# Photoionisation of Unusual States of Matter: Atomic Ions, Excited States and Open-shell Atoms\*

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### Abstract

Our understanding of the photoionisation of ground states of closed-shell atoms is fairly good. The situation is otherwise for open-shell atoms and for ions and excited states throughout the periodic table. Nevertheless, a number of interesting effects have been predicted theoretically in these unusual states of matter. In this paper, some of these predictions, not yet tested by experiment, shall be discussed, along with their implications.

## 1. Introduction

The development of photoelectron spectroscopy, along with increasingly powerful sources of light (notably synchrotrons) in the region below hv = 1000 eV, has opened the door to a number of investigations in atomic physics which had been either marginal or impossible previously. In particular, photoionisation of some unusual states of matter have become possible. In this paper, three general areas of inquiry are discussed, each of which offers attractive possibilities for significant advances in our understanding.

## 2. Photoionisation of Excited States

The study of photoionisation of excited states of atoms is almost virgin territory; only a handful of experimental and theoretical papers on the subject exist. For photoionisation of ground state atoms, whose radii are  $\sim a_0$  (the Bohr radius) we can learn about the continuum wavefunction only in this limited region. For excited states, on the other hand, we can obtain information about the continuum wavefunction over a much larger region than that accessible from a ground state owing to the much larger physical size of an excited state. In addition, owing to its size, the phenomenology of the photoionisation cross sections and photoelectron angular distributions appears to be rather different from that for ground states. For example, it is fairly well established that Cooper minima (Cooper 1962), zeros in the dipole matrix element, occur for ground states only for outer subshells whose wavefunctions have nodes in the  $l \rightarrow l+1$  channel, and then never more than a single zero in a given channel

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(Fano and Cooper 1968; Starace 1981). For excited states, theory predicts a rather different phenomenology.

As an example, the situation for Cs 9d photoionisation, calculated using simple Hartree–Slater (HS) wavefunctions, is shown in Fig. 1 (Lahiri and Manson 1982). The cross section shows a minimum just above threshold, a very deep minimum just above 0.1 Ryd (1 Ryd = 13.605 eV), and a shallow minimum at much higher



Fig. 1. Photoionisation cross section for Cs 9d as a function of photoelectron energy in Rydbergs. The inset shows the higher energy part of the cross section.

Fig. 2. Photoelectron angular distribution asymmetry parameter  $\beta$  for Cs 9d as a function of photoelectron energy in Rydbergs. The inset shows the higher energy part of the results.



energies shown in the inset. These minima are the result of three zeros in the  $9d \rightarrow \epsilon f$  dipole matrix element and are clearly a departure from the ground state case. Basically, it has been found that these zeros result from the difference in the relative phase shift (or quantum defect for a discrete state) between initial and final states (Lahiri and Manson 1982). Roughly speaking, when this phase difference (in units of  $\pi$  radians) is 0.5, one zero can occur, 1.5 for two zeros, etc. In this case, the difference is approximately 2.5 and three zeros are in evidence.

In addition, it is seen from Fig. 1 that the middle minimum drops much more dramatically than either of the others. When the  $9d \rightarrow \epsilon f$  dipole matrix element has a zero, the total cross section, at that energy, is due to the  $9d \rightarrow \epsilon p$  channel. This latter channel is usually small compared with the dominant  $l \rightarrow l+1$  cross section, but not when the  $l \rightarrow l+1$  channel has a zero. On the other hand, the fact that the minimum in Fig. 1 just above 0.1 Ryd is so small, indicates that something peculiar is occurring in the  $9d \rightarrow \epsilon p$  channel also. That peculiarity is a zero in the  $9d \rightarrow \epsilon p$  channel quite close to the zero in  $9d \rightarrow \epsilon f$ . We note that a zero in the  $l \rightarrow l-1$  channel is also never found in ground state photoionisation. Thus it is seen that the calculation predicts multiple zeros in the  $d \rightarrow f$  matrix element and a zero in the  $d \rightarrow p$  as well.

These effects also show up in the photoelectron angular distribution asymmetry parameter  $\beta$  shown for the Cs 9d case in Fig. 2. Here an oscillation in the behaviour of  $\beta$  as a function of energy is seen in the vicinity of each zero. As a matter of fact, at a d  $\rightarrow$  f zero  $\beta = 0.8$  and at a d  $\rightarrow$  p zero  $\beta = 0.2$  (Starace 1981; Manson 1985), and  $\beta$  is seen (Fig. 2) to take on these values at the appropriate energies. Thus, the investigation of  $\beta$  values is an extremely useful tool in uncovering the existence of zeros, particularly in an  $l \rightarrow l-1$  channel whose overall effect on the cross section may not be very large.



Fig. 3. Photoionisation cross section for Cs 6d as a function of photoelectron energy in Hartree–Fock length (HFL), Hartree–Fock velocity (HFV) and Hartree–Slater (HS) approximations.

