

## Enhanced multiphoton ionization driven by quantum light

V. P. Kosheleva<sup>1,\*</sup>, S. Panahiyan<sup>1,2,†</sup>, A. Rubio<sup>1,3</sup> and F. Schlawin<sup>1,2,4</sup><sup>1</sup>*Max Planck Institute for the Structure and Dynamics of Matter, Center for Free Electron Laser Science, Luruper Chaussee 149, 22761 Hamburg, Germany*<sup>2</sup>*Institute for Quantum Physics, University of Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany*<sup>3</sup>*Center for Computational Quantum Physics (CCQ), The Flatiron Institute, 162 Fifth Avenue, New York, New York 10010, USA*<sup>4</sup>*The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, D-22761 Hamburg, Germany*

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We present a first-principles  $S$ -matrix framework for multiphoton ionization driven by arbitrary quantum states of light, retaining the full spatial structure of the light fields. Within this framework, we show that the utilization of momentum-entangled photon pairs emitted by ultrathin nonlinear crystals can enhance resonant two-photon ionization cross sections by more than two orders of magnitude relative to an uncorrelated reference state. The enhancement stems from the broad distribution of the transverse momentum and is captured only by a nonparaxial treatment, while strongly underestimated in the paraxial approximation. Atom-specific estimates for resonant two-photon ionization in sodium indicate that the predicted effect should be observable with currently available photon-pair sources.

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## I. INTRODUCTION

Nanoscale quantum light sources have emerged as highly promising platforms for quantum information science and light-matter interactions. Recent experiments have demonstrated the generation of highly correlated photon pairs from single-layer crystals [1–3], subwavelength nonlinear films [4,5], resonant metasurfaces [6,7], and other compact nonlinear structures [8]. These sources rely on parametric down-conversion in a non-phase-matched regime, where extremely broad bandwidths and emission with very large transverse momenta can be generated [see Fig. 1(a)]. These sources can be engineered to produce tunable polarization [9–12] or spatial [13] entanglement, support multiple entanglement links [1], and offer directional emission control [14,15]. Such capabilities open opportunities for probing matter with engineered spatiotemporal correlations. Research has only recently started to explore these opportunities for, e.g., linear quantum imaging [16], but their wider ramifications for applications in sensing [17–19], imaging [16,20–23], metrology [24–28], high-harmonic generation [29,30], and spectroscopy [31–33] remain largely unexplored.

Investigating this potential requires careful consideration of the nonparaxial emission characteristics of nanoscale sources in these applications [8]. Multiphoton ionization, and its variant resonance-enhanced multiphoton ionization

(REMPI), provides an experimentally accessible and highly sensitive platform for exploring this: Its nonlinear nature is a direct probe of photon correlations, as recently demonstrated with bright squeezed light [34]. Its strong sensitivity to intermediate-state resonances [35], together with its intrinsic dependence on the spatial and correlation structure of the driving field, makes REMPI a clean and controllable setting to identify and quantify quantum advantages beyond the paraxial regime. Beyond its role as a probe of nonclassical fields, REMPI underpins a broad range of applications, including plasma generation [36,37], chemical diagnostics [38,39], high-harmonic generation [40–42], photoelectron spectroscopy [35,43,44], ultracold atom-molecule dynamics and atom-atom collisions [45–47], molecular chirality [48–51], catalytic surface chemistry [52], nuclear-spin conversion [53], and precision metrology [54–56].

Here, we investigate REMPI driven by quantum states of light, taking the full spatial dependence of the photonic fields into account such that broad-angle emission effects are captured properly. Our approach incorporates relativistic effects important for heavy atoms [57–74] and enables accurate predictions of angular distributions [75] and asymmetries [76,77] relevant to chiral discrimination [78] and circular dichroism [79]. Using an  $S$ -matrix formulation, we calculate perturbatively multiphoton ionization cross sections and, as a case study, predict that resonant two-photon ionization of the sodium atom by momentum-entangled photons may be enhanced by several orders of magnitude from momentum entanglement alone. This enhancement can be evaluated only by accounting for broad-angle emission effects via a nonparaxial treatment, and is significantly underestimated by the paraxial approximation. Moreover, our analysis shows that for dipole-mediated REMPI, the enhancement only depends on the photonic quantum state. This breaks down for higher-order multipole transitions, pointing toward an interesting

\*Contact author: [valeriia.kosheleva@mpsd.mpg.de](mailto:valeriia.kosheleva@mpsd.mpg.de)†Contact author: [shahram.panahiyan@mpsd.mpg.de](mailto:shahram.panahiyan@mpsd.mpg.de)

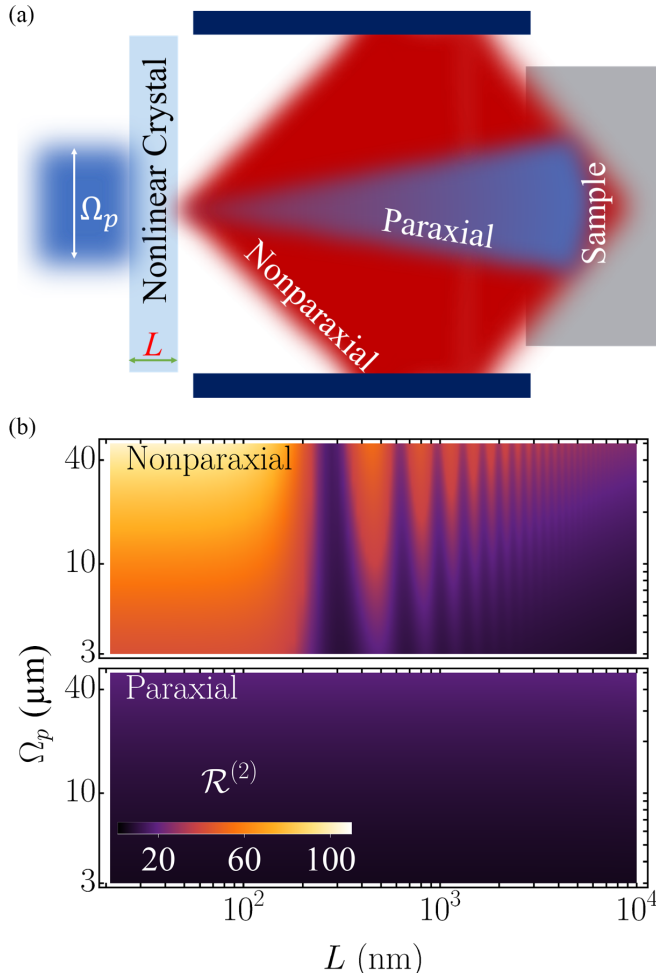


FIG. 1. (a) Schematic presentation of two-photon ionization of the sample with momentum-entangled photons. A pump field beam waist  $\Omega_p$  interacts with a birefringent crystal with length  $L$ , where spontaneous parametric down-conversion (SPDC) generates pairs of momentum-entangled photons. These photon pairs trigger resonant two-photon ionization in the sample. The paraxial approximation accounts only for the narrow emission angles of entangled photons and is valid for sufficiently large crystals, whereas short crystals allow much larger momentum mismatches and correspondingly broader angular spectra, where a nonparaxial treatment is necessary. (b) Enhancement ratio of the REMPI cross sections [Eq. (4)] of entangled photons compared to two separable photons as a function of the pump beam waist  $\Omega_p$  and length of the crystal  $L$  for the ionization through dipole channel: (upper panel) nonparaxial treatment and (lower panel) paraxial approximation. We consider the central frequencies of signal and idler photons to match the energy of the ( $3^2S_{1/2}-4^2P_{3/2}$ ) transition in a neutral sodium atom [80]. The graphs are plotted on a logarithmic scale with base 10, but the scale bar is not in logarithmic scale.

light-matter interaction regime. SI units are used throughout the paper, unless stated otherwise.

## II. TOTAL IONIZATION CROSS SECTION

We model the process as the interaction between a quantum state of light  $|\psi_{\text{in}}\rangle$  and matter  $|\varphi_{\text{in}}\rangle$ , initially prepared in the

state  $|\Psi_{\text{in}}\rangle = |\psi_{\text{in}}\rangle \otimes |\varphi_{\text{in}}\rangle$ . After absorption of  $n$  photons, the system evolves into the total final state  $|\Psi_f\rangle = |\psi_f\rangle \otimes |\varphi_f\rangle$ , where  $|\varphi_f\rangle$  describes the matter state comprising the photoelectron and the *residual system* (e.g., an ion, molecular fragment, or ionized solid-state background), and  $|\psi_f\rangle$  is the final state of the light field.

We define the total cross section  $\sigma^{(n)}$  for  $n$ -photon ionization as (see Appendix A for details)

$$\sigma^{(n)} = \frac{\Gamma^{(n)}}{\phi^{\tilde{n}}}, \quad (1)$$

where  $\Gamma^{(n)}$  is the transition rate associated with the ionization process and  $\phi$  is a projection of the photon flux onto the axis perpendicular to the plane of a target. The transition rate is divided by the  $\tilde{n}$ th power of the photon flux, depending on the initial state of the field: For example, for multiphoton absorption, entangled  $n$ -photon states generate a linear signal at low photon fluxes, such that  $\tilde{n} = 1$  [82,83], whereas the signal of coherent pulses scales with the  $n$ th power of the photon flux, i.e.,  $\tilde{n} = n$ .

