Relativistic Effects in the Photoionization of High-Z Elements: Splittings and Shifts of Minima

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Zeros in dipole matrix elements for high-Z elements are found to occur at significantly higher energies in our relativistic calculations than in nonrelativistic results. The energy separations of the zeros of the relativistic matrix elements are substantially magnified (a factor of $\gtrsim 10$) compared to the initial bound-state spin-orbit splitting.

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One of the interesting aspects of the cross sections for photoionization of atoms is the appearance of minima which are not due to any sort of resonance effect, but rather to the dipole matrix element going through a zero as it changes sign [typically in a $nl \to \epsilon(l+1)$ transition], as a function of energy.[1,2] These minima (generally referred to as Cooper minima but perhaps better called Ditchburn-Bates-Seaton-Cooper minima[3]) are pervasive in outer and near-outer shells of atoms throughout the periodic table. They often have a significant effect on the shape of the cross section,[4-7] and they have an even greater effect upon the character of photoelectron angular distributions[6-9] and subshell branching ratios.[10] As a general rule, it has been observed that the minimum in the cross section for a given subshell first moves out, then moves towards threshold with increasing Z (although not exactly monotonically) until it moves into the discrete.[4,5] This behavior is to be understood from the *relative* shift of bound and continuum wave-function nodes, both of which are moving in with increasing Z. Here we report that the position and dependence of minima can be dramatically altered by relativistic effects.

For high-Z elements, relativistic effects become important in the photoionization process, even for outer electrons and at low energies.[9] (For inner-shell electrons in high-Z atoms, multipole effects with retardation remain important down to threshold, but for outer shells relativistic dipole approximation appears to be adequate in the low-energy regime.) Relativistic effects enter via the change in the central potential itself due to the contraction of the inner shells and resultant relaxation of the outer shells.[11] Relativistic effects also enter through the separate character of large- and small-component radial wavefunctions, G and F, respectively, which the relativistic interaction connects. Although in a nonrelativistic reduction the large component G reduces to the nonrelativistic radial wave function R, and F is proportional to $(d/dr + k/r)rG$, in fact in heavy elements the separate character of F and G and the differences from R are important, especially at small distances (different power dependence for $j = l \pm \frac{1}{2}$, with $j = l + \frac{1}{2}$ closer to nonrelativistic) and large distances (differential exponential decays due to different binding energies). As a result of the relativistic spin-orbit interaction, these wave functions are different for $j = l \pm \frac{1}{2}$. Finally, relativistic effects enter through the relativistic interaction $\vec{\alpha}\cdot\vec{\epsilon}$ which has replaced $\vec{p}\cdot\vec{\epsilon}$, through the use of relativistic kinematics in energy conservation, etc.

When these relativistic effects are considered, each of the $nl \to \epsilon l'$ ($l' = l \pm 1$) nonrelativistic radial matrix elements splits, in general, into three relativistic radial matrix elements, as one applies dipole selection rules to the two initial states $j = l \pm \frac{1}{2}$, and the four final continuum states $j' = l' \pm \frac{1}{2}$. Among the three relativistic matrix elements (which may have zeros) corresponding to a nonrelativistic $l \to l+1$ transition which has a minimum, the separation (in energy) between the zeros of the $nl_{j=l-1/2} \to \epsilon(l+1)_{j'=l+1/2}$ and the $nl_{j=l+1/2} \to \epsilon(l+1)_{j'=l+1/2}$ radial matrix elements (representing transitions from differing initial to the same final state) reflects the spin-orbit splitting of the initial bound state of orbital angular momentum l. A much smaller separation is found between the zeros of the $nl_{j=l+1/2} \to \epsilon(l+1)_{j'=l+1/2}$ and $nl_{j=l+1/2} \to \epsilon(l+1)_{j'=l+3/2}$ radial matrix elements (same initial, differing final states), due to the difference in $j' = l + \frac{1}{2}$ and $l + \frac{3}{2}$ relativistic

