Analytical expression for the angular correlation function of two Lyman-α photons in the photodissociation of hydrogen molecules

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An analytical expression of the angular correlation function of a pair of Lyman-α photons in the photodissociation of a hydrogen molecule is derived theoretically in a manner based on both atomic and molecular physics and quantum optics. The angular correlation function turns out to be expressed in terms of cosine (sine) functions of four angular variables of detectors with five coefficients. The angular correlation function is expanded in terms of the spherical harmonics for investigating which terms are involved, and we discuss the reason why they are involved. Interesting features are revealed in the expansion. We then search for a special detector arrangement where the angular-dependent terms vanish in the angular correlation function expressed in terms of the spherical harmonics. It turns out that no such detector arrangement in fact exists, but there is a special pair of detector arrangements where the angular-dependent terms vanish in the summation of two values of the angular correlation function expressed in terms of the spherical harmonics. We refer to such a pair of detector arrangements as a magic pair.

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I. INTRODUCTION

Entanglement, one of the most profound features of quantum mechanics [1], has been widely used as a resource for quantum information processing [2,3], quantum metrology [4], and quantum simulations [5–7]. The entanglement in atoms (ions) [3,8–10] has been demonstrated with designing and manipulating interactions between subsystems [3,8–10]. However, an idea has been proposed that entangled systems of atoms are spontaneously produced through molecular dissociation even without active control techniques [11,12]. The entanglement in atomic systems would accordingly be ubiquitous. We refer to the idea and the investigations inspired by it in the next paragraph.

Miyagi *et al.* [11] and Jänkälä *et al.* [12] have predicted that an entangled pair of H($2p$) atoms is produced through photodissociation of a hydrogen molecule, and they have shown that the production of entangled atom pairs can be substantiated by measuring the angular correlation function (ACF) of a pair of Lyman-α photons emitted by the two H($2p$) atomic fragments. After the first measurements of the ACFs [13–15], Torizuka *et al.* [16] recently measured the ACFs of a pair of Lyman-α photons in photodissociation of H_2 and D_2 with two photon detectors rotating in a circle perpendicular to the incident beam of the linearly polarized light, and they identified the $2p$ atom-pair state by means of searching for states that reproduce the experimental ACFs. It is remarkable that the identified atom-pair state, a superposition of the $Q_2\,{}^1\Pi_u(1)$ state and the $Q_2\,{}^3\Sigma_u^+(2)$ state at infinite internuclear distance, is entangled, and the entanglement originates from the symmetry properties of the molecular electronic states, the properties which are invariant during dissociation.

In the present study, we aim to theoretically derive a general analytical expression of the ACF of a pair of Lyman-α photons in the photodissociation of a hydrogen molecule following the method described in Ref. [11], an expression which is a function of four angles specifying an arrangement of two detectors and involves a set of physical parameters related to the atomic and photonic systems. The analytical expression would be useful for measuring ACFs over the entire spherical surface. The analytical expression of the ACF is expanded in terms of the spherical harmonics so that we can find out which terms contribute, and we investigate the reason why they do. Interesting construction is revealed in the expansion. We then search for a magic arrangement of two photon detectors, at which arrangement the angular anisotropy in the ACF vanishes and the ACF becomes equal to a constant independent of the incident-photon energy. We are able to measure the angle-integrated cross section for the emission of a pair of Lyman-α photons against the incident-photon energy with both detectors held fixed at the magic arrangement if discovered. The magic arrangement of the two detectors is an analogy to the magic arrangement of a single photon detector, referred to as a magic angle, in the angular intensity distribution of a fluorescence photon emitted by an excited fragment atom in photodissociation [17]. However, in contrast with the emission of a single photon, it has turned out that a magic arrangement of two detectors does not exist in the present two-photon-emission process [see Eq. (1)], but a magic pair

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of detector arrangements does. By virtue of the magic arrangement pair, we are able to measure the angle-integrated cross section for the emission of two Lyman-α photons against the incident-photon energy with only two coincidence measurements between those two photons, i.e., one coincidence measurement at one arrangement in the magic pair and the other measurement at the other arrangement.

II. FORMULATION

A. The process to be investigated and the outline of the formulation

In the present study, we calculate the ACF of a pair of Lyman-α photons emitted in the photodissociation of a hydrogen molecule:

$$\begin{aligned} \mathrm{H}_2(X\,^1\Sigma_g^+) + \gamma_{\mathrm{ex}} &\rightarrow \mathrm{H}_2^{**}(\text{doubly excited states}) + \text{vac} \\ &\rightarrow \mathrm{H}(2p) + \mathrm{H}(2p) + \text{vac} \\ &\rightarrow \mathrm{H}(1s) + \mathrm{H}(1s) + \gamma_{\text{Ly-}\alpha} + \gamma_{\text{Ly-}\alpha}, \end{aligned} \tag{1}$$

where γ_{ex} is a linearly polarized incident photon, $\gamma_{\text{Ly-}\alpha}$ is a Lyman-α photon, and "vac" denotes the photon field in the vacuum state (H_2 may be replaced by D_2 or HD). The internuclear distance in the $\mathrm{H}_2(X\,^1\Sigma_g^+)$ and H_2^{**}(doubly excited states) is around the equilibrium one in the ground electronic state, i.e., the $X\,^1\Sigma_g^+$ state, and the $\mathrm{H}_2(X\,^1\Sigma_g^+)$ is randomly oriented with respect to the space-fixed frame introduced in Sec. II B, whose situations are in accord with those in the experiments [13–16]. The H_2^{**}(doubly excited states) electronically autoionizes and may dissociate into other fragment-pairs, e.g., $\mathrm{H}(2s) + \mathrm{H}(2p) +$ vac. Such processes, however, just decrease the branching ratio of the dissociation into $\mathrm{H}(2p) + \mathrm{H}(2p) +$ vac and does not influence the ACF of two Lyman-α photons. The emission of molecular fluorescence from the H_2^{**}(doubly excited states) is very unlikely during the dissociation because the fluorescent process is, in general, a process of nanosecond or longer time-scale and cannot hence compete with the electronic autoionization or dissociation. The molecular fluorescence, if any, just decreases the branching ratio of the $\mathrm{H}(2p) + \mathrm{H}(2p) +$ vac channel to a very small extent and still does not influence the ACF of two Lyman-α photons

