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Dynamical Relativistic Effects in Photoionization: Spin-Orbit-Resolved Angular Distributions of Xenon 4*d* Photoelectrons near the Cooper Minimum

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Two decades ago, it was predicted [Y. S. Kim *et al.*, Phys. Rev. Lett. **46**, 1326 (1981)] that relativistic effects should alter the dynamics of the photoionization process in the vicinity of Cooper minima. The present experimental and theoretical study of the angular distributions of Xe $4d_{3/2}$ and $4d_{5/2}$ photoelectrons demonstrates this effect for the first time. The results clearly imply that relativistic effects are likely to be important for intermediate-Z atoms at most energies.

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Relativistic effects in atoms have long been known to be important for photoionization dynamics at high Z [1–6]. At low and intermediate Z, where the predominant effect of relativity has been thought to be spin-orbit splitting of states into $j = l \pm 1/2$ with differing threshold energies [2,3,7], recent advances in experiment [8–10] and theory [11–15] have demonstrated observable consequences of relativistic effects on photoionization dynamics. One of the most sensitive dynamical quantities in photoionization is the energy of a Cooper minimum [16,17], where the dipole matrix element for a particular channel goes through (or nearly goes through) zero. Relativistic interactions were predicted to significantly affect Cooper minima two decades ago [1], but this prediction remains unverified.

Finding the location of a Cooper minimum experimentally poses problems because it is often difficult to locate the minimum in a particular channel over the background of other open (and stronger) channels without a minimum in the same energy region. An excellent way to pinpoint Cooper minima is via measurement of the photoelectron angular-distribution parameter β, which takes on specific values at the location of certain Cooper minima [18,19].

In this Letter, we report on a combined experimental and theoretical study of $4d$ photoionization in Xe where the spin-orbit components $4d_{5/2}$ and $4d_{3/2}$ are individually resolved. Experimentally this is difficult in the energy region of the $4d \to \varepsilon f$ Cooper minima because the dominant $d \to f$ contribution to the cross section is very small. In the absence of dynamical effects due to relativistic interactions, Cooper minima for $4d_{5/2}$ and $4d_{3/2}$ photoionization will be located at the same *kinetic energy*. Consequently, $\beta_{5/2}$ and $\beta_{3/2}$ would be identical as a function of photoelectron energy. However, the present measurements clearly exhibit differences in the β parameters and confirm the long-untested theoretical prediction of Kim *et al.* [1]. Furthermore, $\beta_{5/2}$ and $\beta_{3/2}$ differ not only in the immediate vicinity of the Cooper minima, but over a broad energy region, demonstrating the importance of relativistic effects in the photoionization of intermediate-Z atoms over a much larger energy range than previously suspected.

The $4d \to \varepsilon f$ nonrelativistic Cooper minimum splits into three minima relativistically; $4d_{5/2} \to \varepsilon f_{5/2}$, $4d_{5/2} \to \varepsilon f_{7/2}$, and $4d_{3/2} \to \varepsilon f_{5/2}$. Each would appear at the same photoelectron energy in the absence of dynamical effects resulting from relativistic interactions. In terms of matrix elements, along with the $4d \to \varepsilon p$ channels ($4d_{5/2} \to \varepsilon p_{3/2}$, $4d_{3/2} \to \varepsilon p_{3/2}$, and $4d_{3/2} \to \varepsilon p_{1/2}$), the expressions for β are given by [20,21]

$$\beta_{3/2} = \frac{2}{5}\,\frac{-2R_{3/2}{}^2 + 18R_{5/2}{}^2 + 5R_{3/2}R_{1/2}\cos\Delta_{31} + 9R_{3/2}R_{5/2}\cos\Delta_{35} + 45R_{1/2}R_{5/2}\cos\Delta_{15}}{5R_{1/2}{}^2 + R_{3/2}{}^2 + 9R_{5/2}{}^2}, \tag{1}$$

$$\beta_{5/2} = \frac{2}{35}\,\frac{250R_{7/2}{}^2 - 16R_{5/2}{}^2 + 49R_{3/2}{}^2 + 42R_{5/2}R_{3/2}\cos\Delta_{53} + 60R_{5/2}R_{7/2}\cos\Delta_{57} + 840R_{3/2}R_{7/2}\cos\Delta_{37}}{14R_{3/2}{}^2 + R_{5/2}{}^2 + 20R_{7/2}{}^2}, \tag{2}$$

where the R_j denote the moduli of the radial parts of the dipole matrix elements to the final state j, and the Δ's are phase differences. In the absence of relativistic interactions, both expressions reduce to [20]

