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Letter

Dramatic effects of relaxation on many-body interactions: Theoretical and experimental study of atomic photoionization of outer shells in the vicinity of inner-shell thresholds

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A R T I C L E I N F O

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A B S T R A C T

Experimental studies of the Xe $4d_{5/2}$:$4d_{3/2}$ branching ratio in the vicinity of the inner shell 3d thresholds have been made and exhibit significant structure owing to interchannel coupling. New calculations at the Relativistic-Random-Phase Approximation (RRPA) also are reported here in which core relaxation has been included (RRPA-R) and this brings theory and experiment into excellent agreement. Earlier RRPA calculations that ignore relaxation are in both quantitative and qualitative disagreement with the present experimental results.

Many-body effects are of great importance in almost all fields of physics, e.g. [1–4]. Thus, the accurate calculation of many-body correlations is necessary for a wide range of physical phenomena. This is of particular significance in atomic, molecular and optical physics where the inclusion of many-body interactions is crucial to obtaining reliable results for both electronic structure and transition calculations [1]. Clearly, this is of greatest interest in those transition processes where the many-body interactions dominate. Many-body interactions are characterized by wave functions that go beyond a single-particle approximation. For the photoemission process, these can be important either the initial discrete (bound) or final continuum wave functions, or both. Typically, these are known as multi-particle or multiconfiguration wave functions. For discrete wave functions, this is known as configuration interaction, while in the continuum it is called interchannel coupling [5].

Recently, it has been found that the photoionization of atomic electrons in the vicinity of the opening of photoionization channels of subshells with significantly larger threshold energies is greatly influenced by interchannel coupling [6,7]. Theoretical predictions of the situation have been made using the relativistic-random-phase approximation (RRPA) methodology [8] which includes both discrete (bound) state correlations along with interchannel coupling. More specifically,

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calculations of the branching ratios of the spin-orbit outer-shell doublets, the ratio of the $j = l + 1/2$ over the $j = l - 1/2$ cross sections, near inner-shell thresholds were presented. Branching ratios were selected for this investigation because experimentally, they can be obtained more accurately than cross sections because various systematic errors in the cross-section measurements cancel out in the branching ratios. In any case, these calculations predicted significant variations of the branching ratios over small energy regions around the inner-shell thresholds. To test the situation in detail we have embarked upon an experimental program to study these predicted effects. We report here on the first step in this investigation. Measurements have been made on the Xe atom, looking at the branching ratios of outer-shell spin-orbit doublets in the energy region of the 3d thresholds which are split into $3d_{5/2}$ and $3d_{3/2}$ owing to relativistic effects.

The experimental results, as shall be seen, show – as predicted – significant effects around the inner thresholds. However, the variations in the ratio are in significant disagreement, both qualitatively and quantitatively, with the existing calculations [7]. Clearly some important physics is missing from those calculations. Calculations of the near-threshold photoelectron angular distribution parameters for Xe 3d, where interchannel coupling is crucial, have shown the importance of the inclusion of core relaxation [10]. To test the generality of this notion, we have performed new calculations including relaxation, RRPA with relaxation, RRPA-R [11].

RRPA-R is substantially the same as ordinary RRPA except for one major departure; RRPA-R employs relaxed orbitals to describe the final state of the residual ion, while RRPA uses the unrelaxed orbitals of the initial state of the atom. RRPA is well-documented in the literature [8] as is RRPA-R [1] along with the Random-Phase Approximation with Exchange (RPAE) [12] which omits relativity, so we do not detail them here. It is of importance to point out, however, that the interchannel coupling matrix element is obtained with relaxed ionic orbitals in the RRPA-R method vs. unrelaxed atomic orbitals in the standard RRPA calculation, along with continuum wave functions that are calculated in the field generated by the relaxed discrete (bound) orbitals. Also, the threshold energies in the two calculations are significantly different. In the RRPA-R method, the Dirac-Hartree-Fock (DHF) energies of the *N-electron* initial state and the *N-1-electron* final state of the residual ion are calculated using the Oxford-MCDF package [13]. The ionization threshold energy is then taken to be difference in these two self-consistent field (SCF) energies, ΔE_{SCF}. Note that the final state calculation gives the relaxed orbitals. In the RRPA calculation, the threshold energies are taken to be the energy eigenvalues of the DHF equations. Note that the ΔE_{SCF} for Xe $3d_{5/2}$ and $3d_{3/2}$ used in RRPA-R, 676.7 eV and 689.6 eV, respectively are much closer to experiment [14], 676.4 eV and 689.0, than the DHF energies, 694.9 eV and 708.1 eV, used in the RRPA calculation. One *caveat*, however, is that in the RRPA method, length and velocity forms of the dipole matrix element are strictly equal [8,12]. This is not the case for RRPA-R. As a practical matter, our calculations show that the difference between length and velocity results using RRPA-R are less than 10 % at worst, and usually they are within a few percent. Furthermore, since generally the deviation of the velocity cross sections calculated with relaxation for both members of the spin-orbit doublet is in the same direction, the deviation of the ratio is even smaller.

