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Photoelectron angular distributions of *ns* subshells of open-shell atoms as indicators of interchannel coupling: Sc 4*s* photoionization

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It is shown that the photoelectron-angular distribution asymmetry parameter β, arising from ns photoionization in open-shell atoms, is quite a bit more sensitive to interchannel coupling than the integrated cross section. An example of 4s photoionization of atomic Sc is presented. It is demonstrated that this effect can occur throughout the periodic system.

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The study of photoelectron-angular distributions can provide significant information on the photoionization process which is unavailable from integrated cross sections alone. This is because integrated cross sections depend upon the sum of the absolute squares of the amplitudes (matrix elements) for transitions to the various possible final states [1], while the differential cross sections (angular distributions) depend upon the *ratios* of the amplitudes and their *relative phases* [2]. The variation of the angular distribution with energy is a result of the variation of the interferences among the alternative final states. This is reflected in the energy dependence of the angular distribution asymmetry parameter β_i, which, for linerally polarized incident radiation, is related to the differential cross section by [2–4]

$$\frac{d\sigma_i}{d\omega}=\frac{\sigma_i}{4\pi}[1+\beta_i(\cos\theta)], \tag{1}$$

where i is the channel designation, σ_i is the integrated cross section, θ is the angle between photoelectron momentum and photon polarization directions, and $P_2(x)=(3x^2-1)/2$, the Legendre polynomial of order 2.

For the photoionization of ns electrons from closed-shell atoms, β is constant and equal to 2 because only a single $s\rightarrow p$ partial wave is possible. Relativistic effects can modify this behavior by allowing the possiblity of differences between the $s\rightarrow p_{1/2}$ and $s\rightarrow p_{3/2}$ transition amplitudes; from a practical point of view, this occurs only at very high Z [5], or in the vicinity of a Cooper minimum [2,6]. For open-shell atoms, the situation is different. Owing to the possibility of various couplings of the ϵp continuum wave with the open-shell ionic core, multiple partial waves are possible; and these partial waves interfere with each other. At low photoelectron energies (near the ns threshold), the differing exchange interactions among the various channels can provide the difference among the partial-wave transition amplitudes to cause β to differ from 2 and acquire an energy dependence [2]. At high energy (far above threshold), when differences in exchange interactions between photoelectron and ionic core become small, Cooper minima in dipole amplitudes at *slightly* different energies can have a dramatic effect on β. An outstanding example is 3s photoionization in atomic Cl which was predicted to deviate substantially from $\beta=2$ [7]; this prediction was recently confirmed experimentally [8]. In addition, in the vicinity of autoionizing resonances, which can occur at different energies in each of the dipole amplitudes, β can exhibit a rapid variation with energy [9,10].

In this paper, it is pointed out that interchannel coupling can also cause β for an ns photoionization to deviate from 2 and become energy dependent. This is significant because it has recently been discovered that interchannel coupling is of importance for *most subshells of most atoms at most energies* [11,12]. Consequently, scrutiny of the photoelectron angular distribution can lead to a deeper understanding of the details of the dynamics of the photoionization process, details which cannot be obtained via examination of the integrated cross section.

As an example of this phenomenon, the photoionization of atomic Sc is investigated theoretically. Atomic Sc has a ground-state structure $[\mathrm{Ar}]3d4s^2\,{}^2D$, and we look specifically at 4s photoionization leading to Sc^+ $3d4s\,{}^{1,3}D$ final ionic states. The calculation is performed using our recently developed augmented many-body perturbation theory (AMBPT) methodology, which is an outgrowth of the work of Kelly [13,14]. The 32 Sc^+ final ionic states included in the calculation are

$$([\mathrm{Ne}]3s^2\,3p^6\,3d4s\,{}^{1,3}D)kp\ {}^2P,D,F,$$

$$([\mathrm{Ne}]3s^2\,3p^6\,4s^2\,{}^1S)kp\,{}^2P,\ kf\ {}^2F,$$

$$([\mathrm{Ne}]3s^2\,3p^5\,3d4s^2\,{}^{1,3}F)ks\,{}^2F,\ kd\ {}^2P,D,F,$$

$$([\mathrm{Ne}]3s^2\,3p^5\,3d4s^2\,{}^{1,3}D)ks\,{}^2D,\ kd\ {}^2P,D,F,$$

$$([\mathrm{Ne}]3s^2\,3p^5\,3d4s^2\,{}^{1,3}P)ks\,{}^2P,\ kd\ {}^2P,D,F,$$

where $k=n$ for discrete (autoionizing) transitional and $k=\epsilon$ for continuum (ionizing) transitions. Briefly, the method starts with an optimized Hartree-Fock-like basis set [15]. The lowest order dipole matrix elements are corrected via perturbation theory, including all first-order interactions with the ground state which connect to a final state via a dipole matrix