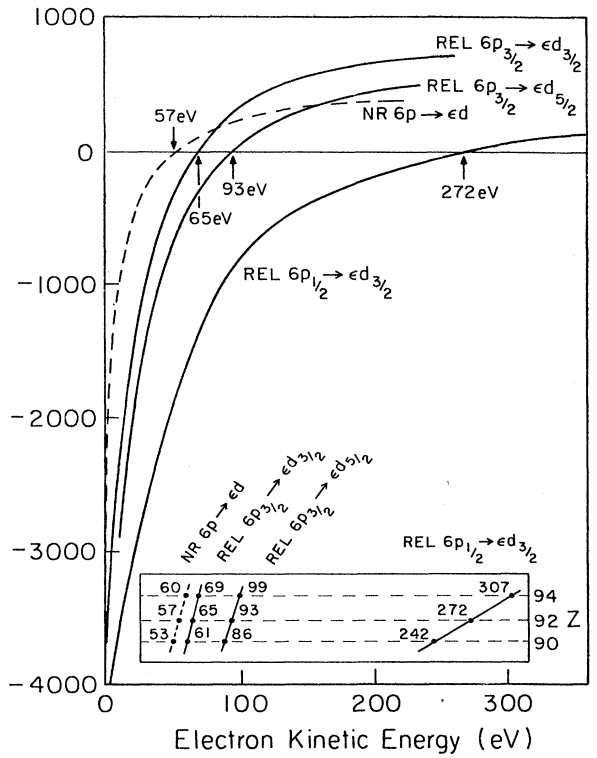

FIG. 1. Uranium $6p \rightarrow \epsilon d$ matrix elements R as a function of ejected-photoelectron kinetic energy (eV), as obtained from the Schrödinger equation with the Hartree-Slater potential and from the Dirac equation with the corresponding relativistic Hartree-Slater potential for $6p_{3/2} \rightarrow \epsilon d_{3/2}$, $6p_{3/2} \rightarrow \epsilon d_{5/2}$, and $6p_{1/2} \rightarrow \epsilon d_{3/2}$. The nonrelativistic ionization energy is 26.1 eV, the two relativistic ionization energies for $6p_{1/2}$ and $6p_{3/2}$ are 34.1 and 24.6 eV, respectively. Matrix elements R are normalized such that the nonrelativistic cross section σ_L and the relativistic cross section σ_J (in barns) are given as

$$\sigma_L = \tfrac{4}{3}(E_b/k)[L\,R_{L-1}{}^2 + (L+1)R_{L+1}{}^2],$$

$$\sigma_J = \frac{2J+1}{6}\,\frac{E_b}{k}\left(\frac{2J-1}{J}\,R_{J-1}{}^2 + \frac{J}{J(J+1)}\,R_J{}^2 + \frac{2J+3}{J+1}\,R_{J+1}{}^2\right).$$

The inset at the bottom of the figure compares the positions of the zeros of these three matrix elements for the cases $Z = 90$, 92, and 94.

continuum wave functions of orbital angular momentum $l+1$.

It has generally been assumed that the positions of the zeros in these three matrix elements should be similar to the common nonrelativistic position and the separation of the zeros corresponding to the $j = l \pm \frac{1}{2}$ splitting of the initial state should be of the same order of magnitude as the spin-orbit splitting of the initial states. This, however, is not the case, as we shall show here, utilizing calculations[12,13] in a single-particle Dirac-Slater (DS) potential.

As an example, Fig. 1 shows the results of our relativistic calculations for the photoionization matrix elements of the three $6p \rightarrow \epsilon d$ channels of atomic U, together with corresponding nonrelativistic Hartree-Slater (HS) results[5,7,14] (with the same approximation to exchange[15]). The most striking feature in these curves is the separation of ~ 150 eV between the $p \rightarrow d$ zero associated with the $6p_{1/2}$ state and the zero associated with the $6p_{3/2}$ state, compared to the spin-orbit energy splitting of the two discrete states of less than 10 eV. For comparison the position of these nodes is also shown for $Z = 90$ and 94. We have found similar effects in U $5p$ (not shown), where only one of the three relativistic zeros ($p_{1/2} \rightarrow d_{3/2}$) occurs in the continuum (~ 1–0 eV above threshold) and the others (and also the nonrelativistic zero) are discrete. This may be compared with $5p$ in Sn, for which our calculations show that the nonrelativistic zero is at 53 eV, the lower relativistic zero at 55 and 57 eV, and the ($p_{1/2} \rightarrow d_{3/2}$) zero at 75 eV above threshold. Based on these results, then, it is fairly certain that the splittings and shifts of minima are not an isolated curiosity, but rather a general phenomenon for high-Z atoms. It seems clear that some of the minima do not behave, as a function of Z, in the same way as is the case for low-Z elements, where relativistic interactions play only a very minor role.

