying orbits. Such atoms have become known as ‘hollow’ and how they are formed and develop in time is not yet fully understood. In contrast to the rapidly increasing number of experiments, the number of theoretical studies of such systems is still very limited. There are several reasons why it is difficult to study such systems. If we, for example, distribute 10 electrons over the $n = 10$ shell, the number of possible initial states becomes so large that a proper statistical treatment is out of the question at the moment. The calculations as such are quite difficult and time consuming since the configurations that need to be considered can be fairly complicated and usually a large number of decay routes are involved. Nevertheless, it is essential to study the stability of such configurations for several reasons. Indeed, although the understanding of the neutralization process of highly-charged ions on metallic surfaces has advanced considerably

§ Senior Research Assistant of the Belgian National Fund for Scientific Research (FNRS).

mainly due to the multiplication of experimental results, uncertainties persist concerning the decay mechanism and the lifetime of a system having a large number of electrons distributed over a number of shells with large n values. It is known that the lifetime of a *doubly*-excited state, in general, is too long at high n values (Hansen 1989, Luc-Koenig and Bauche 1990) to allow such a system to decay in the short time available before impact (10^{-13} – 10^{-14} s). However, very little is known about the decay of *multiply*-excited states and in this paper we present an *ab initio* study of the lifetimes of hollow nitrogen atoms with many inner holes.

In the past few years, nitrogen ions have been used intensively in a number of neutralization experiments involving multiply-charged ions on metal surfaces. For example, Kurz *et al* (1992) and Aumayr *et al* (1993) have measured the total electron emission from slow N^{q+} ($q \leq 6$) ions impinging on a clean gold surface. Folkerts and Morgenstern (1991) and Das *et al* (1992) have studied the secondary electron energy spectra of N^{6+} and N^{7+} on W and Ni surfaces at high and low energies while Zeijlmans van Emmichoven *et al* (1991, 1993) have analysed the low-energy electron spectra produced by N^{6+} ions at Au and Cu surfaces. N^{2+} , N^{5+} and N^{6+} ions have been used by Hughes *et al* (1993) to study kinetic and potential electron emission on an Au surface. This proliferation of experimental studies is one of the main motivations for the choice of hollow nitrogen ions as the subject of the present work. However, we believe that the behaviour of the lifetimes for multiply-excited states in other atoms will be similar.

We have already studied triply-excited states of the type $(3\ell)^3$ in nitrogen both with and without a $1s^2$ core and found average lifetimes considerably shorter than for the equivalent $(3\ell)^2$ doubly-excited states independently of whether a $1s$ core is present or not (Vaeck and Hansen 1992a). We have also studied the average lifetimes of $1s7p^N$ configurations in nitrogen ions (Vaeck and Hansen 1991a) and found a significant shortening of the lifetimes when the ion becomes neutralized, i.e. when a truly hollow *atom* is formed.

The n value of the shell in which the electrons from the solid are initially captured during the neutralization process depends mainly on the charge of the ion and the work function of the metal and although the $n = 7$ shell has been found to be a good approximation for the first pick-up of the electrons from the conduction band of a clean gold surface for example (Burgdörfer *et al* 1991), a variation in the n value is expected for the interaction with other metal surfaces (Meyer *et al* 1993). In order to check the effect of a variation of n on the decrease of the lifetime with N , calculations were performed for the $1snp^N$ configurations with $n = 2$ – 7 and $N = 2$ – 6 in nitrogen (Vaeck and Hansen 1992b). It was found that the calculated lifetimes fall on two 'universal' curves with a tendency to longer lifetimes for higher n values unless the ion is completely neutralized. We have been interested in checking the 'universal' character of these curves and here we present new results concerning the lifetimes of $1s^M np^N$ states. The restriction to p electrons is for calculational convenience only and unfortunately does not reflect the expected complexity of the experimental situation. Therefore we have also considered some other ℓ values and the results support the view that the simplicity of the $1s^M np^N$ results is no accident which gives some hope that the behaviour of such systems is less fickle than could have been expected.

In the following, we will use the notation $1s^M(n\ell)^N$ where M is the number of $1s$ electrons, i.e. one, two or zero, n is the principal quantum number of the ℓ subshell and finally N is the number of electrons in the $n\ell$ shell.

2. Method of calculation

The calculations were performed with the suite of programs written by Cowan (1981). We have used the single-configuration approximation (Cowan 1981) to calculate the 'average'

autoionization rates (Hansen 1989, Luc-Koenig and Bauche 1990, Vaeck and Hansen 1991a, 1992a) for configurations of the type $1s^M(n\ell)^N$ with $M = 0-2$, $n = 2-7, 10$ and $N = 2-6$ in neutral and ionized nitrogen. We calculate the average decay rate to a particular final configuration from the initial configuration assuming a statistical population of the initial levels:

$$A^{stat} = \frac{\sum_i g_i A_i}{\sum_i g_i} \quad (1)$$

where A_i is the decay rate of the level i with degeneracy g_i . From the summed decay rates we obtain an upper limit to the *average* lifetime, τ , of the initial configuration from

$$\tau = \frac{1}{\sum_j A_j^{stat}} \quad (2)$$

where the summation, in principle, is over all the possible final configurations j but since usually many final configurations are possible, of which perhaps not all have been considered, our values are in general, as mentioned, upper limits to the exact lifetime. In the following the average lifetime will usually be called 'the lifetime' for short.

By explicit comparison with calculations including the main correlation effects, this approach, which does not take the correlation between electrons into account, has been found to adequately reproduce the *average* decay properties of the triply-excited $1s^2(3\ell)^3$ and $(3\ell)^3$ states in N^{2+} and N^{4+} (Vaeck and Hansen 1992a). In the same way, we show in section 6 that the average approximation is valid also for multiply-excited states $1s^2np^N$ with $n = 4$ and $3 \leq N \leq 5$ which provides further support for the general validity of this result for multiply-excited states. A similar conclusion has been reached by Omar and Hahn (1991) in calculations for ions with at most two holes (in the $1s$ shell).

3. Lifetimes of the $1s^Mnp^N$ configurations

All the lifetimes of the $1s^Mnp^N$ configurations with $M = 0-2$, $n = 2-7, 10$ and $N = 2-6$ for the nitrogen ions calculated using (2), taking into account the main decay channels, are given in table 1. We will discuss the results for the different cores separately.

3.1. Ions with a $1s$ core

In our previous paper concerning the theoretical lifetimes of the $1s7p^N$ configurations in $N^{(6-N)+}$ (Vaeck and Hansen 1991a) it was found that the lifetime of the multiply-excited states decreases when N increases, the shortest lifetime corresponding to the neutral atom with $N = 6$. This was explained by the fact that the largest autoionization decay rate usually occurs for the transition with the smallest free electron energy and the large decrease in the lifetime at the neutral end of the sequence is in fact due to the opening of new decay channels to the limits $1s6\ell7p^4$ with $\ell = s, p, d$ and f ; i.e. $\Delta n = 1$ for the jumping electron. This corresponds to Coster-Kronig transitions with free electron energies varying from 0.044 Ry to 0.004 Ry (Vaeck and Hansen 1991a).

The apparent 'universality' of these curves was suggested by the fact that the same behaviour was found for the lifetimes of $1s6p^N$ in $C^{(5-N)+}$ and $1s9p^N$ in $O^{(7-N)+}$ (Vaeck and Hansen 1991a) as well as for other values of n (Vaeck and Hansen 1992b). Figure 1 shows average lifetimes for the $1snp^N$ configurations in nitrogen for $n = 2-7$ and 10. We see, as mentioned already, that all values up to $n = 7$ fall on two curves, one 'fast' and one 'slow'. As N increases, more and more values move from the 'fast' to the 'slow' curve. However, in all cases with n less or equal to 7 the neutral atom is found on the 'fast' curve with a lifetime of about 4×10^{-16} s.

Table 1. Lifetimes (τ in s) of the $1s^M np^N$ configurations with $M = 0-2$, $n = 2-7$, 10 and $N = 2-6$ for nitrogen ions.

