Strong Electron Correlation in Photoionization of Spin-Orbit Doublets

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A new and explicitly many-body aspect of the "leveraging" of the spin-orbit interaction is demonstrated, spin-orbit activated interchannel coupling, which can significantly alter the photoionization cross section of a spin-orbit doublet. As an example, it is demonstrated *via* a modified version of the spin-polarized random phase approximation with exchange, that a recently observed unexplained structure in the Xe $3d_{5/2}$ photoionization cross section [A. Kivimäki *et al.,* Phys. Rev. A **63**, 012716 (2000)] is entirely due to this effect. Similar features are predicted for Cs $3d_{5/2}$ and Ba $3d_{5/2}$.

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More than 30 years ago, Ugo Fano published a paper [1] explaining how the spin-orbit force is "leveraged" to produce substantial effects in atoms. It had just been demonstrated that the weak spin-orbit force, being a small relativistic correction to the Coulomb nuclear force, could lead to a significant polarization of photoelectrons [2,3]. This discovery opened up an entirely new domain in atomic physics. A decade later, it was predicted [4] and soon observed [5], that this same small force causes large distortions in the energy dependence of *s* electrons angular distribution asymmetry parameters, in particular to the 5*s* in xenon. Research in this direction supplies a stringent test for many-body theories of photoionization [6].

In both of the previous examples of the leveraging of the spin-orbit force in atoms, photoelectron spin polarization and distortion of the angular distribution of photoelectrons, the effect was present in the single-particle picture. Of course, many-body interactions altered the effect quantitatively a substantial amount, but still, the qualitative effect was there at the single-particle level.

In this paper, we present an entirely new example of a strong effect that is "activated" only due to the action of this weak spin-orbit interaction. Furthermore, this new example differs from the previous manifestations in that it is an explicitly many-body effect, a correlation effect, with no single-particle analog. The correlation effect that is activated in this case is what is known as interchannel coupling, which is really just configuration interaction among continuum states. In recent studies, substantial effects of interchannel coupling have been shown to be pervasive in the photoionization of both inner and outer shells, not only near thresholds, but at intermediate and high energy as well [7–9]. It has even been found that interchannel coupling alters the asymptotic nonrelativistic high-energy behavior of most subshell cross sections [10].

This new example of the leveraging of the spin-orbit force was stimulated by a recent experimental investigation [11] of the photoionization cross section of the 3*d* subshell of Xe, where an additional broad structure in the $3d_{5/2}$ partial photoionization cross section was discovered. Multiconfiguration direct-fock calculations (MCDF) were performed [11] and the results exhibited no hint of this newly discovered maximum, although the same theoretical technique gave good agreement for Kr $3d_{3/2}$ photoionization where this extra maximum was not found. The MCDF calculations, however, omit many-body interactions among the various possible ionization channels. In this paper, a new manifestation of interchannel coupling is uncovered, one that requires the action of the spin-orbit interaction to activate it.

To demonstrate how this works, calculations of the photoionization cross sections and photoelectron angular distribution asymmetry parameters have been performed within the framework of the newly developed version of the Generalized spin-polarized random phase approximation with exchange (SPRPAE) [12] which includes core relaxation and improved threshold energies. This structure was a result of strong interaction between electrons belonging to two components of the $3d_{5/2}$ and $3d_{3/2}$ doublets, which, however, becomes observable only due to the spin-orbit interaction that splits $3d_{5/2}$ and $3d_{3/2}$ levels. This observation presents an entirely new area of manifestations of the role played by interaction between electrons of different atomic levels.

For deep enough subshells, such as Xe 3*d*, the corrections to the single-particle photoionization amplitude introduced within the framework of the random phase approximation with exchange (RPAE) were usually thought to be quite small; taken to be of greater importance were usually rearrangement and/or relaxation effects [13]. But the new understanding of the widespread influence of interchannel coupling suggests, however, that RPAE corrections in the form of interchannel coupling can still be important. Thus, to treat the mutual influence of $3d_{5/2}$ and $3d_{3/2}$, one must take into account RPAE and rearrangement simultaneously.