## III. PHOTON FLUX

Without loss of generality, we assume that the target is placed in the  $xy$  plane; therefore,  $\phi$  is the projection of the photon flux onto the  $z$  axis. We define the photon flux of an arbitrary quantum state of light  $|\psi_{\text{in}}\rangle$  as

$$\phi = c \frac{\sum_{\lambda=1,2} \int_{-\infty}^{\infty} d\mathbf{k} \frac{k_z}{k} \langle \psi_{\text{in}} | \hat{a}_{\lambda}^{\dagger}(\mathbf{k}) \hat{a}_{\lambda}(\mathbf{k}) | \psi_{\text{in}} \rangle}{V_{\psi_{\text{in}}}}, \quad (2)$$

where  $c$  is the speed of light in vacuum,  $\hat{a}_{\lambda}(\mathbf{k})$  is an annihilation operator of a photon with momentum  $\mathbf{k}$  and polarization  $\lambda$ ,  $k_z$  is projection of  $\mathbf{k}$  onto  $z$  axis,  $k = |\mathbf{k}|$ , and  $V_{\psi_{\text{in}}}$  is an *effective volume* that quantifies the localization of the photonic state in space. This definition allows us to account for the strong wave packet dispersion beyond the paraxial regime. It naturally incorporates the spatial and temporal confinement of realistic photon states, and Eq. (1) reduces to the established semiclassical cross sections in the appropriate limits: Taking a plane wave as the initial state of light, the effective volume coincides with the full quantization volume since the state is completely delocalized [84]. For a Gaussian pulse, the volume is determined by the transverse beam waist and longitudinal pulse length, and for entangled photons, it is further reduced due to correlations inherent in the quantum state, as we will discuss below Eq. (5). Our first-principles framework described above is general and can be applied to compute cross sections for both resonant and nonresonant ionizations. As an illustration, we focus here on REMPI driven by entangled photons as a nonclassical light source.

## IV. ENHANCEMENT RATIO

To study the enhancement of the REMPI cross section due to quantum correlations, we introduce the ratio between the REMPI cross sections induced by entangled light fields,  $\sigma_{\text{ent}}$ , and by suitable separable states,  $\tilde{\sigma}_{\text{sep}}$  [see discussion after

Eq. (5)],

$$\mathcal{R}^{(n)} = \frac{\sigma_{\text{ent}}^{(n)}}{\tilde{\sigma}_{\text{sep}}^{(n)}}. \quad (3)$$

Both cross sections are calculated from Eq. (1) with a linear photon flux dependence,  $\tilde{n} = 1$ , such that  $\mathcal{R}^{(n)}$  is unitless. Crucially, if the ionization is resonant with intermediate dipole transitions and the field polarization is independent of the photons' propagation direction,  $\mathcal{R}^{(n)}$  becomes independent of the material: For narrow-band separable or entangled states with  $n$ -photon wave functions  $F_{\text{ent/sep}}(\mathbf{k}_1, \dots, \mathbf{k}_n)$ , we find (for details, see Appendix B)

$$\mathcal{R}^{(n)} = \frac{V_{\text{ent}}}{V_{\text{sep}}} \frac{f_{\text{ent}}^{(n)}}{f_{\text{sep}}^{(n)}}, \quad (4)$$

where  $V_{\text{ent/sep}}$  is the effective volume of the respective state, and  $f_{\text{ent/sep}}^{(n)} = \frac{|\int_{-\infty}^{\infty} d\mathbf{k}_1 \dots d\mathbf{k}_n F_{\text{ent/sep}}(\mathbf{k}_1, \dots, \mathbf{k}_n)|^2}{\int_{-\infty}^{\infty} d\mathbf{k}_1, \dots, d\mathbf{k}_n |F_{\text{ent/sep}}(\mathbf{k}_1, \dots, \mathbf{k}_n)|^2 (\frac{k_{1,z}}{k_1} + \dots + \frac{k_{n,z}}{k_n})}$  quantifies the focusing of the  $n$ -photon wave function at the sample. Notably, the enhancement depends only on the light field, not on the sample. As we will demonstrate by simulations below, however, this result [Eq. (4)] breaks down when the quantum state of light is in resonance with a higher-order multipole transition.

## V. MOMENTUM-ENTANGLED PHOTON PAIRS

We illustrate this enhancement in the case of the cross section of two-photon ionization with momentum-entangled photons. The general setup is depicted in Fig. 1(a). A nonlinear crystal is pumped by a laser (shown in blue) to generate entangled photon pairs. The generated photons are subsequently focused on the sample, where they induce two-photon ionization. The emitted photoelectrons are then detected. We consider a model of two narrow-band entangled photons denoted by signal and idler and produced in SPDC, both centered around frequency  $\omega$ , which are momentum entangled in the  $xz$  plane; i.e., the  $y$  components of the momentum for both photons are very small,  $k_{i/s,y} \approx 0$ , as investigated in Ref. [16]. This leads to  $|\psi_{\text{in}}\rangle \equiv |\psi_{\text{ent}}\rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_i d\mathbf{k}_s F_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_i) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_s) |0, 0\rangle$ , with  $\mathbf{k}_s$  and  $\mathbf{k}_i$  being the momentum of signal and idler photons, respectively, and  $\lambda_y$  being a linear polarization in the  $y$  direction. The two-photon wave function is given by (for details, see Appendix C)

$$F_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s) = \frac{C_{\text{ent}}}{\sqrt{2}} \text{sinc}\left(\frac{L\Delta k_z}{2}\right) u_p(k_{i,x} + k_{s,x}; k_{i,y} + k_{s,y}; \Omega_p) \times e^{-\frac{\Omega_y^2(k_{i,y}^2 + k_{s,y}^2) - T^2((\omega_i - \omega)^2 + (\omega_s - \omega)^2)}{2}} \theta(k_{i,z}) \theta(k_{s,z}), \quad (5)$$

where  $\text{sinc}$  is a sinc function,  $L$  is the length of the crystal in  $z$  direction, and  $\Delta k_z$  is the momentum mismatch in the  $z$  direction. The  $u_p$  is the pump transverse momentum-space envelope function, which depends on the  $x$  and  $y$  components of the signal and idler wave vectors,  $k_{s/i,x}$  and  $k_{s/i,y}$ , and on the pump beam waist parameter  $\Omega_p$  (see Appendix C for the full form). The pulse duration is given by  $T$ ,  $\Omega_y$  characterizes the spread of  $k_{i/s,y}$  for the idler and signal photons, and  $\theta(k_{i/s,z})$

is the Heavisine function, which enforces propagation in the positive  $z$  direction.  $C_{\text{ent}}$  is a normalization constant.

Before we continue, it is important to comment on the paraxial approximation and its relation to our formalism. The paraxial approximation assumes that the photons are emitted only within small angles relative to the pump propagation axis, irrespective of the crystal length, typically not exceeding a few degrees (e.g.,  $\lesssim 5^\circ$ ). In contrast, Eq. (5) is derived within a fully nonparaxial treatment of the SPDC-generated two-photon state. This means that no small-angle approximation is imposed on the transverse momentum components of the emitted photons. Consequently, the formalism remains valid for arbitrary emission angles and hence arbitrary crystal lengths, allowing one to accurately describe broad angular spectra and strong transverse-momentum correlations.

The narrow-angle (long-crystal) and broad-angle (ultrathin-crystal) emission regimes, on the other hand, are physical characteristics of the emitted radiation, irrespective of their theoretical modeling. For a fixed central frequency  $\omega$ , the crystal length  $L$  controls the angular spread of the emitted photons through the phase-matching sinc function. As  $L$  decreases, the sinc function broadens in momentum space, allowing increasingly large transverse momenta and correspondingly larger emission angles with respect to the pump axis. This defines the broad-angle (ultrathin-crystal) emission regime central to our analysis. Conversely, for sufficiently long crystals, the phase-matching function becomes narrow in momentum space, restricting the emitted photons to small transverse momenta and small propagation angles, thereby recovering the narrow-angle (long-crystal limit) emission regime. Hence, while the nonparaxial treatment is formally applicable for all crystal lengths, nonparaxial physical features (broad-angle emission) become particularly pronounced for short-crystal configurations.

The two-photon state is localized within an effective volume  $V_{\text{ent}} = C_{\text{ent}}$ , and its degree of entanglement is controlled by the crystal length  $L$  and the pump-beam waist  $\Omega_p$  [85]. This volume is inversely related to the joint momentum-space correlation volume, i.e., to the overall extent of the *unnormalized* joint spectrum in  $(\mathbf{k}_i, \mathbf{k}_s)$  space. For two separable Gaussian photons, the joint spectrum is confined to the product of two narrow single-photon distributions, yielding a relatively small joint correlation volume in momentum space. In contrast, for momentum-entangled SPDC pairs in the ultrathin-crystal regime, longitudinal phase matching allows a much broader joint angular spectrum, resulting in a larger joint correlation volume in momentum space. Since the normalized two-photon amplitude scales inversely with this correlation volume in momentum space, the broadened joint spectrum corresponds to a smaller effective normalization volume  $V_{\text{ent}}$  compared to  $V_{\text{sep}}$  in real space.