Configuration	τ		
	$M = 1$	$M = 2$	$M = 0$
$1s^M 2p^2$	2.463×10^{-14}		8.970×10^{-15}
$1s^M 2p^3$	1.060×10^{-14}		3.666×10^{-15}
$1s^M 2p^4$	7.007×10^{-15}		2.289×10^{-15}
$1s^M 2p^5$	5.674×10^{-15}	1.246×10^{-16}	1.743×10^{-15}
$1s^M 2p^6$	1.184×10^{-16}		1.498×10^{-15}
$1s^M 3p^2$	3.242×10^{-15}	3.156×10^{-15}	3.235×10^{-15}
$1s^M 3p^3$	1.229×10^{-15}	1.237×10^{-15}	1.201×10^{-15}
$1s^M 3p^4$	7.187×10^{-16}	7.585×10^{-16}	6.820×10^{-16}
$1s^M 3p^5$	5.189×10^{-16}	5.848×10^{-16}	4.746×10^{-16}
$1s^M 3p^6$	4.314×10^{-16}		3.759×10^{-16}
$1s^M 4p^2$	2.592×10^{-14}	3.835×10^{-14}	3.745×10^{-14}
$1s^M 4p^3$	1.293×10^{-15}	1.298×10^{-15}	1.307×10^{-15}
$1s^M 4p^4$	7.312×10^{-16}	7.598×10^{-16}	7.227×10^{-16}
$1s^M 4p^5$	5.460×10^{-16}	5.561×10^{-16}	4.855×10^{-16}
$1s^M 4p^6$	4.042×10^{-16}		3.709×10^{-16}
$1s^M 5p^2$	3.228×10^{-14}	3.212×10^{-14}	3.304×10^{-14}
$1s^M 5p^3$	1.234×10^{-14}	1.270×10^{-14}	1.247×10^{-14}
$1s^M 5p^4$	5.678×10^{-15}	7.766×10^{-16}	7.135×10^{-15}
$1s^M 5p^5$	5.662×10^{-16}	5.556×10^{-16}	5.253×10^{-16}
$1s^M 5p^6$	3.939×10^{-16}		3.919×10^{-16}
$1s^M 6p^2$	3.048×10^{-14}	3.256×10^{-14}	3.253×10^{-14}
$1s^M 6p^3$	1.143×10^{-14}	1.248×10^{-14}	1.192×10^{-14}
$1s^M 6p^4$	6.674×10^{-15}	7.516×10^{-15}	6.987×10^{-15}
$1s^M 6p^5$	3.843×10^{-15}	5.297×10^{-16}	4.782×10^{-15}
$1s^M 6p^6$	3.801×10^{-16}		3.849×10^{-16}
$1s^M 7p^2$	2.927×10^{-14}	3.296×10^{-14}	3.262×10^{-14}
$1s^M 7p^3$	1.102×10^{-14}	1.239×10^{-14}	1.253×10^{-14}
$1s^M 7p^4$	6.295×10^{-15}	7.278×10^{-15}	6.907×10^{-15}
$1s^M 7p^5$	4.930×10^{-15}	5.686×10^{-16}	4.676×10^{-15}
$1s^M 7p^6$	3.588×10^{-16}		3.598×10^{-15}
$1s^M 10p^2$	9.804×10^{-14}	1.147×10^{-13}	1.170×10^{-13}
$1s^M 10p^3$	3.659×10^{-14}	4.327×10^{-14}	4.298×10^{-14}
$1s^M 10p^4$	2.140×10^{-14}	6.263×10^{-15}	2.391×10^{-14}
$1s^M 10p^5$	4.407×10^{-15}	4.222×10^{-15}	1.623×10^{-14}
$1s^M 10p^6$	3.121×10^{-15}		3.015×10^{-15}

For $n = 10$, we find the first deviation from the two 'universal' curves shown on figure 1. However, there still is a considerable reduction in the lifetime at the neutral end of the sequence. The $n = 10$ results are discussed in more detail in section 4.

It is interesting to compare the results with the prediction of the statistical model due to Larkins (1971) which has been used by Briand *et al* (1990) to predict the decay rates in Ar^{17+} . With regard to Auger decay rates this model is based on the observation by McGuire (1969) that for autoionization rates averaged over the initial states of a configuration and summed over all final states, i.e. as calculated here, the dependence on the number of electrons in the initial state can be mimicked by the statistical, i.e. $N(N-1)/2$, dependence where N is the number of electrons in the shell under consideration. This prediction is of

Figure 1. Lifetimes (in s) of the $1snp^N$ configurations of the $N^{(6-N)+}$ ions as a function of the occupation number of the np shell.

course only valid if the same decay channels are considered for all N values, so it cannot describe the jump from one curve to another which is such a prominent feature of our results. Another assumption is that the radial integrals do not change and this assumption can be tested on our results, for example, for the $1s3p^N$ configurations, which all fall on the same curve. If we compare the calculated ratios between the lifetimes for different values of N we find 7.52:2.85:1.67:1.20:1 for $N = 2, 3, 4, 5$ and 6 compared to the statistical 15:5:2.5:1.5:1. Thus, in this case the statistical approximation is valid only within a factor of two, which is only adequate for qualitative estimates. The variation with N is seen to be smaller than predicted by the statistical model and this conclusion applies more generally to the results in table 1.

3.2. Ions with a $1s^2$ core

The lifetimes of the $1s^2np^N$ configurations with $n = 2-7, 10$ and $N = 2-5$ in $N^{(5-N)+}$ are presented in figure 2. The similarity between figures 1 and 2 is striking. For $N = 2$ and 3 the lifetimes for the different n values fall on the same two curves, one 'slow' and one 'fast' and the lifetimes of the $1s^210p^N$ configurations lie above the 'slow' curve exactly as in figure 1. The first deviation between the two figures occurs for $N = 4$ where the configurations with $n = 5$ and $n = 10$ lie on the 'fast' curve because of the opening of decay channels to $1s^24p5p^2$ and $1s^28p10p^2$, respectively. This corresponds, in fact, to the situation for $N = 5$ in figure 1. Similarly, the lifetimes of the neutralized configurations $1s^2np^5$ show the same behaviour as the lifetimes of $1snp^6$ in figure 1.

One of the main differences between figures 1 and 2 concerns the lifetimes of the $1s^M2p^N$ configurations. Because the decay to $1s$ is impossible for the $1s^22p^N$ configurations, the only possible autoionization decay in the LS approximation is the super Coster-Kronig channel which is energetically forbidden until $N = 5$; the neutral end of the sequence. The magnitude of this super Coster-Kronig decay is similar to that for the $1s2p^6$ configuration.

3.3. Ions without a core

The lifetimes of the np^N configurations with $n = 2-7, 10$ and $N = 2-6$ in $N^{(7-N)+}$ are presented in figure 3. Once again we find the lifetimes located on two parallel curves with the lifetimes of the $10p^N$ configurations lying on a third 'slower' curve. However, compared to figures 1 and 2, figure 3 presents some new features. First, a fourth curve appears in this figure which corresponds to the lifetimes of the $2p^N$ configurations. This curve is not exactly parallel to the others. The reason is probably that the decay of the np^N

Figure 2. Lifetimes (in s) of the $1s^2np^N$ configurations of the $N^{(5-N)+}$ ions as a function of the occupation number of the np shell.

Figure 3. Lifetimes (in s) of the np^N configurations of the $N^{(7-N)+}$ ions as a function of the occupation number of the np shell.

configurations with $n > 2$ is dominated by autoionization to the $(n-1)pnp^{(N-2)}$ limits, thus corresponding to a $p \rightarrow p'$ jump. In the case of $2p^N$ the only possible decay is to the $1s2p^{(N-2)}$ limit corresponding to a $2p \rightarrow 1s$ transition. However, the same transition $2p \rightarrow 1s$ also appears in the decay of the $1s2p^N$ configurations (figure 1) and if the proposed explanation is correct it is surprising that the lifetime of the latter configurations *does* follow the 'slow' curve, although not exactly.

Since in this case the p shell is full before the ion is neutralized, the super Coster-Kronig channel for the $2p^N$ configurations remains energetically forbidden even for $N = 6$ and no 'jump' in the lifetime is observed at this point. This is also the case for the $7p^N$ lifetimes which do not jump to the 'fast' curve for $N = 6$. To neutralize the atom in this case, we need to start filling another shell. The addition of a $7s$, $8s$ or $9s$ electron to the $7p^6$ configuration shortens the lifetime to 3.57×10^{-16} , 3.89×10^{-16} and 3.72×10^{-16} s, respectively, thus exactly on the 'fast' curve. On the other hand, the super Coster-Kronig channels to the $2s2p^4n\ell$ limits are energetically forbidden for any $n\ell$ electron we have considered.

3.4. General comments

The similarity of the behaviour of the lifetimes as a function of the occupation number for the np shell is, in fact, very surprising. Indeed, it should be kept in mind that the decay schemes for the different n values are quite different. For instance, the $1s2p^N$ configurations

with $N = 2-5$ for which the lifetimes are shown in figure 1, can only decay to the $1s^2 2p^{(N-2)}$ configurations and it is only for $N = 6$ that the super Coster-Kronig decay channel to the $1s 2s 2p^4$ configuration is energetically allowed. The lifetime of a $1s 2p^N$ configuration with $N = 2-5$ is nearly the same as the lifetime of the $1s 7p^N$ configuration with the same N value. However, the $1s 7p^N$ configurations can decay to all the $1sn\ell 7p^{N-2}$ configurations with n values between 1 and 5 and ℓ values going up to $\ell = 4$. Moreover, the kinetic energies of the continuum electrons are very different in the case of $1s 2p^N$ and $1s 7p^N$ (around 25 Ry for the $1s 2p^N$ configurations and around 0.2 Ry for the main decay channel of the $1s 7p^N$ configurations). For the $1s 7p^6$ configurations the decay channel to the $1s 6\ell 7p^4$ configurations becomes allowed which leads to a large decrease in the lifetime (Vaeck and Hansen 1991a) but because of the very large decay rate for the super Coster-Kronig transition of the $1s 2p^6$ state, these two lifetimes do differ (by a factor of three).