The experiments were performed at the PLEIADES beamline [9] at the synchrotron SOLEIL in France. At this beamline a high-resolution plane-grating monochromator (PGM) is installed. The photoelectrons were collected using a VG-Scienta 4000 hemispherical electron analyzer equipped with a gas cell using a pass energy of 200 eV and a curve slit width of 800 μm. In combination with a 600 lines/mm grating and an exit slit of 100 μm for the monochromator a total energy resolution between 0.5 eV at 630 eV and 0.6 eV at 730 eV was achieved. Note that this resolution is sufficient to resolve well the spin-orbit split Xe 4d photoelectron peaks. The spectra were measured at magic angle, i.e., an angle of 54.7 degrees between the polarization direction of the light and the detector direction. The spectra were calibrated using the Xe 5p photoelectron lines in first order light in combination with the Xe 3d photoelectron lines in second order light resulting in an accuracy of about 100 meV for the photon energy axis. The intensity of the 4d photoelectron lines was extracted using Lorentzian line shapes with a lifetime broadening of 115 meV convoluted with a Gaussian function in order to simulate the experimental resolution.

The experimental branching ratios for Xe 4d in the vicinity of the 3d thresholds are shown in Fig. 1. Clearly something significant is going on in this range. Away from the 3d thresholds the branching ratio is more or less constant at the statistical value of 1.5. Close to the 3d thresholds, however, it rises to a value of about 1.7 and drops to about 1.1, a fairly large traverse over a small (30 eV) energy range, before moving back to the statistical value at higher energies. Previous work has shown that the structure of the branching ratio in the vicinity of inner-shell thresholds is due to correlation in the form of interchannel coupling, i.e., configuration interaction in the continuum [6,7]. The RRPA result of Ref. [7] is also shown in Fig. 1 and, while it also shows significant variation of the branching ratio in this region, the agreement with the experimental result in the region of significant variation is seen to be quite poor. Note, however, that away from this region, at higher and lower energies where the experimental branching ratio is constant, agreement is quite good. Our calculated RRPA-R branching ratio is also shown and excellent agreement with experiment is seen in the region of the 3d thresholds. Thus, it is clear that the inclusion of relaxation is crucial to the accuracy of the calculations. But why?

To answer this question, we look first at why interchannel coupling leads to variations in the cross sections, and therefore, in the ratio. After this we shall discuss the influence of relaxations on the variations. Perturbation theory provides a framework to explain the variations depicted in Fig. 1. The dipole matrix element for channel i with interchannel coupling included, $D_i(E)$, is related to the matrix elements which do not include the interchannel coupling, $M_j(E)$, as [15]

$$D_i(E) = M_i(E) + \sum_j \int dE' \frac{< \varphi_i(E)|V|\varphi_j(E') >}{E - E'} M_j(E'), \tag{1}$$

where the integral is over all energies from threshold to ∞ for each open channel, the sum is over all open photoionization channels and V is the