We may tentatively identify some of the mechanisms which lead to these features. Considering the cross sections for the $6p \rightarrow \epsilon d_{3/2}$ transitions, the final state is the same, but the initial states differ in that $6p_{1/2}$ is more tightly bound than $6p_{3/2}$. Outer lobes of the $6p_{1/2}$ wave function are shifted toward the nucleus in comparison both to $6p_{3/2}$ and to the nonrelativistic $6p$ wave function, reflecting an entirely different small-distance behavior, which is then propagated outward as a shift in nodes. [While at small distances, Schrödinger wave functions behave as r^l, Dirac wave functions behave as $r^{\gamma-1}$, with $\gamma = (k^2 - a^2)^{1/2}$, where $a \equiv Z\alpha$ and $k = -(l+1)$ for $j = l + \frac{1}{2}$, $k = l$ for $j = l - \frac{1}{2}$. At small distances $p_{1/2}$ states behave approximately as $a^2 r^{-a^2/2}$, the same as $s_{1/2}$ (and with an amplitude comparable to the nonrelativistic-like $r^{1-1/2a^2}$ term for large Z when a is large), while $p_{3/2}$ behaves as $r^{1-1/4a^2}$, closer to the nonrelativistic p wave.] The continuum wave func-

tion moves toward the nucleus with increasing energy, so that we may expect that a change in sign of the matrix element occurs first for $6p_{3/2}$ and then at a higher energy for $6p_{1/2}$ (which can be understood by assuming that the position of the zero is controlled by the region of the outer lobes). Since the d-wave potential has a large centrifugal barrier, we can expect that the continuum energy must be increased significantly for the ϵd wave function to move in a small distance in the region of p-wave nodes, thereby magnifying (in the matrix element) the consequences of the spin-orbit splitting of the initial bound state.

With similar arguments we may discuss the smaller $6p_{3/2} \rightarrow \epsilon d$ splittings, for which the initial state is the same but the final continuum states differ by a spin-orbit interaction, attractive for $d_{3/2}$ but repulsive for $d_{5/2}$. For the same energy we may expect the $d_{3/2}$ continuum state nodes to be shifted toward smaller distances in comparison with those of $d_{5/2}$; consequently we expect a zero in $d_{3/2}$ at lower energy. However, since the spin-orbit interaction for a higher-angular-momentum state (d waves) is smaller than for p waves, a smaller shift in continuum energies suffices for the two continuum states to have the same overlap with the bound state, explaining the much smaller splitting of these minima. The fact that the $6p_{3/2}$ matrix elements are closer to the nonrelativistic $6p$ matrix element than the $6p_{1/2}$ matrix element reflects the fact that $6p_{3/2}$ nodes are closer to nonrelativistic, while $6p_{1/2}$ has been pulled in because of the very different small-distance behavior.

Other relativistic effects may also contribute to these features. Since the change in potential causes outer-shell relativistic wave functions to be more extended this will shift zeros to higher energies. However our calculations indicate that this shift due to the change in potential is only about a rydberg, small compared to the observed shift of the zero for the $p_{1/2}$ state. Other effects, such as those arising from the breakdown of the nonrelativistic limit connection between small- and large-component wave-function shapes, need to be investigated.

At present there is a paucity of experimental data on high-Z atoms, where these relativistic effects are important. The behavior of these minima presents an experimental opportunity to gain insight into relativistic effects, since the positions of the minima can be obtained quite well via photoelectron spectroscopy through angular-distribution[6-8] or electron-spin-polarization measurements.[16]

Finally, it is important to note that a more proper inclusion of some of the interactions approximated in these calculations, such as exchange or interchannel coupling, is likely to change the results quantitatively, but not qualitatively, just as is the case for nonrelativistic calculations.[6,7,17] Thus we expect that the effects described here are real and we would strongly urge some exploratory experimental studies.

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