In table 2, we show explicitly the different decay channels for the $4p^N$ configurations with $N = 2-6$ as well as the corresponding autoionization decay rates and the energy of the free electron. For the $4p^N$ configurations the jump to the 'fast' curve in figure 3 occurs already between $N = 2$ and $N = 3$ when the decay channel to the $3p 4p^{N-2}$ limits becomes

Table 2. Autoionization decay channels for the $4p^N$ configurations with $N = 2-6$ in nitrogen ions. Indicated are, the initial and final configurations, the summation over all calculated autoionization rates (A^a in s^{-1}) weighted by the degeneracy of the levels in the initial configuration g and the kinetic energy of the free electron (ϵ in Ry) corresponding to the energy difference between the centres of gravity of the initial and final configurations.

Initial configuration	Final configuration	$\sum g A^a$	ϵ
$4p^2$	$\rightarrow 1s$	1.51×10^{13}	43.4
	$\rightarrow 2s$	1.05×10^{13}	6.59
	$\rightarrow 2p$	3.75×10^{14}	6.59
$4p^3$	$\rightarrow 1s 4p$	5.08×10^{13}	43.5
	$\rightarrow 2s 4p$	3.53×10^{13}	6.83
	$\rightarrow 2p 4p$	1.31×10^{15}	6.82
	$\rightarrow 3s 4p$	2.89×10^{14}	0.14
	$\rightarrow 3p 4p$	1.28×10^{16}	0.13
	$\rightarrow 3d 4p$	8.24×10^{14}	0.10
$4p^4$	$\rightarrow 1s 4p^2$	6.30×10^{13}	43.7
	$\rightarrow 2s 4p^2$	4.36×10^{13}	7.11
	$\rightarrow 2p 4p^2$	1.69×10^{15}	7.08
	$\rightarrow 3s 4p^2$	3.89×10^{14}	0.49
	$\rightarrow 3p 4p^2$	1.74×10^{16}	0.47
	$\rightarrow 3d 4p^2$	1.20×10^{15}	0.42
$4p^5$	$\rightarrow 1s 4p^3$	3.44×10^{13}	43.9
	$\rightarrow 2s 4p^3$	2.37×10^{13}	7.38
	$\rightarrow 2p 4p^3$	9.51×10^{15}	7.34
	$\rightarrow 3s 4p^3$	2.28×10^{14}	0.82
	$\rightarrow 3p 4p^3$	1.04×10^{16}	0.80
	$\rightarrow 3d 4p^3$	7.56×10^{14}	0.73
$4p^6$	$\rightarrow 1s 4p^4$	6.91×10^{12}	44.2
	$\rightarrow 2s 4p^4$	4.77×10^{12}	7.65
	$\rightarrow 2p 4p^4$	1.97×10^{14}	7.61
	$\rightarrow 3s 4p^4$	4.94×10^{13}	1.14
	$\rightarrow 3p 4p^4$	2.26×10^{15}	1.12
	$\rightarrow 3d 4p^4$	1.74×10^{14}	1.03

energetically allowed. In fact, when this decay is possible, it represents 84% of the total transition probability. This percentage is constant along the $n = 4$ sequence for $N = 3$ to $N = 6$. As n increases the percentage of the main decay channel decreases because the number of energetically allowed limits is larger. For example, the decay of the $3p^N$ configurations ($N = 2-6$) to the $2p3p^{(N-2)}$ limits contributes 97% of the total decay rate while the decay of the $6p^6$ configuration to the $5p6p^4$ limits is only 78% of the total decay rate.

Table 2 also shows that the fastest decay does not always occur to the closest limit. There is a dependence on the angular momentum of the active electron. For example, the decay of $4p^N$ to the $2p4p^{(N-2)}$ limits with an averaged continuum energy of 7.2 Ry is faster than the decay to the $3d4p^{(N-2)}$ limits which are located on average less than 1 Ry away from the decaying configuration. This $\Delta\ell$ dependence of the autoionization rates is the same for all the $1s^M np^N$ configurations that we have studied. Similarly, the autoionization rates to the $1s4p^{(N-2)}$ limits are larger than the rates to the $2s4p^{(N-2)}$ limits which are located more than 36 Ry closer to the autoionizing state. Also this behaviour, which is not due to angular momentum restrictions, is a feature of the decay of all the $1s^M np^N$ configurations we have studied and is found for other ions too. As a check, we have made more detailed studies of the $1S$ states $3s^2$, $3p^2$ and $3d^2$ in He using the MCHF-AUTO program (Froese Fischer and Brage 1992) which is part of the MCHF-ASP library (Froese Fischer 1991). The autoionization probabilities to the $1s$ and $2s$ limits are, respectively, $6.56 \times 10^{12} \text{ s}^{-1}$ and $1.03 \times 10^{14} \text{ s}^{-1}$ for the $3s^2 1S$, $7.37 \times 10^{12} \text{ s}^{-1}$ and $7.02 \times 10^{12} \text{ s}^{-1}$ for the $3p^2 1S$ and $9.07 \times 10^9 \text{ s}^{-1}$ and $5.25 \times 10^{13} \text{ s}^{-1}$ for the $3d^2 1S$ state. Thus only for $3p^2 1S$ is the decay rate to the $1s$ limit larger than the rate to the $2s$ limit and this result is no longer true when we include correlation in the wavefunction of the $3p^2$ state. A simple MCHF expansion $3p^2 + 3s^2 + 3d^2 1S$ for the $3p^2 1S$ term gives an autoionization decay rate to the $1s$ limit of $9.90 \times 10^{11} \text{ s}^{-1}$ which is considerably smaller than the rate to the $2s$ limit ($1.47 \times 10^{14} \text{ s}^{-1}$). Thus, this feature of the results for the $1s^M np^N$ configurations seems to be a peculiarity of the single-configuration approximation for the p^N configurations.

4. Higher n values

The 'fast' curves for $n = 2-7$ in figures 1-3 correspond to a dominant decay to the $1s^M(n-1)\ell np^{(N-2)}$ limits ($\Delta n = 1$ transitions) while the 'slow' curves correspond to the decay to the $1s^M(n-2)\ell np^{(N-2)}$ limits ($\Delta n = 2$ transitions). All the configurations we have considered show the same behaviour with their lifetimes lying on these two curves. However, when we look at configurations with higher n values such as, for example, the $1s^M 10p^N$ configurations, the $\Delta n = 1$ transitions are energetically forbidden even for the neutral atom. Therefore the decays to the $1s^M(n-2)\ell np^{(N-2)}$ thresholds become the fastest decays but are only allowed when the ion is close to being neutralized. The (super) 'slow' curves for these configurations in figures 1-3 correspond to $\Delta n = 3$ transitions.

In figure 4, we show the lifetimes of the $1s^2 np^2$ and $1s^2 np^5$ configurations for $n = 2$ to $n = 14$ calculated by taking into account only the dominant decay to the $1s^2 n'p$ and $1s^2 n'pnp^3$ limits. The super Coster-Kronig channel is only open for $n = 2$ and $N = 5$ and corresponds to the fastest lifetime on figure 4. For $n = 3$ to $n = 7$, the fast decays correspond to $\Delta n = 1$ transitions and the slow ones to $\Delta n = 2$ transitions. The $\Delta n = 1$, $\Delta\ell = 0$ transitions are then energetically forbidden for the $n = 8$ to $n = 11$ configurations for which the fast decays go to the $1s^2(n-2)pnp^{(N-2)}$ limits and the slow ones to the $1s^2(n-3)pnp^{(N-2)}$ thresholds with a corresponding increase in the lifetimes by nearly one order of magnitude. Finally, for $n = 12$ to 14 , the accessible limits are $1s^2(n-4)p$

Figure 4. Lifetimes (in s) of the $1s^2np^2$ configurations of the N^{3+} ion (●) and of the $1s^2np^5$ configurations of the N atom (□) as a function of the principal quantum number of the np shell.

Figure 5. Lifetimes (in s) of the $1snp^6$ configurations of the Ar^{11+} ion as a function of the principal quantum number of the np shell.

and $1s^2(n-3)pn^3$ for the $1s^2np^2$ and $1s^2np^5$ configurations, respectively, giving rise as usual to a sudden increase of the lifetimes. The results reported in figure 4 confirm that the shortest lifetime is always obtained for the neutral configurations but also show that the lifetime increases in stages with n . We expect this behaviour to be the same for even higher n values until the moment when the difference in energy between the different limits becomes so small that a smooth change with n will appear.

The lifetimes behave in the same way as well for other systems. In figure 5, we show the lifetimes of the $1snp^6$ configurations with $n = 2-14$ for Ar^{11+} . We have chosen this system because Ar ions have been used in several recent experiments (Donets 1985, Briand *et al* 1990, Schulz *et al* 1991, Briand 1993, d'Etat *et al* 1993). The figure shows exactly the same pattern although the increase of the lifetime with n does not occur for the same n values. For the $n = 2$ configuration, the super Coster-Kronig channel to $1s2s2p^4$ is not open so that $1s2p^6$ can only decay to the $1s^22p^4$ limit which explains the long lifetime obtained for this configuration.