We compare the REMPI cross section of two entangled photons using Eq. (5) with a separable counterpart  $F_{\text{sep}}$ , which describes two narrow-band Gaussian photons propagating along the  $z$  axis, but features the same beam waist, pulse duration, central frequencies, and linear  $y$  polarization as the signal and idler photons (see Appendix C for explicit form of  $F_{\text{sep}}$ ). With these two wave

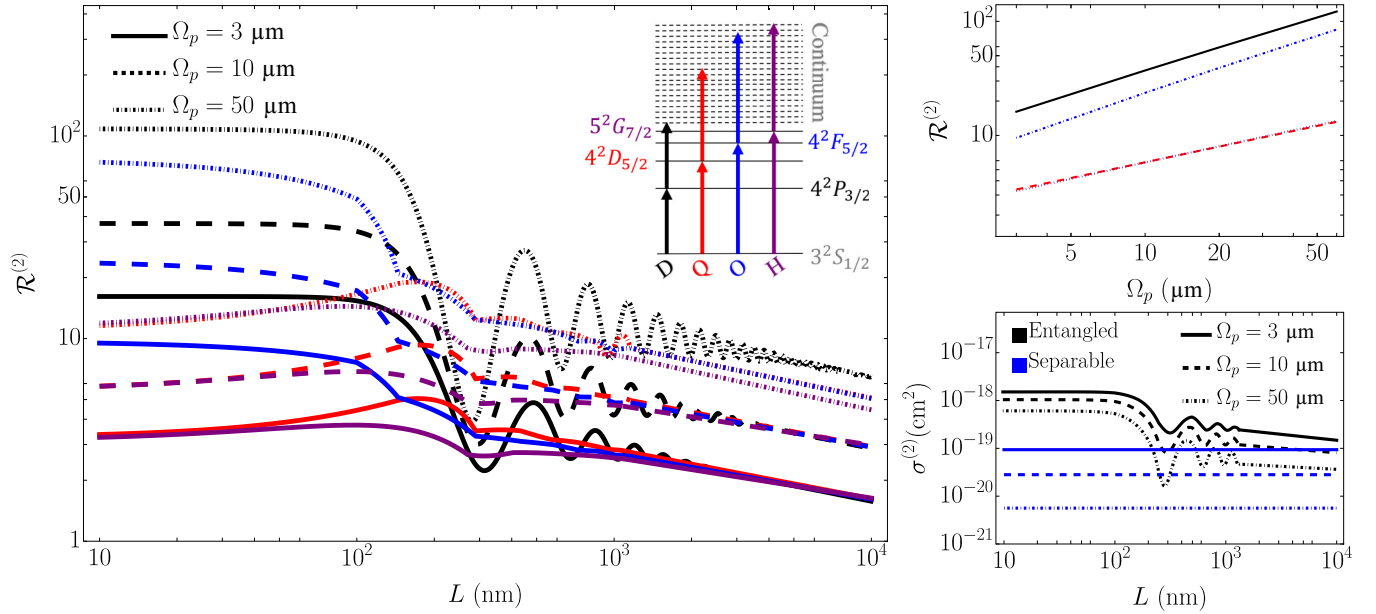


FIG. 2. (a) The enhancement ratio of the REMPI cross sections ( $\mathcal{R}^{(2)}$ ) [Eq. (3)] of a neutral sodium atom for dipole (black lines), quadrupole (red lines), octupole (blue lines), and hexadecapole (purple lines) as a function of the crystal length  $L$  (which quantifies angular emissions of entangled photons). The considered beam waists of the pump field are  $\Omega_p = 3 \mu\text{m}$  (solid lines),  $\Omega_p = 10 \mu\text{m}$  (dashed lines), and  $\Omega_p = 50 \mu\text{m}$  (dot-dashed lines). (b) The enhancement ratio of the cross section of neutral sodium atoms for dipole (solid black line), quadrupole (dashed red line), octupole (dot-dashed blue line), and hexadecapole (dotted blue line) as a function of the beam waists of the pump field ( $\Omega_p$ ) for crystal length  $L = 10 \text{ nm}$ . (c) Total REMPI cross sections,  $\sigma_{\text{ent}}^{(2)}$ , with entangled (black lines) and separable (blue lines) photons via dipole channel as a function of crystal length  $L$  for different beam waist. The transverse beam waists is  $\Omega_y = 50 \mu\text{m}$ , chosen large enough that the transverse momentum can be neglected. The pulse duration is  $T = 1.33 \text{ ps}$ , corresponding to a photon bandwidth smaller than the  $4^2P_{3/2}$ - $4^2P_{1/2}$  splitting, ensuring exclusive population of  $4^2P_{3/2}$ . The transition energies considered for the dipole, quadrupole, octupole, and hexadecapole channels are 3.753 293, 4.283 461 4.288 194, and 4.594 759, respectively [80] and lifetimes of the intermediate  $4^2P_{3/2}$ ,  $4^2D_{5/2}$ ,  $4^2F_{5/2}$ , and  $5^2G_{7/2}$  states are 90, 55, 72, and 235 ns, respectively [81]. All the graphs are plotted on a logarithmic scale with base 10, but the scale bar is not in logarithmic scale. All the results presented here are obtained via the nonparaxial treatment.

functions and Eq. (4), we can evaluate the enhancement without specifying the sample. The results are presented in Fig. 1(b).

The enhancement increases with the beam waist and with decreasing crystal length, but plateaus at very short lengths [see also Fig. 2(a)]. The formation of the plateau is a distinct feature emerging only in the ultrathin-crystal regime. It arises because the sinc function governing longitudinal phase matching in Eq. (5) approaches unity, i.e.,  $\text{sinc}(\Delta kL/2) \simeq 1$ , effectively removing the dependence on the propagation length within the crystal. This is the non-phase-matched regime, which is characteristic of nanoscale entangled light sources with subwavelength crystal lengths [1–3,8]. This saturation effect indicates an ultimate enhancement limit for momentum-entangled two-photon interactions, which has not been previously reported. It emerges in the nonlinear interactions considered here, and is absent, e.g., in linear quantum imaging [16]. At intermediate lengths, the enhancement oscillates with the crystal length, since the two-photon amplitude is proportional to a sinc function, as predicted, e.g., in entangled two-photon transparency [83]. An enhancement of several orders of magnitude is shown to be possible from this analysis. This pronounced enhancement arises from the large longitudinal mismatch leading to a very broad angular spectrum of photons.

## VI. PARAXIAL VERSUS NONPARAXIAL TREATMENT

We repeat the same calculation using the paraxial treatment. The results for these calculations (paraxial and nonparaxial treatment) are plotted in Fig. 1(b). Strikingly, the paraxial treatment strongly underestimates the achievable enhancement, incorrectly suggesting that only an  $\mathcal{O}(1)$  enhancement is possible in the depicted parameter range. In addition, the paraxial treatment completely misses the oscillatory features in the intermediate-length crystal that we discussed above. Hence, it cannot describe the most interesting regime of quantum-enhanced REMPI.

## VII. REMPI BEYOND DIPOLE TRANSITIONS

Given the results for the dipole channel, a natural question is whether higher-order multipole ionization channels can be enhanced in the same way. Here, each “channel” refers to its multipole character, namely, electric dipole, quadrupole, octupole, or hexadecapole, of the transition from the ground state to the intermediate excited bound state in the course of the two-photon ionization. First, we note that Eq. (4) breaks down because the multipole moments matrix elements depend explicitly on the photonic wave vectors, such that photonic and sample correlation functions cannot be separated, and

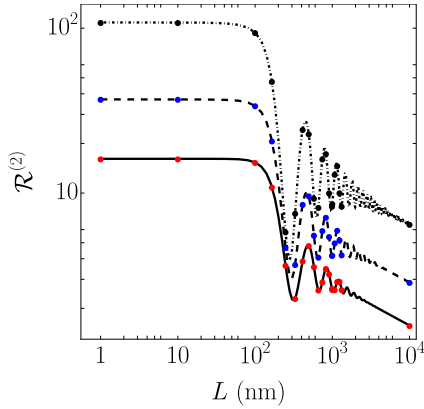


FIG. 3. Enhancement ratio of the dipole channel as a function of the crystal length for three different beam waists for  $n = 2$ :  $\Omega_p = 3 \mu\text{m}$  (solid line),  $\Omega_p = 10 \mu\text{m}$  (dashed line), and  $\Omega_p = 50 \mu\text{m}$  (dash-dotted line). The curves are obtained from Eq. (4), while the discrete markers represent the numerical evaluation of Eq. (3), showing excellent agreement between analytical and numerical results.

the potential enhancement now becomes explicitly sample dependent. We thus consider a case study in which our sample is a neutral sodium atom, and we model the process in the framework of a single-electron approximation (see computational details [81,86,87] in the Appendix A). We present the simulations of the enhancement ratios using Eq. (3) for REMPI via dipole, quadrupole, octupole, and hexadecapole transitions in Fig. 2. For ionization via the dipole channel, the results obtained from Eqs. (3) and (4) coincide with very high accuracy (see Fig. 3).

In the dipole channel, the most significant enhancement in REMPI occurs for ultrathin crystals ( $L < 300 \text{ nm}$ ), where broad-angle emission effects are the most pronounced [see Fig. 2(a)]. This remains true in the octupole channel, but surprisingly, the enhancement in both the quadrupole and hexadecapole channels peaks at a finite crystal length, approximately given by the wavelength of the quadrupole and hexadecapole transitions. In any channel, as the crystal length increases, moving toward the narrow-angle emission regime, the enhancement of the cross section decreases and vanishes for sufficiently large crystal lengths. The dipole transition exhibits the most pronounced enhancement in the cross section, followed by the octupole [see Figs. 2(a) and 2(b)]. As we already discussed for the ionization via the dipole channel, the former enhancement ratio is determined solely by the light properties. In contrast, the quadrupole and hexadecapole transitions display significantly weaker enhancement across the depicted parameter ranges.