To take into account the interaction between two components SPRPAE was applied [14]. This approach treats electrons with $+1/2$ and $-1/2$ spin projections as different particles, without exchange between them. Therefore, a ten-electron subshell is split into two levels with five electrons in each. The photoionization amplitude is then given by

$$\hat{D}_u(\omega) = d_u + \hat{D}_d \times \hat{\chi}_d \times \hat{V}_{du}. \quad (1)$$

Here $\hat{D}_u(\omega)$ is the "up" photoionization amplitude with account of interaction between "up" and "down" electrons, d_u is the photoionization amplitude with account of interaction among up electrons only. The operator $\hat{\chi}_d(\omega) \equiv (\omega - \hat{H}^d_{ev})^{-1} - (\omega + \hat{H}^d_{ev})^{-1}$ describes the propagation of noninteracting virtually created electron and vacancy, with the one-electron Hartree-Fock Hamiltonian $\hat{H}^d_{ev}$ and $\hat{V}_{du}$ denoting the interelectron Coulomb potential $V_{12} = 1/|\vec{r}_1 - \vec{r}_2|$. The equation for down electrons can be obtained from Eq. (1) by interchanging the indexes u by d. A detailed description of how to solve these equations and how to take into account the electron shell rearrangement after the $3d$ vacancy creation can be found in Ref. [14].

The photoionization cross section is determined by

$$\sigma_u(\omega) = \frac{4\pi\omega}{c} |\langle i_u|\hat{D}_u(\omega)|\varepsilon_u\rangle|^2. \quad (2)$$

Here $\varepsilon_u = \omega - I_u$, with I_u being the up electrons ionization potential. The expression for down electrons is similar, with u substituted by d.

However, this formulation must be adapted to the present case, because the number of electrons in $3d_{5/2}$ and $3d_{3/2}$ subshells is equal to six and four, respectively, instead of five, as implied by the up-down approach. To take this difference into account, we (slightly) modified Eq. (1) introducing into the second term in Eq. (1) the factor $\eta_{u,d} = 2(2j_{n,d} + 1)/N_{3d}$, where N_{3d} is the number of $3d$ electrons, $j_{u,d} = 5/2(3/2)$. Thus, we relate the up equation to the $3d_{5/2}$ electrons and the down equation to $3d_{3/2}$; the ionization potentials are taken from experiment, 676 and 689 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively [15]. The second term in the up equation has to be multiplied by $4/5$ while for down equation it is $6/5$. The corresponding $3d_{5/2}$ and $3d_{3/2}$ cross sections that are determined by square modulus of the up and down amplitudes have to be multiplied by factors $6/5$ and $4/5$, respectively.

The results of our model calculations for the Xe $3d$ cross sections are presented in Fig. 1, along with experimental data [11]. Reasonably good agreement is evident. The interchannel coupling of the $3d_{3/2}$ photoionization channels with the $3d_{5/2}$ channels is manifested by the second maximum in the $3d_{5/2}$ partial cross section, which is well predicted by our model calculation. Fundamentally, this second maximum in the $3d_{5/2}$ partial cross section is a result of the mixing of a small amount of the continuum wave functions of the $3d_{3/2}$ channels with the $3d_{5/2}$ continuum functions; the change to the matrix element is represented by the second term in Eq. (1). Since the $3d_{3/2}$ cross section is much larger than the $3d_{5/2}$ around 700 eV, the mixing of even a small amount of $3d_{3/2}$ with $3d_{5/2}$ can alter the latter considerably. Furthermore, as see from Eq. (1), the alteration in the $3d_{5/2}$ matrix element is proportional to V_{du} or $\langle 3d_{3/2}kl|1/r_{12}|3d_{5/2}k'l\rangle$. This matrix element is quite large since the $3d_{5/2}$ and $3d_{3/2}$ wave functions are virtually the same, leading to excellent overlap. This combination of factors results in a second maximum in the $3d_{5/2}$ cross section, as seen in Fig. 1. But this mixing is complicated, and, as the sum over energy in second order perturbation theory shows, the mixing does not occur only between states of the same energy. Thus, the new structure in the $3d_{5/2}$ cross section does not occur exactly at the maximum of the $3d_{3/2}$ cross section. Needless to say that the total photoabsorption cross section, which is a sum of the partial contributions, is also in good agreement with the experimental data.

