Correlation structure in nondipole photoionization

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(Dated: December 24, 2021)

The nondipole parameters that characterize the angular distribution of the photoelectrons from the 3d subshell of Cs are found to be altered qualitatively by the inclusion of correlation in the form of interchannel coupling between the 3d_{5/2} and 3d_{3/2} photoionization channels. A prominent characteristic maximum is predicted only in the parameters for 3d_{5/2} photoionization, while the effect for 3d_{3/2} is rather weak. The results are obtained within the framework of the Generalized Random Phase Approximation with Exchange (GRPAE), which in addition to the RPAE effects takes into account the rearrangement of all atomic electrons due to the creation of a 3d vacancy.

PACS numbers: 31.20Tz, 31.50.+b, 32.80.Dz, 32.80.Fb, 32.80.Hd

Nondipole effects in the photoionization of atoms and molecules were thought to be of any importance only at multi-keV photon energies[1, 2] despite indications to the contrary[3, 4, 5]. However, in an upsurge of work on the subject, it was found both theoretically and experimentally that nondipole effects are often of significance at photon energies of hundreds and even tens of eV[6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16]. It has been determined that photoelectron angular distributions are particularly affected by these nondipole photoionization channels. In lowest order, the effect of the non-dipole channels is to add two new terms to the well-known dipole expression for the photoelectron angular distribution, along with their associated dynamical parameters, \( \gamma \) and \( \delta \), the nondipole parameters[5, 7, 8, 17, 18]. These parameters arise from the interference of dipole and quadrupole (E1 and E2) channels in much the same manner that the \( \beta \) parameter, which characterizes the dipole photoelectron angular distribution, arises from dipole-dipole interference[19].

Studies of these nondipole parameters have found \( \gamma \) and \( \delta \) to be essentially structureless, except in regions of dipole or quadrupole resonances[11, 16] or Cooper minima[13]. It has also been averred that correlation effects are unimportant for nondipole effects[20]. In this communication, we show that assertion to be incorrect. In fact, we report on a new phenomenon, a new kind of structure in nondipole parameters that has nothing to do with resonances or Cooper minima. This structure, as shall be shown below, is due solely to many-body correlations; it has no analogue in a single-particle picture. Furthermore, the structure is induced by relativistic interactions; it does not arise in a non-relativistic calculation. Thus, the study of this structure is a direct measure of relativistic correlation effects.

To understand the basic origin of this structure, note that it was demonstrated recently[21] that the interaction between photoionization channels belonging to different components of the spin-orbit doublets 3d_{5/2} and 3d_{3/2} in Xe, Cs and Ba affect dramatically the partial photoionization cross sections. Specifically, it was shown that due to this interchannel coupling interaction, the partial 3d_{5/2} cross section acquires an additional prominent maximum. This result gave the explanation for the recent experimental observation of this effect in Xe[22] and also predicted similar, even more dramatic effects for 3d photoionization in Cs and Ba.

In this communication we present the results of our studies, based on the approach developed earlier[21], of the nondipole angular distribution parameters for 3d photoionization in Cs to illustrate a new phenomenon where impressive manifestations of intra-doublet interchannel interactions producing new structures in nondipole parameters are predicted, thereby also contradicting the notion that correlation does not affect nondipole parameters significantly.

The theoretical results were obtained using a specially modified random-phase-approximation with exchange (RPAE) approach previously developed for half-filled subshells[23, 24]. This calculation showed clearly the physics of the phenomenon observed[22] and led to results[21] that are in both qualitative and quantitative agreement with experimental 3d Xe data. Explicitly relativistic calculations[25] were subsequently performed using the relativistic-random-phase approximation (RRPA)[26] which confirmed the qualitative and quantitative accuracy of the results in[21].

To summarize the theoretical approach, we consider the 3d_{5/2} and 3d_{3/2} subshells each as half-filled atomic subshells. This permits us to apply straightforwardly the RPAE methodology to include many-body correlations (including interchannel coupling) for half-filled subshells.
Exchange is neglected between these two sorts of electrons, the six that form the 3d_{5/2} (called "up") and the four forming 3d_{3/2} (called "down") electrons. However, in the real half-filled 3d shell one would have five electrons. But these corrections, 6/5 and 4/5, respectively can be introduced easily into the calculational scheme.

