

## Subshell branching ratios of partial photoionization cross sections

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We examine subshell branching ratios of partial photoionization cross sections, within a relativistic single-electron screened potential, as a function of energy and principal quantum number, for uranium, tin, and carbon. We focus on features beyond the simple kinetic-energy effects made visible by the shift in photon energy, resulting from the fine-structure splitting, which corresponds to the same shape-resonance energy of the outgoing continuum electron. At low energies, deviations from statistical  $(L + 1)/L$  ratios are amplified by the presence and by the separation of Cooper minima in dominant matrix elements. Effects are largest for outer  $p$  shells of high- $Z$  elements because the separation of Cooper minima is largest. At higher energies in a given element all the  $nL$  ratios for a given  $n$  tend to merge into a common curve.

It is well known both experimentally and theoretically<sup>1-12</sup> that branching ratios of partial photoionization cross sections often depart from their statistical ratio. This subject was discussed by Walker *et al.*,<sup>6,7</sup> who noted that these deviations arise both due to the different energies of the photoelectron (kinetic-energy effect, arising from the fine-structure splitting of the two states) and to the different spatial extent of the wave functions of the two states. We have also recently pointed out large deviations of relativistic origin.<sup>12</sup> Like the photoelectron angular distributions, subshell branching ratios permit study of other aspects of the atomic matrix elements than are determined in total-cross-section measurements.

Here we want to give a somewhat more systematic survey of the nonstatistical values of the subshell branching ratios of photoionization cross sections. We report the branching ratios for  $J = L \pm \frac{1}{2}$  subshells of uranium, tin, and carbon as functions of photoelectron kinetic energy (1 eV–100 keV), and of principal quantum number  $n$ . We will see how, at low energies, deviations from statistical values  $(L + 1)/L$  are amplified by the presence and by the separation of Cooper minima in dominant matrix elements.

Our numerical single-electron photoeffect code developed by Ron solves the Dirac equation in a self-consistent relativistic Hartree-Fock-Slater (HFS) field (known also as Dirac-Slater or DS field) by partial-wave expansion, and includes all multipole contributions with retardation as well as relativistic and screening effects.

Figure 1 summarizes our results. Note that the branching ratios are plotted against photoelectron kinetic energy rather than photon energy. Experimentally, a branching ratio would be obtained corresponding to cross sections resulting

from the same incident photon energy. From a theoretical viewpoint it is clearer to plot for given photoelectron energy so that the simple kinetic-energy effects on the ratios related to different threshold energies have already been factored out. (When plotted against photon energy these kinetic-energy effects are large, particularly when there is a prominent shape resonance at a given final continuum electron kinetic energy close to threshold, which appears in the cross sections at two different photon energies owing to the fine-structure energy splitting of the bound state. There are no such features near threshold in the cases of Fig. 1.) Figures 1(a) for  $np$  subshells of uranium and 1(d) for tin show that cross section ratios may vary substantially as a function of photoelectron energy. The ratio of uranium  $4p$  subshell cross sections reaches more than 3 times the statistical ratio at low energies, the  $5p$  ratio curve has a maximum, while the ratio curve of uranium  $6p$  subshells has a minimum followed by a maximum at a higher energy. We note that all the  $nL$  ratios for fixed  $L$  show a tendency to merge into a common curve at high energies, as we have observed also for high-energy photoelectron angular distributions.<sup>13</sup> The ratio of the outermost  $p$  shells ( $5p$  of tin and  $6p$  of uranium) are a little different from the common curve of the other  $p$  states at high energies due to the larger screening effects. (We shall discuss this high-energy region elsewhere,<sup>14</sup> focusing our attention here on the region of Cooper minima.) The  $nd$  and  $nf$  subshell ratios show the same tendencies but the variations have smaller amplitudes. The amplitudes of the variations also decrease as  $Z$  decreases.

