Two-photon decay of inner-shell vacancies in heavy atoms

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Based on the second-order perturbation theory, we investigate the two-photon decay of K-shell vacancies in heavy atoms. The many-electron transition amplitude that occurs in the theory is evaluated by means of the independent particle approximation (IPA). By using this approach, computations are performed for the decay of neutral gold and are directly compared with recent experimental data, not relying on any scaling assumptions. The obtained results confirm previously identified discrepancies between the IPA theory and the experiment for the $2s \to 1s$ transition, and an apparent "resonance" region of the $3s \to 1s$ transition, but they show a moderate agreement with the measured data for the $3d \to 1s$ and $4s + 4d \to 1s$ cases. Moreover, with the help of the IPA we discuss the validity of the nonrelativistic scaling that was employed in the past to estimate the relative two-photon transition probabilities P in heavy atoms based on calculations done for lighter elements and different decay geometries. We find, in particular, that the electric-dipole angular distribution of emitted photons holds rather well even in the high-Z domain, while the assumption that the relative probability P is independent of nuclear charge may result in 10–30% inaccuracy of theoretical predictions.

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I. INTRODUCTION

Two-photon transitions in atoms and ions have been intensively studied for decades, both in theory and experiments, as has been reviewed in detail in Refs. [1,2]. Originally focused on neutral hydrogen and low-Z atoms, nowadays these investigations often deal with heavier atomic systems. For example, much current attention is paid to two-photon transitions in highly charged heavy ions up to uranium [3–11]. For these ions, a number of measurements of total as well as energy-differential (two-photon) decay rates have been performed recently. The experimental results are typically in good agreement with theoretical predictions, based on the relativistic second-order perturbation theory.

In addition to few-electron ions, there is particular interest in the two-photon decay of K-shell vacancies in neutral atoms. Novel advances in x-ray detection techniques allow one to explore such a decay not only in the medium-Z [12–15] but also in the high-Z domain, where the effects of relativity and the nondipole contributions to the electron-photon interaction can become of paramount importance. For example, the relative (with respect to the total decay rate of a K hole) differential probabilities of the two-photon decay of K-shell vacancies in gold atoms were measured recently by Dunford *et al.* [16]. In that work, photons emitted in the $2s \to 1s$, $3s \to 1s$, $3d \to 1s$, and $(4s + 4d) \to 1s$ transitions were observed in coincidence by two detectors arranged at right angles to each other. No theoretical predictions were available, however, for such a heavy system ($Z = 79$), that could help in analyzing the experimental data. To overcome the lack of (theoretical) knowledge, Dunford and coworkers utilized the results of calculations performed in Refs. [17–20] for silver ($Z = 47$) and xenon ($Z = 54$) atoms and *scaled* them to $Z = 79$. Two important assumptions were made to perform such a scaling: (i) the relative decay probability P is independent of Z for all photon energies and angles, and (ii) the angular distributions of emitted photons are $1 + \cos^2\theta$ and $1 + (1/13)\cos^2\theta$ for the $ns \to 1s$ and $nd \to 1s$ transitions, respectively. As we will see later, both these assumptions are based on a nonrelativistic theory describing the electric dipole $2E1$ decay of a hydrogen-like atom [21,22].

When the experimental data of Dunford *et al.* was compared with their *scaled* calculations, utilizing results from Refs. [17–20], a rather large discrepancy was found for some of the two-photon transitions. For example, theoretical predictions underestimated significantly the measured probabilities of the $2s \to 1s$ and $3d \to 1s$ decay and were unable to explain the anomalous resonance structure observed for the $3s \to 1s$ transition. In order to understand the reasons for these discrepancies, further theoretical studies of the two-photon decay of K-shell vacancies in heavy atoms were highly needed.

In this contribution, therefore, we apply the second-order perturbation theory based on the Dirac equation to reinvestigate (inner-shell) two-photon transitions in heavy ions. Since the details of such an approach have been given in Ref. [19], in Sec. II we will restrict ourselves to a rather short compilation of the basic ideas and notations, just enough to discuss later our predictions and experimental data. In particular, we mention that the complete basis of atomic states, needed for the two-photon calculations, can be generated within the independent particle approximation (IPA) in which many-electron wavefunctions are approximated by one-particle solutions of the Dirac equation in a screened potential. While such an IPA method can be employed to analyze inner-shell transitions in any medium- and high-Z atom, here we focus our study on the gold atom. Results of calculations are presented later in Sec. III A and are compared with the experimental data of Dunford *et al.* Moderate

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agreement between the theory and experiment is found for the decay of the highly excited $3d$ and $4s + 4d$ states. In contrast, our calculations strongly overestimate the measured probabilities of the $2s \to 1s$ transition and do not confirm the peak structure observed in the $3s \to 1s$ decay channel, thus verifying the discrepencies previously reported in Ref. [16].