Then we concentrate on the investigation of the influence of "up" and "down" electrons upon each other and demonstrate that the effect of the 3d_{3/2} ("down") electrons upon the 3d_{5/2} ("up") manifests itself not only in the partial cross sections $\sigma_{5/2}(\omega)$, $\sigma_{3/2}(\omega)$ [21] and somewhat in the respective angular anisotropy parameters $\beta_{5/2}(\omega)$, $\beta_{3/2}(\omega)$ [25], but also in the nondipole parameters of the photoelectron angular distributions, $\gamma(\omega)$ and $\delta(\omega)$. In all these cases the effect of the 3d_{3/2} photoionization channels upon the 3d_{5/2} leads to the creation of an additional maximum, while the action of the 3d_{3/2} electrons upon 3d_{5/2} proved to be generally negligible. Note that since the matrix elements for the photoionization process are strongly modified by correlation in the form of interchannel coupling, it is evident that characteristics of the process other than the integrated cross section; for example, the photoelectron spin polarization (see [27] and references therein) are also modified.

The angular distribution of photoelectrons from an nl subshell created by linearly polarized light, including the lowest order nondipole parameters [5, 7, 8, 17, 18] is given by

$$\frac{d\sigma_{nl}(\omega)}{d\Omega} = \frac{\sigma_{nl}(\omega)}{4\pi} [1 + \beta_{nl}(\omega)P_2(\cos \theta)] + [\delta_{nl}(\omega) + \gamma_{nl}(\omega)\cos^2 \theta \sin \theta \cos \phi],$$  

where $\sigma_{nl}(\omega)$ is the partial cross section, $\beta_{nl}(\omega)$ is the dipole angular anisotropy parameter, $\gamma_{nl}(\omega)$ and $\delta_{nl}(\omega)$ are nondipole parameters, $P_2(\cos \theta)$ is a Legendre polynomial, $\theta$ is the angle between the photoelectron and the photon polarization directions, and $\phi$ is the angle between the photon momentum and the projection of the photoelectron momentum in the plane perpendicular to the photon polarization. The expressions for $\gamma_{nl}(\omega)$ and $\delta_{nl}(\omega)$ in terms of dipole and quadrupole matrix elements were first obtained in a slightly different form in [5] and later in [7, 8, 13, 28]. Most of the attention in the past was given to $l = 0$ and $l = 1$, where the expressions for $\gamma_{nl}$ and $\delta_{nl}$ are relatively simple. Here we are interested in the more complex case of $l = 2$, and the explicit expressions are given elsewhere [8]. For present purposes, however, it is necessary to point out that the expressions involve ratios of quadrupole to dipole matrix elements, along with cosines of phase shift differences.

In the present calculation, the 3d $\rightarrow \epsilon p, \epsilon f$ dipole amplitudes and 3d $\rightarrow \epsilon s, \epsilon d, \epsilon g$ quadrupole amplitudes are taken into account for both 3d_{5/2} and 3d_{3/2} photoionization. The matrix elements for dipole, $d_{l\pm 1}$, and quadrupole, $q_{l\pm 2,0}$, are defined as

$$d_{l\pm 1} \equiv d_{nl\pm 1} = \int_0^{\infty} \phi_{nl}(r)r \phi_{l\pm 1}(r) dr,$$

$$q_{l\pm 2,0} \equiv q_{nl\pm 2,0} = \frac{1}{2} \int_0^{\infty} \phi_{nl}(r)r^2 \phi_{l\pm 2,0}(r) dr. \quad (2)$$

Here $\phi_{nl}(r)$ and $\phi_{l\pm 1}(r)$ are the radial parts of the Hartree-Fock (HF) one-electron wave functions. In the uncorrelated (HF) approximation, the formulae for $\gamma_{nl}(\omega)$ and $\delta_{nl}(\omega)$ can be used directly with the dipole and quadrupole amplitudes.