For both uranium and tin the ratios for subshells of larger  $n$  have sharper variations as functions of

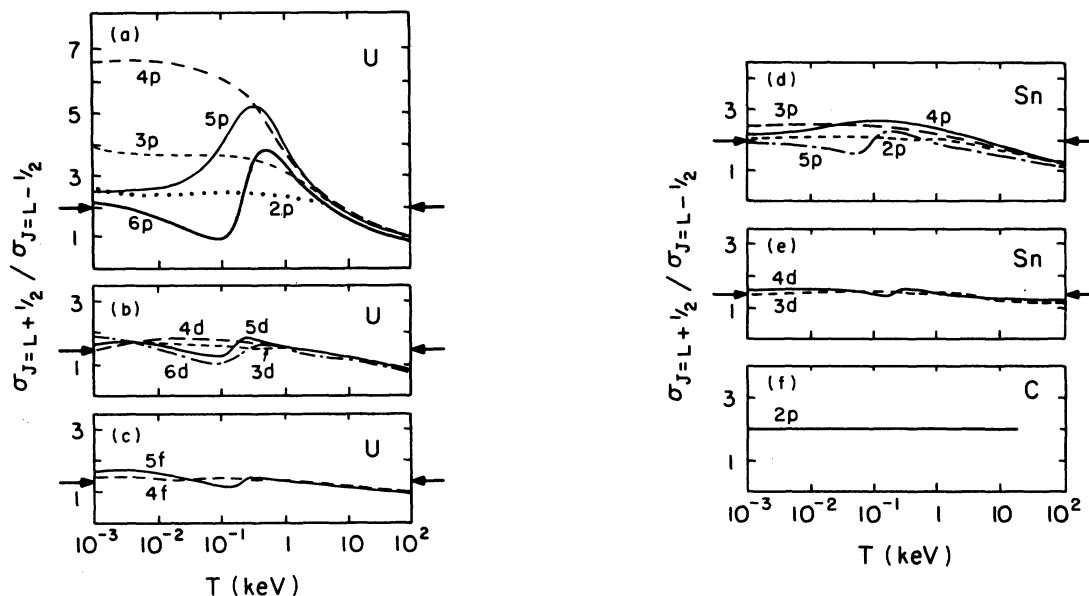


FIG. 1. Subshell branching ratios of photoionization cross sections: (a), (b), and (c) for uranium  $p$ ,  $d$ , and  $f$  subshells, (d) and (e) for tin  $p$  and  $d$  subshells, and (f) for carbon  $p$  subshells, respectively, as a function of photoelectron kinetic energy. Arrows indicate the statistical values.

energy. For states having nodeless wave functions ( $2p$ ,  $3d$ , and  $4f$ ) there are no appreciable deviations from the statistical value. These are the cases where no Cooper minimum occurs.<sup>15</sup>

Figure 2 shows corresponding total cross sections for some sample cases. We clearly see that, although the total cross sections for outer

$d$  and  $f$  shells show more variation with energy, (corresponding to shape resonances and to Cooper minima which may in fact overlap<sup>16</sup>), the two  $J = L \pm \frac{1}{2}$  subshell cross-section curves for given ( $nL$ ) on a logarithmic scale are almost parallel, so that their ratio varies little with energy. By contrast the total cross sections of outer  $p$  sub-