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$$\beta = \frac{2R_p^2 + 12R_f^2 - 36R_pR_f\cos\Delta_{pf}}{10R_p^2 + 15R_f^2}, \tag{3}$$

where R_p and R_f are the two radial partial-wave amplitudes and Δ_{pf} is their phase-shift difference.

A fair bit of experimental data exists for Xe $4d$ photoionization. The cross section [22,23], spin-orbit branching ratio [24,25], and angular-distribution parameter [23,26–28] have been measured from threshold (67.5 eV) to 280 eV photon energy, and dipole transition matrix elements have been determined using electron-spin [29,30] and coincidence [31,32] measurements at a few energies. Two characteristic features of the $4d$ cross section appear in the energy range of these studies: the broad maximum (22 Mb) of the shape resonance at approximately 100 eV at the Cooper minimum near 185 eV. In most of the angular-distribution measurements [23,26,27], the $4d$ spin-orbit components were unresolved; only one unpublished report [28] measured spin-orbit-resolved $\beta_{5/2}$ and $\beta_{3/2}$, in the 72–128 eV range. Despite all this previous experimental work on Xe, there is no extant data resolving $\beta_{5/2}$ and $\beta_{3/2}$ in the vicinity of the Cooper minima.

The angle-dependent intensity of emitted electrons is described by the differential cross section $d\sigma/d\Omega$. Within the dipole approximation, for 100% linearly polarized light, the differential cross section is given by [17,18]

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}[1 + \beta P_2(\cos\theta)], \tag{4}$$

where σ is the partial cross section and P_2 is the second-order Legendre polynomial: $P_2(x) = (3x^2 - 1)/2$. The angle θ is between the electric field vector of the radiation and the direction of the outgoing electrons, measured in the plane perpendicular to the light propagation vector. This geometry is well suited for determination of β parameters, because first-order-nondipole contributions to the photoionization process vanish in the perpendicular plane [33].

To check possible systematic errors related to a particular experimental method, the measurements were done independently with hemispherical and time-of-flight (TOF) electron spectrometers at two different undulator beam lines at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. One experiment was carried out at beam line 10.0.1 using an end station designed for gas-phase angle-resolved studies based on the Scienta SES-200 hemispherical electron analyzer (HEA) [34,35]. The analyzer is rotatable in the perpendicular plane, allowing electron angular-distribution studies. Measurements at the θ angles of 0°, 54.7°, and 90° were performed, and angular-distribution parameters were determined using a method described by Kivimäki *et al.* [36]. This method uses intensity ratios of different lines within the spectrum at each angle. If the photoelectron angular distribution is sufficiently different for a pair of lines, then the β parameters for that pair can be determined accurately from measurements at three angles. In the TOF measurements, performed at ALS beam line 8.0 [37], two analyzers are mounted in the perpendicular plane at $\theta = 0°$ and $\theta = 54.7°$, allowing simultaneous measurements for accurate determination of β parameters. Details of the experiment are described elsewhere [38]. To determine β parameters, the data were calibrated with the Ne-$2s$ photoline, which has a fixed β value of 2. In both experiments, for most of the data, the photon energy was increased in 2 eV steps, because the energy splitting of the spin-orbit components is 2.0 eV. This approach permitted the measurement of $\beta_{5/2}$ and $\beta_{3/2}$ at the same photoelectron *kinetic energy,* and the difference $\beta_{3/2} - \beta_{5/2}$ could be calculated easily. At higher energies, where larger energy steps were used (TOF measurements only), continuous curves were interpolated through the measured values of β and used to estimate the difference $\beta_{3/2} - \beta_{5/2}$.