In all channels, the enhancement increases monotonically with beam waist, as the excitation probability of separable states naturally decreases with beam waist (i.e., with focusing). However, the rate of increase is channel dependent [Fig. 2(b)]: The octupole and hexadecapole transitions show steeper growth compared to the dipole and quadrupole cases. Consequently, there is a crossover for very large beam waists, where the enhancement of higher-order multipole channels (octupole and hexadecapole) can surpass their lower-order counterparts (dipole and quadrupole). This can be observed

in Fig. 2(b), where the hexadecapole transition eventually exceeds the quadrupole in enhancement for sufficiently large beam waists. Overall, the results presented in Figs. 2(a) and 2(b) clearly confirm that Eq. (4) breaks down when other ionization channels are considered, and the enhancement depends on the material explicitly.

### VIII. SYMMETRY OF THE IONIZATION CHANNELS

The observed variation in enhancement originates from the interplay between the photonic wave function and the material response. For the quadrupole and octupole ionization channels, the photon fluxes are nearly identical, since the corresponding frequencies  $\omega$  are almost the same in both cases. The enhancement, therefore, cannot be attributed to flux differences alone. Instead, it arises from the overlap between the photonic wave function  $F_{\text{ent}}$  and the material response in  $\mathbf{k}$  space, which is larger for the octupole (even-parity) channel than for the quadrupole (odd-parity) one. A similar trend holds for other channels: The enhancement ratio  $\mathcal{R}^{(2)}$  is maximal for the dipole (odd-parity) channel, reflecting the largest  $\mathbf{k}$ -space overlap, as the material response effectively decouples from  $F_{\text{ent}}$ .

Consequently, at short crystal lengths, where the angular range for signal and idler photons is broad, odd multipole transitions with parity-favored pathways (dipole and octupole) exhibit significantly enhanced coupling, resulting in the highest enhancement. As the crystal length increases, the angular range for signal and idler photons narrows, reducing the distinctiveness between channels and diminishing the enhancement differences in any excitation channel.

### IX. QUANTUM-ENHANCED REMPI CROSS SECTION

We can express the entangled two-photon ionization cross section  $\sigma_{\text{ent}}^{(2)}$  in terms of the classical cross section, using  $\sigma_{\text{cl}}^{(2)} = \frac{\tilde{\sigma}_{\text{sep}}^{(2)}}{\phi_{\text{sep}}}$ . This yields

$$\sigma_{\text{ent}}^{(2)} = \mathcal{R}^{(2)} \phi_{\text{sep}} \sigma_{\text{cl}}^{(2)}, \quad (6)$$

where the material properties are encoded in the classical cross section  $\sigma_{\text{cl}}^{(2)}$  [57,88]. The classical cross section is weighted by the ratio  $\mathcal{R}^{(2)}$  that quantifies the momentum correlations of the entangled photon pair. We note an important distinction between Eq. (6) and similar expressions in the literature: Earlier expressions for entangled cross sections accounted for quantum correlations in momentum and energy separately [83], such that the factor  $\mathcal{R}^{(2)} \phi_{\text{sep}}$  can be replaced by the inverse of the so-called entanglement area and time. Equation (6) instead allows for arbitrary spatial profiles and propagation directions, and can account, e.g., for spatiotemporal entanglement [89,90].

In Fig. 2(c), we show estimates of the total REMPI cross section for entangled and separable photons via the dipole channel as a function of the crystal length and different beam waists of a pump beam  $\Omega_p$ . To this end, we have to choose realistic values for the pulse duration and the transverse beam waist.

The cross sections up to  $\lesssim 10^{-18} \text{ cm}^2$  are on par with the largest reported entangled two-photon absorption cross

sections in molecules [33,91] or with phase-matched sum frequency generation [90,92], and orders of magnitude larger than those measured in competing experiments [92–97]. The large ionization cross section in our study has a twofold origin: first, the resonant nature of the REMPI pathway, and second, the additional enhancement arising from momentum correlations in photon pairs generated by ultrathin crystals. This is evident from comparing Eq. (6) and Fig. 2(c). Experimentally, REMPI is particularly attractive because the signal is read out via photoelectrons, where the signal is less prone to be spoiled by other processes, as is the case in a purely photon-detecting scheme [98]. Hence, our simulations establish REMPI as an attractive platform to explore entangled two-photon physics and for entanglement-enhanced sensing, spectroscopy, and imaging.

As a final remark, we note that thin nonlinear crystals and tight focusing conditions may generally lead to relatively low SPDC efficiencies and, consequently, reduced entangled-photon fluxes. Thus, despite the potentially large enhancement factor, the experimentally achievable ionization yield may remain limited by the available photon-pair production rate. However, recent advances in engineered nanophotonic platforms, including resonantly enhanced metasurfaces and exciton-assisted SPDC in low-dimensional materials, have demonstrated significantly improved entangled-photon generation efficiencies [99,100]. These developments may pave the way toward thin nonlinear media capable of efficient entangled-photon generation and thereby may help mitigate these limitations in future implementations.

## X. CONCLUSION

We have investigated resonant multiphoton ionization driven by entangled light produced by nanoscale sources. By describing the ionization processes beyond the paraxial approximation, we uncovered a large enhancement of the ionization cross section. We further found channel-dependent enhancements that are entirely missed in paraxial models. These results demonstrate that the metrological advantages of entangled light emerge most strongly in the broad-angle emission regime, where large momentum correlations determine the ionization efficiency. This insight highlights the relevance of emerging nonclassical light sources based on ultrathin crystals, metasurfaces, and subwavelength nonlinear films, which naturally operate in this regime. Beyond revealing this effect, our framework provides a general foundation for exploring quantum-light-driven ionization, chiral and symmetry-sensitive photoreponses, and precision spectroscopy with modern nanoscale light sources.

We close by mentioning that we only analyzed the impact of momentum correlations in this paper. Extending the analysis to higher-dimensional spatiotemporal entanglement [101] will likely enhance the total cross section even further. Although our case study focuses on neutral sodium atoms, the perturbative  $S$ -matrix formalism is fully general and applies to both finite systems, such as molecules or other atomic species, and extended periodic systems, including solids.

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The authors declare no conflicts of interest.

## DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

## APPENDIX A: DEFINITION OF THE CROSS SECTION FOR TWO-PHOTON IONIZATION WITH QUANTUM STATES OF LIGHT

The total cross section  $\sigma^{(n)}$  is given by

$$\sigma^{(n)} = \frac{\Gamma^{(n)}}{\phi^{\tilde{n}}} = \frac{1}{g_{\text{in}}} \sum_{\text{in}} \sum_f \frac{|S_{\text{in};f}^{(n)}|^2}{T \phi^{\tilde{n}}}, \quad (\text{A1})$$

where  $T$  is the effective interaction time of the incident radiation at the target and  $S_{\text{in};f}^{(n)}$  is the transition matrix element from the total initial state  $|\Psi_{\text{in}}\rangle$  to the total final state  $|\Psi_f\rangle$ . We sum over the final states ( $\sum_f$ ) and average over the initial degenerate matter states ( $\frac{1}{g_{\text{in}}} \sum_{\text{in}}$ ), with  $g_{\text{in}}$  being a degeneracy of the initial matter state. All quantum numbers required to characterize the initial state of the system,  $|\Psi_{\text{in}}\rangle$  (and also final state  $|\Psi_f\rangle$ ), are specified by the multi-index in  $(f)$ . We note that in the case when these quantum numbers are continuous, the sums in Eq. (A1) must be interpreted as integrals with proper normalizations.

For the case of the ionization by two-photon state, Eq. (A1) reduces to

$$\sigma^{(2)} = \frac{\Gamma^{(2)}}{\phi^{\tilde{n}}} = \frac{1}{g_{\text{in}}} \sum_{\text{in}} \sum_f \int_{-\infty}^{\infty} d\mathbf{p}_e |S_{\text{in};f}^{(2)}(\mathbf{p}_e)|^2, \quad (\text{A2})$$

where  $S_{\text{in};f}^{(2)}(\mathbf{p}_e)$  is a transition matrix element from the total initial state given by  $|\Psi_{\text{in}}\rangle = |\psi_{\text{in}}\rangle \otimes |\varphi_{\text{in}}\rangle$ , with  $|\varphi_{\text{in}}\rangle$  being an initial electronic ground state to the total final state  $|\Psi_f\rangle = |0, 0\rangle \otimes |\varphi_f\rangle$ , with  $|\varphi_f\rangle = |\varphi_{\text{res}}; \mathbf{p}_e \mu_e\rangle$  being a wave function of the final state of a system comprising the residual system state  $|\varphi_{\text{res}}\rangle$  and photoelectron wave function  $|\mathbf{p}_e \mu_e\rangle$ . Here, the photoelectron is characterized by helicity  $\mu_e$  and definite asymptotic momentum  $\mathbf{p}_e = (p_e, \theta_e, \phi_e)$ , with  $p_e = |\mathbf{p}_e|$ , and  $\theta_e$  and  $\phi_e$  being polar and azimuthal angles, respectively.

The initial photonic state  $|\psi_{\text{in}}\rangle$  has the general form

$$|\psi_{\text{in}}\rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_1 d\mathbf{k}_2 F(\mathbf{k}_1, \mathbf{k}_2) \hat{a}_{\lambda_1}^{\dagger}(\mathbf{k}_1) \hat{a}_{\lambda_2}^{\dagger}(\mathbf{k}_2) |0, 0\rangle, \quad (\text{A3})$$

where  $F(\mathbf{k}_1, \mathbf{k}_2)$  denotes the normalized joint two-photon momentum-space amplitude for two photons with momenta

$\mathbf{k}_1$  and  $\mathbf{k}_2$  and polarizations  $\lambda_1$  and  $\lambda_2$ . For the symmetric two-photon state considered here, we assume that  $F(\mathbf{k}_1, \mathbf{k}_2) = F(\mathbf{k}_2, \mathbf{k}_1) = \frac{C_0}{\sqrt{2}} \tilde{F}(\mathbf{k}_1, \mathbf{k}_2)$ , with  $C_0 = \sqrt{\frac{1}{\int d\mathbf{k}_1 \int d\mathbf{k}_2 |\tilde{F}(\mathbf{k}_1, \mathbf{k}_2)|^2}}$  being the normalization factor. Note that  $C_0 \equiv V_{\psi_{\text{in}}}$ , where  $V_{\psi_{\text{in}}}$  is the effective volume of the photonic state.