An effect of correlation, however, is to render these transition matrix elements complex; the correlated dipole amplitudes are termed $D_{l\pm 1}$ and the correlated quadrupole amplitudes $Q_{l\pm 2,0}$. To obtain the corresponding expressions for $\gamma_{nl}$ and $\delta_{nl}$, one has to perform the following substitutions [5, 17]

$$|d_{l\pm 1}|^2 \rightarrow |ReD_{l\pm 1}|^2 + |ImD_{l\pm 1}|^2$$

$$|q_{l\pm 2,0}|^2 \rightarrow |ReQ_{l\pm 2,0}|^2 + |ImQ_{l\pm 2,0}|^2$$

$$d_{l\pm 1}q_{l\pm 2,0} \cos(\delta_{l\pm 2,0} - \delta_{l\pm 1}) \rightarrow [ReD_{l\pm 1}ReQ_{l\pm 2,0} + ImD_{l\pm 1}ImQ_{l\pm 2,0}] \cos(\delta_{l\pm 2,0} - \delta_{l\pm 1}) - [ReD_{l\pm 1}ImQ_{l\pm 2,0} - ImD_{l\pm 1}ReQ_{l\pm 2,0}] \sin(\delta_{l\pm 2,0} - \delta_{l\pm 1}) \quad (3)$$

where the $\delta_l$ are the single-particle (HF) phase shifts for the designated channel, and $Re$ and $Im$ stand for real and imaginary parts, respectively.

The method that we use here, just as in [21], is the spin-polarized random-phase approximation with exchange (SPRPAE). However, for the intermediate 3d subshell SPRPAE is not sufficient; the effects of core rearrangement (relaxation) must be taken into account. This is done by going from RPAE to the generalized (GRPAE) or, in our case, from SPRPAE to SPGRPAE which takes into account that while a slow photoelectron leaves the atom, the field seen is modified due to the alteration (rearrangement) of the wave functions of all other atomic electrons as a result of the creation of the inner-subshell vacancy. GRPAE is discussed at length in [29]. Its extension for a system with two types of electrons "up" and "down", the transition from SPRPAE to SPGRPAE, is straightforward.

The results of our calculations for $\gamma$ for photoionization of Cs 3d_{5/2} and 3d_{3/2} are shown in Fig. 1; both the correlated and the uncorrelated Hartree-Fock (HF) results are shown to emphasize the features brought about by correlation. As seen from the figure, the outstanding difference between correlated and uncorrelated results appears in the value of $\gamma$ for 3d_{5/2} photoionization in the region just above a photon energy of 740 eV. The fact that this
significant structure in $\gamma$ is not seen in the uncorrelated, HF, calculation is proof that its existence is due to correlation. Specifically, we have found that it is due to interchannel coupling among the $3d_{5/2}$ and $3d_{3/2}$ photoionization channels; by interchannel coupling we mean simply configuration interaction in the continuum. Since the "real" wave function for the final continuum state in a photoionization process is multichannel, there is mixed in with the final state wave functions for $3d_{3/2}$ photoionization a small amount of $3d_{3/2}$ channels. Then, due to the $3d \rightarrow \epsilon f$ shape resonance in the region just above the $3d_{3/2}$ threshold, the $3d_{3/2}$ dipole cross section is much larger than the $3d_{5/2}$. Thus mixing a small amount of the wave function of the $3d_{3/2} \rightarrow \epsilon f$ channel with the wave function of the much smaller $3d_{5/2}$ channel alters the $3d_{5/2}$ dipole matrix elements significantly; the $3d_{5/2}$ cross section maximizes with the $3d_{5/2} \rightarrow \epsilon f$ just above its threshold, and drops off considerably at the energy of the $3d_{3/2} \rightarrow \epsilon f$ shape resonance.

But the $\gamma$ parameter, as discussed above, is essentially a ratio of quadrupole to dipole matrix elements. There is also interchannel coupling among the quadrupole channels, $3d_{5/2} \rightarrow es, df$ and $3d_{3/2} \rightarrow es, df$. But there are no significant resonances in any of these channels in the energy range of interest, and all of the channels are of more or less the same size. Thus, interchannel coupling does not introduce any important changes in the quadrupole photoionization matrix elements like it does in the dipole case. Since only one participant in the ratio that yields $\gamma$ changes significantly because of correlation, then it is evident that the ratio itself must be altered as well. This is the reason for the significant structure seen in Fig. 1 for $\gamma$ of $3d_{5/2}$ in the vicinity of the $3d_{3/2}$ threshold.