We consider a system composed of a photon field and a pair of hydrogen atoms for the present calculation, a system which is referred to as a total system. As for each hydrogen atom in a hydrogen molecule with infinite internuclear distance, the infinite nuclear-mass approximation is used, and only the electronic motion is considered in reference to a nucleus at rest against the space-fixed frame introduced in Sec. II B. The total system is hence composed of the electronic partial system and the photonic partial system. The nuclear state is taken into account through the distribution function of dissociation direction with respect to the space-fixed frame as mentioned in Sec. II D because the nuclear state at infinite internuclear distance is expressed as a state with definite dissociation direction. The two nuclei (protons) are labeled a and b, and the two electrons are labeled 1 and 2. Each electron is bound by either the nucleus a or b. We do not consider the possibility that both electrons are bound by either nucleus. As for atomic fluorescence, only electric dipole photons are taken into account, and the Weisskopf-Wigner theory (e.g., Sec. 6.3 in Ref. [18]) is used for the spontaneous emission of fluorescence. In process 1, the step from $\mathrm{H}_2(X\,^1\Sigma_g^+) + \gamma_{\mathrm{ex}}$ to $\mathrm{H}(2p) + \mathrm{H}(2p) +$ vac is much faster than the successive step from $\mathrm{H}(2p) + \mathrm{H}(2p) +$ vac to $\mathrm{H}(1s) + \mathrm{H}(1s) + \gamma_{\text{Ly-}\alpha} + \gamma_{\text{Ly-}\alpha}$ [the lifetime of $\mathrm{H}(2p)$ atoms is 1.6 ns (pp. 200–201 in Ref. [19])] and the origin of time is taken at the point when a pair of fragment $\mathrm{H}(2p)$ atoms is formed with the photon field being in the vacuum state.

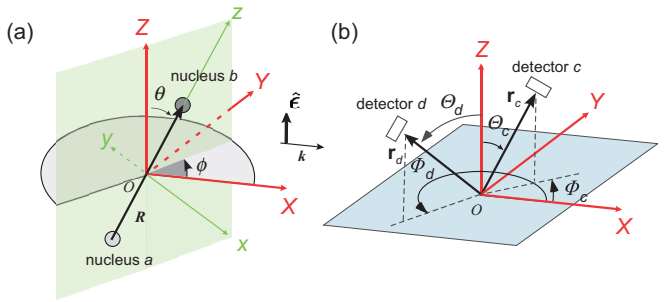

FIG. 1. (a) The space-fixed XYZ frame and the molecular xyz frame used for calculating the angular correlation function of a pair of Lyman-α photons in the photodissociation of hydrogen molecules. $\hat{\boldsymbol{\epsilon}}$, the unit polarization vector of the linearly polarized incident light; $\boldsymbol{k}$, the wave-number vector of the incident light. The green panel shows the xz plane, which involves the Z axis. See Sec. II B for details. (b) An arrangement of the photon detectors c and d. A detector arrangement is specified with a set of four angles $(\Theta_c, \Phi_c, \Theta_d, \Phi_d)$. The blue panel shows the XY plane. See Sec. II D for details.

We first calculate the ACF under the assumption that only one doubly excited state, which does not need to be specified, is involved in process 1 for a given energy of the incident photon (the single-state case), and then we calculate the ACF under the other assumption that many doubly excited states are involved in process 1 for a given energy of the incident photon (the many-state case). In fact, the same analytical form has been obtained for the single-state case and the many-state case. As for the spherical harmonics, we follow the definition described in Sec. 2.5 in Ref. [19].

B. The frames of reference

As shown in Fig. 1(a), we first introduce a frame of reference held fixed to the incident light beam, a frame that is referred to as the space-fixed frame. The origin O of the space-fixed XYZ frame is taken on the incident light beam. The positive direction of the Z axis points to the direction of the unit polarization vector of the linearly polarized incident light $\hat{\boldsymbol{\epsilon}}$, and the positive direction of the X axis points to the propagation direction of the incident light. The Y axis is taken so that the space-fixed XYZ frame is a right-handed system. As mentioned in Sec. II A, the nuclei a and b are held at rest against the space-fixed XYZ frame and they are hence put on the line passing through the origin O of the space-fixed XYZ frame.