5. Other configurations

One of the motivations behind this work is to provide autoionization rates which can help to understand the mechanisms involved in the creation and de-excitation of the hollow atoms populated when highly-charged ions approach a surface. In this type of experiment the ion is very slow and therefore we expect that mainly configurations with small angular momenta are populated. However, we must also consider that a distribution in ℓ values is possible.

We have calculated the lifetimes of the $1s(3\ell)^6$ and $1s(5\ell)^6$ configurations with different values of ℓ . The results are shown in table 3. All the lifetimes are of the same order of magnitude, the largest difference (a factor of 2) is found between the $1s3p^6$ and the $1s3d^6$ configurations. Since no $d \rightarrow d$ transition is possible in this case, the short lifetime for the $1s3d^5$ configuration is noteworthy. The same behaviour is obtained for the $1s(5\ell)^6$ configurations of which $1s5d^6$ also has the longest lifetime although the variation with ℓ is smaller in this case, as could be expected since $d \rightarrow d$ transitions are now possible.

Table 3. Lifetimes for the $1s(3\ell)^6$ and $1s(5\ell)^6$ configurations in nitrogen with different values of ℓ . The table shows the initial $1s(3\ell)^6$ and $1s(5\ell)^6$ configurations, the final configurations, the summation over all calculated autoionization rates (A^a in s^{-1}) weighted by the degeneracy of the levels in the initial configuration g and an upper limit to the average lifetime τ in s.

Initial configuration		Final configurations	$\sum gA^a$	τ
$1s3s^23p^4$	$\rightarrow$	$1s2\ell(3\ell)^4$	6.05×10^{16}	5.0×10^{-16}
$1s3s3p^5$	$\rightarrow$	$1s2\ell(3\ell)^4$	5.17×10^{16}	4.6×10^{-16}
$1s3p^6$	$\rightarrow$	$1s2\ell(3\ell)^4$	4.62×10^{15}	4.3×10^{-16}
$1s3d^6$	$\rightarrow$	$1s2\ell(3\ell)^4$	4.94×10^{17}	8.5×10^{-16}
$1s5s^25p^4$	$\rightarrow$	$1s4\ell(5\ell)^4$	7.14×10^{16}	3.9×10^{-16}
	$\rightarrow$	$1s3\ell(5\ell)^4$	5.61×10^{15}	
	$\rightarrow$	$1s2\ell(5\ell)^4$	8.25×10^{14}	
	$\rightarrow$	$1s4\ell(5\ell)^4$	5.79×10^{16}	
$1s5s5p^5$	$\rightarrow$	$1s3\ell(5\ell)^4$	4.64×10^{15}	3.8×10^{-16}
	$\rightarrow$	$1s2\ell(5\ell)^4$	7.21×10^{14}	
	$\rightarrow$	$1s4\ell(5\ell)^4$	4.72×10^{15}	
	$\rightarrow$	$1s3\ell(5\ell)^4$	3.85×10^{14}	
$1s5p^6$	$\rightarrow$	$1s2\ell(5\ell)^4$	6.69×10^{13}	3.9×10^{-16}
	$\rightarrow$	$1s4\ell(5\ell)^4$	7.00×10^{17}	
	$\rightarrow$	$1s3\ell(5\ell)^4$	6.67×10^{16}	
	$\rightarrow$	$1s2\ell(5\ell)^4$	9.57×10^{15}	

A reason for considering in some detail the decay probabilities for the different $1s(5\ell)^N$ configurations is that it has been proposed by Andra *et al* (1992) that in neon these particular configurations are populated by a 'screening dynamics' effect (SD) corresponding to a successive transfer of the initial resonant population of the n manifold into the $n-1$ manifold during the first part of the approach of the ion to the surface. (A similar mechanism has been discussed by Aumayr and Winter (1994).) These SD cycles stop at a characteristic value n' . In the case of Ne^{9+} interacting with a conducting surface n' was estimated to be equal to 5. The $1s(5\ell)^N$ configurations are then the starting point of the Auger cascades filling the M, L and K shells and are responsible for an important part of the observed secondary electron yield. Keeping the variation in n' as a function of the nuclear charge in mind, for N^{6+} ions we can expect that the initial configurations will have $n' = 5$ or 4. This process is important because a straightforward extrapolation of the Hagstrum model (1954) predicts that the initial transfer takes place to levels which have such large n values

(n larger than 20 in the case of Ar^{17+}) that the de-excitation times are expected to be longer than the time needed to reach the surface as discussed for Ar^{17+} by d'Etat *et al* (1993).

In order to obtain an estimate of the lifetimes of the intermediate states in the Auger cascades populated in such a scheme, we have considered the following decays:

$1s5p^6$	Lifetime $= 3.94 \times 10^{-16}$ s
↓	
$1s4p5p^4$	Yield 80%
↓	
$1s4p5p^5$	Pick-up of a 5p electron, lifetime $= 1.02 \times 10^{-15}$ s
↓	
$1s4p^25p^3$	Yield 80%
↓	
$1s4p^25p^4$	Pick-up of a second 5p electron, lifetime $= 2.02 \times 10^{-15}$ s
↓	
$1s3p5p^4$	Yield 50%
↓	
⋮	

The yields shown are a measure of how much of the initial configuration will decay to the configuration shown. Not all possible decays have been included so yields and lifetimes are approximate but all configurations shown have a lifetime shorter than 3×10^{-15} s. d'Etat *et al* (1993) have pointed out that transitions of electrons in the outermost shell are likely to be the most probable decay mode until that shell is more or less empty: in the present case another $5p \rightarrow 4p$ transition. The inference was that the first $4p \rightarrow 3p$ transition will occur only after the 4p shell is reasonably full. This leads to a rather large number of time steps before the first electron arrives in the $n = 3$ shell which would slow up the filling of the inner shells. The result above (for another case) does not completely confirm this scenario. Already in the second decay, there is a 20% probability for a transition to 3p instead of 4p and the third decay has a branching ratio of nearly 50% with the rest going into the $n = 4$ shell. Despite this the results illustrate the difficulty involved in filling the lower shells in the available time.

We have also considered some configurations with mixed values of n such as $1s(5\ell)^2(6\ell)^2(7\ell)^2$. We obtain lifetimes of 4.63×10^{-15} s for the $1s5s^26s^27p^2$ configuration and 6.41×10^{-15} s for the $1s5s^26s^27s^2$ configuration (we note that this state is strongly mixed with the $1s5p^26s^27s^2$ 2S state and that this mixing might be responsible for a shortening of the lifetime). We therefore conclude that the typical lifetime of configurations with mixed values of n is, in most cases, shorter than 5×10^{-15} s when n lies between 3 and 7 where the primary decay usually consists of an electron jump with the smallest Δn consistent with energy conservation.

6. Correlation effects

We have already published a study of the properties of the $(3\ell)^3$ states in N^{4+} and the $1s^2(3\ell)^3$ states in N^{2+} using a CI approach (Vaeck and Hansen 1991b, 1992a). Our basis set included all the configurations of the Layzer complex (Layzer 1959) as well as some $(3\ell)^24\ell'$ configurations. The autoionization rates to the $2\ell3\ell'$ limits were calculated for each of the 64 states of the $(3\ell)^3$ manifold for both ions and the results show that the dispersion of the autoionization rates is very small, i.e. the total variation between the fastest and the

slowest decay rate is a factor of 8 for N^{2+} and about 15 for N^{4+} . Moreover, when the CI values of the autoionization rates are averaged over the entire configuration and compared with the average decay rates calculated from (1), the agreement between both sets of values is good. This was the original justification for performing average calculations in this work.

In order to check the importance of the correlation effects on the decay properties of the multiply-excited states considered here we have made similar CI calculations using a Hartree-Fock basis set limited to the Layzer complex. However, even restricting the basis to the complex, the number of configurations increases dramatically with n and N . For example, the Layzer complex for the even parity $1s^2(3\ell)^2$ states contains only four configurations while in contrast 16 configurations constitute the complex for the even parity $1s^2(7\ell)^2$ states due to the increase in the number of possible ℓ values. In addition, when the 4ℓ shell is occupied by two electrons six configurations of even parity belong to the complex, while with four electrons in the same shell 17 even configurations are possible.

A special problem appears when the multiply-excited states are located just below a threshold. Then the states interact with high members of those Rydberg series which converge to the threshold. This situation has been studied in detail for the $(4\ell)^2$ states interacting with the $3\ell n\ell'$ Rydberg series in N^{5+} , O^{6+} and Ne^{8+} (van der Hart *et al* 1994, 1995, van der Hart and Hansen 1994). It was shown that this interaction strongly modifies the decay properties of those $(4\ell)^2$ states which lie in the range of energy where the Rydberg states are very dense, on average the effect being an increase in the radiative decay rates for these states (Roncin *et al* 1991, van der Hart *et al* 1994, 1995), while for individual terms the effect can be either an increase or a decrease in the decay rates (van der Hart *et al* 1994, 1995).