Beside providing theoretical results for the relative differential probabilities of the two-photon decay of gold K-shell vacancy, we used the IPA approach to examine the validity of the simple nonrelativistic scaling used by Dunford *et al.* [16]. Calculations of the $2s \to 1s$ and $3d \to 1s$ transition probabilities were carried out for atoms with nuclear charges in the range $47 \leqslant Z \leqslant 85$ and for various photon emission geometries. Even though these calculations are restricted to the case of equal energy sharing between the photons, the obtained results are representative of other energies lying in the nonresonant region. In Sec. III B we discuss that in such a region performing a nonrelativistic angular scaling from Dunford *et al.* generally holds within 5% even for heavy atoms. In contrast, the assumption that the relative transition probability is independent of Z may results in about 10% and 30% underestimation of the IPA predictions for the decay of $2s$ and $3d$ states, respectively. Finally, the resonant behavior of the two-photon decay rates is briefly discussed in Sec. III B3. In particular, we argue that the nonrelativistic Z-scaling of the relative transition probabilities leads to a wrong description of the peak structures attributed to the cascade transitions from highly excited states. A summary of these results and brief outlook will be given in Sec. IV.

II. THEORY AND COMPUTATIONS

Analysis of experimental and theoretical data on the two-photon decay of the K-shell vacancy in atoms can be performed most conveniently if one introduces the *relative differential transition probability*

$$P = \frac{1}{W_K} \frac{d^3 w}{d\omega_1\, d\Omega_1\, d\Omega_2}\,. \quad (1)$$

Here, $d^3 w/d\omega_1\, d\Omega_1\, d\Omega_2$ is the rate of a particular (two-photon) transition and W_K is the *total* decay rate for a K hole, which account for both, the radiative and Auger channels. In the high-Z domain, the autoionization is significantly suppressed and contributes not more than 5% to the total decay probability [23]. The behavior of the W_K for heavy atoms is governed, therefore, by the *radiative* decay rate $W_K^{\rm rad}$, whose values are tabulated, for example, in Ref. [24,25].

Not much has to be said about the differential two-photon decay rate $d^3 w/d\omega_1\, d\Omega_1\, d\Omega_2$ from Eq. (1), whose evaluation has been discussed in detail by Tong and coworkers [19]. Here we just mention that such an evaluation is based on the second-order perturbation theory and requires the knowledge about the complete atomic spectrum, including bound- as well as (positive- and negative-energy) continuum states. For the treatment of the two-photon decay of K-shell vacancies in heavy atoms, this spectrum can be generated within the framework of the independent particle approximation (IPA). In the high-Z domain and for strongly bound states, the IPA is known to be fairly good as a first approximation for the analysis of single-photon decay, photo- and impact-ionization [26,27], recombination [28], as well as high-energy Rayleigh and Compton scattering [29–31]. The performance of the IPA method depends, however, on the particular choice of single-electron wavefunctions. In the present study, these functions are obtained as solutions of the Dirac equation in a screened potential $V_{\rm DF}(r)$, generated within the Dirac-Fock theory [32], and are expanded in terms of B-splines (see Refs. [33–35] for further details). Recently, such a "screened" IPA approach was used for the treatment of two-photon transitions in few-electron heavy ions and its predictions were found in a good agreement with rigorous QED calculations [10,11].

Before we proceed with the relativistic IPA calculations of the relative probability Eq. (1), let us note its simple scaling proposed in Ref. [16]. Namely, based on the nonrelativistic single-electron approach, Dunford and coworkers assumed that P can be written

$$P(Z,y,\theta) = W(\theta)\, g(y), \quad (2)$$

independent of the nuclear charge Z. Here W is the relative probability of photon emission at the opening angle θ, given by

$$W_s(\theta) \sim 1 + \cos^2\theta \quad (3)$$

for the $ns \to 1s$ transitions and

$$W_d(\theta) \sim 1 + (1/13)\cos^2\theta \quad (4)$$

for the $nd \to 1s$ transitions, respectively. The function g describes the two-photon spectral distribution as a function of the energy sharing parameter $y = \omega_1/(\omega_1 + \omega_2)$; it can be determined from calculation, as for example, the data of Tong *et al.* [19]. In Sec. III we will employ Eq. (2) to scale theoretical predictions obtained from medium-Z atoms to the high-Z regime. Comparing these (scaled) results with the experimental data and relativistic calculations, we will discuss the validity of the nonrelativistic approach of Dunford *et al.*