We then introduce one more frame of reference, called a molecular frame, whose z axis points from the nucleus a to b as shown in Fig. 1(a). The origin of the molecular xyz frame is taken at the midpoint between the nucleus a and b, and is taken to coincide with the origin of the space-fixed XYZ frame. The

relative position vector of the two nuclei with respect to the nucleus a is denoted by $\boldsymbol{R}$ as seen in Fig. 1(a). The molecular xyz frame is specified with respect to the space-fixed XYZ frame with the Euler angles $(\phi, \theta, 0)$, where the azimuth angle ϕ ranges from 0 to 2π and the polar angle θ ranges from 0 to π. We label the molecular frame (MF) specified with the Euler angles $(\phi, \theta, 0)$ MF(θ, ϕ), which is held fixed with respect to the space-fixed XYZ frame throughout the step from H$(2p)$ + H$(2p)$ + vac (the time $t = 0$) to H$(1s)$ + H$(1s)$ + $\gamma_{\text{Ly-}\alpha}$ + $\gamma_{\text{Ly-}\alpha}$ $(t \to \infty)$ in process 1. The MF(θ, ϕ) implies that the internuclear distance $R \to \infty$. We consider the ensemble of the total systems related to an MF(θ, ϕ), and the MF(θ, ϕ) ranges with the probability-distribution function discussed in Sec. II F.

C. The linear spaces, the ket vectors, and the density operators involved

We first consider the total system at $t = 0$ based on an MF(θ, ϕ) with (θ, ϕ) held fixed. To this end, a linear space $S_i(\theta, \phi)$ spanned by an orthonormal basis set $E_i(\theta, \phi)$ is introduced:

$$\begin{aligned} E_i(\theta, \phi) = \Big\{ \Big| & 2p^a_{m_a}(k)\, 2p^b_{m_b}(\ell)\, m_s(1)\, n_s(2); \theta, \phi \Big\rangle_e |\text{vac}\rangle_p \Big| \\ & m_a = -1, 0, 1, \text{ and } m_b = -1, 0, 1, \text{ and} \\ & (k, \ell) = (1, 2), (2, 1), \text{ and} \\ & m_s = \pm\tfrac{1}{2}, \text{ and } n_s = \pm\tfrac{1}{2} \Big\}, \end{aligned} \tag{2}$$

where $|\cdots\rangle_e$ denotes a ket vector of the electronic partial system and $|\cdots\rangle_p$ is a ket vector of the photonic partial system. A ket vector of the total system is thus denoted by $|\cdots\rangle$ without subscripts. If it is clear to which partial system a given ket vector belongs, the subscripts e and p will be omitted. The ket vector $|\text{vac}\rangle_p$ expresses the vacuum state of the photonic partial system. As for ket vectors of the electronic partial system, $|2p^a_m(k)\rangle$ $(m = -1, 0, 1)$, for example, means that the electron k $(k = 1, 2)$ is bound by the nucleus a and a projection of the electron orbital angular momentum on the z axis is m in the unit of $\hbar$. The ket vector $|2p^a_m(k)\rangle$ is hence given through the translation of a ket vector $|2p_m(k)\rangle$ along the z axis by $-(1/2)\boldsymbol{R}$, and the ket vector $|2p^b_m(k)\rangle$ is given through the translation of a ket vector $|2p_m(k)\rangle$ along the z axis by $(1/2)\boldsymbol{R}$, where the ket vector $|2p_m(k)\rangle$ is a $2p$ state at the origin O in Fig. 1(a) with the projection quantum number m onto the z axis. The translation of electronic ket vectors along the z axis does not change the projection quantum number m onto the z axis. The ket vectors $|\pm\frac{1}{2}(k)\rangle_e$ $(k = 1, 2)$ are spin eigenstates of the electron k with the projection of the electron spin angular momentum on the z axis being $\pm\frac{1}{2}$ in the unit of $\hbar$ (double-sign corresponds). It is a custom to symbolically write $|\frac{1}{2}(k)\rangle_e$ and $|-\frac{1}{2}(k)\rangle_e$ as $|\alpha(k)\rangle$ and $|\beta(k)\rangle$, respectively. We note that the linear space $S_i(\theta, \phi)$ and the basis set $E_i(\theta, \phi)$ are based on the MF(θ, ϕ).

We assume that a doubly excited state "ex" alone is involved in process 1 for a given energy of the incident photon (the single-state case). Any state "α" of the total system at the time $t = 0$ associated with the MF(θ, ϕ), $|\text{ex}, \alpha; \theta, \phi; t = 0\rangle$, belongs to the linear space $S_i(\theta, \phi)$ and is thus expanded in terms of $E_i(\theta, \phi)$ as

$$|\text{ex}, \alpha; \theta, \phi; t = 0\rangle = \sum C_{\text{ex},\alpha}(m_a, m_b, (k, \ell), m_s, n_s) \Big| 2p^a_{m_a}(k)\, 2p^b_{m_b}(\ell)\, m_s(1)\, n_s(2); \theta, \phi \Big\rangle_e |\text{vac}\rangle_p , \tag{3}$$

where the summation is taken over all the possible values of the indices, i.e., m_a, m_b, (k, ℓ), m_s, and n_s. The expansion coefficients $C_{\text{ex},\alpha}(\cdots)$ are independent of (θ, ϕ) because in process 1 the processes proceed in the same manner irrespective of the MF(θ, ϕ) after the photoexcitation to the doubly excited state "ex." The state $|\text{ex}, \alpha; \theta, \phi; t = 0\rangle$ is evolved in time as follows [11]:

$$|\text{ex}, \alpha; \theta, \phi; t = 0\rangle \to |\text{ex}, \alpha; \theta, \phi; t \to \infty\rangle , \tag{4a}$$

$$|\text{ex}, \alpha; \theta, \phi; t \to \infty\rangle = \sum C_{\text{ex},\alpha}(m_a, m_b, (k, \ell), m_s, n_s) \, |(m_a)_a (m_b)_b; \theta, \phi\rangle_p \, |1s^a(k)\, 1s^b(\ell)\, m_s(1)\, n_s(2); \theta, \phi\rangle_e . \tag{4b}$$