In the following we evaluate the effect of correlation on the autoionization rate of the $1s^2 4p^N$ configurations. This appears to be the first attempt to include correlation in the calculation of autoionization rates for multiply-excited states with more than three excited electrons. The correlation effects are much more significant for hollow atoms since the absence of a core means that the different configurations within the complex are more closely degenerate than in a normal atom where screening by the core electrons leads to a larger difference between the single-particle energies. Also the correlation effects in the complex become more important when n increases. For instance, the two $^3P^o$ states of the $1s^2(3\ell)^2$ configurations are both 96% pure in $3s3p$ and $3d3p$ character, respectively. On the other hand, the dominant eigenvector component of the six $1s^2(7\ell)^2$ $^3P^o$ terms are [82%]7s7p, [50%]7d7f, [45%]7f7g, [42%]7g7h, [52%]7h7i and [33%]7g7h, the mixing being so strong that no state is dominantly 7d7p.

The method of calculation is described in our earlier paper (Vaeck and Hansen 1992a). In brief, CI is introduced in the initial state via a HF basis set. The basis sets are usually limited to the configurations belonging to the Layzer complex but sometimes further restrictions had to be made as described in connection with the individual cases. Autoionization rates to the accessible limits are calculated separately making use of Fermi's golden rule (Cowan 1981, chapter 18) without including the coupling between degenerate continuum states. (The same procedure is used for the single-configuration calculations discussed earlier.) This is expected to be a satisfactory approximation (Martín *et al* 1989), in particular for a several times ionized system, when total decay rates are considered.

6.1. Doubly-excited states

We do not expect the doubly-excited states to show a statistical behaviour. Indeed, all studies of doubly-excited states agree on the large spread of the autoionization rates inside

Table 4. Autoionization decay rates (A^a in s^{-1}) of the $1s^2(4\ell)^2\ ^1S$ states to the $1s^2(2, 3)\ell$ limits in N^{3+} . The notation $n\ ^1S$ corresponds to an ordering according to energy ($n = 1$ being the lowest).

Limit	1 1S	2 1S	3 1S	4 1S
2s	8.54×10^{12}	1.20×10^{13}	1.69×10^{11}	5.81×10^{10}
2p	1.21×10^{12}	7.89×10^{13}	1.82×10^{11}	7.29×10^{10}
3s	—	5.29×10^{13}	1.17×10^{14}	4.96×10^{12}
3p	—	—	4.16×10^{14}	3.43×10^{12}
3d	—	—	8.48×10^{14}	2.36×10^{13}
Total	9.75×10^{12}	1.44×10^{14}	1.38×10^{15}	3.21×10^{13}

a manifold. For instance, the difference between the fastest and the slowest autoionization decay rate for the $1s^2(3\ell)^2$ states in N^{3+} is a factor 15 000 (Vaeck and Hansen 1989).

Of the four $1s^2(4\ell)^2\ ^1S$ states of N^{3+} , the lowest state is dominantly $4s^2$ (82%) and is located below the 3s limit of N^{4+} . The second state has 52% $4d^2$ character and 37% $4p^2$. It is located between the 3s and the 3p limits. Finally, the two highest states lie above the $N = 3$ thresholds; the third state being dominant (58%) $4f^2$ while the highest one is severely mixed (39% $4f^2$, 36% $4d^2$ and 20% $4p^2$). The autoionization rates of these states, shown in table 4, are dominated by their location relative to the $N = 3$ limits.

If we compare the decays to the $N = 2$ limits, which are common to all states, the decay rate of the highest 1S state is between one and three orders of magnitude smaller than the rates for the other three 1S states. The same behaviour has been found for the highest 1S states in the $(2\ell)^2$ and $(3\ell)^2$ manifold labelled $2p^2\ ^1S$ and $3d^2\ ^1S$, respectively. These states have been termed anti-Wannier states because the two electrons are found preferentially on the same side of the atom. In our calculation, the opening of the decay channel to $N = 3$ limits leads to a large increase of the total autoionization rate of this state. It nevertheless remains the state with the smallest decay rate of the three states which are energetically allowed to decay to the $N = 3$ limits. We note that the two lowest 1S states can interact with the $3\ell n\ell'$ Rydberg states which can modify their eigenvectors and therefore their decay properties. On the other hand, the Layzer complex is probably a good approximation for the two upper states.

6.2. Triply-excited states

The $1s^24p^3$ configuration gives rise to a $^4S^o$, a $^2P^o$ and a $^2D^o$ state. We have performed a CI calculation for these three symmetries using a basis set which includes the ten odd configurations in the Layzer complex. As expected from our previous work on the triply-excited $1s^2(3\ell)^3$ states (Vaeck and Hansen 1991b, 1992a) the mixing between the configurations of the complex is very strong, so strong in fact that it is nearly impossible to give a mono-configurational label to the states. The eigenvectors of the states with a $4p^3$ component of more than 12% are given in table 5 together with the autoionization rates. When possible, the corresponding $1s^2(3\ell)^3$ eigenvectors and autoionization rates are given for comparison. The table shows that, as already mentioned, the mixing in the Layzer complex increases with n . There are two reasons for this. Firstly, the increase of the number of states (for example, there are seven $^2P^o$ states in the $1s^2(3\ell)^3$ manifold compared to 17 in the $1s^2(4\ell)^3$ manifold) and secondly, the differences in energy between the states of the complex decrease with n (the $^2P^o$ states are spread over 17.5 eV for the $1s^2(3\ell)^3$ and over

Table 5. Eigenvectors and autoionization rates (A^a in s^{-1}) of the $1s^2(4\ell)^3\ 4S^o$, $2P^o$ and $2D^o$ states in N^{2+} with a percentage of $4p^3$ character larger than 12%. Only contributions of more than 10% are given and the states are arranged according to symmetry and within a given symmetry according to energy. The mono-configurational label given to the state is in most of the cases insignificant due to the strong mixing discussed in the text. The eigenvectors and autoionization rates for the $1s^2(3\ell)^3$ states (Vaeck and Hansen 1992a) are given for comparison when possible.

Label	Symmetry	Eigenvector	A^a
$4p^3$	$4S^o$:	$0.858\ 4p^3 + 0.480\ 4d^2\ ^3P\ ^1J4p$	5.53×10^{14}
$3p^3$	$4S^o$:	$0.936\ 3p^3 + 0.350\ 3d^2\ ^3P\ ^3P$	7.64×10^{14}
$4d^2\ ^3P\ ^1J4p$	$4S^o$:	$0.623\ 4d^2\ ^3P\ ^1J4p + 0.501\ 4d^2\ ^3F\ ^1J4f - 0.456\ 4p^3 + 0.322\ 4f^2\ ^3P\ ^1J4p$	9.14×10^{14}
$3d^2\ ^3P\ ^3P$	$4S^o$:	$0.918\ 3d^2\ ^3P\ ^3P - 0.350\ 3p^3$	2.34×10^{14}
$4p^3$	$2P^o$:	$0.535\ 4s4p\ ^3P\ ^1J4d - 0.522\ 4p^3 + 0.422\ 4s4p\ ^1P\ ^1J4d - 0.332\ 4d^2\ ^1S\ ^1J4p$	8.00×10^{14}
$3p^3$	$2P^o$:	$0.596\ 3p^3 + 0.562\ 3s3p\ ^3P\ ^3D + 0.468\ 3s3p\ ^1P\ ^3D - 0.264\ 3d^2\ ^1S\ ^3P$	8.57×10^{14}
$4s4p\ ^3P\ ^1J4d$	$2P^o$:	$0.557\ 4s4p\ ^3P\ ^1J4d + 0.407\ 4p^3 + 0.388\ 4s4p\ ^3D\ ^1J4f + 0.333\ 4d^2\ ^1S\ ^1J4p$	1.06×10^{15}
$3s3p\ ^3P\ ^3D$	$2P^o$:	$0.443\ 3s3p\ ^3P\ ^3D + 0.549\ 3p^3 - 0.435\ 3d^2\ ^1D\ ^3P + 0.328\ 3s3p\ ^1P\ ^3D$	8.42×10^{14}
$4s4p\ ^3P\ ^1J4d$	$2D^o$:	$0.822\ 4s4p\ ^3P\ ^1J4d + 0.465\ 4p^3$	4.52×10^{14}
$3s3p\ ^3P\ ^3D$	$2D^o$:	$0.855\ 3s3p\ ^3P\ ^3D + 0.481\ 3p^3$	5.31×10^{14}
$4s4p\ ^1P\ ^1J4d$	$2D^o$:	$0.638\ 4s4p\ ^1P\ ^1J4d + 0.474\ 4p^3 + 0.344\ 4d^2\ ^1D\ ^1J4p + 0.326\ 4d^2\ ^3F\ ^1J4p$	5.73×10^{14}
$3s3p\ ^1P\ ^3D$	$2D^o$:	$0.700\ 3s3p\ ^1P\ ^3D + 0.527\ 3p^3 + 0.291\ 3d^2\ ^1D\ ^3P + 0.272\ 3d^2\ ^3F\ ^3P$	7.03×10^{14}
$4p^3$	$2D^o$:	$0.435\ 4p^3\ ^3P\ ^1J4f + 0.414\ 4p^2\ ^1D\ ^1J4f + 0.397\ 4s4p\ ^1P\ ^1J4d - 0.385\ 4p^3 + 0.357\ 4d^2\ ^3P\ ^1J4p$	8.66×10^{14}
$3p^3$	$2D^o$:	$0.535\ 3p^3 - 0.483\ 3d^2\ ^3P\ ^3P - 0.478\ 3s3p\ ^1P\ ^3D + 0.434\ 3d^2\ ^1D\ ^3P$	6.24×10^{14}
$4d^2\ ^1D\ ^1J4f$	$2D^o$:	$0.463\ 4d^2\ ^1D\ ^1J4f + 0.354\ 4p^3$	8.01×10^{14}

Table 6. Eigenvectors and autoionization rates (A^a in s^{-1}) of the $1s^2(4\ell)^4$ $1S^e$, $3P^e$ and $1D^e$ states in N^+ with a percentage of $4p^4$ character larger than 12%. Only contributions of more than 10% are given and the states are arranged according to symmetry and within a given symmetry according to energy.