III. RESULTS AND DISCUSSIONS

A. Two-photon decay in gold atoms

Having discussed the basics of the independent particle approximation and the computational details, we are ready now to explore the relative differential probability Eq. (1) of the two-photon decay of atomic K vacancies. We begin with the gold atom, which was the focus of recent experimental studies by Dunford and coworkers [16]. As mentioned above, the measurements were made for a number of $nl \to 1s$, $n = 2$, 3, and 4, transitions and for the geometry where the photons were detected at the angle $\theta = 90^\circ$ with respect to each other. In Fig. 1 we display the calculations performed for such an *opening* angle and for the $2s \to 1s$ (top panel) and $3s \to 1s$ (bottom panel) decay. Together with our IPA predictions, depicted by solid squares, the experimental findings (up triangles) from Ref. [16] are also shown for the energy-sharing parameters in the range $0.2 \leqslant y \leqslant 0.5$. Furthermore, for completeness we present data of Tong *et al.* [19], computed for a perpendicular photon emission ($\theta = 90^\circ$) following the decay of $2s$ and $3s$ states of the silver atom, and applied for gold according to the nonrelativistic rule $P(Z) =$ const. While the validity of such a "scaling" will be discussed

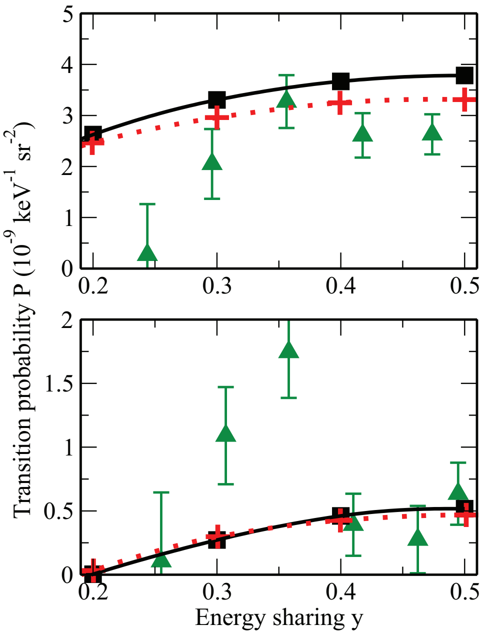

FIG. 1. (Color online) Relative differential probability P, defined by Eq. (1), at opening angle $\theta = 90^\circ$ for the $2s \to 1s$ (top panel) and $3s \to 1s$ (bottom panel) transitions in a gold atom as a function of the energy sharing y. Experimental results from Ref. [16] (up triangles) are compared with predictions of the IPA approach (squares connected for guidance by solid line). Moreover, the theoretical data of Tong and coworkers [19], derived for a perpendicular photon emission from silver atoms are also displayed by crosses (connected for guidance by dotted line).

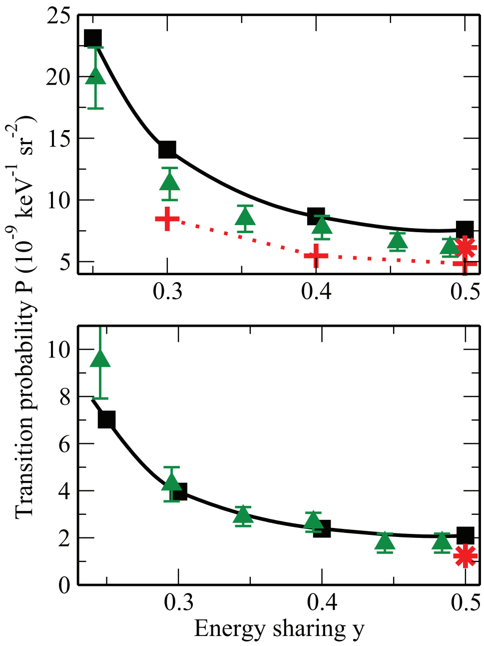

FIG. 2. (Color online) Relative differential probability P, defined by Eq. (1), at opening angle $\theta = 90^\circ$ for the $3d \to 1s$ (top panel) and $4s + 4d \to 1s$ (bottom panel) transitions in a gold atom as a function of the energy sharing parameter y. Experimental results from Ref. [16] (up triangles) are compared with predictions of the IPA approach (squares connected for guidance by solid line). Moreover, the theoretical data of Tong and coworkers [19], derived for (i) a perpendicular photon emission from silver atoms (crosses connected by dotted line) as well as (ii) a back-to-back emission from xenon atoms and multiplied by 13/14 (stars), are also displayed.