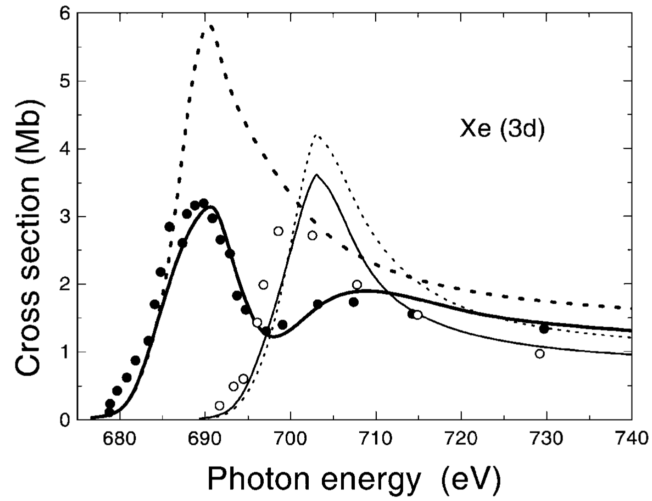

FIG. 1. Photoionization cross sections for the spin-orbit components of the $3d$ subshell of Xe. The thick and thin solid curves are the present correlated (RPAE) theoretical results for Xe $3d_{5/2}$ and $3d_{3/2}$, respectively, while the dashed curves present the respective uncorrelated (HF) results. The solid and open circles are the experimental results of Ref. [11] for Xe $3d_{5/2}$ and $3d_{3/2}$, respectively.

The effect of this spin-orbit activated interchannel coupling is particularly striking in the case of Xe $3d$ owing to the shape resonances that occur above each threshold of the $3d \rightarrow kf$ channels [5]. But, from the explanation of the origins of this phenomenon, it is clear that this effect could be of importance for any innershell spin-orbit doublet. The interchannel coupling matrix element between the channels spin-orbit doublet will *always* be large since the spin-orbit interaction exerts so small a perturbation on the radial wave functions so that the $j = l \pm 1/2$ orbits of the doublet are nearly identical; this is evident from the small splitting of their binding energies (~10 eV) compared to the ~700 eV binding energies themselves. Note that, in addition to the strength of the interchannel coupling matrix element, for this spin-orbit activated interchannel coupling to be significant, it is necessary for the splitting of the thresholds of the spin-orbit doublet be large enough so that the $j = l + 1/2$ cross section be rather smaller than the $j = l - 1/2$ in the vicinity of the $j = l - 1/2$ threshold. Thus, it is not expected (or found) for this effect to appear for outer or near-outer atomic subshells, such as Kr $3d$ where the splitting is only $\sim$1 eV.

To emphasize the generality of spin-orbit activated interchannel coupling effect in atomic photoionization, calculations have also been performed for the photoionization of Cs $3d$ and Ba $3d$ employing the same methodology described above in connection with Xe. The cross sections obtained for Cs $3d$ are shown in Fig. 2, along with the corresponding HF cross sections, and show a close qualitative similarity to the Xe results. A very strong structure is seen in the $3d_{5/2}$ cross section in a region where the corresponding HF cross section is monotone decreasing. As in the Xe $3d_{5/2}$ case, this is due to interchannel coupling. This result further emphasizes the complexity of the interchannel coupling interaction, which can also decrease the cross section, as evidenced by the pronounced dip just below 740 eV seen in Fig. 2. But it is clear that in both the case of Xe $3d_{5/2}$ and Cs $3d_{5/2}$ cross sections, the interchannel coupling with the $d \rightarrow f$ shape resonance in the $3d_{3/2}$ channel produces new structures.