Symmetry	Eigenvector	A^a
$1S^e$:	$0.720\ 4s^2 4p^2 + 0.448\ 4s^2 4d^2 + 0.403\ 4p^4$	1.09×10^{15}
$1S^e$:	$0.515\ 4p^4 - 0.468\ 4s^2 4d^2 - 0.372\ 4p^2[1D]4d^2$	1.63×10^{15}
$3P^e$:	$0.534\ 4s^2 4d^2 + 0.415\ 4p^4 + 0.394\ 4p^2[1D]4s4d$	1.27×10^{15}
$3P^e$:	$-0.441\ 4s^2 4d^2 + 0.436\ 4p^2[3P]4s[2P]4p + 0.370\ 4p^4 - 0.327\ 4p^2[3P]4s[2P]4d$	1.24×10^{15}
$1D^e$:	$0.597\ 4p^2[1D]4s4d - 0.403\ 4p^4 + 0.374\ 4s^2 4d^2$	1.13×10^{15}
$1D^e$:	$0.525\ 4s^2 4d^2 - 0.369\ 4s^2 4p4f + 0.367\ 4p^4$	1.16×10^{15}

only 13.1 eV for the $1s^2(4\ell)^3$ configurations). All the interactions already present in the $(3\ell)^3$ states of table 5 are also found in the corresponding $(4\ell)^3$ eigenvectors but in the latter the number of perturbers increase because of the appearance of configurations with one or two electrons in the 4f orbital.

The $1s^2(4\ell)^3$ states lie above the $1s^2 3\ell 4\ell'$ limits and their decay properties are dominated by the autoionization to these thresholds. We have calculated the autoionization decay rates of the $4S^o$, $2P^o$ and $2D^o$ states to all possible $1s^2 3\ell 4\ell'$ limits but neglecting the mixing between the limits. The average autoionization decay rate of the $1s^2 4p^3$ configuration to the $3\ell 4\ell'$ states is $7.06 \times 10^{14}\ s^{-1}$ which is in very good agreement with the rate averaged over the three $4p^3$ terms given in table 5 ($7.84 \times 10^{14}\ s^{-1}$). Moreover, the slowest decay ($2.85 \times 10^{14}\ s^{-1}$) has been obtained for the $4d^2[3F]4f\ 4S^o$ state and the fastest decay ($1.06 \times 10^{15}\ s^{-1}$) for both $4s4p[3P]4d\ 2P^o$ and $4f^3\ 2D^o$ which corresponds to a factor of 4 difference to be compared with a factor of 5 between the slowest and the fastest decay among the three symmetries of the $1s^2(3\ell)^3$ manifold.

6.3. Quadruply-excited states

There are 25 $1S^e$, 63 $3P^e$ and 66 $1D^e$ states in the $1s^2(4\ell)^4$ complex (for simplicity we have neglected the $1s^2 4f^4$ configuration). Among those, 13 $1S^e$, 49 $3P^e$ and 58 $1D^e$ states have a leading eigenvector component less than 20%. Moreover, in the $1D^e$ symmetry, which is the most strongly mixed of the three, 18 states have a dominant component of less than 10%. The purest configuration is $4s^2 4p^2$ which is dominant in the lowest $1S$ (52%), the lowest $1D$ (60%) and the lowest $3P$ term (64%). The leading eigenvector component of the states with a $4p^4$ character of more than 12% are given in table 6. Only two states of each symmetry have more than 12% $4p^4$ character and none of them except the second $1S^e$ state (i.e. the third lowest $1S^e$ state of the entire complex) is really dominant $4p^4$. It is also interesting to note that one of the main components of all six eigenvectors belongs to the $4s^2 4d^2$ configuration which, in fact, represent a quadruple excitation from $4p^4$ and only interact with $4p^4$ via intermediate configurations like for instance $4s^2 4p^2$. It therefore has a second-order effect on the wavefunction and from this point of view the importance of the $4s^2 4d^2$ component in all the eigenvectors of table 6 is surprising. The same second-order interaction already appeared in the eigenvectors of the triply-excited states (table 5) but only for some states which illustrates the increase in the importance of correlation with N .

The $1s^2(4\ell)^4$ configurations are located above the $1s^2(4\ell)^2 3\ell'$ limits. To calculate the autoionization probabilities for the $1S^e$, $3P^e$ and $1D^e$ states we have taken into account

Table 7. Eigenvectors and autoionization rates (A^a in s^{-1}) of the $1s^2(4\ell)^5\ ^2P^o$ states in neutral nitrogen with a percentage of $4p^5$ character larger than 8%. Only contributions of more than 8% are given and the states are arranged according to symmetry and within a given symmetry according to energy.

Symmetry	Eigenvector	A^a
$^2P^o$:	$0.671\ 4s^24p^3 + 0.351\ 4p^5 + 0.298\ 4s^24p4d^2[{}^1S] + 0.291\ 4s4p^3[{}^2D]({}^3D)4d$	1.50×10^{15}
$^2P^o$:	$0.535\ 4s4p^3[{}^2D]({}^3D)4d - 0.428\ 4s^24p^3 + 0.291\ 4p^5$	1.73×10^{15}
$^2P^o$:	$0.388\ 4p^5 + 0.326\ 4s^24p4d^2[{}^1D] + 0.309\ 4p^3[{}^2D]4d^2[{}^2D] + 0.295\ 4s4p^3[{}^2D]({}^1D)4d$	1.68×10^{15}
$^2P^o$:	$0.296\ 4p^5 - 0.293\ 4p^4[{}^1D]4f$	1.70×10^{15}

all the 30 possible limits since there is a high degree of mixing in the wavefunctions of the decaying states. Again we have neglected the interaction between the limits. The total autoionization rates are given in table 6. The autoionization rates in table 6 are very similar, the ratio between the largest and the smallest decay rate is only 1.5. Moreover, we have checked a number of other states and find autoionization rates of the same size. The decay rate averaged over the states included in table 6 is 1.22×10^{15} to be compared with the configuration average result, 1.24×10^{15} obtained by considering only the three $4p^23\ell$ limits. Of course we do not expect this excellent agreement between the two sets of results for all configurations but this result again confirms that the average autoionization rate reflects the properties of each individual state to a good approximation.

6.4. Quintuply-excited states

A complete treatment of the $1s^24p^5\ ^2P^o$ state in neutral nitrogen is beyond our present computational capabilities even if the basis set is restricted to the Layzer complex. There are 234 $^2P^o$ states in the complex belonging to 24 different configurations. We have included all the configurations constructed from single ($4p^44f$) and double excitations ($4s^24p^3$, $4p^34d^2$, $4p^34f^2$ and $4s4p^34d$) from $4p^5$. We have also included all the configurations in the Layzer complex which have a component larger than 1.2% in the eigenvectors of the states for which the $4p^5$ character is larger than 4%. Because of the extent of the mixing, only seven configurations can be neglected, i.e. $4s4p4d4f^2$, $4d^44f$, $4p4d^24f^2$ and the four $4f^3(4\ell)^2$ configurations. We have also excluded the $4f^5$ and $4f^44p$ configurations, leaving 95 $^2P^o$ states. The mixing is so strong that 81 states have a leading component smaller than 15% and, in fact, for 46 states the leading component is smaller than 10%. The mixings are even larger if all the $^2P^o$ states of the complex are included in the calculation. In table 7, the eigenvectors of those states which have more than 8% $4p^5$ character are shown.

To calculate the autoionization rates of the $^2P^o$ states described by a superposition of only 95 configuration functions, we need to consider the decay to 51 $1s^2(4\ell)^33\ell$ limits. These rates are given in table 7. The ratio between the smallest and the largest decay rates is only 1.15 and the average value is $1.65 \times 10^{15}\ s^{-1}$ to be compared with $1.67 \times 10^{15}\ s^{-1}$ from the average calculation to the $4p^33\ell$ limits. We note that this comparison (as well as the previous ones) is somewhat arbitrary due to the somewhat arbitrary selection criteria for the terms included in tables 5–7. Table 7, for example, includes only 45% of the total $4p^5$ character which on the other hand illustrates the severity of the mixing since no term with more than 8% $4p^5$ character has been omitted.