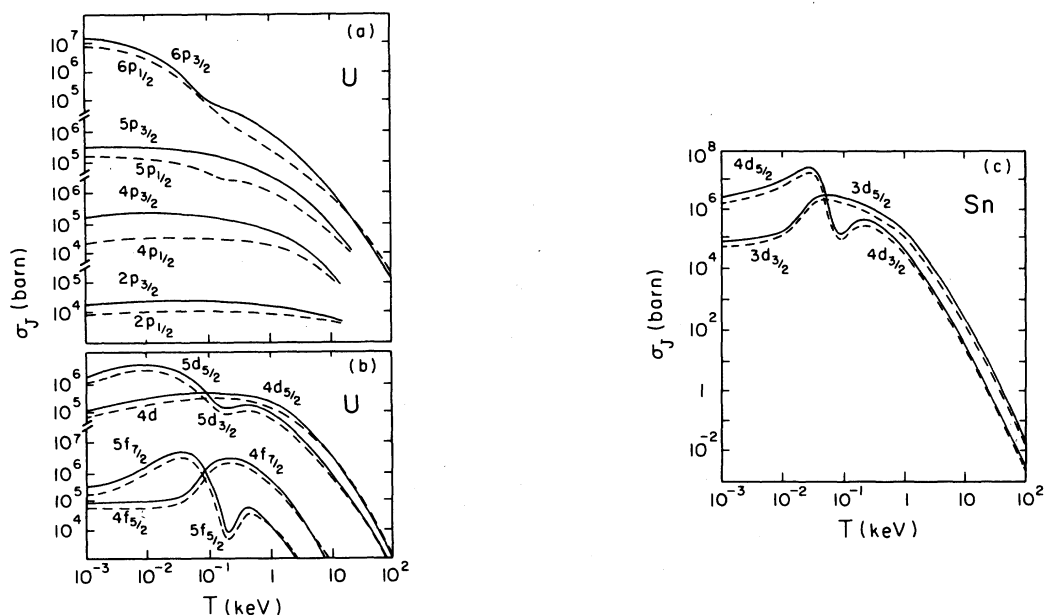


FIG. 2. Total subshell cross sections, as a function of photoelectron kinetic energy, for (a) uranium  $2p$ ,  $4p$ ,  $5p$ , and  $6p$  subshells, (b) uranium  $4d$  and  $5d$ , and  $4f$  and  $5f$  subshells, and (c) tin  $3d$  and  $4d$  subshells.

shells vary less dramatically with energy, but the relative shifts of the  $J = L \pm \frac{1}{2}$  subshell partial cross sections are larger, resulting in larger variations of the ratios. The uranium  $4p_{1/2}$  subshell cross section is suppressed near threshold, resulting in a large branching ratio at low energy, while the shift in the relative position of structure in the uranium  $6p$  subshell cross sections produce a minimum followed by a maximum in the branching ratio. Since only the uranium  $5p_{1/2}$ , and not the  $5p_{3/2}$ , subshell cross section has a similar structure as in the two  $6p$  subshells, this leads to a pronounced maximum in the ratio of the subshell cross sections. We will see below that these structures in the cross sections are due to zeros in the dominant matrix elements, which correspond to  $L \rightarrow L + 1$  transitions.

Figure 3 shows some sample dipole matrix elements, which dominate total cross sections at low energies, up to 1 keV photoelectron energy, for the  $3p$ ,  $6p$ , and  $5f$  subshells of uranium and the  $4d$  subshells of tin. We can see that the minima and maxima observed in the branching ratios, as well as the structures in the cross sections, are associated with the zeros (Cooper minima) of the  $L \rightarrow L + 1$  transition matrix elements which

dominate the cross section.<sup>17</sup> There exist situations for which the total subshell cross section, with a zero in the  $L \rightarrow L + 1$  matrix element, does not have an obvious minimum (e.g., uranium  $5p_{1/2}$  and  $6p$  subshells). In these cases the  $L \rightarrow L - 1$  matrix elements are masking the zeros of the  $L \rightarrow L + 1$  transitions.

We can see that the suppression of the  $4p_{1/2}$  cross section near threshold in comparison to  $4p_{3/2}$  is connected with the occurrence of matrix element zeros at higher energies in the  $p_{1/2}$  cases. For  $n=3$  neither matrix is dropping by threshold while for  $n=5$  the  $p_{1/2}$  zero is already above threshold. ( $p_{3/2}$  does not have zeros above threshold until  $n=6$ .) The  $n=4$  case is intermediate and the  $p_{1/2}$  matrix element is significantly suppressed, though not yet zero, by threshold.