later, here we compare the Tong *et al.* results with our calculations. As seen from the figure, the discrepancy between the predictions of both *theoretical* models does not exceed 10% for the $2s \to 1s$ transition, where the scaled data slightly underestimate the IPA results, and is on the percent level for the $3s \to 1s$ case. A more remarkable difference can be observed between experimental and theoretical data. For example, the measured values of the relative probability $P_{2s\to 1s}$ lie generally below the theoretical curves; the effect becomes most pronounced for small energy sharing, $y \leqslant 0.3$. For the two-photon decay of the $3s$ state, in contrast, good agreement between experiment and theory is found for most of the energy-sharing parameters except for the region near $y = 0.35$. As seen from the bottom panel of Fig. 1, a resonance-like feature was detected in this region, which corresponds to the case where the energy of one photon is approximately twice the energy of the other. Such a "resonance" should not be attributed to the $3s \to 2p_{1/2,3/2} \to 1s$ cascades, which lead to singularities of the decay rate at $y \approx 0.11$ and $y \approx 0.13$ [36]. Moreover, no peak is predicted at $y = 0.35$ in two independent theoretical approaches (the present and Tong *et al.*), thus suggesting that the experimentally observed "resonance" might be caused by some not yet understood systematic error.

Beside the $2s, 3s \to 1s$ two-photon transitions, experimental data for the $3d \to 1s$ and $4s + 4d \to 1s$ decay channels were reported in Ref. [16]. These results are displayed in Fig. 2 for the opening angle $\theta = 90^\circ$ and energy sharing parameters in the range $0.25 \leqslant y \leqslant 0.5$, and they are compared with the predictions of the IPA model. Since the atomic fine structure was not resolved in the experiment, we added the decay rates of the states $nd_{3/2}$ and $nd_{5/2}$, $n = 4, 5$, in order to obtain the relative probabilities $P_{3d} = P_{3d_{3/2}} + P_{3d_{5/2}}$ (top panel) and $P_{4s+4d} = P_{4s} + P_{4d_{3/2}} + P_{4d_{5/2}}$ (bottom panel). As seen from the figure, better agreement between the measured data and the IPA calculations is found for these two cases in comparison to the results discussed above for the $2s$ and $3s$ levels. While the theory overestimates the experimental findings by not more than 10–20% for the $3d \to 1s$ transition, the IPA values P_{4s+4d} lie within the error bars for a wide range of the sharing parameter y.

Apart from predictions of our IPA approach, we also display in Fig. 2 results derived in Ref. [19] for (i) Ag atoms at the opening angle $\theta = 90^\circ$ (crosses connected by dotted line) and (ii) Xe atoms at the opening angle $\theta = 180^\circ$ (stars). In the latter case, we followed Dunford and coworkers [16] and rescaled the Tong *et al.* data as $P(\theta = \pi/2) = 13/14 \cdot P(\theta = \pi)$ to utilize them for the geometry where photons are emitted perpendicular to each other. Again, the details and validity of this transformation will be discussed later. Here we just mention that a pretty good agreement between the IPA- and the scaled Xe results can be found for both $3d \to 1s$ and $4s + 4d \to 1s$ transitions and for an equal energy sharing. In contrast, the Ag data of Tong and coworkers, available for the decay of the $3d$ state and for a rather

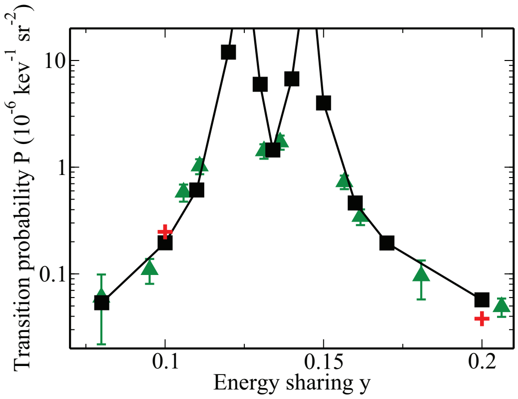

FIG. 3. (Color online) Relative differential probability P, defined by Eq. (1), at opening angle $\theta = 90^\circ$ for the $3d \to 1s$ transition in a gold atom as a function of the energy sharing parameter y. Experimental results from Ref. [16] (up triangles) are compared with predictions of the IPA approach (squares connected for guidance by solid line). Moreover, the theoretical data of Tong and coworkers [19], derived for a perpendicular photon emission from silver atoms, are also displayed by crosses.

wide range of energies, underestimate the IPA predictions by about 30%.