The transition matrix element  $S_{\text{in};f}^{(2)}(\mathbf{p}_e)$  is given by [84,88]

$$S_{\text{in};f}^{(2)}(\mathbf{p}_e) = -\frac{2\pi i e^2 c^2}{\hbar^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_1 d\mathbf{k}_2 F(\mathbf{k}_1, \mathbf{k}_2) \left[ \sum_n \frac{\langle \varphi_{\text{res}}; \mathbf{p}_e \mu_e | \hat{R}_{\mathbf{k}_2, \lambda_2} | \varphi_n \rangle \langle \varphi_n | \hat{R}_{\mathbf{k}_1, \lambda_1} | \varphi_{\text{in}} \rangle}{\frac{E_f}{\hbar} - \omega_2 - \frac{1}{\hbar} \left( \varepsilon_n - \frac{i\hbar}{2t_n} \right)} + \sum_n \frac{\langle \varphi_{\text{res}}; \mathbf{p}_e \mu_e | \hat{R}_{\mathbf{k}_1, \lambda_1} | \varphi_n \rangle \langle \varphi_n | \hat{R}_{\mathbf{k}_2, \lambda_2} | \varphi_{\text{in}} \rangle}{\frac{E_f}{\hbar} - \omega_1 - \frac{1}{\hbar} \left( \varepsilon_n - \frac{i\hbar}{2t_n} \right)} \right] \delta \left( \frac{E_f}{\hbar} - \omega_1 - \frac{\varepsilon_{\text{in}}}{\hbar} - \omega_2 \right), \quad (\text{A4})$$

in which  $t_n$  and  $\varepsilon_n$  are lifetime and energy of the intermediate matter state  $\varphi_n$ , respectively,  $\varepsilon_{\text{in}}$  is the energy of the initial matter state  $\varphi_{\text{in}}$ , and  $E_f = \varepsilon_e + E_{\text{res}}$ , with  $\varepsilon_e$  and  $E_{\text{res}}$  being an energy of photoelectron and residual matter system, respectively. Here, the interaction operator  $\hat{R}_{\mathbf{k}, \lambda} = \sum_i^{N_e} \boldsymbol{\alpha}_i \cdot \mathbf{A}_{\mathbf{k}, \lambda}(\mathbf{r}_i)$ , where  $N_e$  is the number of electrons in a system and  $\boldsymbol{\alpha}_i$  is the Dirac matrix acting on  $i$ th electron. The amplitudes  $\mathbf{A}_{\mathbf{k}, \lambda}(\mathbf{r}_i)$  are given by  $\mathbf{A}_{\mathbf{k}, \lambda}(\mathbf{r}_i) = \sqrt{\frac{\hbar}{2\omega_k \epsilon_0 (2\pi)^3}} e^{i\mathbf{k} \cdot \mathbf{r}_i} \mathbf{e}_{\lambda}(\mathbf{k})$ , with  $\mathbf{e}_{\lambda}(\mathbf{k})$  being a polarization vector such as  $\mathbf{e}_{\lambda}(\mathbf{k}) \perp \mathbf{k}$ ,  $\omega_k = c|\mathbf{k}|$  is frequency of the photon, and  $\epsilon_0$  is vacuum permittivity.

The photon flux is obtained using Eq. (2):

$$\phi = c \frac{\sum_{\lambda=1,2} \int_{-\infty}^{\infty} d\mathbf{k} \frac{\mathbf{k} \cdot \mathbf{e}_{\lambda}}{k} \langle \psi_{\text{in}} | \hat{a}_{\lambda}^{\dagger}(\mathbf{k}) \hat{a}_{\lambda}(\mathbf{k}) | \psi_{\text{in}} \rangle}{V_{\psi_{\text{in}}}} = \frac{2c}{V_{\psi_{\text{in}}}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_1 d\mathbf{k}_2 |F(\mathbf{k}_1, \mathbf{k}_2)|^2 \left( \frac{k_{1,z}}{k_1} + \frac{k_{2,z}}{k_2} \right), \quad (\text{A5})$$

where  $k_{1/2} = |\mathbf{k}_{1/2}|$  and  $k_{1/2,z}$  is the projection of  $\mathbf{k}_{1/2}$  onto the  $z$  axis.

**REMPI.** Now, we consider the REMPI case, i.e., when the energy of (at least) one absorbed photon is resonant with the transition energy from the initial matter state  $\varphi_{\text{in}}$  to an intermediate matter state  $\varphi_c$  with the energy  $\varepsilon_c$ . This corresponds to tuning the photon frequency to  $\hbar\omega \approx \varepsilon_c - \varepsilon_{\text{in}}$ . In practice, achieving such a resonance requires at least one of the photons to be narrow band. Here, we focus on the case where both photons are narrow band and centered at the same frequency  $\omega$ . Accordingly, we set  $\omega_1 = \omega_2 = \omega$  in Eq. (A4). Then, upon inserting Eq. (A4) into Eq. (A2), we encounter the square of a Dirac delta distribution. For sufficiently long pulses, i.e., in the narrow-band limit, we regularize it using the standard finite-time identity [84]

$$\begin{aligned} & \delta^2 \left( \frac{E_f}{\hbar} - 2\omega - \frac{\varepsilon_{\text{in}}}{\hbar} \right) \\ &= \lim_{T \rightarrow \infty} \delta \left( \frac{E_f}{\hbar} - 2\omega - \frac{\varepsilon_{\text{in}}}{\hbar} \right) \int_{-T/2}^{T/2} \frac{dt}{2\pi} e^{i \left( \frac{E_f}{\hbar} - 2\omega - \frac{\varepsilon_{\text{in}}}{\hbar} \right) t} \\ &= \lim_{T \rightarrow \infty} \delta \left( \frac{E_f}{\hbar} - 2\omega - \frac{\varepsilon_{\text{in}}}{\hbar} \right) \frac{T}{2\pi}. \end{aligned} \quad (\text{A6})$$

Using the identity  $d\mathbf{p}_e = \frac{1}{c^2} p_e \varepsilon_e d\varepsilon_e d\Omega_e$  (in which  $d\Omega_e = \sin\theta_e d\theta_e d\phi_e$  denotes the solid angle) and integrating over  $d\varepsilon_e$ , we get the expression for total cross section as

$$\sigma^{(2)} = \frac{\hbar p_e \varepsilon_e}{2\pi c^2} \frac{1}{g_{\text{in}}} \sum_{\text{in}} \sum_f \int d\Omega_e \frac{|\tau_{\text{in};f}^{(2)}(\mathbf{p}_e)|^2}{\phi^{\tilde{n}}}, \quad (\text{A7})$$

where the transition amplitude  $\tau_{\text{in};f}^{(2)}(\mathbf{p}_e)$  is given by

$$\begin{aligned} \tau_{\text{in};f}^{(2)}(\mathbf{p}_e) &= -\frac{4\pi e^2 c^2 t_c}{i\hbar^3} \sum_c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_1 d\mathbf{k}_2 F(\mathbf{k}_1, \mathbf{k}_2) \\ &\times \left( \langle \varphi_{\text{res}}; \mathbf{p}_e \mu_e | \hat{R}_{\mathbf{k}_2, \lambda_2} | \varphi_c \rangle \langle \varphi_c | \hat{R}_{\mathbf{k}_1, \lambda_1} | \varphi_{\text{in}} \rangle \right. \\ &\left. + \langle \varphi_{\text{res}}; \mathbf{p}_e \mu_e | \hat{R}_{\mathbf{k}_1, \lambda_1} | \varphi_c \rangle \langle \varphi_c | \hat{R}_{\mathbf{k}_2, \lambda_2} | \varphi_{\text{in}} \rangle \right). \end{aligned} \quad (\text{A8})$$

Here,  $\varepsilon_e = \varepsilon_{\text{in}} + 2\omega - E_{\text{res}}$  and  $t_c$  is a lifetime of the intermediate state  $\varphi_c$ .