The above results were obtained using simple wavefunctions. In the absence of experiment it is important to be sure that these zeros are not simply artifacts of the calculation. To investigate this point, calculations of Cs 6d have been performed using both Hartree–Slater (HS) and Hartree–Fock (HF) wavefunctions (Msezane

and Manson 1984). The results are shown in Fig. 3 where two significant points emerge. Firstly, the HF results, which show good agreement between length and velocity formulations (Starace 1981), and the HS results show exactly the same phenomenology; both have a  $d \rightarrow f$  zero in the low energy region, shown in Fig. 3, and a higher energy zero (not shown). Thus it appears that the qualitative predictions of the HS calculation are indeed correct. Secondly, the HF calculation shows the zero at significantly higher energy than the HS prediction. This very dramatic shift is due primarily to the f-wave shape resonance which is very sharp in the HS approximation but much more gradual in HF (Msezane and Manson 1984). This is perhaps one of the worst cases, but it does show that the actual positions of the HS zeros (although not their existence) may be suspect.



Fig. 4. Zeros in 5d  $\rightarrow \epsilon p$  dipole matrix elements. The lower curve is the energy at which the minimum occurs in Rydbergs above the threshold plotted against Z. The upper curve is the difference between the p-wave phase shift at threshold,  $\delta_p(0)$  in units of  $\pi$  radians, and the quantum defect of the discrete 5d state,  $\sigma_{5d}$ .

Another important question to investigate is the generality of these multiple minimum phenomena. As an example, the location of the  $5d \rightarrow \epsilon p$  zeros, as a function of Z, is shown in the lower part of Fig. 4 (Msezane and Manson 1982). From these HS results, it is clear that these minima are not an isolated phenomenon, occurring for Z values from 9 to 55 in this one case. Also shown in Fig. 4 is the relative phase shift difference between the continuum p wave and the discrete 5d. It is clear that the 'trajectory' of the zero mimics the relative phase shift difference very closely, at least at the lower Z values. At the higher Z values, the 5d wavefunction becomes progressively more compact, so that an appreciable part of the matrix element comes from the inner, non-hydrogenic region where the phase shift (quantum defect) does not describe the wavefunctions. In fact, the effect of the inner region is always to move the zero to lower energy, or into the discrete region (Lahiri and Manson 1986).

Although there are no experimental results for excited state photoionisation in the neighbourhood of these zeros, some work does exist. In Fig. 5, the experimental photoionisation cross section of Na 3p is shown, along with the results of HS and HF calculations (Preses *et al.* 1985). The agreement is seen to be excellent. This gives confidence in the calculations and implies that the predictions concerning zeros are most likely correct.



Fig. 5. Photoionisation cross section for Na 3p. Theoretical results are Hartree– Fock (HF) and Hartree–Slater (HS). The experimental cross section is absolute and *not* normalised to theory.

# 3. Photoionisation of Atomic Ions

The investigation of the photoionisation of atomic ions is in very poor shape from an experimental point of view; nevertheless, the subject has been investigated theoretically (Reilman and Manson 1979) owing to its importance in various areas, for example, astrophysical and CTR plasmas. From the theoretical point of view, the calculations should become more accurate in going from the neutral atom to progressively more highly charged ions. This is because the electrostatic interaction between electrons, which is the part of the Hamiltonian being approximated, becomes proportionally less important as the state of ionisation increases. This has not yet been properly tested because the existing measurements over an energy range have yielded only very rough cross sections (Lucatorto and McIlrath 1976; McIlrath and Lucatorto 1977).

Furthermore, an interesting phenomenon is revealed by the calculations. To a high degree of accuracy, photoionisation cross sections for inner shells of ions are virtually unaffected by the removal of outer shell electrons, except for a shift of threshold (Reilman and Manson 1978; Ong *et al.* 1979; Chao and Manson 1981). More explicitly, it has been found that the photoionisation cross section for a subshell nl as a function of photon energy remains constant to within about 3%, when electrons with a higher principal quantum number are removed. As an example, the



Fig. 6. Calculated 2s photoionisation cross section (per 2s electron) for the Fe isonuclear sequence from the neutral atom to  $Fe^{+23}$ . The vertical lines are the theoretical thresholds for the given stage of ionisation.

situation for Fe 2s is shown in Fig. 6 where it is seen that for ionisation stages up to +15, where only n = 3 and n = 4 electrons have been removed, the cross section remains on the same curve with only the threshold moving to higher energy. But by +17 and higher, which involves removal of 2p electrons, the cross section changes. This phenomenon is due to the fact that  $\langle r \rangle$  for a subshell nl depends on n and very little else. To a first approximation, the ionic electrons are thought of as spherical shells of charge. Since a shell of charge exerts no force inside the shell, the removal of an outer shell electron does not change anything in the interior except by an overall constant, thereby leading to the shift in threshold.

This phenomenon has practical consequences in that, where applicable, it allows the transfer of our knowledge from individual subshells of atoms to ions, thus making ionic calculations considerably less time consuming. In addition, there are a few cases where this simplification is not likely to be true such as Ca 3d and Ba 4f where removal of an outer shell electron causes the orbital in question to collapse, totally or partially. Such cases would be particularly useful to investigate experimentally to gain a better understanding of this notion of wavefunction collapse.