Nevertheless, the results support our previous conclusions (Vaeck and Hansen 1992a) that not only are the average autoionization rates a good approximation to the decay

rates of the multiply-excited states but the autoionization rates are also very similar for all the members of the manifold we have considered and therefore for different types of configurations which agrees with the results shown in table 3.

7. Other theoretical results on hollow atoms

Very few theoretical studies have been performed concerning hollow atoms. In the past some work has been carried out on ions with two vacancies in the 1s shell sometimes in combination with holes in the $n = 2$ shell. Such ions can be obtained in ion-atom collisions and their decay properties have been studied in some detail (Gavrila and Hansen 1978 and references therein, Omar and Hahn 1991). The light ions are particularly interesting as model systems for the study of electron correlation and this has led to a number of studies in the past. For example, the observation of triply-excited states in atomic lithium (Kuyatt *et al* 1965, Bruch *et al* 1975, Rødbro *et al* 1979, Agentoft *et al* 1984, Mannervik *et al* 1989, Müller *et al* 1989) has resulted in a number of theoretical studies (Ahmed and Lipsky 1975, Nicolaides and Beck 1977, Safronova and Senashenko 1978, Simons *et al* 1979, Chung 1982). Recently the autoionization width of the $2s^2 2p^2 P^o$ state in Li has been measured (Kiernan *et al* 1994) and more work on such systems is expected.

In contrast, studies of systems with several empty inner shells are very scarce indeed. The study of neutralization processes of ions at surfaces is the origin of the recent interest in such systems. For nitrogen ions, a calculation of the Auger decays of multiply-excited states has been carried out by Zeijlmans van Emmichoven *et al* (1991) which was used in a simulation of the population of the different n levels during the neutralization of N^{6+} ions on a Cu(100) surface. The authors use the same approach as us but they do not give any information about the type of configuration they have considered and only the n values of the initial and final shells as well as the number of electrons in these shells are reported. When comparison is possible, our values are of the same order of magnitude as the results of Zeijlmans van Emmichoven *et al*, the main difference being that these authors did not consider the decay of $1s(7\ell)^6$ to the $1s6\ell(7\ell)^4$ limits or the decay channel $1s(5\ell)^5 \rightarrow 1s4\ell(5\ell)^3$. As we pointed out already (Vaeck and Hansen 1992b), the effect of the inclusion of these decays in the model of Zeijlmans van Emmichoven *et al* (1991) is not obvious because, although the rates are much faster, two additional steps have been introduced in the cascade namely $n = 7 \rightarrow n = 6$ and $n = 5 \rightarrow n = 4$.

Other simulations based on the classical over-barrier model, originally developed for one-electron capture by highly charged ions during ion-atom collisions (Bárány *et al* 1985, Niehaus 1986), have been used to describe above-surface charge exchange and relaxation processes (Burgdörfer *et al* 1991, Burgdörfer and Meyer 1993, Meyer *et al* 1993). Auger rates are used in the simulations but were not reported in the papers.

The latter is the case in the work of d'Etat *et al* (1993) on the neutralization of Ar^{17+} on metallic surfaces. This work contains results of detailed Dirac-Fock calculations of Auger rates for hollow Ar atoms with 5 or 17 electrons distributed in the shells $n = 10, 6, 4$ and 3 in a single-configuration approximation. (A few results were reported in an earlier letter (Briand *et al* 1990).) Based on extensive calculations these authors were able to draw some general conclusions about the behaviour of the Auger rates of hollow atoms which are closely similar to ours. It was, for example, found that the Auger rates depend mainly on the n value and not on the J quantum number of the state under consideration. This is in agreement with the conclusion in section 6 that the autoionization rates are largely the same for an entire manifold and depend very weakly on the type of configuration. d'Etat *et al* also confirmed that the fastest autoionization

rates generally occur when the kinetic energy of the free electron is minimal, thus for transitions with Δn minimum. Similarly, they observed an angular dependence which favours the transitions $\Delta \ell = 0$, for example the transitions $s \rightarrow s$ or $p \rightarrow p$, in agreement with the angular dependence described in section 3.4. Finally, d'Etat *et al* noticed a large increase in the autoionization rates as a function of the number of electrons in a specific n shell when the limit corresponding to the minimum Δn becomes energetically allowed. Also this is in agreement with the jump from the 'slow' to the 'fast' curves reported here.

d'Etat *et al* (1993) report Auger rates for the transitions $1sns^2np^2 \rightarrow 1sn'snp^2$ in Ar^{13+} and $1sns^2np^6nd^8 \rightarrow 1sn'snp^6nd^8$ in Ar^+ where $n = 3, 4, 6$ and 10 . We have compared these results with our values for the transitions $1snp^6 \rightarrow 1sn'pnp^4$ in Ar^{11+} . The results of d'Etat *et al* are obtained by calculating the decay $s \rightarrow s$. The rates are reported 'per electron' and the total rates are obtained by multiplying by the number of electrons assuming that p and d electrons give similar contributions which agrees with our explicit results (for nitrogen) in table 3. Except for the $n = 3$ states for which the decay to $n = 2$ is the only possibility for both the 5 and 17 electrons states, the Auger rates of d'Etat *et al* for Ar^{13+} are roughly an order of magnitude smaller per electron than the rates for Ar^+ . In other words, the lifetimes of the five-electron states are lying on a 'slow' and the lifetimes of the 17-electron states on a 'fast' curve. This means that to compare results with the same Δn value we must compare our results for Ar^{11+} with the values for Ar^{13+} for $n = 6$ and 10 (i.e. $4.5 \times 10^{13} s^{-1}$ and $1.0 \times 10^{13} s^{-1}$ compared to $1.7 \times 10^{13} s^{-1}$ and $4.3 \times 10^{12} s^{-1}$) and to the results for Ar^+ for $n = 3$ and 4 (i.e. $6.2 \times 10^{14} s^{-1}$ and $5.2 \times 10^{14} s^{-1}$ compared to $9.4 \times 10^{13} s^{-1}$ and $1.1 \times 10^{14} s^{-1}$). (Our results are also given 'per electron' i.e. average rates (equation (1)) divided by six: the number of electrons in the initial state that participates in the decay.) Thus our results are from two to nearly seven times larger per electron than the values of d'Etat *et al*. To understand the reason for the difference we have calculated the autoionization rates for (i) the $1sns^2np^2 \rightarrow 1sn'snp^2$, (ii) the $1sns^2np^2 \rightarrow 1sn'pns^2$ and (iii) the $1snp^4 \rightarrow 1sn'pnp^2$ transitions in Ar^{13+} for $n = 3, 6$ and 10 . The autoionization rates per electron in (i) ($s \rightarrow s$) are somewhat smaller than the values of d'Etat *et al*. We obtain $0.9 \times 10^{14} s^{-1}$, $0.9 \times 10^{13} s^{-1}$ and $2.2 \times 10^{12} s^{-1}$ for $n = 3, 6$ and 10 , respectively, to be compared with $1.4 \times 10^{14} s^{-1}$, $1.8 \times 10^{13} s^{-1}$ and $4.7 \times 10^{12} s^{-1}$ reported by d'Etat *et al*. The rates per electron for type (ii) transitions ($p \rightarrow p$) are very similar to case (i) (1.4×10^{14} , 1.0×10^{13} and $2.3 \times 10^{12} s^{-1}$ for $n = 3, 6$ and 10 , respectively) vindicating the assumption of d'Etat *et al*. However, in case (iii) the rates per electron are larger (4.0×10^{14} , 3.0×10^{13} and $6.5 \times 10^{12} s^{-1}$ for $n = 3, 6$ and 10 , respectively) although the radial integrals involved in the two cases, (ii) and (iii), are of the same type ($R^{0,2}(np, np; n'p, \epsilon \ell)$ with $\ell = p$ and f) and, in fact, also numerically very similar ($R^0 = 0.481$ and $R^2 = 0.471$ for the decay of $1s10s^210p^2$ with a continuum p electron compared to $R^0 = 0.480$ and $R^2 = 0.483$ for the decay of $1s10p^4$). The difference between (ii) and (iii) thus comes from the difference in the number of limits which are allowed in the decay of these configurations. Considering the decay with an ϵp continuum electron, there are seven possible $1sn'pns^2\epsilon p$ final states to which the $1sns^2np^2$ configuration can decay. On the other hand, the $1snp^4$ configuration can decay to 48 different $1sn'pnp^2\epsilon p$ states. This explains why in a mono-configurational approach the lifetime of the $1snp^4$ configuration is shorter by one order of magnitude than the lifetime of $1sns^2np^2$. However, the mixing between configurations due to the correlation in the $1sns^2np^2$ states (see table 6) is important and will lead to the opening of a large number of additional decay channels thereby shortening the lifetime of the $1sns^2np^2$ states. We conclude that the configurations used to model the decay rate by d'Etat *et al* (1993)

probably lead to lifetimes that are somewhat longer than would be obtained by a calculation including configuration interaction. Only two examples of total rates are given in the work of d'Etat *et al* (1993) and we note that both lead to lifetimes which are slightly longer than our estimates.