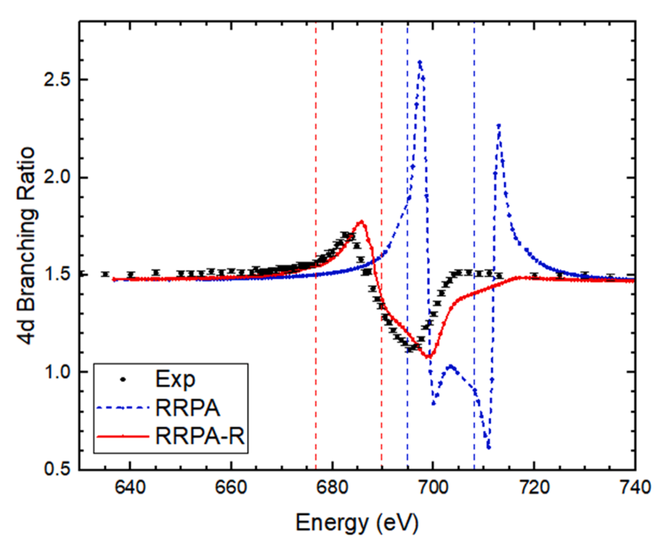

Fig. 1. (color online) Xe $4d_{5/2}$:$4d_{3/2}$ photoionization branching ratio in the vicinity of the 3d thresholds. The points with error bars are the present experimental results, the dashed curve is the RRPA calculation from Ref. [7] and the solid curve is the present RRPA-R result. The vertical dashed lines indicate the calculated 3d thresholds; the lower pair the ΔESCF $3d_{5/2}$ and $3d_{3/2}$ relevant to the RRPA-R calculation and the higher-energy pair the DHF results used in the RRPA calculation.

perturbation. The continuum wave functions $\varphi_i(E)$ and $\varphi_j(E')$ are the unperturbed (without interchannel coupling) final-state wave functions. The first term in this equation is the unperturbed dipole matrix element, and the second term the correction to this matrix element owing to the interchannel coupling. In the present context, i represents the Xe $4d_{5/2}$ or $4d_{3/2}$ photoionization channels, while j stands for the Xe $3d_{5/2}$ and $3d_{3/2}$ channels. This equation demonstrates that the interchannel coupling correction to the unperturbed dipole matrix element depends upon many things. However, it is clear that it is likely to be the largest when the denominator goes to zero, i.e., when $E = E'$ that occurs when both channels i and j are open at the photon energy under consideration. Furthermore, if $M_j(E)$ is significantly larger than $M_i(E)$, which is typical close to the inner ionization threshold, then the interchannel coupling correction will be enhanced. In short, when two photoionization channels are open at the same energy, the stronger one can alter the weaker one greatly *via* interchannel coupling [16]. This is also enhanced by the fact that near the 3d thresholds, the photoelectrons emitted from the 3d subshells have very low energy so that their wave functions do not oscillate very much. This means that the interchannel coupling matrix element will be much larger near the 3d thresholds than at higher energy where the oscillations in the 3d photoelectron wave functions tend to damp it. In any case, it is clear that the structure in the branching ratio is caused by the second (interchannel coupling) term of Eq. (1).

At energies E below the inner shell thresholds, contributions to the interchannel coupling term can only be found for large values of the energy denominator E - E' because the 3d photoionization channels are closed here, i.e., $M_j(E') = 0$ for E' below the corresponding ionization threshold. As a result, this term is no longer important and the matrix element is dominated by the first term in Eq. (1). In addition, at energies well above the 3d thresholds the interchannel coupling matrix element diminishes from the oscillations on the 3d photoelectron wave functions, as discussed above, and, where the energy denominator is small, the 3d matrix elements are no longer so large compared to those of the outer shell. This combination of effects diminishes considerably the importance on the interchannel coupling term in Eq. (1). Thus, at energies well above the inner shell thresholds, the matrix element is also dominated by the first term in Eq. (1).

The discussion up to this point applies to both calculations, without and with relaxation. Now we turn to the individual results of both calculations. From Fig. (1) it is clear that away from the inner thresholds, RRPA and RRPA-R branching ratios agree well with each other and with experiment. In fact, the cross sections themselves (only the RRPA-R cross sections are shown in Fig. 2) are also in agreement away from the inner threshold. That means that the uncoupled continuum wave functions for all of the photoionization channels, the $\varphi_i(E)$, and thus the $M_i(E)$, are not strongly affected by relaxation. Looking at the second term in Eq. (1) then, it must be the interchannel coupling matrix element that is significantly changed by the use of relaxed wave functions. The reason that the interchannel coupling matrix element is strongly affected by the relaxation, but not the uncoupled dipole matrix elements, the $M_i(E)$, is that the former is sensitive to the wave functions, discrete and continuum, at small radial distance, r, because the operator V in Eq. (1) is essentially e^2/r_{ij} which is large at small radial distances. The $M_i(E)$, on the other hand, are sensitive to the wave functions at large r because they are matrix elements of the dipole operator $\boldsymbol{r}$ which obviously emphasizes large radial distances. Evidently, relaxation induces more significant changes in the wave functions at small r than at large r.