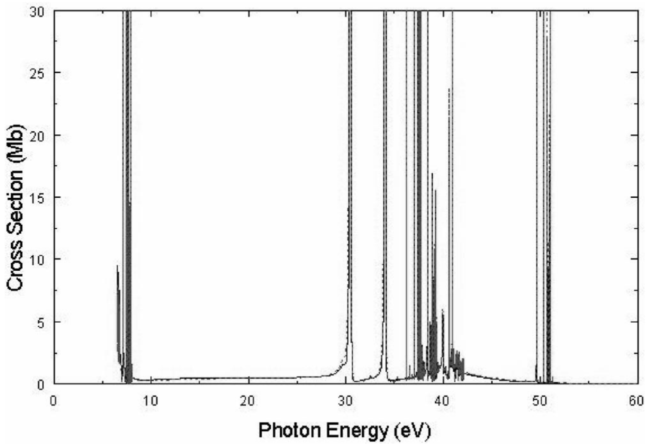

FIG. 1. Photoionization cross sections for Sc$3d4s^2\ ^2D \rightarrow$ Sc$^+$ $3d4s\ ^3D$. The cross section is summed over Sc$^+$ $(3d4s)\ ^3D\epsilon p\ ^2L$ for $L=1$, 2, and 3. The solid curve in each is the ''length'' formulation, while the dashed curve is the ''velocity.''

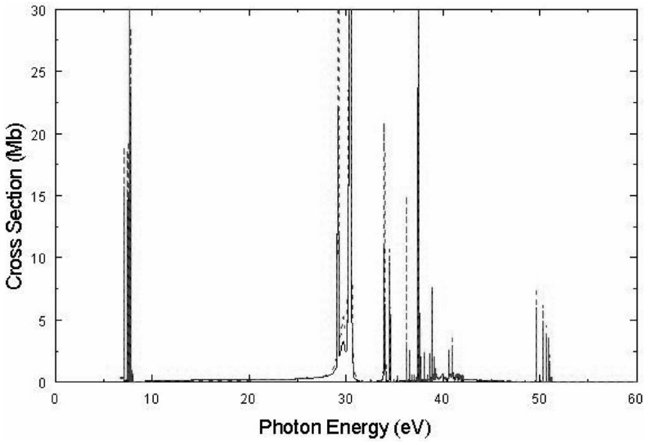

FIG. 2. Photoionization cross sections for Sc$3d4s^2\ ^2D \rightarrow$ Sc$^+$ $3d4s\ ^1D$. The cross section is summed over Sc$^+$ $(3d4s)\ ^1D\epsilon p\ ^2L$ for $L=1$, 2, and 3. The solid curve in each is the ''length'' formulation, while the dashed curve is the ''velocity.''

element. Threshold energies are obtained via a multiconfiguration Hartree-Fock procedure [16], with care taken to avoid double counting and to insure orthogonality to lower states of the same symmetry. In particular, the important $3d^2\ ^1D$ mixing in the $3d4s\ ^1D$ state of Sc$^+$ is included. The interaction among the degenerate continuum channels (interchannel coupling) is effected through a matrix diagonalization technique, but not before including the most important higher-order interactions among the degenerate channels via perturbation theory; this procedure amounts to close-coupling with corrections for final states not included in the above list, including the $(3d^2\ ^1D)kp$ states. The details of this AMBPT method, as applied to atomic Sc, are given elsewhere [17].

From the channel listing above, it is seen that $4s$ photoionization leads to final states of the system $[3d4s\ ^{1,3}D]\epsilon p\ ^2P$, ^2D, ^2F for both singlet and triplet ionic cores. Although it is, in principle, possible to measure the angular momentum of the total (photoelectron plus ionic core) final state [18,19], such a measurement requires an oriented initial state. Thus what can be reasonably measured is the sum over ^2P, ^2D, and ^2F channels for each of the states of the Sc$^+$ core; the Sc$^+$ states can be separated via photoelectron energy.

The results for the total Sc$^+$ $[3d4s^{1,3}D]$ cross sections are shown in Figs. 1 and 2, where it is seen that the two cross sections are qualitatively similar; the ^3D cross section is roughly a factor of 3 larger than the ^1D owing the the statistical factor. In each case, a resonant region near threshold is seen, followed by a Cooper minimum, a ''recovery'' from the Cooper minimum, then a smooth monotone decreasing region, another (very broad) resonance region, and finally a smooth region where the cross section is quite small. From our earlier work, and that of others [17,20,21], it is known that the resonances in the threshold region are due to $4s$ and $3d$ excitation: the $3d4snp$, $4s^2np$, and $4s^2nf$ series. The higher-energy resonances arise from $3p$ excitation converging to the six different $3p^53d4s^2$ thresholds $3p^53d4s^2ns$ and $3p^53d4s^2nd$, including the $3p^53d^24s^2$ which are the strongest resonances.