The electronic ket vectors, $|1s^a(k)\rangle$ and $|1s^b(k)\rangle$ $(k = 1, 2)$, are given through the translation of a ket vector $|1s(k)\rangle$ along the z axis by $-(1/2)\boldsymbol{R}$ and $(1/2)\boldsymbol{R}$, respectively, where the ket vector $|1s(k)\rangle$ is the $1s$ state at the origin O in Fig. 1(a) with the projection of the electron orbital angular momentum on the z axis being zero in the unit of $\hbar$. We again note that the translation of the electronic ket vectors along the z axis does not change the projection of the electron orbital angular momentum on the z axis. The photonic ket vector $|(m_a)_a; \theta, \phi\rangle_p$, for example, is a state of a single photon emitted by an electron bound by the nucleus a through the $2p^a_{m_a} \to 1s^a$ transition. It is convenient to symbolically write $|(m_a)_a; \theta, \phi\rangle_p$ and $|(m_b)_b; \theta, \phi\rangle_p$ as [11]

$$|(1)_{a/b}; \theta, \phi\rangle_p = |\gamma_{a/b}; \theta, \phi\rangle_p , \tag{5a}$$

$$|(0)_{a/b}; \theta, \phi\rangle_p = |\phi_{a/b}; \theta, \phi\rangle_p , \tag{5b}$$

$$|(-1)_{a/b}; \theta, \phi\rangle_p = |\rho_{a/b}; \theta, \phi\rangle_p . \tag{5c}$$

The Euler angles ϕ and θ in ket vectors are often omitted for simplicity. It is a good approximation that the spin-orbit coupling is neglected in the radiative transition in a hydrogen atom, and the spin eigenstates of the electronic partial system consequently remain unaltered. In the experiments [13–16], the fine structure of the Lyman-α fluorescence was not resolved.

The density operator for the ensemble of the total systems at the time $t = 0$, $\hat{\rho}_{\text{ex}}(\theta, \phi; t = 0)$, is written as

$$\hat{\rho}_{\text{ex}}(\theta, \phi; t = 0) = \sum_\alpha p_{\text{ex},\alpha} \, |\text{ex}, \alpha; \theta, \phi; t = 0\rangle \langle \text{ex}, \alpha; \theta, \phi; t = 0| , \tag{6}$$

where the fractional population $p_{\text{ex},\alpha}$ for the $|\text{ex}, \alpha; \theta, \phi; t = 0\rangle$ state is independent of the MF(θ, ϕ) such

as the expansion coefficients $C_{\mathrm{ex},\alpha}(m_a, m_b, (k,\ell), m_s, n_s)$ in Eq. (3) because of the same reason as that for the coefficients. The density operator $\hat{\rho}_{\mathrm{ex}}(\theta,\phi;t=0)$ is an operator in the linear space $S_i(\theta,\phi)$ and is evolved in time following the time evolution of the $|\mathrm{ex},\alpha;\theta,\phi;t=0\rangle$ state shown in Eqs. (4):

$$\hat{\rho}_{\mathrm{ex}}(\theta,\phi;t=0) \to \hat{\rho}_{\mathrm{ex}}(\theta,\phi;t\to\infty), \tag{7a}$$

$$\hat{\rho}_{\mathrm{ex}}(\theta,\phi;t\to\infty) = \sum_{\alpha} p_{\mathrm{ex},\alpha}\,|\mathrm{ex},\alpha;\theta,\phi;t\to\infty\rangle \langle \mathrm{ex},\alpha;\theta,\phi;t\to\infty|\,. \tag{7b}$$

The fractional population $p_{\mathrm{ex},\alpha}$ is not changed as the time evolves because the ensemble of the total systems is left undisturbed.

We introduce one more linear space $S_f(\theta,\phi)$ spanned by an orthonormal basis set $E_f(\theta,\phi)$,

$$E_f(\theta,\phi) = \{|(i)_a(j)_b;\theta,\phi\rangle_p\,|1s^a(k)\;1s^b(\ell)\;m_s(1)\;n_s(2);\theta,\phi\rangle_e\,| \\ i=\gamma,\phi,\rho,\ \text{and}\ j=\gamma,\phi,\rho,\ \text{and}\quad (k,\ell)=(1,2),(2,1),\ \text{and}\quad m_s=\alpha,\beta,\ \text{and}\ n_s=\alpha,\beta\}, \tag{8}$$

where photonic ket vectors and electron spin ket vectors are symbolically written. The ket vector of the total system $|\mathrm{ex},\alpha;\theta,\phi;t\to\infty\rangle$ shown in Eq. (4b) is an element of the linear space $S_f(\theta,\phi)$, and the density operator for the ensemble of the total systems $\hat{\rho}_{\mathrm{ex}}(\theta,\phi;t\to\infty)$ shown in Eq. (7b) is an operator in $S_f(\theta,\phi)$. This is the reason why the linear space $S_f(\theta,\phi)$ is introduced in addition to the linear space $S_i(\theta,\phi)$. Both the linear space $S_f(\theta,\phi)$ and the basis set $E_f(\theta,\phi)$ are based on the MF(θ,ϕ) on which $S_i(\theta,\phi)$ and $E_i(\theta,\phi)$ are based too, and the MF(θ,ϕ) is held fixed with respect to the space-fixed XYZ frame during the step from H$(2p)$ + H$(2p)$ + vac $(t=0)$ to H$(1s)$ + H$(1s)$ + $\gamma_{\text{Ly-}\alpha}$ + $\gamma_{\text{Ly-}\alpha}$ $(t\to\infty)$ in process 1 as mentioned at the end of Sec. II B. The total system at $t=0$ is described in the linear space $S_i(\theta,\phi)$ and that at $t\to\infty$ is described in the linear space $S_f(\theta,\phi)$. In what follows, the state of the total system $|\mathrm{ex},\alpha;\theta,\phi;t\to\infty\rangle$ and the density operator for the ensemble of the total systems $\hat{\rho}_{\mathrm{ex}}(\theta,\phi;t\to\infty)$ are simply written as $|\mathrm{ex},\alpha;\theta,\phi\rangle$ and $\hat{\rho}_{\mathrm{ex}}(\theta,\phi)$, respectively.