We note that the separation between the zero in uranium  $6p_{1/2} \rightarrow \epsilon d_{3/2}$  and the zeros in the  $6p_{3/2} \rightarrow \epsilon d_{3/2}$ ,  $\epsilon d_{5/2}$  is more than ten times larger than the corresponding binding energy difference of the two subshells.<sup>18</sup> This large separation of zeros, leading to a large separation in cross-section structures, is important for the production of a large effect on the branching ratio. For  $d$  and  $f$  subshells, the binding energy difference

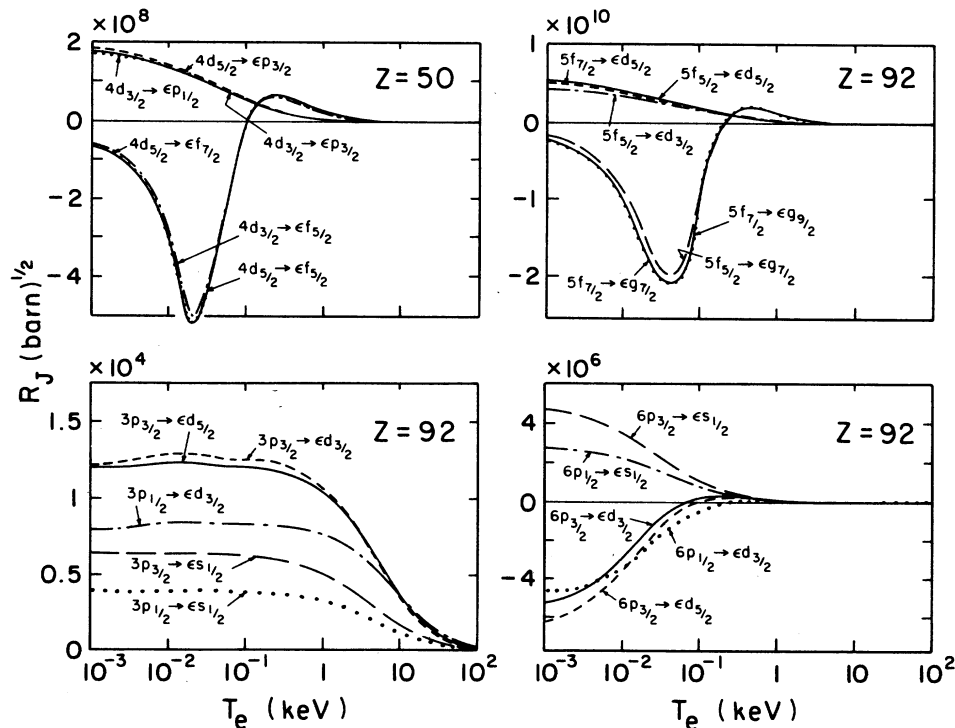


FIG. 3. Radial dipole matrix elements  $R_J(nl_J \rightarrow \epsilon l_J)$  for  $4d$  subshells of tin and  $5f$ ,  $3p$ , and  $6p$  subshells of uranium, as a function of photoelectron kinetic energy.  $R_J$  is normalized such that the subshell cross section  $\sigma_J$  (in barns) is given as

$$\sigma_J = \frac{2J+1}{18} \left( \frac{2J-1}{J} R_{J-1}^2 + \frac{1}{J(J+1)} R_J^2 + \frac{2J+3}{J+1} R_{J+1}^2 \right).$$

is less due to smaller spin-orbit interactions, leading to a smaller separation between the zeros of the outer shell  $L \rightarrow L+1$  transition matrix elements (the magnification is in fact less).

If the zeros of the transition matrix elements are closely spaced (e.g., uranium  $5f$  case) then both partial cross sections,  $5f_{5/2}$  and  $5f_{7/2}$ , are similar and their ratio does not change drastically. However, if the zeros are separated (e.g., uranium  $6p$  case) then the minimum in the two partial cross sections occur at very different energies, giving rise to a rapid variation in the ratio of the cross sections without having a major change in the cross sections themselves.

It is clear that in order to better understand the photoelectric effect at relatively low energies

(1–100 eV) one needs to further investigate the behavior of the zeros of these matrix elements. From our examples one can see that this is the key to predicting the nature of the structure in the cross sections, the branching ratios, and the angular distributions.<sup>11</sup> The dependence upon  $n$ ,  $L$ , and especially  $Z$  (which involves examining relativistic versus nonrelativistic effects) should be studied in more detail.

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