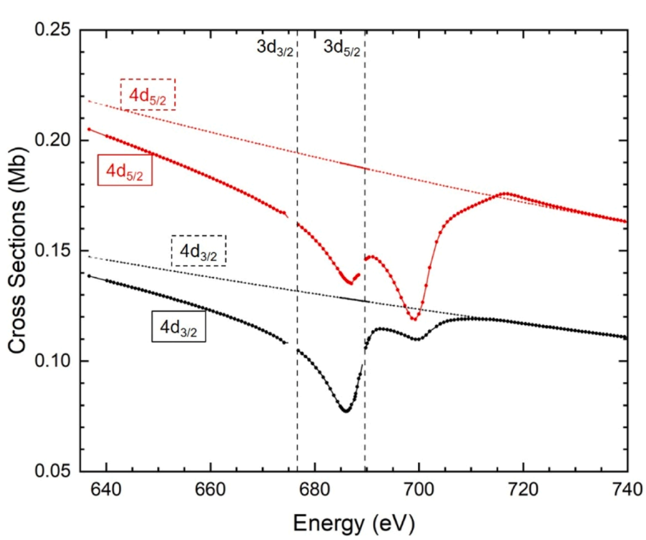

Fig. 2. (color online) Calculated Xe 4d RRPA-R cross sections with (full lines) and without (dotted lines) coupling to the 3d channels.

To emphasize these points, the 4d cross sections calculated using the RRPA-R, i.e., with relaxation, are shown in Fig. 2 with and without coupling to the 3d photoionization channels. The uncoupled cross sections are seen to be smooth and monotone decreasing in this energy range while the coupled cross sections show dramatic variations. Since leaving out the coupling is essentially ignoring the second term in Eq. (1), this plot shows its influence in the region of the 3d thresholds. Note that at the higher energies, above about 710 eV, the coupled and uncoupled cross sections coalesce, indication that the second term in Eq. (1) is of no real importance that far away from the 3d thresholds.

In conclusion, our measurements of the branching ratios for the 4d subshells of the Xe atom have shown that the existing theoretical RRPA calculations [7] were both qualitatively and quantitatively incorrect in the region of the inner-shell 3d thresholds, where the interchannel coupling aspect of many-body interactions are known to be of importance. However, the introduction of core relaxation into the calculation, using RRPA-R, results in quite good agreement with our experimental values. The improvement was traced to a change in the interchannel coupling matrix elements driven by the change in the ion core wave functions induced by the relaxation. It is expected that this will be a general phenomenon for all aspects of photoemission processes for outer shells in the neighborhood of inner-shell thresholds of atomic and molecular systems (including both positive and negative ions). Furthermore, there is no reason that these considerations should be limited to optically allowed final-state wave functions, so relaxation should be important for charged-particle and multiphoton ionization as well.

CRediT authorship contribution statement

R.V. Silva: Writing – review & editing, Visualization, Software, Formal analysis. **C.R. Munasinghe:** Writing – review & editing, Visualization, Supervision, Software, Methodology, Investigation. **A. Ganesan:** Writing – review & editing, Software, Methodology, Formal analysis. **P.C. Deshmukh:** Writing – review & editing, Validation, Supervision, Software, Formal analysis. **S.T. Manson:** Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization. **A. Verma:** Writing – review & editing, Investigation, Formal analysis. **D. Peng:** Writing – review & editing, Investigation. **I. Ismail:** Writing – review & editing, Investigation. **T. Marchenko:** Writing – review & editing, Investigation. **O. Travnikova:** Writing – review & editing, Investigation. **R. Guillemin:** Writing – review & editing, Investigation. **N. Velasquez:** Writing – review & editing, Investigation. **M.N. Piancastelli:** Writing – review & editing, Supervision. **J.D. Bozek:** Writing – review & editing, Investigation, Formal analysis. **M. Simon:** Writing – review & editing, Supervision, Investigation. **R. Püttner:** Writing – original draft, Supervision, Project administration, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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