D. Photon-pair detection operator and the two-photon correlation function

The outline of calculating the ACFs for the single-state and many-state cases is as follows. We first calculate a two-photon correlation function of a pair of Lyman-α photons for the ensemble of the total systems specified by the density operator $\hat{\rho}_{\mathrm{ex}}(\theta,\phi)$ with the angles θ and ϕ held fixed, i.e., we first calculate a two-photon correlation function for pairs of fragment hydrogen atoms held fixed against the space-fixed XYZ frame with the internuclear distance $R\to\infty$ [Eq. (10)]. As mentioned at the end of Sec. II B, the azimuth angle ϕ ranges from 0 to 2π and the polar angle θ ranges from 0 to π. Each two-photon correlation function for each $\hat{\rho}_{\mathrm{ex}}(\theta,\phi)$ is then averaged with the weight of $w_{\mathrm{ex}}(\theta,\phi)$, the distribution function of MF(θ,ϕ), so that we can obtain the two-photon correlation function for the ensemble of the total systems specified by both $\hat{\rho}_{\mathrm{ex}}(\theta,\phi)$ and $w_{\mathrm{ex}}(\theta,\phi)$ under the assumption of the single-state case [Eq. (11)]. The ACF of a pair of Lyman-α photons is derived from the two-photon correlation function. The two-photon correlation function for the many-state case is calculated from that for the single-state case as mentioned in Sec. II G

In this subsection, we introduce the operator for detecting a photon-pair and then the ensemble average of the operator, referred to as the two-photon correlation function of a pair of Lyman-α photons. The two-photon correlation function is a generator of both the ACF of a pair of Lyman-α photons and the angle-differential cross section for the emission of a pair of Lyman-α photons.

Suppose that a photon is detected at the time t_c by the detector c at the position $\boldsymbol{r}_c$ and the other photon is detected at the time t_d by the detector d at the position $\boldsymbol{r}_d$. Those detectors are arranged as shown in Fig. 1(b), and their directions are specified by the Euler angles $(\Phi_{c/d},\ \Theta_{c/d},\ \Psi_{c/d}=0)$ in reference to the space-fixed XYZ frame, provided that those detectors are originally on the $+Z$ axis. The detection of a photon-pair is expressed by the operator $\hat{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ defined as (see p. 33 in Ref. [18])

$$\hat{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d) \\ = [\boldsymbol{E}^{(-)}(\boldsymbol{r}_c,t_c)\boldsymbol{E}^{(-)}(\boldsymbol{r}_d,t_d)\boldsymbol{E}^{(+)}(\boldsymbol{r}_d,t_d)\boldsymbol{E}^{(+)}(\boldsymbol{r}_c,t_c)]\otimes\hat{I}_e \\ = \hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\otimes\hat{I}_e, \tag{9}$$

where $\boldsymbol{E}^{(+)}$ and $\boldsymbol{E}^{(-)}$ are the positive and negative frequency parts of the electric-field operator, respectively, and line up in the normal order. The operator $\hat{I}_e$ in Eq. (9) is the identity operator in the space for the electronic partial system. The expectation value or the ensemble average of the photon-pair detection operator $\hat{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ is referred to as the two-photon correlation function (p. 33 in Ref. [18]), which is proportional to the probability density of detecting a photon pair at $(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ (Secs. 4.2 and 4.3 in Ref. [18]).

The ensemble average of $\hat{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ for the ensemble of the total systems specified by the density operator $\hat{\rho}_{\mathrm{ex}}(\theta,\phi)$ is written as

$$[\hat{\mathscr{E}}^{(2)}](\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi) \\ = \mathrm{Tr}[\tilde{\rho}_{\mathrm{ex}}(\theta,\phi)\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)], \tag{10}$$

where $\tilde{\rho}_{\mathrm{ex}}(\theta,\phi)$ and $\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$ are representation matrices of the density operator $\hat{\rho}_{\mathrm{ex}}(\theta,\phi)$ and the photon-pair detection operator $\hat{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ in terms of $E_f(\theta,\phi)$ defined in Eq. (8), respectively, and both of them are hence 72×72 matrices. Symbols with ˜ express representation matrices in the present paper. The ensemble average $[\hat{\mathscr{E}}^{(2)}](\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$ is based on the MF(θ,ϕ), and it is again averaged with the weight of $w_{\mathrm{ex}}(\theta,\phi)$, the distribution function of MF(θ,ϕ) in reference to the space-fixed XYZ frame, so that we can obtain $G^{(2)}_{\mathrm{ex}}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$, the two-photon

correlation function of a pair of Lyman-α photons in process 1 for the single-state case,

$$G_{\rm ex}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d) = \int \mathrm{Tr}[\tilde{\rho}_{\rm ex}(\theta,\phi)\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)] \times w_{\rm ex}(\theta,\phi)\sin\theta\, d\theta\, d\phi. \quad (11)$$

We use the function $w_{\rm ex}(\theta,\phi)$ which takes account of the random orientation of the $H_2(X\,^1\Sigma_g^+)$ with respect to the space-fixed frame in process 1.