## 4. Photoionisation of Open-shell Atoms

Of all the elements in the periodic table (>100), only a dozen or so are closed-shell atoms; the rest have open shells. Nevertheless, over 95% of the experimental work on atomic photoionisation has been carried out on closed-shell atoms, particularly the noble gases. Aside from the fact that the paucity of data for open-shell atoms requires experimental work to bench-mark the theory, there is a whole extra dimension to open-shell atoms. Namely, the open shell has various angular momentum couplings (multiplet structure). Thus photoionisation of Cl  $(3p^5)^2P$ , for example, can go to Cl<sup>+</sup>  $(3p^4)^1D$ , <sup>1</sup>S or <sup>3</sup>P, i.e. three possible states (Manson *et al.* 1979). Experimental studies of the cross sections to each of the final ionic states, as well as their ratios, would greatly advance our understanding of the process. At present, there exist a number of theoretical cross sections (Brown *et al.* 1980); experiment is required to see which, if any, are correct.



Fig. 7. The Al 3s photoionisation cross sections for  ${}^{3}P$  and  ${}^{1}P$  channels of Al<sup>+</sup>, divided by statistical weights (3 for  ${}^{3}P$ , 1 for  ${}^{1}P$ ), in Hartree–Fock length and velocity formulations.

Not only outer shells, but inner shells as well can be significantly affected by the multiplet structure, particularly near threshold. As an example, the photoionisation of Al 3s can yield a final 3s, 3p state of Al<sup>+</sup> in either the <sup>1</sup>P or <sup>3</sup>P state. The results of our HF calculations are shown in Fig. 7 where the cross sections divided by their statistical weights are found to differ very markedly in the threshold region, owing primarily to the difference in the exchange effects on the continuum p wavefunction in the two channels; in the absence of such effects, the <sup>3</sup>P and <sup>1</sup>P curves would coincide. It is interesting to note that while the <sup>1</sup>P cross section shows good agreement between length and velocity, the <sup>3</sup>P in the threshold region does not. This indicates that multichannel effects are important in the <sup>3</sup>P channel, but may not be in the <sup>1</sup>P. A few Rydbergs above threshold, however, the curves do come together, indicating that multichannel effects are no longer likely to be important and that exchange effects for the two channels are the same. Thus, in this case, it is the threshold region which warrants further scrutiny.

Before proceeding, it is of importance to point out that HF calculations, as used in this paper, are not necessarily the same as diagonalising the intrachannel coupling, due to the orthogonalisation of the continuum orbitals to the discrete ionic orbitals of the same symmetry *via* off-diagonal Lagrange multipliers. Basically, when dealing with wavefunctions that cannot be represented by a single determinant, the matter of orthogonalisation can be of importance. In the case discussed above, then, this incomplete diagonalisation of the intrachannel coupling is likely also to contribute to the discrepancy between length and velocity. Nevertheless, the results show that it becomes unimportant at a few Rydbergs above threshold.

As another example, the branching ratio for B 2s photoionisation resulting from a HF calculation is shown in Fig. 8. Boron, it is to be noted, lies in the same column

as aluminium in the periodic table and the 2s, 2p configuration of  $B^+$  gives rise to  ${}^{3}P$  and  ${}^{1}P$  states. The branching ratio is below the statistical value of 3 in the threshold region, in both length and velocity formulations, and gradually rises towards the statistical value with increasing energy. Thus the  ${}^{3}P$  cross section is anomalously small in this case, while it was anomalously large for Al as was seen in Fig. 7. Also shown in Fig. 8, labelled K, is an estimate of the kinetic energy effect obtained by assuming that the shapes of the  ${}^{3}P$  and  ${}^{1}P$  cross sections were identical but displaced by the difference in thresholds. Clearly the kinetic energy effects are still seen to be of importance.



Fig. 8. The  ${}^{3}P_{-}{}^{1}P$  photoionisation branching ratio for B 2s photoionisation in Hartree–Fock length (L) and velocity (V) formulations. The curve K is the result of the kinetic energy effect described above.

In addition, photoelectrons leaving an open-shell atom do not 'see' a central field, as is the case for closed-shell atoms. The non-central or anisotropic field can exert a torque, thus allowing for the possibility of angular momentum exchanges between the photoelectron and the ionic core. This, in turn, leads to dramatic effects in the photoelectron angular distributions, particularly for atomic s electrons. A particularly striking example has been found for Cl 3s photoionisation (Starace *et al.* 1977) where, at certain energies, instead of the expected  $\cos^2\theta$  distribution, a  $\sin^2\theta$  distribution is predicted.

## 5. Final Remarks

The examples shown in the areas of photoionisation of excited states, atomic ions, and open-shell atoms are meant to be indicative of the richness of phenomena yet to be studied experimentally; it is not to be taken as a comprehensive review of these areas. The examples, however, do point out the need for experimental work, particularly studies that obtain photoionisation cross sections and angular distributions for individual subshells. Photoelectron spectroscopy is a technique ideally suited for that purpose.

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