Our theoretical cross sections for the case of Ba $3d$ are shown in Fig. 3, along with the corresponding HF results. These results appear to be completely different qualitatively from the Xe and Cs results. To understand this phenomenology, note that the shape resonances in the HF cross sections are gone in the case of Ba, as seen in Fig. 3. This is because the resonances have moved into the discrete region; specifically the $4f$ has *collapsed* into the inner region, thereby dramatically increasing the overlap with the innershell $3d$ wave functions. Thus, the Ba $3d_{5/2}$ RPAE cross section is dramatically altered through interchannel coupling, not with the continuum part of the $3d_{3/2}$ photoionization channels, but the discrete part, specifically, the $3d_{3/2} \rightarrow 4f$ autoionizing transition. This autoionizing resonance is seen to completely dominate the character of the Ba $3d_{5/2}$ cross section just below the opening of the $3d_{3/2}$ channel. Thus, from a theoretical point of view, the physics of the Ba situation is almost the same as in Xe and Cs; the one difference is that the resonance now lies in the discrete (autoionizing) region rather than in the open continuum. Nevertheless, in all three cases, it is spin-orbit activated interchannel coupling that introduces the new structures.

In addition, the effect should not be limited to atoms; it is expected that it will be exhibited in ions, molecules, clusters, and condensed matter as well; particularly for innershell photoabsorption, where aggregates of matter tend to behave substantially like their atomic constituents. Thus, the effect should be very general.

Calculations of the photoelectron angular distribution anisotropy parameter β have also been performed for both members of the Xe $3d$ spin-orbit doublet. The calculated β's are in reasonable agreement with the experimental results, as seen from Fig. 4. More importantly, the calculation shows no noticeable effect of the extra structure in the $3d_{5/2}$ cross section in the angular distribution; the experimental results seem to show a slight structure, but it is well below the noise level and cannot be taken seriously. The reason that the structure shows up in the cross section, but not in β, is that β is a ratio [12,16,17]. The spin-orbit activated interchannel coupling affects both $d \rightarrow p$ and $d \rightarrow f$ channels and their ratio is not significantly altered,

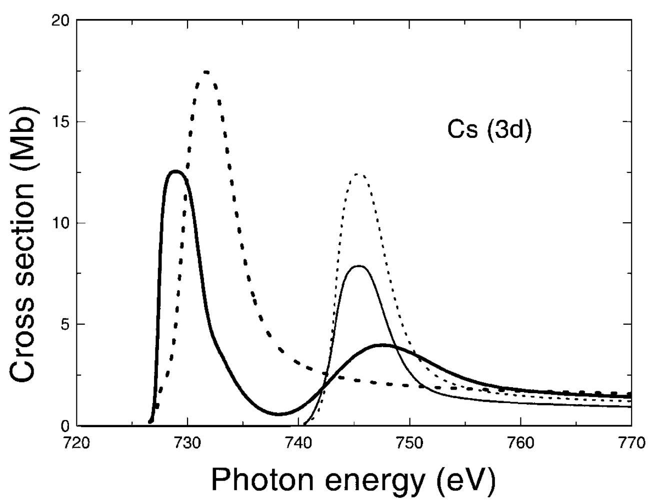

FIG. 2. Photoionization cross sections for the spin-orbit components of the $3d$ subshell of Cs. The thick and thin solid curves are the present correlated (RPAE) results for Cs $3d_{5/2}$ and $3d_{3/2}$, respectively, while the dashed curves present the respective uncorrelated (HF) results.