Until now we have restricted our study of the two-photon decay to the energy regions that are free of the resonance peaks in the relative differential probability Eq. (1). As briefly mentioned above, these peaks arise when transition $|n_i j_i\rangle \to |n_f j_f\rangle + \gamma_1 + \gamma_2$ can proceed via an intermediate state $|n_\nu j_\nu\rangle$ with energy $E_i > E_\nu > E_f$, thus leading to *two sequential* one-photon emissions. One pronounced example of such a (resonant) behavior can be observed for the $3d \to 1s$ decay, whose differential rate has singularities at energies corresponding to the $3d \to 2p_{1/2} \to 1s$ and $3d \to 2p_{3/2} \to 1s$ cascades. In order to explore the $3d \to 1s$ resonances, special attention to the energy range $0.1 \leqslant y \leqslant 0.2$ was paid in the experiment by Dunford and coworkers [16]. The differential probability $P_{3d\to 1s}$, measured in this range, is depicted by up triangles in Fig. 3 and compared with the predictions of the IPA approximation (squares, connected for guidance by solid line). As seen from the figure, theoretical calculations suggest two peaks at $y = 0.12$ and $y = 0.145$ corresponding to the cascades through the $2p_{3/2}$ and $2p_{1/2}$ states, correspondingly. Good agrement with the measured data is observed on the "wings" of these resonances and even in the region between the peaks.

The theoretical results obtained by Tong and coworkers [19] for the decay of Ag atoms are also presented in Fig. 3. The predictions are available only for the sharing parameters $y = 0.1$ and $y = 0.2$, i.e., far from the peak positions. At these energies, the Tong *et al.* calculations reproduce pretty well both the experimental data and the IPA results. In Sec. III B3, however, we will show that such an agreement would not hold near the resonances, thus indicating a limitation of the scaling approach proposed by Dunford and coworkers.

B. Scaling properties of the relative transition probability

As seen from Figs. 1–3 and the discussion above, the relativistic results of Tong *et al.* [19] for the decay of silver and xenon atoms were utilized—more or less successfully—to understand the two-photon transitions in gold. The application of these results, obtained for *other* elements and decay geometries, is based on the assumption that the relative differential probability Eq. (1) follows simple scaling rules in both the nuclear charge Z and the opening angle θ [cf. Eqs. (2)–(4)]. In the next two subsections we shall discuss the validity of these scalings for $2s \to 1s$ and $3d \to 1s$ transitions. Even though we focus our analysis on the case of equal energy sharing between photons, our conclusions hold also for other parameters $y < 0.5$. Finally, in Sec. III B3 the performance of the nonrelativistic scaling rule Eq. (2) in the resonant region will be briefly discussed.

1. Nuclear charge scaling

We begin with the naïve scaling of the relative transition probability, $P(Z) = \text{const}$. It follows immediately from Eq. (1) and the fact that both the total K-shell- and the differential two-photon decay rate, evaluated within the nonrelativistic hydrogenic approximation, behave as Z^4 [21,22,38]. This scaling allowed Dunford *et al.* in Ref. [16] and us in Figs. 1–3 to use *directly* previous theoretical calculations for silver and xenon atoms [19] for the investigation of the two-photon decay of the K-shell vacancy in gold. However, the constant behavior of the transition probability $P = P(Z)$ should be questioned for heavy atoms for which the relativistic and many-electron effects can be of paramount importance. (In fact, it could be also questioned for lighter atoms and more outer shells due to the neglect of screening.)

In order to better understand the Z-scaling of the relative probability Eq. (1), we display in Fig. 4 this quantity for a wide range of nuclear charges $47 \leqslant Z \leqslant 85$ and for the $2s \to 1s$ (top panel) as well as the $3d \to 1s$ (bottom panel) transitions. Our calculations, based on the IPA model, were performed for equal energy sharing ($y = 0.5$) between the photons that are emitted in the "back-to-back" direction, $\theta = 180^\circ$. As seen from the figure, both $P_{2s\to 1s}$ and $P_{3d\to 1s}$ are not constant but *increase* with nuclear charge. Since the total K-shell decay rate scales approximately as $W_K \propto Z^4$ even in the high-Z regime [24,25], such a Z-behaviour implies that the two-photon IPA rate grows faster than the nonrelativistic hydrogen prediction $(d^3 w/d\omega_1\, d\Omega_1\, d\Omega_2)_{\rm nr} \propto Z^4$. This can be attributed to the interplay between the many-electron (mainly screening) and relativistic effects. The screening of the nucleus by relativistically contracted inner-shell electrons expands outer-shell orbitals and leads to a decrease of the overlap between the initial- and final-state wavefunctions and, hence, to a reduction of the IPA rates in comparison to the hydrogenic predictions. However, this reduction becomes gradually smaller as the wavefunctions become more hydrogen-like with the growth of Z. The (direct as well as indirect) relativistic effects on the wavefunctions cause also the different Z-behavior of the quantities $P_{2s\to 1s}$ and $P_{3d\to 1s}$. In particular, the decay probability of the $3d$ state, whose delocalized orbital is more affected by the screening, rises faster with Z than $P_{2s\to 1s}$ (cf. Fig. 4).