As will be mentioned in Eq. (51), the two-photon correlation function $G_{\rm ex}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ is separated into a temporal part and a spatial part as

$$G_{\rm ex}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d) = g(t_c,t_d)F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d), \quad (12a)$$

$$g(t_c,t_d) = \left(\frac{\omega^2 p}{4\pi\epsilon_0 c^2}\right)^4\left(\frac{1}{R_0^4}\right) \times e^{-\Gamma(t_c-\frac{R_0}{c})}e^{-\Gamma(t_d-\frac{R_0}{c})} \times \Theta\left(t_c-\frac{R_0}{c}\right)\Theta\left(t_d-\frac{R_0}{c}\right), \quad (12b)$$

where c is the light velocity in vacuum, ϵ_0 is the permittivity of free space, ω is the angular frequency of the Lyman-α fluorescence in vacuum, and Γ is the reciprocal of the lifetime of $H(2p)$ atoms, i.e., $\Gamma^{-1} = 1.6$ ns (pp. 200–201 in Ref. [19]). In Eqs. (12), $R_0 = |\boldsymbol{r}_c| = |\boldsymbol{r}_d|$, which is a constant independent of $\boldsymbol{r}_c$ and $\boldsymbol{r}_d$ because we put the detectors on a spherical surface of the radius R_0, $\hat{\boldsymbol{r}}_c = \boldsymbol{r}_c/R_0$, $\hat{\boldsymbol{r}}_d = \boldsymbol{r}_d/R_0$, and $p = |\langle 1s|(-e\boldsymbol{r})|2p_{m=1}\rangle| = |\langle 1s|(-e\boldsymbol{r})|2p_{m=0}\rangle| = |\langle 1s|(-e\boldsymbol{r})|2p_{m=-1}\rangle|$, where e is the elementary charge ($e>0$), $|2p_m\rangle$ ($|1s\rangle$) is a $2p$ state ($1s$ state) at the origin O in Fig. 1(a) with the projection of the electron orbital angular momentum on the z axis being m (for the $|1s\rangle$ state, $m=0$), and $\boldsymbol{r}$ is the position of the electron in reference to the nucleus at the origin O. The projection of the electron orbital angular momentum m is associated with the z axis as mentioned in Sec. II C. $\Theta(\cdots)$ is the step function representing the causality. The two-photon correlation function $G_{\rm ex}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$, from the definition, should have the dimensions of an (electric field)^4, and the temporal part, $g(t_c,t_d)$, turns out to have the same dimensions. The spatial part, $F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$, is hence dimensionless.

We deduce two quantities from $F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$, the spatial part of the two-photon correlation function, as shown below. The function $c_{\rm ex}F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$, where $c_{\rm ex}$ is a constant independent of $(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$, gives the ACF of a pair of Lyman-α photons if $c_{\rm ex}$ is determined such that

$$\int c_{\rm ex}F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)d\Omega_c d\Omega_d = 1, \quad (13)$$

where $d\Omega_{c/d} = \sin\Theta_{c/d}d\Theta_{c/d}d\Phi_{c/d}$. The product of $c_{\rm ex}F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ and $\sigma_{\rm ex}^{L_\alpha L_\alpha}$, the angle-integrated cross section for emitting a pair of Lyman-α photons, yields the angle-differential cross section for emitting the photon pair $\frac{d^2\sigma_{\rm ex}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}$:

$$\frac{d^2\sigma_{\rm ex}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d} = \sigma_{\rm ex}^{L_\alpha L_\alpha}(c_{\rm ex}F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)). \quad (14)$$

E. The method for calculating the two-photon correlation function

In this subsection, we show that Eq. (11) is rewritten in terms of 9×9 matrices [$\tilde{\rho}_{\rm ex}(\theta,\phi)$ and $\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$ are 72×72 ones]. To this end, we first derive useful properties of the matrix $\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$ and $\tilde{\rho}_{\rm ex}(\theta,\phi)$.

We rewrite an element of $E_f(\theta,\phi)$ in Eq. (8) in a simpler form,

$$|I;\theta,\phi\rangle_p\,|K;\theta,\phi\rangle_e = |(i)_a(j)_b;\theta,\phi\rangle_p\,|1s^a(k)\;1s^b(\ell)\;m_s(1)\;n_s(2);\theta,\phi\rangle_e\,, \quad (15)$$

where an index I collectively stands for (i,j) and an index K collectively stands for $((k,\ell),m_s,n_s)$. The $((I',K'),(I'',K''))$ element of the matrix $\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$ is simplified as

$$_p\langle I';\theta,\phi|_e\,\langle K';\theta,\phi|\,\hat{\mathscr{E}}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\,|I'';\theta,\phi\rangle_p\,|K'';\theta,\phi\rangle_e = \delta_{K'K''}\;{}_p\langle I';\theta,\phi|\,\hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\,|I'';\theta,\phi\rangle_p\,, \quad (16)$$

because of the orthonormality of the set $\{|K;\theta,\phi\rangle_e\}$. We note that $\delta_{K'K''} = \delta_{(k',\ell')(k'',\ell'')}\delta_{m_s'm_s''}\delta_{n_s'n_s''}$. Equation (16) is useful for simplifying Eq. (11) as shown later.