**Single-active electron approximation in sodium atom.** In the sodium case study ( $Z = 11$ ), the matrix elements entering Eq. (A8) are evaluated within the single-active-electron (SAE) approximation. Accordingly, the many-electron states in Eq. (A8) are approximated in factorized form as  $|\varphi_{\text{in}}\rangle \simeq |\varphi_{\text{core}}\rangle \otimes |\tilde{\varphi}_{\text{in}}\rangle$ ,  $|\varphi_c\rangle \simeq |\varphi_{\text{core}}\rangle \otimes |\tilde{\varphi}_c\rangle$ , and  $|\varphi_{\text{res}}; \mathbf{p}_e \mu_e\rangle \simeq |\varphi_{\text{core}}\rangle \otimes |\mathbf{p}_e \mu_e\rangle$ , where  $|\varphi_{\text{core}}\rangle$  denotes the frozen (spectator) core and  $|\tilde{\varphi}_{\text{in}}\rangle$ ,  $|\tilde{\varphi}_c\rangle$ , and  $|\mathbf{p}_e \mu_e\rangle$  are one-electron Dirac spinors of the active (valence) electron in an effective central potential describing the screened nuclear field. Within SAE, the interaction operator  $\hat{R}_{\mathbf{k}, \lambda}$  in Eq. (A8) retains only the contribution of the active electron, since the core is frozen and core excitations are neglected. Consequently, the core factor yields  $\langle \varphi_{\text{core}} | \varphi_{\text{core}} \rangle = 1$ , and the matrix elements in Eq. (A8) reduce to one-electron matrix elements between  $|\tilde{\varphi}_{\text{in}}\rangle$ ,  $|\tilde{\varphi}_c\rangle$ , and  $|\mathbf{p}_e \mu_e\rangle$ . The initial state is taken as the ground  $3s$  orbital. We choose the  $z$  axis as the quantization axis. The continuum wave function of the photoelectron  $|\mathbf{p}_e \mu_e\rangle$  is

expanded in the partial waves [43],

$$|p_e \mu_e\rangle = \sqrt{\frac{c^2}{4\pi \varepsilon_e p_e}} \sum_{\kappa m_j} C_{j_1 m_1 j_2 m_2}^{j \mu_f} 1_{1/2 \mu_f} i^l \sqrt{2l+1} e^{-i\delta_k} \times D_{m_j \mu_e}^j(\phi_e, \theta_e, 0) \Phi_{\varepsilon \kappa m_j}(\mathbf{r}). \quad (\text{A9})$$

Here,  $\kappa = (-1)^{l+j+1/2}(j+1/2)$  is the Dirac quantum number determined by the total angular momentum  $j$  and the parity  $l$ ,  $\delta_k$  is the phase shift induced by the scattering potential,  $C_{j_1 m_1 j_2 m_2}^{j \mu_f}$  is the Clebsh-Gordan coefficient,  $D_{MM'}^j$  is the Wigner matrix [102], and  $\Phi_{\varepsilon \kappa m_j}(\mathbf{r})$  is the partial-wave solution of the Dirac equation in the scattering field [86,87]. The summation over intermediate states in Eq. (A8) is taken as  $\sum_c \equiv \sum_{m_c}$ , where  $m_c$  is the projection of the total angular momentum of the intermediate state  $|\tilde{\varphi}_c\rangle$  onto the  $z$  axis. In Eq. (A7), the average over the degenerate initial states is written explicitly as  $\frac{1}{g_{\text{in}}} \sum_{\text{in}} \equiv \frac{1}{2j_{\text{in}}+1} \sum_{m_{\text{in}}}$ , with  $j_{\text{in}}$  being the total angular momentum of the initial electronic state  $|\tilde{\varphi}_{\text{in}}\rangle$  and  $m_{\text{in}}$  its projection onto the quantization axis ( $z$ ). The summation over final states is taken as  $\sum_f \equiv \sum_{\mu_e}$ . In all SAE calculations, we assume both photons to be linearly polarized along the  $y$  axis ( $\mathbf{e}_\lambda(\mathbf{k}) \simeq \mathbf{e}_{\lambda_y}$ ); i.e., this choice is used for the polarization entering  $\hat{R}_{k,\lambda}$  in Eq. (A8). In general, the polarization vector depends on  $\mathbf{k}$ ; however, in the parameter regime considered here, the photon momenta satisfy  $k_y \simeq 0$  (see Appendix C and the main text), so that the polarization can be taken as linearly polarized along the  $y$  axis.

As effective potential, we utilize the so-called  $X\alpha$  central potential whose parameters are adjusted in such a way as to reproduce the energy of dipole ( $3^2S_{1/2} - 4^2P_{3/2}$ ), quadrupole ( $3^2S_{1/2} - 4^2D_{5/2}$ ), octupole ( $3^2S_{1/2} - 4^2F_{5/2}$ ), and hexadecapole ( $3^2S_{1/2} - 5^2G_{7/2}$ ) transitions, respectively, namely, 3.753 293, 4.283 461, 4.288 194, and 4.594 759 eV [80]. The corresponding lifetimes  $t_c$  of the intermediate  $4^2P_{3/2}$ ,  $4^2D_{5/2}$ ,  $4^2F_{5/2}$ , and  $5^2G_{7/2}$  states are 90, 55, 72, and 235 ns, respectively [81]. The modified radial package solves the radial Dirac equation with the effective potential [86].

Now, to obtain  $\sigma_{\text{ent}}^{(2)}$  from the main text, one should use  $F(\mathbf{k}_1, \mathbf{k}_2)$  given by Eq. (C16),  $C_0 = C_{\text{ent}} \equiv V_{\text{ent}}$ , and  $\tilde{n} = 1$ . To obtain  $\tilde{\sigma}_{\text{sep}}^{(2)}$  from the main text, one should use  $F(\mathbf{k}_1, \mathbf{k}_2)$  given by Eq. (C18),  $C_0 = C_{\text{sep}} \equiv V_{\text{sep}}$ , and  $\tilde{n} = 1$ .

## APPENDIX B: CALCULATION OF ENHANCEMENT RATIO: THE DIPOLE CHANNEL

When considering the transition amplitude  $\tau_{\text{in},f}^{(2)}(\mathbf{p}_e)$  [Eq. (A8)] through the dipole channel in a dipole approximation, we can approximate the interaction operator  $\hat{R}_{k,\lambda_y}$  as  $\hat{R}_{k,\lambda_y} = \sum_i^{N_e} \boldsymbol{\alpha}_i \cdot \mathbf{A}_{k,\lambda}(\mathbf{r}_i) = \sqrt{\frac{\hbar}{2\omega_k \varepsilon_0 (2\pi)^3}} \sum_i^{N_e} e^{i\mathbf{k} \cdot \mathbf{r}_i} \boldsymbol{\alpha}_i \cdot \mathbf{e}_{\lambda_y} \simeq \sqrt{\frac{\hbar}{2\omega_k \varepsilon_0 (2\pi)^3}} \sum_i^{N_e} \boldsymbol{\alpha}_i \cdot \mathbf{e}_{\lambda_y}$ . As a result, the absorption operator is independent of momentum  $\mathbf{k}$ , i.e.,  $\hat{R}_{k,\lambda_y} \equiv \hat{R}_{\lambda_y}$ . Then, the two-photon ionization amplitude for entangled photons,  $\tau_{\text{ent}}^{(2)}(\mathbf{p}_e)$ , can be expressed in terms of the corresponding amplitude for separable photons,  $\tau_{\text{sep}}^{(2)}(\mathbf{p}_e)$  (for both amplitudes, for simplic-

ity we have omitted lower indices in;  $f$ ),

$$\begin{aligned} \tau_{\text{ent}}^{(2)}(\mathbf{p}_e) &\approx -\frac{8\pi e^2 c^2 t_c}{i\hbar^3} \sum_c \langle \varphi_{\text{res}}; \mathbf{p}_e \mu_e | \hat{R}_{\lambda_y} | \varphi_c \rangle \langle \varphi_c | \hat{R}_{\lambda_y} | \varphi_{\text{in}} \rangle \\ &\times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_i d\mathbf{k}_s F_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s) \\ &= \frac{\tau_{\text{sep}}^{(2)}(\mathbf{p}_e) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_i d\mathbf{k}_s F_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s)}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_1 d\mathbf{k}_2 F_{\text{sep}}(\mathbf{k}_1, \mathbf{k}_2)}. \end{aligned} \quad (\text{B1})$$

Using Eq. (B1) together with Eqs. (A5) and (A7), we obtain the enhancement ratio as

$$\mathcal{R}^{(2)} = \frac{V_{\text{ent}}}{V_{\text{sep}}} \frac{f_{\text{ent}}^{(2)}}{f_{\text{sep}}^{(2)}}, \quad (\text{B2})$$

$$\text{where } f_{\text{ent/sep}}^{(2)} = \frac{|\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_{i/1} d\mathbf{k}_{s/2} F_{\text{ent/sep}}(\mathbf{k}_{i/1}, \mathbf{k}_{s/2})|^2}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\mathbf{k}_{i/1} d\mathbf{k}_{s/2} |F_{\text{ent/sep}}(\mathbf{k}_{i/1}, \mathbf{k}_{s/2})|^2 \left( \frac{k_{i/1,z}}{k_{i/1}} + \frac{k_{s/2,z}}{k_{s/2}} \right)}.$$

Similarly, one can extend the enhancement ratio to the case of REMPI with  $n$  entangled photons ( $n$  is even),

$$\tau_{\text{ent}}^{(n)}(\mathbf{p}_e) = \frac{\tau_{\text{sep}}^{(n)}(\mathbf{p}_e) \int_{-\infty}^{\infty} d\mathbf{k}_1 \cdots d\mathbf{k}_n F_{\text{ent}}(\mathbf{k}_1, \dots, \mathbf{k}_n)}{\int_{-\infty}^{\infty} d\mathbf{k}_1 \cdots d\mathbf{k}_n F_{\text{sep}}(\mathbf{k}_1, \dots, \mathbf{k}_n)}, \quad (\text{B3})$$

in which we assumed that  $|\psi_{\text{in}}\rangle = \int_{-\infty}^{\infty} d\mathbf{k}_1 \cdots d\mathbf{k}_n F_{\text{ent}}(\mathbf{k}_1, \dots, \mathbf{k}_n) a_{\lambda}^{\dagger}(\mathbf{k}_1) \cdots a_{\lambda}^{\dagger}(\mathbf{k}_n)$  and that  $F_{\text{ent}}(\mathbf{k}_1, \dots, \mathbf{k}_n)$  is symmetric to any permutations of  $\mathbf{k}_n$  and that polarization of the photons is independent of the direction of the vectors  $\mathbf{k}_n$  (which is true for the case of paraxial approximation or the case when the wave vectors are confined in  $2d$  plane). Then, the flux is given by