The IPA calculations, presented in Fig. 4, allow us to estimate the error of the simple nonrelativistic rule $P(Z) = \text{const}$ that was utilized by Dunford and coworkers [16]. For example,

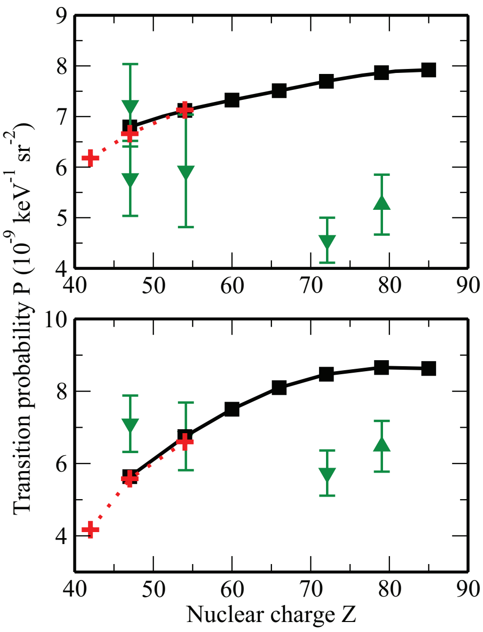

FIG. 4. (Color online) Relative differential probability P, defined by Eq. (1), for the $2s \to 1s$ (top panel) and $3d \to 1s$ (bottom panel) transitions as a function of the nuclear charge Z. Results are presented for equal energy sharing between the photons emitted in the back-to-back directions, $\theta = 180^\circ$. The predictions of the IPA approach (squares connected by solid line) are compared with experimental data of Ilakovac *et al.* [13,14] and Mokler *et al.* [15] (down triangles) and of Dunford *et al.* [16] (up triangles). Since the latter results have been measured for the perpendicular photon emission, we multiplied them by 2 (in the top panel) and by 14/13 (in the bottom panel). The theoretical data of Tong and coworkers [19], derived for the decay of Mo, Ag, and Xe atoms, and $\theta = 180^\circ$, are also displayed by crosses (connected for guidance by dotted line).

by scaling theoretical predictions for the two-photon decay of the K-shell vacancy of xenon to $Z = 79$, as it was done in Ref. [16], one underestimates the IPA results by about 10% and 30% for the $2s \to 1s$ and $3d \to 1s$ transitions, respectively. One may note that the so-scaled results are in better agreement with experimental findings (depicted in Fig. 4 by triangles) than our computations. This is caused by (i) the fact that the measured values of $P_{2s\to 1s}$ and $P_{3d\to 1s}$ stay rather constant or even slightly decrease with Z, and (ii) by a fortunate choice of the "input data" to scale. If in place of xenon results one would employ the calculations for heavier (or lighter) elements, the agreement will be worse. The dependence of the (simple) scaling procedure on the "input data" is especially noticeable for the $3d \to 1s$ decay, whose probability, evaluated within the IPA in the middle-Z domain, grows very fast with the nuclear charge. This was illustrated already in the top panel of Fig. 2: while the Tong *et al.* calculations for Xe and $y = 0.5$ reproduce the measured value $P(Z = 79)$ rather well, the predictions for Ag significantly underestimate the experimental data.

The above discussion on the scaling of the relative transition probabilities $P_{2s\to 1s}$ and $P_{3d\to 1s}$ was restricted to the case of equal energy sharing between the photons. Similar Z-behavior can be observed also for other than $y = 0.5$ parameters. That is, the IPA values of the $P_{2s\to 1s}(y < 0.5)$ and—in the nonresonance region—the $P_{3d\to 1s}(y < 0.5)$ increase with nuclear charge Z, thus resulting in about 10–30% inaccuracy of the nonrelativistic hydrogenic approach Eq. (2).

2. *Angular dependence of the relative transition probability*

In the previous sections we compared measured data for the two-photon decay of the K-shell vacancy of heavy atoms with the IPA calculations and the theoretical predictions using data of Tong *et al.* [19]. Since the latter results are restricted not only to a limited number of nuclear charges Z but also to just a few photon-photon opening angles, they were scaled also over the θ to reproduce experimentally relevant emission geometries. In order to perform properly such a transformation, one needs a knowledge about the angular correlations between the emitted photons. As mentioned already in Sec. II, within the electric-dipole approach these correlations are given by the well-known Eqs. (3) and (4) for the $ns \to 1s$ and $nd \to 1s$ transitions, respectively.