We then show that the matrix $\tilde{\rho}_{\rm ex}(\theta,\phi)$ is in fact independent of (θ,ϕ). As mentioned in Sec. II C, the expansion coefficients in Eq. (4b), $C_{{\rm ex},\alpha}(m_a,m_b,(k,\ell),m_s,n_s)$, are independent of (θ,ϕ) and the fractional population $p_{{\rm ex},\alpha}$ in Eq. (7b) is also independent of (θ,ϕ). The matrix elements of $\tilde{\rho}_{\rm ex}(\theta,\phi)$ are determined by only a set of those expansion coefficients and the fractional populations, and $\tilde{\rho}_{\rm ex}(\theta,\phi)$ is consequently independent of (θ,ϕ).

Equation (16) and the (θ,ϕ) independence of $\tilde{\rho}_{\rm ex}(\theta,\phi)$ being used, Eq. (11) is simplified as

$$G_{\rm ex}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d) = \sum_{I'}\left[\sum_{I''}\left\{\left({}_p\langle I';\theta,\phi|\,\hat{\rho}_{\rm ex}^{\rm ph}(\theta,\phi)\,|I'';\theta,\phi\rangle_p\right) \times\left(\int \sin\theta\, d\theta\, d\phi\; w_{\rm ex}(\theta,\phi) \times{}_p\langle I'';\theta,\phi|\,\hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\,|I';\theta,\phi\rangle_p\right)\right\}\right], \quad (17)$$

where $\hat{\rho}_{\rm ex}^{\rm ph}(\theta,\phi)$ is defined as

$$\hat{\rho}_{\rm ex}^{\rm ph}(\theta,\phi) = \sum_{K'}{}_e\langle K';\theta,\phi|\,\hat{\rho}_{\rm ex}(\theta,\phi)\,|K';\theta,\phi\rangle_e, \quad (18)$$

and is the reduced density operator for the photonic partial system.

We introduce two 9×9 matrices to rewrite Eq. (17) with the trace of the product of them. One is $\tilde{\rho}_{\rm ex}^{\rm ph}$, the representation matrix of the reduced density operator $\hat{\rho}_{\rm ex}^{\rm ph}(\theta,\phi)$ in terms of the orthonormal basis set $E_p(\theta,\phi)$,

$$E_p(\theta,\phi) = \{|(i)_a(j)_b;\theta,\phi\rangle_p\,|i=\gamma,\phi,\rho \text{ and } j=\gamma,\phi,\rho\} = \{|I;\theta,\phi\rangle_p\}. \quad (19)$$

The reason why the representation matrix is denoted not by $\tilde{\rho}_{\rm ex}^{\rm ph}(\theta,\phi)$ but by $\tilde{\rho}_{\rm ex}^{\rm ph}$ is that the matrix element

${}_p\langle I';\theta,\phi|\,\hat{\rho}_{\rm ex}^{\rm ph}(\theta,\phi)\,|I'';\theta,\phi\rangle_p$ is a sum of some elements of $\tilde{\rho}_{\rm ex}(\theta,\phi)$ and the elements of $\tilde{\rho}_{\rm ex}(\theta,\phi)$ are independent of (θ,ϕ) as mentioned just above. The explicit expression of the $((i',j'),(i'',j''))$ element of $\tilde{\rho}_{\rm ex}^{\rm ph}$ is

$$\begin{aligned}&\big(\tilde{\rho}_{\rm ex}^{\rm ph}\big)_{(i',j')(i'',j'')}\\&\quad={}_p\langle(i')_a(j')_b;\theta,\phi|\,\hat{\rho}_{\rm ex}^{\rm ph}(\theta,\phi)\,|(i'')_a(j'')_b;\theta,\phi\rangle_p\,.\end{aligned}\tag{20}$$

The other 9×9 matrix is $[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$, the $w_{\rm ex}(\theta,\phi)$-averaged representation matrix of $\hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ in terms of $E_p(\theta,\phi)$ defined in Eq. (19). The $((i',j'),(i'',j''))$ element of $[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ is explicitly written as

$$\begin{aligned}&[\tilde{E}^{(2)}]^b_{(i',j')(i'',j'')}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\\&=\int\sin\theta\,d\theta\,d\phi\;w_{\rm ex}(\theta,\phi)\\&\quad\times{}_p\langle(i')_a(j')_b;\theta,\phi|\,\hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\,|(i'')_a(j'')_b;\theta,\phi\rangle_p\,.\end{aligned}\tag{21}$$

The parameter "b" comes from Eq. (31), the analytical expression of $w_{\rm ex}(\theta,\phi)$. The two 9×9 matrices $\tilde{\rho}_{\rm ex}^{\rm ph}$ and $[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ being used, Eq. (17) is simplified in matrix form as

$$G_{\rm ex}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)=\mathrm{Tr}\big[\tilde{\rho}_{\rm ex}^{\rm ph}[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\big].\tag{22}$$

We note that $\tilde{\rho}_{\rm ex}^{\rm ph}$, the reduced density matrix for the photonic partial system, is independent of the detector arrangement $(\boldsymbol{r}_c,\boldsymbol{r}_d)$ and independent of the detection time (t_c,t_d) as well. Detecting a pair of photons is involved in $[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$. In the end, we have reached Eq. (22), which is much simpler than the equivalent equation, Eq. (11), since the former equation is written in terms of the 9×9 matrices and the latter one is in terms of the 72×72 matrices. Following Eq. (22), we calculate the two-photon correlation function, a generator of the ACF.

For the discussion in Sec. II F, we introduce one more 9×9 matrix, a generator of the matrix $[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$. On the right-hand side of Eq. (21), a part ${}_p\langle(i')_a(j')_b;\theta,\phi|\,\hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\,|(i'')_a(j'')_b;\theta,\phi\rangle_p$ is the $((i',j'),(i'',j''))$ element of the representation matrix for the operator $\hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ in terms of the basis set $E_p(\theta,\phi)$ defined in Eq. (19), the matrix which is denoted by $\tilde{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$.