$$\begin{aligned} \phi_{\text{ent/sep}} &= \frac{2c}{V_{\text{ent/sep}}} \int_{-\infty}^{\infty} d\mathbf{k}_1 \cdots d\mathbf{k}_n |F_{\text{ent/sep}}(\mathbf{k}_1, \dots, \mathbf{k}_n)|^2 \\ &\times \left( \frac{k_{1,z}}{k_1} + \cdots + \frac{k_{n,z}}{k_n} \right), \end{aligned} \quad (\text{B4})$$

and the enhancement ratio  $\mathcal{R}^{(n)}$  is given by

$$\mathcal{R}^{(n)} = \frac{V_{\text{ent}}}{V_{\text{sep}}} \frac{f_{\text{ent}}^{(n)}}{f_{\text{sep}}^{(n)}}, \quad (\text{B5})$$

$$\text{where } f_{\text{ent/sep}}^{(n)} = \frac{|\int_{-\infty}^{\infty} d\mathbf{k}_1 \cdots d\mathbf{k}_n F_{\text{ent/sep}}(\mathbf{k}_1, \dots, \mathbf{k}_n)|^2}{\int_{-\infty}^{\infty} d\mathbf{k}_1 \cdots d\mathbf{k}_n |F_{\text{ent/sep}}(\mathbf{k}_1, \dots, \mathbf{k}_n)|^2 \left( \frac{k_{1,z}}{k_1} + \cdots + \frac{k_{n,z}}{k_n} \right)}.$$

In Fig. 3, we plot the enhancement ratio  $\mathcal{R}^{(2)}$  for the case of the ionization of a sodium atom in SAE approximation through the intermediate  $4p_{3/2}$  state. The curves are obtained from Eq. (4) with  $n = 2$ , while the discrete markers represent the numerical evaluation of Eq. (3) with  $n = 2$ , showing excellent agreement between analytical and numerical results.

## APPENDIX C: THE TWO-PHOTON AMPLITUDE

In the current investigation, we assume that entangled photons are generated via the SPDC process and the entangled state  $|\psi_{\text{ent}}\rangle$  is given by [16]

$$\begin{aligned} |\psi_{\text{ent}}\rangle &\propto \int_{-T_{\text{int}}}^{T_{\text{int}}} dt \int_{V_{\text{crystal}}} d\mathbf{r} \sum_{\alpha, \beta, \gamma \in \{x, y, z\}} \chi_{\alpha\beta\gamma}^{(2)}(\mathbf{r}) \\ &\times E_{P,\gamma}(\mathbf{r}, t) \hat{E}_{\alpha}^{(-)}(\mathbf{r}, t) \hat{E}_{\beta}^{(-)}(\mathbf{r}, t) |0, 0\rangle, \end{aligned} \quad (\text{C1})$$

where  $\chi_{\alpha\beta\gamma}^{(2)}$  is the second-order nonlinear susceptibility tensor of the crystal. Note that the present analysis assumes an idealized two-photon Fock state  $|\psi_{\text{ent}}\rangle$ , which captures the leading-order physics of SPDC in the low-gain regime. In realistic sources, higher-order Fock components corresponding to multipair emissions are present; however, their contribution scales with higher powers of the pump intensity and can be strongly suppressed under typical experimental conditions using low pump powers [103], temporal gating [104], and coincidence detection. Such multipair events primarily introduce an incoherent background and are therefore expected to reduce the absolute visibility of the effect rather than qualitatively alter the predicted enhancement.

We integrate Eq. (C1) over the interaction volume of the crystal  $V_{\text{crystal}}$  and interaction time  $T_{\text{int}}$ , with  $E_{p,\gamma}(\mathbf{r}, t)$  being  $\gamma$ th component of the pump field, which we assume to be linearly polarized in  $y$  direction and propagate along positive  $z$  axis:

$$E_p(\mathbf{r}, t) = \int_{-\infty}^{\infty} d\mathbf{k}_p u_p(k_{p,x}, k_{p,y}) e^{i\mathbf{k}_p \cdot \mathbf{r} - i\omega_p t} \theta(k_{p,z}) \mathbf{e}_y, \quad (\text{C2})$$

where  $u_p$  is the pump transverse momentum-space envelope function that depends on  $x$  and  $y$  components of pump mo-

mentum  $\mathbf{k}_p$ ,  $k_{p,x}$  and  $k_{p,y}$ , respectively. The shape of  $u_p$  is determined by the pump-beam parameters, which are kept implicit for the moment.  $\theta(k_{p,z})$  is a Heaviside function, which makes photons propagate in the positive  $z$  direction, and  $\mathbf{e}_y$  is the polarization vector in the  $y$  direction. The quantized electric field  $\hat{\mathbf{E}}^{(-)}(\mathbf{r}, t)$  that corresponds to idler and signal photons is given by

$$\hat{\mathbf{E}}^{(-)}(\mathbf{r}, t) = \frac{-i}{(2\pi)^{3/2}} \sum_{\lambda=1,2} \int_{-\infty}^{\infty} d\mathbf{k} \left( \frac{\hbar\omega_{\mathbf{k}}}{2\epsilon_0} \right)^{1/2} \times \hat{a}_{\lambda}^{\dagger}(\mathbf{k}) e^{-i(\mathbf{k} \cdot \mathbf{r} - \omega_{\mathbf{k}} t)} \theta(k_z) \mathbf{e}(\mathbf{k}, \lambda), \quad (\text{C3})$$

where  $\hbar$  is the reduced Planck constant,  $\epsilon_0$  is the vacuum permittivity, and  $\hat{a}_{\lambda}(\mathbf{k})$  and  $\hat{a}_{\lambda}^{\dagger}(\mathbf{k})$  are the creation and annihilation operators of a photon with momentum  $\mathbf{k}$  and helicity  $\lambda$ , respectively, such as

$$[\hat{a}_{\lambda}(\mathbf{k}), \hat{a}_{\lambda'}^{\dagger}(\mathbf{k}')] = \delta^{(3)}(\mathbf{k} - \mathbf{k}') \delta_{\lambda\lambda'}. \quad (\text{C4})$$

The frequency of the photon is  $\omega_{\mathbf{k}} = c|\mathbf{k}|$  and  $\mathbf{e}(\mathbf{k}, \lambda)$  is the transversal dimensionless polarization vector that obeys  $\mathbf{k} \cdot \mathbf{e}(\mathbf{k}, \lambda) = \mathbf{e}(\mathbf{k}, 1)^* \cdot \mathbf{e}(\mathbf{k}, 2) = 0$ . The two-photon state can thus be written as

$$\begin{aligned} |\psi_{\text{ent}}\rangle &\propto \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-L/2}^{+L/2} dz \sum_{\alpha, \beta \in \{x, y, z\}} \chi_{\alpha\beta\gamma}^{(2)}(x, y, z) \int_{-\infty}^{+\infty} d\mathbf{k}_p u_p(k_{p,x}, k_{p,y}) e^{i(k_{p,x}x + k_{p,y}y + k_{p,z}z - \omega_p t)} \theta(k_{p,z}) \\ &\times \sum_{\lambda_i} \int_{-\infty}^{\infty} d\mathbf{k}_i \omega_{\mathbf{k}_i}^{1/2} e^{-i(k_{i,x}x + k_{i,y}y + k_{i,z}z - \omega_i t)} \theta(k_{i,z}) e_{\alpha}(\mathbf{k}_i, \lambda_i) \hat{a}_{\lambda_i}^{\dagger}(\mathbf{k}_i) \sum_{\lambda_s} \\ &\times \int_{-\infty}^{\infty} d\mathbf{k}_s \omega_{\mathbf{k}_s}^{1/2} e^{-i(k_{s,x}x + k_{s,y}y + k_{s,z}z - \omega_s t)} \theta(k_{s,z}) e_{\beta}(\mathbf{k}_s, \lambda_s) \hat{a}_{\lambda_s}^{\dagger}(\mathbf{k}_s) |0, 0\rangle. \end{aligned} \quad (\text{C5})$$

To take the spatial and time integrals, we use the following relations:

$$\int_{-\infty}^{+\infty} dx e^{i(k_{p,x} - k_{s,x} - k_{i,x})x} \propto \delta(k_{p,x} - k_{s,x} - k_{i,x}), \quad (\text{C6})$$

$$\int_{-\infty}^{+\infty} dy e^{i(k_{p,y} - k_{s,y} - k_{i,y})y} \propto \delta(k_{p,y} - k_{s,y} - k_{i,y}), \quad (\text{C7})$$

$$\int_{-L/2}^{+L/2} dz e^{i(k_{p,z} - k_{s,z} - k_{i,z})z} \propto \text{sinc}\left(\frac{\Delta k_z L}{2}\right), \quad (\text{C8})$$

$$\int_{-\infty}^{+\infty} dt e^{i(\omega_s + \omega_i - \omega_p)t} \propto \delta(\omega_s + \omega_i - \omega_p) \propto \delta(\omega_s/c + \omega_i/c - k_p), \quad (\text{C9})$$

in which  $\Delta k_z = k_{p,z} - k_{s,z} - k_{i,z}$ , and consequently, Eq. (C5) reduces to