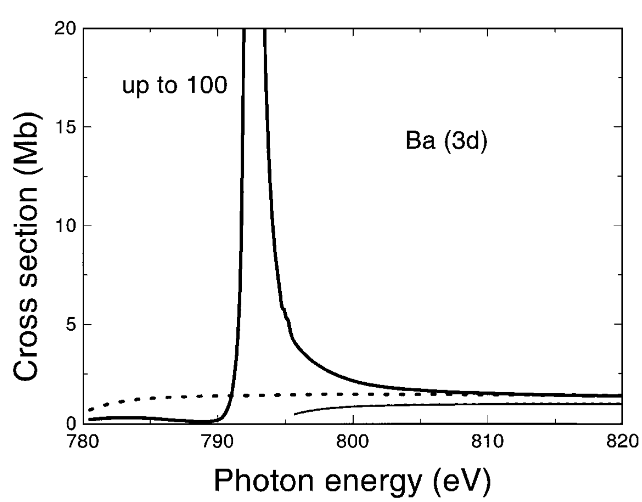

FIG. 3. Photoionization cross sections for the spin-orbit components of the $3d$ subshell of Ba. The thick and thin solid curves are the present correlated (RPAE) results for Ba $3d_{5/2}$ and $3d_{3/2}$, respectively, while the dashed curves present the respective uncorrelated (HF) results.

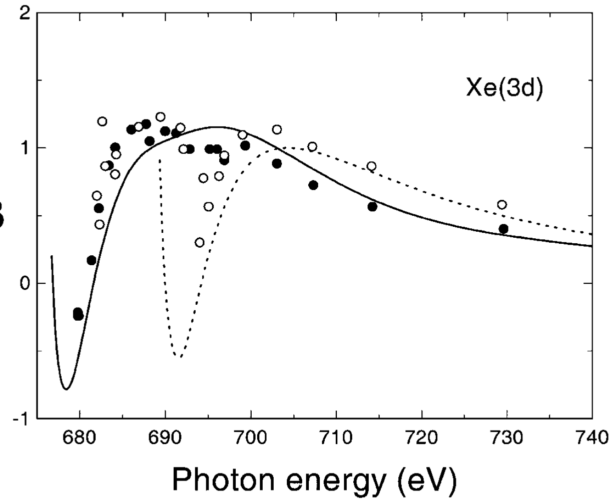

FIG. 4. Photoelectron angular distribution asymmetry parameter β for the spin-orbit doublet of Xe $3d$. The solid and dashed curves are the present correlated (RPAE) results for Xe $3d_{5/2}$ and $3d_{3/2}$, respectively. The solid and open circles are the experimental results of Ref. [11] results for Xe $3d_{5/2}$ and $3d_{3/2}$, respectively.

thereby producing no second maximum in β for the case of $3d_{5/2}$. A more detailed study of the β's will be presented separately.

In summary then, a new phenomenon has been discovered, spin-orbit activated interchannel coupling, in which the interaction among photoionization channels from the members of a spin-orbit doublet produces marked changes in partial cross sections. This is the first example of spin-orbit leveraging that has no single-particle aspect; the leveraging is only in the realm of correlation. To confirm the existence of this effect, model calculations were performed and good agreement was obtained with a previously unexplained structure in the Xe $3d_{5/2}$ partial cross section found in a recent experimental measurement of the Xe $3d$ partial cross sections. In addition, the effect was shown to exist for Cs and Ba $3d$ photoionization as well. Furthermore, the generality of this effect over the periodic table and for ions, molecules, clusters, and condensed matter was pointed out. It is important to note the idea of this effect is more general still. The essence of this interaction involves the spin-orbit force breaking the degeneracy among the electrons of a subshell; once the degeneracy is broken the photoionization channels arising from the distinct degenerate groups can interact. But electric or magnetic fields other than those produced through the spin-orbit interaction can also remove this degeneracy, e.g., molecular or crystal fields. Thus, it is expected that effects similar to the spin-orbit activated interchannel coupling will be ubiquitous in many physical systems.

Finally, note that the calculations performed have been aimed at a qualitative explanation of the phenomenon of spin-orbit activated interchannel coupling, along with its generality, and to provide an explanation of the experimental observation of a new structure in the photoionization of Xe $3d$. However, to achieve higher quantitative accuracy, fully relativistic *ab initio* calculations are in progress.

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