Calculations were performed using the relativistic random-phase approximation (RRPA) [21,39,40] based upon the Dirac equation; relativistic effects are included on an *ab initio* basis. All relativistic single-excitation channels from the $4s$, $4p$, $4d$, $5s$, and $5p$ subshells were included in the calculation, a total of 20 interacting channels. As noted above, in the absence of relativistic effects, β_j *must* be independent of j as a function of photoelectron energy. Any observed difference between $\beta_{5/2}$ and $\beta_{3/2}$ is an unambiguous manifestation of relativistic effects.

The present results for $\beta_{5/2}$ and $\beta_{3/2}$ as a function of photoelectron energy are shown in the lower panel of Fig. 1, where a clear difference is evident. To focus on this difference more clearly, values of $\beta_{3/2} - \beta_{5/2}$ are shown in the upper panel of Fig. 1, where zero corresponds to the nonrelativistic expectation. Also shown in Fig. 1 are the results of our RRPA calculations. The agreement is remarkably good between theory and experiment. The part missing from the theoretical curve is the $4p \rightarrow ns, nd$ resonance region where the theoretical results are affected by autoionization. There is also excellent agreement between the two sets of experimental results, providing confidence in the reliability of the measurements. Note particularly that the β-parameter curves are not simply shifted, but have different shapes, e.g., $\beta_{3/2}$ goes lower than $\beta_{5/2}$, and the difference persist to higher energy.

From Eq. (3), nonrelativistically, when there is a Cooper minimum in the $d \rightarrow f$ channel, $\beta = 0.2$. From Eqs. (1) and (2), relativistically, $\beta_{3/2} = 0.2$ at the $4d_{3/2} \rightarrow \varepsilon f_{5/2}$ Cooper minimum to an excellent approximation because dynamical effects on the radial matrix elements for the εp transitions are insignificant. The same is true for $\beta_{5/2}$, but with the value of 0.2 coming somewhere between the two εf minima. In the 105–110 eV region in Fig. 1, it is evident $\beta_{5/2}$ reaches a value of 0.2 about 2 eV lower in kinetic energy than $\beta_{3/2}$. Thus, purely from the experimental results, it can be inferred that the Cooper minimum in the $4d_{3/2} \rightarrow \varepsilon f_{5/2}$ channel lies about 2 eV above the "average" position of the Cooper minima in the $4d_{5/2} \rightarrow \varepsilon f_{5/2,7/2}$ channels. The calculated positions of the Cooper