Looking now at the photoelectron angular distribution asymmetry parameter β, shown in Figs. 3 and 4, it is seen that there are dramatic variations in the resonance regions, as expected. In addition, at the Cooper minima, just above the threshold resonances in each case, the predicted significant deviation of β from 2 is seen. Above the Cooper minima, the β's tend rapidly toward 2, again as expected.

At the highest energies shown, above the last series of resonances (51-60 eV), there is also a deviation from $\beta=2$ in each case. This is actually due to Cooper minima, induced by interchannel coupling in these cases, but is too small to be seen on the scales of Figs. 1 and 2. These induced Cooper minima, which have been known for some time in other atoms [5,22], behave in all respects just like ''natural'' Cooper minima.

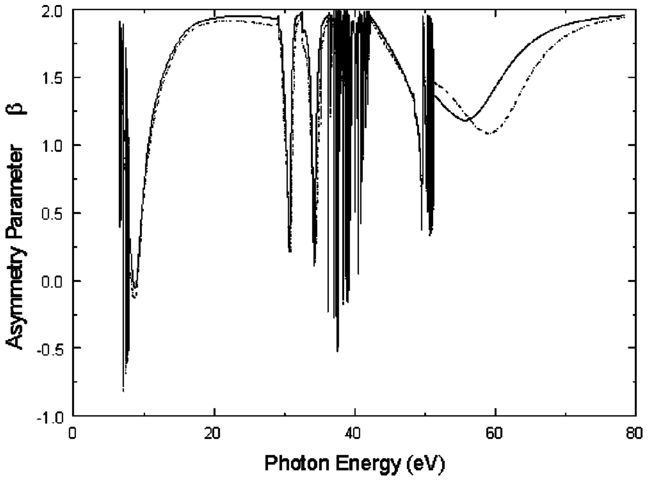

FIG. 3. Photoelectron-angular distribution asymmetry parameter β for the Sc$3d4s^2\ ^2D \rightarrow$ Sc$^+$ $3d4s\ ^3D$ transition. The solid curve in each is the ''length'' formulation, while the dashed curve is the ''velocity.''

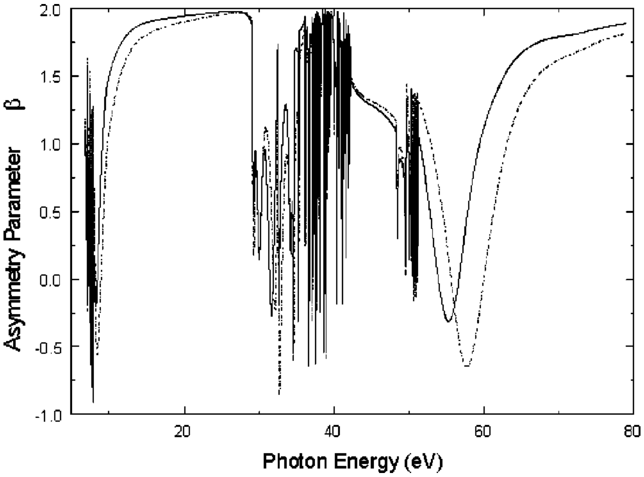

FIG. 4. Photoelectron-angular distribution asymmetry parameter β, for the $\mathrm{Sc}3d4s^2\,{}^2D \rightarrow \mathrm{Sc}^+\ 3d4s\ {}^1D$ transition. The solid curve in each is the ''length'' formulation, while the dashed curve is the ''velocity.''