$$\begin{aligned} |\psi_{\text{ent}}\rangle &\propto \sum_{\alpha, \beta \in \{x, y, z\}} \chi_{\alpha\beta\gamma}^{(2)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} d\mathbf{k}_s d\mathbf{k}_i d\mathbf{k}_p \delta(k_{p,x} - k_{s,x} - k_{i,x}) \delta(k_{p,y} - k_{s,y} - k_{i,y}) \delta(\omega_s/c + \omega_i/c - k_p) \\ &\times \text{sinc}\left(\frac{\Delta k_z L}{2}\right) u_p(k_{p,x}, k_{p,y}) \theta(k_{p,z}) \sum_{\lambda_i} \omega_{\mathbf{k}_i}^{1/2} \theta(k_{i,z}) e_{\alpha}(\mathbf{k}_i, \lambda_i) \hat{a}_{\lambda_i}^{\dagger}(\mathbf{k}_i) \sum_{\lambda_s} \omega_{\mathbf{k}_s}^{1/2} \theta(k_{s,z}) e_{\beta}(\mathbf{k}_s, \lambda_s) \hat{a}_{\lambda_s}^{\dagger}(\mathbf{k}_s) |0, 0\rangle, \end{aligned} \quad (\text{C10})$$

where we have assumed that the crystal is uniform without poling (making  $\chi^{(2)}$  independent of  $\mathbf{r}$ ). In the next step, we use the following identity for the delta function:

$$\delta(\omega_s/c + \omega_i/c - k_p) = \frac{\delta(k_{p,z} - \sqrt{(k_s + k_i)^2 - k_{p,x}^2 - k_{p,y}^2})(\omega_s + \omega_i)}{\sqrt{(k_s + k_i)^2 - k_{p,x}^2 - k_{p,y}^2} c}, \quad (\text{C11})$$

where we took into account that  $k_{p,z} > 0$ . Using the above delta function, the entangled state can be simplified further to

$$|\psi_{\text{ent}}\rangle \propto \sum_{\alpha, \beta \in \{x, y, z\}} \chi_{\alpha\beta}^{(2)} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dk_s dk_i \frac{(\omega_s + \omega_i)}{\sqrt{(k_s + k_i)^2 - (k_{s,x} + k_{i,x})^2 - (k_{s,y} + k_{i,y})^2}} \text{sinc}\left(\frac{\Delta k_z L}{2}\right) u_p(k_{s,x} + k_{i,x}; k_{s,y} + k_{i,y}) \\ \times \sum_{\lambda_i} \omega_{k_i}^{1/2} \theta(k_{i,z}) e_{\alpha}(\mathbf{k}_i, \lambda_i) \hat{a}_{\lambda_i}^{\dagger}(\mathbf{k}_i) \sum_{\lambda_s} \omega_{k_s}^{1/2} \theta(k_{s,z}) e_{\beta}(\mathbf{k}_s, \lambda_s) \hat{a}_{\lambda_s}^{\dagger}(\mathbf{k}_s) |0, 0\rangle, \quad (\text{C12})$$

where  $\Delta k_z = k_{p,z} - k_{s,z} - k_{i,z} = \sqrt{(k_s + k_i)^2 - k_{p,x}^2 - k_{p,y}^2} - k_{s,z} - k_{i,z} = \sqrt{(k_s + k_i)^2 - (k_{s,x} + k_{i,x})^2 - (k_{s,y} + k_{i,y})^2} - k_{s,z} - k_{i,z}$ . Considering that we want to have a fixed frequency and  $k_y \approx 0$ , we apply the filter to both the signal and the idler. This means that we should add a corresponding filter function  $e^{-\frac{k_{s,y}^2 \Omega_p^2}{2}} e^{-\frac{k_{i,y}^2 \Omega_p^2}{2}} e^{-\frac{(\omega_s - \omega)^2 T^2}{2}} e^{-\frac{(\omega_i - \omega)^2 T^2}{2}}$ , where the first two exponents filter out signal and idler photons with  $k_{s/y} \approx 0$  and the last ones filter out single frequency  $\omega$  for sufficiently long pulse duration  $T$ . Since  $k_y \approx 0$  for both signal and idler, then in summation over polarization  $\lambda_{i/s}$ , one can take one of the polarizations being along  $y(\lambda_y)$  and another perpendicular. We also assume that  $\chi_{yyy}^{(2)} = \text{const}$  is the largest contribution, which is true for most crystals [16]. Using the vacuum dispersion relationship for signal and idler photons, we get

$$|\psi_{\text{ent}}\rangle \propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dk_i dk_s \frac{\sqrt{\omega_s \omega_i} (k_s + k_i)}{\sqrt{(k_s + k_i)^2 - (k_{s,x} + k_{i,x})^2 - (k_{s,y} + k_{i,y})^2}} \text{sinc}\left(\frac{\Delta k_z L}{2}\right) \\ \times u_p(k_{s,x} + k_{i,x}; k_{s,y} + k_{i,y}) e^{-\frac{(k_{s,y}^2 + k_{i,y}^2) \Omega_p^2}{2}} e^{-\frac{((\omega_s - \omega)^2 + (\omega_i - \omega)^2) T^2}{2}} \theta(k_{i,z}) \theta(k_{s,z}) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_i) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_s) |0, 0\rangle. \quad (\text{C13})$$

We note that we leave the dependence on  $k_{s/y}$  because we would like to construct a normalizable state. The use of the vacuum dispersion relation eliminates the need to account for crystal-specific refractive index variations, which would require detailed knowledge of the material dispersion and reduce the generality of the analysis [16]. Since only photons with transverse wave vectors smaller than the free-space wave vector can exit the crystal, the accessible mode range is fundamentally determined by the vacuum dispersion condition. Deviations from this condition due to the actual crystal dispersion affect only the detailed shape of the phase-matching function, without altering the accessible transverse momentum range (especially in the case of a very thin crystal) or the main conclusions of this work.

From here on, we use the explicit Gaussian form for the envelope function  $u_p$ :

$$u_p(k_{p,x}, k_{p,y}) = u_p(k_{s,x} + k_{i,x}; k_{s,y} + k_{i,y}) \equiv u_p(k_{s,x} + k_{i,x}; k_{s,y} + k_{i,y}; \Omega_p) = e^{-\frac{\Omega_p^2 (k_{s,x} + k_{i,x})^2}{2}}, \quad (\text{C14})$$

where  $\Omega_p$  is the pump beam waist, characterizing the pump momentum spread in the  $x$  direction. We consider a loosely focused pump beam; i.e.,  $\Omega_p$  is sufficiently large such that  $k_{p,z} \gg k_{p,x}$ . In this paraxial regime, one has  $k_{p,z} \approx k_p$  and hence  $\frac{(k_s + k_i)}{\sqrt{(k_s + k_i)^2 - (k_{s,x} + k_{i,x})^2 - (k_{s,y} + k_{i,y})^2}} \approx 1$ . Since, we assume that the signal and idler photons are both centered around the same frequency  $\omega$ , i.e.,  $\omega_i \approx \omega_s \approx \omega$ , the entangled-photon state can be written as

$$|\psi_{\text{ent}}\rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dk_i dk_s F_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_i) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_s) |0, 0\rangle, \quad (\text{C15})$$

where  $F_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s) = \frac{C_{\text{ent}}}{\sqrt{2}} \tilde{F}_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s)$ , with  $C_{\text{ent}}$  being a normalization factor and  $\tilde{F}_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s)$  is given by

$$\tilde{F}_{\text{ent}}(\mathbf{k}_i, \mathbf{k}_s) = \text{sinc}\left(\frac{\Delta k_z L}{2}\right) u_p(k_{s,x} + k_{i,x}; k_{s,y} + k_{i,y}; \Omega_p) e^{-\frac{(k_{s,y}^2 + k_{i,y}^2) \Omega_p^2}{2}} e^{-\frac{((\omega_s - \omega)^2 + (\omega_i - \omega)^2) T^2}{2}} \theta(k_{i,z}) \theta(k_{s,z}). \quad (\text{C16})$$

Here,  $\Delta k_z = k_{p,z} - k_{s,z} - k_{i,z} = \sqrt{(k_s + k_i)^2 - k_{p,x}^2 - k_{p,y}^2} - k_{s,z} - k_{i,z} = \sqrt{(k_s + k_i)^2 - (k_{s,x} + k_{i,x})^2 - (k_{s,y} + k_{i,y})^2} - k_{s,z} - k_{i,z} \approx \sqrt{(k_s + k_i)^2 - (k_{s,x} + k_{i,x})^2} - k_{s,z} - k_{i,z}$  and  $k_{s/y} \approx \sqrt{k_{s/i}^2 - k_{s/i,x}^2}$ . For the case of separable photons, we use the following expression for the two-photon amplitude:

$$|\psi_{\text{sep}}\rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dk_1 dk_2 F_{\text{sep}}(\mathbf{k}_1, \mathbf{k}_2) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_1) \hat{a}_{\lambda_y}^{\dagger}(\mathbf{k}_2) |0, 0\rangle, \quad (\text{C17})$$

where  $F_{\text{sep}}(\mathbf{k}_1, \mathbf{k}_2) = \frac{C_{\text{sep}}}{\sqrt{2}} \tilde{F}_{\text{sep}}(\mathbf{k}_1, \mathbf{k}_2)$ , with  $C_{\text{sep}}$  being a normalization constant and  $\tilde{F}_{\text{sep}}(\mathbf{k}_1, \mathbf{k}_2)$  is given by

$$\tilde{F}_{\text{sep}}(\mathbf{k}_1, \mathbf{k}_2) = u_p(k_{1,x}; k_{1,y}; \Omega_p) u_p(k_{2,x}; k_{2,y}; \Omega_p) e^{-\frac{(k_{1,y}^2 + k_{2,y}^2) \Omega_p^2}{2}} e^{-\frac{((\omega_1 - \omega)^2 + (\omega_2 - \omega)^2) T^2}{2}} \theta(k_{1,z}) \theta(k_{2,z}). \quad (\text{C18})$$

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