Based on Eqs. (3) and (4), one can estimate the (relative) probabilities of photon emission at different opening angles θ. Of special interest are two angles, $\theta = 90^\circ$ and 180°, which were available in the past for the experimental two-photon studies [2,15,16]. The ratios $W_s(\theta = 180^\circ)/W_s(\theta = 90^\circ) = 2$ and $W_d(\theta = 180^\circ)/W_d(\theta = 90^\circ) = 14/13$, derived for these angles, were employed by Dunford *et al.* to transform the relative transition probability Eq. (1) between the "perpendicular" and the "back-to-back" emission geometries. One should verify, however, the accuracy of such an (angular) scaling in the medium- and high-Z domain, where the nondipole contributions to the electron-photon interaction may influence the *shape* of the angular correlation function Eqs. (3) and (4). In Fig. 5 we display, therefore, the ratio $W(\theta = 180^\circ)/W(\theta = 90^\circ)$ for $2s \to 1s$ (left panel) and $3d \to 1s$ (right panel) transitions, evaluated within the electric-dipole approximation and by taking into account a full multipole expansion of the electron-photon interaction operator. The IPA calculations have been performed for the equal energy sharing between the photons, for which the nondipole effects on the angular correlations are known to be generally

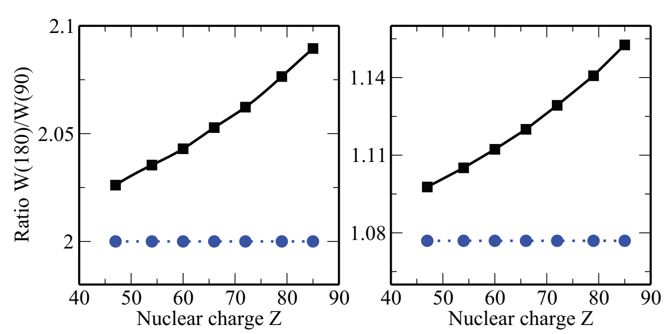

FIG. 5. (Color online) Intensity ratio $W_s(\theta = 180^\circ)/W_s(\theta = 90^\circ)$ for the two-photon $2s \to 1s$ (left panel) and $3d \to 1s$ (right panel) transitions at equal energy sharing. Results from the nonrelativistic electric dipole approximation (circles linked by dashed line) and compared with the predictions of the IPA model, which involves a full multipole expansion of the electron-photon interaction (squares linked by solid line).

most pronounced [37]. As seen from the figure, the higher multipole terms result in an enhancement of the ratio $W(\theta = 180^\circ)/W(\theta = 90^\circ)$ with respect to its dipole estimates 2 and $14/13 = 1.076$. However, even for the heaviest elements the enhancement does not exceed 5% and 7% for the decay of $2s$ and $3d$ states, respectively. These nondipole corrections are small in comparison to the accuracy of current two-photon measurements, which justifies the use of the simple dipole scaling applied by Dunford and coworkers [16].

3. *Resonant behavior of the relative transition probability*

In Sec. III B1 we have discussed the Z-scaling of the relative differential transition probability Eq. (1). Our analysis has been restricted, however, to the *nonresonant* region where P behaves smoothly as a function of the energy sharing y and does not exhibit peak structures. For the decay of highly excited states, these peaks arise at small parameters, $y < 0.2$, and have been clearly observed in Ref. [16], in particular for the $3d \to 1s$ transition in gold atoms (see Fig. 3). Application of the simple nonrelativistic scaling $P(Z) = \text{const}$ for the description of such a peak structure may cause significant errors, mainly because of the shift of the resonance *positions* for different elements. In Fig. 6 we display, for example, the Z-dependence of the positions of resonances corresponding to the $3d \to 2p_{1/2} \to 1s$ (circles) and $3d \to 2p_{3/2} \to 1s$ (squares) cascades in atoms with a K-shell vacancy. As seen from the figure, while the $2p_{3/2}$-peak is observed at almost the same energy sharing $y \approx 0.12$ for a wide range of nuclear charges, the $2p_{1/2}$ resonance moves from $y \approx 0.126$ for $Z = 47$ to almost $y \approx 0.145$ for $Z = 79$. Therefore, by scaling theoretical predictions derived for the medium-Z atoms toward the high-Z end, one may introduce about 15% error in estimating the position of the $2p_{3/2}$ intermediate-state resonance. This, and comparable errors found for the decay of $3s$, $4s$, and $4d$ states, are essential in the near-resonant regions but have little influence on the "wings" of the peaks where the usual (nonresonant) scaling works reasonably well. That is why the Tong *et al.* predictions obtained in Ref. [19] for the decay of silver atoms at $y = 0.1$ and $y = 0.2$ show a reasonable agreement with experimental data for gold (see Fig. 3).