8. Conclusions

We have calculated upper limits for the lifetimes of hollow nitrogen atoms in configurations of the type $1s^M np^N$ with $M = 0-2$, $n = 2-7$, 10 and $N = 2-6$. We have shown that these lifetimes follow very regular patterns as a function of N . For each n value, the lifetimes decrease with N following a 'slow' curve. At a certain n value, they jump to a 'fast' curve when the transition with minimal Δn becomes energetically allowed. The fastest lifetimes are found for the neutral system for all n values. For $n = 3-7$, this lifetime is typically of the order of 3 to 6×10^{-16} s.

We have shown that the lifetime increase 'in stages' with n . Already for $n = 8$ in nitrogen ions, the lifetimes are nearly one order of magnitude longer than for $n = 7$. We believe that the behaviour described above is valid for a larger range of ions and indeed we found the same increase 'in stages' with n for the lifetimes of Ar^{11+} with six electrons in the outer n shell.

In the $1s^2 4p^N$ sequence ($N = 2-5$) we have checked the influence of correlation on the autoionization rates and found that although the mixing between configurations in these multiply-excited states increases dramatically with N , the effect on the autoionization rates is small reflecting the fact that nearly all the configurations within a manifold have very similar lifetimes although some exceptions exist as we have discussed for Ar.

In this work we have only considered non-radiative decay but it is not clear that it is possible to entirely neglect radiative decay. Although this probably is a good approximation in nitrogen, it clearly is less justified for high degrees of ionization. In fact, several groups have observed x-rays in experiments with Ar^{17+} (Donets 1985, Briand *et al* 1990, Schulz *et al* 1991) and even in Ne radiative decay has been reported (Bonnet *et al* 1991).

To conclude we would like to draw attention to the fact that knowledge of the decay properties of hollow atoms is becoming important for other fields of research. Indeed, it has become clear recently that in collision experiments between highly charged ions and neutral atomic or molecular targets, hollow atoms can be created by virtue of multiple charge-transfer processes from the target to excited states of the projectile and in this case theoretical data is urgently needed as well. This work should be considered as a start towards providing such data.

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References

- Agentoft M, Andersen T and Chung K T 1984 *J. Phys. B: At. Mol. Phys.* **17** L433-8
- Ahmed M and Lipsky L 1975 *Phys. Rev. A* **12** 1176-96
- Andrä H J *et al* 1992 *Electronic and Atomic Collisions, Proc. XVII ICPEAC (Brisbane)* ed W R MacGillivray *et al* (Bristol: Hilger) pp 89-104
- Aumayr F, Kurz H, Töglhofer K and Winter H P 1993 *VI Int. Conf. on the Physics of Highly Charged Ions (AIP Conf. Proc. 274)* ed P Richard *et al* (New York: AIP) pp 573-82
- Aumayr F and Winter H P 1994 *Comments At. Mol. Phys.* **29** 275-303
- Bárány A, Astner G, Cederquist H, Danared H, Hult S, Hvelplund P, Johnson A, Knudsen H, Liljeby L and Rensfelt K-G 1985 *Nucl. Instrum. Methods B* **9** 397-9
- Bonnet J J, Fleury A, Bonnefoy M, Chassevent M, Lamy T, Brenac A, Simionovici A, André H J and Andriamonje S 1991 *Z. Phys. D* **21** S343-5
- Briand J P 1993 *The Physics of Electronic and Atomic Collisions (AIP Conf. Proc. 295)*, XVIII ICPEAC (Aarhus) ed T Andersen *et al* (New York: AIP) pp 731-40
- Briand J P, de Billy L, Charles P, Essabaa S, Briand P, Geller R, Desclaux J P, Bliman S and Ristori C 1990 *Phys. Rev. Lett.* **65** 159-62
- Bruch R, Paul G, André H J and Lipsky L 1975 *Phys. Rev. A* **12** 1808-24
- Burgdörfer J, Lerner P and Meyer F W 1991 *Phys. Rev. A* **44** 5674-85
- Burgdörfer J and Meyer F 1993 *Phys. Rev. A* **47** R20-2
- Chung K T 1982 *Phys. Rev. A* **25** 1596-603
- Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California Press)
- Das J, Folkerts L and Morgenstern R 1992 *Phys. Rev. A* **45** 4669-74
- Das J and Morgenstern R 1993 *Comments At. Mol. Phys.* **29** 205-27
- d'Etat B, Briand J P, Ban G, de Billy L, Desclaux J P and Briand P 1993 *Phys. Rev. A* **48** 1098-106
- Donets E D 1985 *Nucl. Instrum. Methods B* **9** 522-5
- Folkerts L and Morgenstern R 1991 *Z. Phys. D* **21** S351-2
- Froese Fischer C 1991 *Comput. Phys. Commun.* **64** 369-98
- Froese Fischer C and Brage T 1993 *Comput. Phys. Commun.* **74** 381-98
- Gavrila M and Hansen J E 1978 *J. Phys. B: At. Mol. Phys.* **11** 1353-81
- Hagstrum H D 1954 *Phys. Rev.* **96** 336-65
- Hansen J E 1989 *J. Physique Coll.* **1** 603-7
- Hughes I G, Burgdörfer J, Folkerts L, Havener C C, Overbury S H, Robinson M T, Zehner D M, Zeijlmans van Emmichoven P A and Meyer F W 1993 *Phys. Rev. Lett.* **71** 291-4
- Kiernan L M, Kennedy E T, Mosnier J-P, Costello J T and Sonntag B F 1994 *Phys. Rev. Lett.* **72** 2359-62
- Kurz H, Töglhofer K, Winter H P and Aumayr F 1992 *Phys. Rev. Lett.* **69** 1140-3
- Kuyatt C E, Simpson J A and Mielczarek S R 1965 *Phys. Rev. A* **138** 385-99
- Larkins F P 1971 *J. Phys. B: At. Mol. Phys.* **4** L29-32
- Layzer D 1959 *Ann. Phys., NY* **8** 271-96
- Luc-Koenig E and Bauche J 1990 *J. Phys. B: At. Mol. Opt. Phys.* **23** 1763-82
- Mannervik S, Short R T, Sonnek D, Träbert E, Möller G, Ludwig V, Heckmann P H, Blanke J H and Brand K 1989 *Phys. Rev. A* **39** 3964-8
- Martín F, Sánchez I and Bachau H 1989 *Phys. Rev. A* **40** 4245-55
- McGuire E J 1969 *Phys. Rev.* **185** 1-6
- Meyer F W, Folkerts L, Hughes I G, Overbury S H, Zehner D M, Zeijlmans van Emmichoven P A and Burgdörfer J 1993 *Phys. Rev. A* **48** 4479-84
- Müller A, Hofmann G, Weissbecker B, Stenke M, Tinschert K, Wagner M and Salzborn E 1989 *Phys. Rev. Lett.* **63** 758-61
- Nicolaides C A and Beck D R 1977 *J. Chem. Phys.* **66** 1982-7
- Niehaus A 1986 *J. Phys. B: At. Mol. Phys.* **19** 2925-37
- Omar G and Hahn Y 1991 *Phys. Rev. A* **43** 4695-701
- Rødbro M, Bruch R and Bisgaard P 1979 *J. Phys. B: At. Mol. Phys.* **12** 2413-47
- Roncín P, Gaboriaud M N and Barat M 1991 *Europhys. Lett.* **16** 551-6
- Safronova U I and Senashenko V S 1978 *J. Phys. B: At. Mol. Phys.* **11** 2623-40
- Schulz M, Cocke C L, Hagmann S, Stöckli M and Schmidt-Bücking H 1991 *Phys. Rev. A* **44** 1653-8
- Simons R L, Kelly H P and Bruch R 1979 *Phys. Rev. A* **19** 682-7
- van der Hart H W and Hansen J E 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** L395-400
- van der Hart H W, Vaeck N and Hansen J E 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 3489-514

- van der Hart H W, Vaeck N and Hansen J E 1995 *J. Phys. B: At. Mol. Opt. Phys.* submitted
- Vaeck N and Hansen J E 1989 *J. Phys. B: At. Mol. Opt. Phys.* **22** 3137-53
- 1991a *J. Phys. B: At. Mol. Opt. Phys.* **24** L469-75
- 1991b *Z. Phys. D* **21** S221-3
- 1992a *J. Phys. B: At. Mol. Opt. Phys.* **25** 883-905
- 1992b *Surf. Sci.* **269/270** 596-600
- Zeijlmans van Emmichoven P A, Havener C C and Meyer F W 1991 *Phys. Rev. A* **43** 1405-15
- Zeijlmans van Emmichoven P A, Havener C C, Hughes I G, Zehner D M and Meyer F W 1993 *Phys. Rev. A* **47** 3998-4006