The only other real effect of correlation on the $\gamma$ parameter is for $3d_{3/2}$ right at threshold, where the HF result is noticeably lower than the correlated value. This again is due to interchannel coupling, but in this case the effect of the $3d_{5/2}$ photoionization channels on the $3d_{3/2}$ causes the modification. In particular, the $3d_{3/2} \rightarrow \epsilon f$ amplitude, which is extremely small at the $3d_{3/2}$ threshold, is strongly modified by its interchannel interaction with the much larger $3d_{5/2}$ amplitudes.

The situation for the $\delta$ parameter is shown in Fig. 2 and we find here a story similar to that of the $\gamma$ parameter. A significant correlation structure in the $3d_{5/2}$ channel, seen just above the $3d_{1/2}$ threshold is evident, along with changes in $\delta$ in the $3d_{3/2}$ channel just at its threshold. These effects of correlation occur for exactly the same reason as discussed above for $\gamma$. It is apparent from comparison of Figs. 1 and 2 that the changes in $\delta$ due to correlation are qualitatively larger than for $\gamma$. This is probably due to the fact that the values of $\delta$ are roughly an order of magnitude smaller than $\gamma$.

Owing to the geometry of a number of experimental setups to measure nondipole photoelectron angular distributions, $\gamma$ and $\delta$ are often not measured individually[9, 10]; instead, $\zeta = \gamma + 3\delta$ is investigated. To connect with such experimental investigations, $\zeta$ for the $3d_{5/2}$ and $3d_{3/2}$ channels of Cs are shown in Fig. 3. Since $\zeta$ is simply a linear combination of $\gamma$ and $\delta$, the explanation for the correlation structure here simply follows from the previous discussion for $\gamma$ and $\delta$ individually.

In conclusion then, it has been shown that, due to spin-orbit induced interchannel coupling between the dipole photoionization channels arising from the two members of the $3d$ spin-orbit doublet in Cs, a new structure results in the nondipole photoelectron angular distribution parameters $\gamma$ and $\delta$ (and, of course, $\zeta$). Similar results are found for Xe 3d and Ba 3d; these will be presented in a future publication. This is the first case of structure in the energy dependence of nondipole parameters discovered that is not related to resonances (dipole or quadrupole) or Cooper minima. And, it was shown explicitly that correlation in the form of interchannel coupling can indeed be important for the nondipole photoelectron angular distribution parameters, in contradistinction to the conventional wisdom. Experimental scrutiny into this prediction is highly desirable.

Research at Clark Atlanta University is supported by DoE, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research (AZM) and NSF. The work of MYaA was supported by the Hebrew University Intramural Fund. MYaA and LVC acknowledge the support of the International Science and Technology Center (grant No 1358). The work of ASB and STM was supported by the US Civilian Research & Development Foundation for the Independent States of the Former Soviet Union, Award No. ZP1-2449-TA-02. STM also acknowledges the support of NSF and NASA.

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Figure Captions

FIG. 1 Calculated values of the nondipole photoelectron angular distribution parameter $\gamma$ for Cs $3d_{5/2}$ and $3d_{3/2}$ subshells in correlated (SRPAE) and uncorrelated (HF) approximations.

FIG. 2 Calculated values of the nondipole photoelectron angular distribution parameter $\delta$ for Cs $3d_{5/2}$ and $3d_{3/2}$ subshells in correlated (SRPAE) and uncorrelated (HF) approximations.

FIG. 3 Calculated values of the nondipole photoelectron angular distribution parameter $\zeta$ for Cs $3d_{5/2}$ and $3d_{3/2}$ subshells in correlated (SRPAE) and uncorrelated (HF) approximations.
Cs 3d

Photon energy (eV)
Cs 3d

Photon energy (eV)