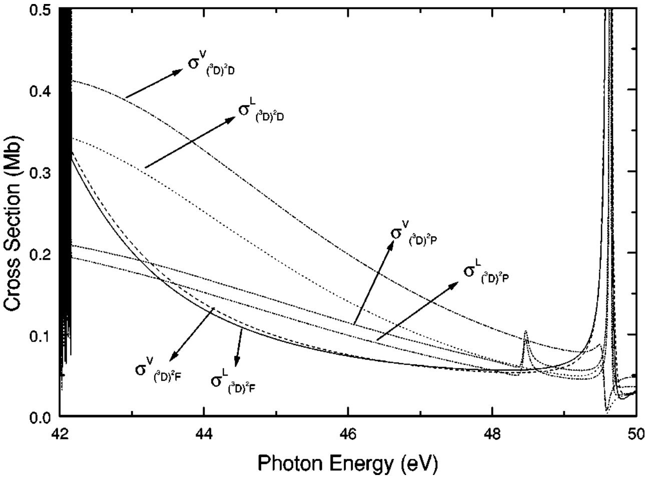

FIG. 5. Photoionization cross sections for $\mathrm{Sc}3d4s^2\,{}^2D \rightarrow \mathrm{Sc}^+\ (3d4s)\ {}^3D\epsilon p\ {}^2L$ for $L=1$, 2, and 3. The solid curve in each is the ''length'' formulation, while the dashed curve is the ''velocity.''

There is also, however, another region, from about 42 to 48 eV in each case, where β deviates from 2 where there are no Cooper minima or resonances. Furthermore, this energy region begins more than 35 eV above threshold, so exchange effects are not likely to be important here. In fact, in the photon energy range of about 20 eV, β is seen to be approaching 2, thereby demonstrating the weakness of exchange effects only 15 eV above threshold. Having eliminated all of the other possibilities, then, it is evident that the deviation of β from 2 *must* be a result of interchannel coupling causing differences among the transition amplitudes for the ${}^2P$, ${}^2D$, and ${}^2F$ channels. In one sense, however, this might be considered a Cooper minimum effect due to the minima at about 60 eV, in each case. But, since these Cooper minima are induced by interchannel coupling, the distinction is purely a semantic one; without interchannel coupling neither the Cooper minima at about 60 eV, nor the variations of β in the 42–48 eV region, occur. It is important to note that, in this energy range, where β deviates significantly from 2, the cross section, shown in Figs. 1 and 2, is completely smooth in each case, giving no indication that anything unusual is going on.

Furthermore, it is useful to note that interchannel coupling with the $3p$ ionization channels significantly affects the $4s$ β's over a broad energy range, starting from the opening of the $3p$ channels. In most of the region, however, the resonances strongly affect the β's, making it rather difficult to isolate interchannel effects. Thus it is only in the 42–48-eV region, in these cases, where the β's would be constant and equal to 2 without interchannel effects, that their dramatic influence is demonstrated unequivocally.

To show that it is indeed the case that interchannel coupling plays the essential role in this deviation of β from 2, a magnified view of the ${}^3D$ cross section in this energy region is shown in Fig. 5, where the large differences among the cross sections for ${}^2P$, ${}^2D$, and ${}^2F$ channels is clear. The situation for the ${}^1D$ cross section (not shown) is essentially the same. Each of the channels comprising the total ${}^3D$ cross section is seen to behave quite differently, as a function of energy, in this region. In the absence of interchannel coupling, however, our calculations show that these cross sections are virtually identical, thereby demonstrating conclusively that interchannel coupling affects each of these channels differently. Each one of the cross sections is seen to have a significantly different shape. In addition the magnitudes differ by as much as a factor of 2. It should be reiterated that, in principle, each of these cross sections could be measured. In practice, however, such a measurement is extremely difficult. But, as shown above, β gives both qualitative and quantitative information on the phenomenon, information which is not even hinted at in the total channel cross sections.

Now, what about the accuracy of the calculated cross sections? In each of the figures presented, both for σ and β, results from the ''length'' and ''velocity'' formulations are depicted. The results of these two formulations must be equal for exact wave functions. In all cases it is evident that agreement between them is rather good, indicating the likelihood that the calculations reported in this paper are indeed accurate. The largest limitation of the methodology is that relativistic and spin-orbit effects are not included. While they will have some quantitative effect on the results, their inclusion should not in any way alter the qualitative phenomenology presented in this paper.

The importance of the results presented is that they are by no means limited to atomic Sc. It is known that strong interchannel interactions generally occur for outer-shell cross sections in the vicinity of inner-shell thresholds throughout the periodic system [22]. Thus it is expected that this will be a general phenomenon. Furthermore, by looking experimentally at both *σ and β* for ns photoionization in open-shell atoms in regions where β deviates from 2, information can be gleaned about the importance of interchannel coupling, information which generally cannot be obtained from σ alone. In addition, even a knowledge of the integrated cross sections to the individual total channels (^2P, ^2D, and ^2F in the present case of atomic Sc) only yields the absolute squares of the matrix elements; β provides information on their relative phases as well.

In conclusion, then, we have demonstrated an interesting aspect of what the scrutiny of β's of ns subshells in open-shell atoms can reveal. We urge that β's for ns states be measured over a broad energy region for open-shell atoms throughout the periodic system. There is a wealth of information there that has not yet been tapped.

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