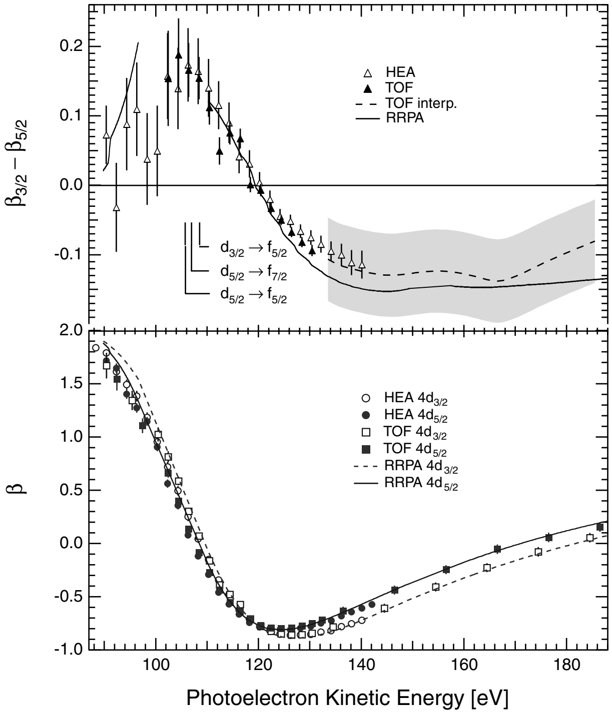

FIG. 1. Lower panel: Photoelectron angular-distribution parameters, $\beta_{5/2}$ and $\beta_{3/2}$, for Xe 4d ionization as a function of photoelectron energy. The points are the present experiment and the curves are our theoretical results. Upper panel: $\beta_{3/2} - \beta_{5/2}$ as a function of photoelectron energy derived from the data in the lower panel. The points are experiment and the solid curve is theory. The dashed curve was obtained via interpolation of the TOF data, and the shaded area represents error bars. Omitted from theory is the region of the $4p \to ns, nd$ resonances. Also shown are theoretical predictions for the locations of the Cooper minima.

minima, found at photoelectron kinetic energies of 105.74, 106.97, and 108.54 eV for $4d_{5/2} \to \varepsilon f_{5/2}$, $4d_{5/2} \to \varepsilon f_{7/2}$, and $4d_{3/2} \to \varepsilon f_{5/2}$, respectively (see Fig. 1), confirm this interpretation. To understand the ordering of the Cooper minima, we note the spin-orbit interaction is attractive for the $j = l - 1/2$ state, and repulsive for $j = l + 1/2$. Thus, the $4d_{3/2}$ wave function is more compact than $4d_{5/2}$, so the εf wave function, which moves towards the nucleus with increasing energy, reaches the Cooper minima with $4d_{5/2}$ at lower energy than $4d_{3/2}$. Similarly, the $4d_{5/2} \to \varepsilon f_{5/2}$ Cooper minimum occurs at lower energy than the $4d_{5/2} \to \varepsilon f_{7/2}$ minimum because the $\varepsilon f_{5/2}$ continuum wave function is pulled in relative to the $\varepsilon f_{7/2}$ owing to the spin-orbit interaction.

The same interactions influencing the discrete and continuum wave functions of Xe and splitting the Cooper minima are equally important over the entire energy range shown in Fig. 1. As a result, the wave functions for the various channels differ somewhat. This difference leads to differences in the dipole matrix elements, which in turn lead to observable differences in the β parameters. The reason the interchannel effects are pervasive over a broad energy region is the various matrix elements for transitions to εf, owing to the existence of the Cooper minima, remain quite small over this whole range. Because interchannel coupling tends to strongly affect weak channels degenerate with strong ones [17,41,42], the result is significant quantitative alteration of the εf matrix elements over an extended range, even up to the highest energies investigated experimentally, ~100 eV above the Cooper-minimum region.

At still higher energies, recent work has shown that interchannel interactions are pervasive and often dominant for most subshells of most atoms at most energies [42,43], so much so that even the asymptotic form of the high-energy nonrelativistic photoionization cross section for non-s states is altered [44]. Thus, as long as 4d photoionization does not dominate the total cross section, significant interchannel interactions will modify the 4d transition amplitudes. But there is no reason to expect these interchannel interactions will modify each relativistic amplitude in the same way, i.e., interchannel coupling will cause observable differences between $\beta_{3/2}$ and $\beta_{5/2}$ for *all* higher energies. Near threshold, it is also known that $\beta_{3/2}$ and $\beta_{5/2}$ differ [23,26–28,45] due to differing exchange interactions among the relativistic channels. Only in the shape-resonance region, 30–80 eV kinetic energy, are there no differences between $\beta_{3/2}$ and $\beta_{5/2}$, because the 4d cross section dominates here, and the energy is high enough so exchange interactions are no longer important; interchannel interactions are negligible *only* in this narrow region. Thus, except for a small energy region near the 4d shape resonance, equality of $\beta_{3/2}$ and $\beta_{5/2}$ is the exception, not the rule.

Finally, there is no reason to suspect Xe 4d is a special case; the results found in this work should be quite general. We thus expect effects of relativistic interactions on interchannel coupling will be widespread over all intermediate-Z atoms. These effects also should be manifest in molecules, clusters, surfaces, and solids.

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