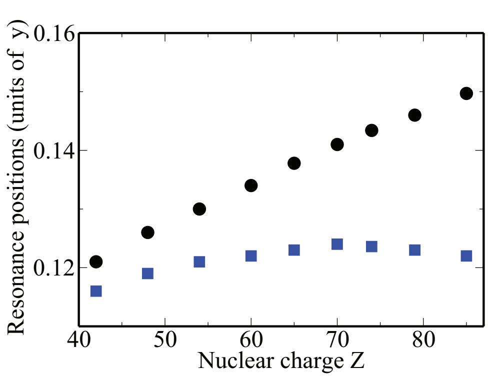

FIG. 6. (Color online) Positions of the $2p_{1/2}$ (circles) and $2p_{3/2}$ (squares) resonances in the relative differential probability of the $3d \to 1s$ two-photon decay. The results are presented in units of energy sharing parameter y.

IV. SUMMARY

In summary, we have reinvestigated the two-photon decay of K-shell vacancies in heavy atoms. The relative energy- and angle-differential probability of this process was obtained within the framework of the independent particle approximation. In such a model, many-electron wavefunctions are approximated by (one-electron) solutions of the Dirac equation in which electron-nucleus interaction is described by the effective frozen-core Dirac-Fock potential. Even though the formalism can be applied to any medium- and high-Z atom, we use it here primarily to investigate $2s \to 1s$, $3s \to 1s$, $3d \to 1s$, and $4s + 4d \to 1s$ transitions in gold. Extensive experimental data have been reported recently for these transitions [16], whose interpretation required detailed theoretical analysis. Good agreement between results of our calculations and experimental findings was found for the decay of highly excited $3d$ and $4s + 4d$ states in a wide range of photon energies. Beside a smooth nonresonant behavior, the IPA model reproduced very well the peak structure of the differential probability P, which is attributed to the cascade transitions from the excited- to the $1s$ state via $2p$ intermediate levels. For the $3s \to 1s$ decay, theoretical and experimental values of P also agree for most of the energy sharings except the region $0.3 \lesssim y \lesssim 0.38$. The resonance-like structure, reported at these y by Dunford and coworkers [16], was not obtained in our computations. Finally, the most pronounced discrepancy between the experiment and theory was found for the $2s \to 1s$ transition, where the IPA predictions underestimate significantly the P_{exp}.

Beside the analysis of inner-shell two-photon transitions in gold atoms, we have employed the IPA approach in order to verify the validity of a simple scaling of the relative differential probability P utilized in Ref. [16]. This scaling is derived within the nonrelativistic hydrogenic model and assumes that (i) the quantity P is independent of nuclear charge Z, and (ii) the angular dependence of P is governed by Eqs. (3) and (4). Based on our calculations, we found that while the (nonrelativistic) angular behavior holds generally within about 5% accuracy for a wide range of elements, P increases by about 10% for the $2s \to 1s$ and 30% for the $3d \to 1s$ decay if the nuclear charge changes from $Z = 47$ to $Z = 79$. Furthermore, the rule $P(Z) = \text{const}$ may fail to describe the resonant behavior of the two-photon decay probability since positions of the peaks, corresponding to the cascade transitions, vary with the nuclear charge of the atom. We can conclude, therefore, that the simple scaling proposed by Dunford *et al.* [16] can be applied in the nonresonant regime and within small intervals of the nuclear charge, $\Delta Z \lesssim 15$. Its use requires, moreover, the knowledge about the probability P of (i) the transition of interest obtained at (ii) a particular energy scaling y. Only based on such input data can the scaling in the other two parameters, θ and Z, be performed with a fair accuracy.

The discrepancy between the measured and theoretical values of the $2s \to 1s$ transition probability and (within a "resonance" region) the $3s \to 1s$ transition probability, reported by Dunford *et al.* [16] and confirmed by the present IPA calculations, still remains an open question. It may indicate some experimental inconsistencies and/or the failure of the independent particle approach. Our results, therefore, emphasize the need of further studies of inner-shell two-photon transitions in neutral atoms, both in experiment and theory. For the latter, investigations beyond the IPA approach are needed which make use of correlated many-body wavefunctions as currently employed in atomic-structure calculations (see, e.g., Ref. [39]).

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