F. Matrix representation of the photon-pair detection operator

In this subsection, two matrix representations are shown of the photon-pair detection operator. They are $\tilde{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$ and $[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$, both of which have been defined in Sec. II E. Once the former matrix has been obtained, the latter matrix is calculated on the basis of Eq. (21) and the latter one yields the two-photon correlation function $G_{\rm ex}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ according to Eq. (22).

Following Ref. [11], we have calculated the matrix $\tilde{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d;\theta,\phi)$ to find out that the $((i',j'),(i'',j''))$ element is separated into a temporal part and spatial part as

$$\begin{aligned}&{}_p\langle(i')_a(j')_b;\theta,\phi|\,\hat{E}^{(2)}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\,|(i'')_a(j'')_b;\theta,\phi\rangle_p\\&\quad=g(t_c,t_d)\,f_{(i',j')(i'',j'')}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d;\theta,\phi),\end{aligned}\tag{23}$$

where $i'=\gamma,\phi,\rho$, $j'=\gamma,\phi,\rho$, $i''=\gamma,\phi,\rho$, and $j''=\gamma,\phi,\rho$. The temporal part $g(t_c,t_d)$ has been defined in Eq. (12b). The dimensionless functions $f_{(i',j')(i'',j'')}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d;\theta,\phi)$ are arranged in matrix form as

$$\begin{array}{c|cccc|cccc|c}
 & |\gamma\gamma\rangle & |\rho\rho\rangle & |\gamma\rho\rangle & |\rho\gamma\rangle & |\gamma\phi\rangle & |\phi\gamma\rangle & |\rho\phi\rangle & |\phi\rho\rangle & |\phi\phi\rangle \\
\hline
\langle\gamma\gamma| & f_{D1} & f_2 & f_1 & f_1 & f_6 & f_6 & f_4 & f_4 & -f_7 \\
\langle\rho\rho| & f_2^* & f_{D1} & f_1^* & f_1^* & -f_4^* & -f_4^* & -f_6^* & -f_6^* & -f_7^* \\
\langle\gamma\rho| & f_1^* & f_1 & f_{D1} & f_3 & -f_6^* & f_5^* & -f_5 & f_6 & -f_8 \\
\langle\rho\gamma| & f_1^* & f_1 & f_3 & f_{D1} & f_5^* & -f_6^* & f_6 & -f_5 & -f_8 \\
\hline
\langle\gamma\phi| & f_6^* & -f_4 & -f_6 & f_5 & f_{D2} & f_8 & f_9 & f_7 & f_{10} \\
\langle\phi\gamma| & f_6^* & -f_4 & f_5 & -f_6 & f_8 & f_{D2} & f_7 & f_9 & f_{10} \\
\langle\rho\phi| & f_4^* & -f_6 & -f_5^* & f_6^* & f_9^* & f_7^* & f_{D2} & f_8 & -f_{10}^* \\
\langle\phi\rho| & f_4^* & -f_6 & f_6^* & -f_5^* & f_7^* & f_9^* & f_8 & f_{D2} & -f_{10}^* \\
\hline
\langle\phi\phi| & -f_7^* & -f_7 & -f_8 & -f_8 & f_{10}^* & f_{10}^* & -f_{10} & -f_{10} & f_{D3}
\end{array},\tag{24}$$

where the ket vector $|\gamma\rho\rangle$ and the bra vector $\langle\gamma\rho|$, for example, stand for $|\gamma_a\rho_b;\theta,\phi\rangle_p$ and ${}_p\langle\gamma_a\rho_b;\theta,\phi|$, respectively. The matrix is composed of three diagonal elements f_{D1}–f_{D3} and ten off-diagonal elements f_1–f_{10}, which are explicitly written as

$$f_{D1}=2|\hat{\boldsymbol{r}}_c\times\hat{\boldsymbol{p}}_\gamma|^2|\hat{\boldsymbol{r}}_d\times\hat{\boldsymbol{p}}_\gamma|^2,\tag{25a}$$

$$f_{D2}=|\hat{\boldsymbol{r}}_c\times\hat{\boldsymbol{p}}_\gamma|^2|\hat{\boldsymbol{r}}_d\times\hat{\boldsymbol{p}}_\phi|^2+|\hat{\boldsymbol{r}}_c\times\hat{\boldsymbol{p}}_\phi|^2|\hat{\boldsymbol{r}}_d\times\hat{\boldsymbol{p}}_\gamma|^2,\tag{25b}$$

$$f_{D3}=2|\hat{\boldsymbol{r}}_c\times\hat{\boldsymbol{p}}_\phi|^2|\hat{\boldsymbol{r}}_d\times\hat{\boldsymbol{p}}_\phi|^2,\tag{25c}$$

$$f_1=-|\hat{\boldsymbol{r}}_c\times\hat{\boldsymbol{p}}_\gamma|^2(\hat{\boldsymbol{r}}_d\times\hat{\boldsymbol{p}}_\gamma^*)^2-(\hat{\boldsymbol{r}}_c\times\hat{\boldsymbol{p}}_\gamma^*)^2|\hat{\boldsymbol{r}}_d\times\hat{\boldsymbol{p}}_\gamma|^2,\tag{25d}$$

$$f_2=2(\hat{\boldsymbol{r}}_c\times\hat{\boldsymbol{p}}_\gamma^*)^2(\hat{\boldsymbol{r}}_d\times\hat{\boldsymbol{p}}_\gamma^*)^2,\tag{25e}$$

$$f_3 = (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*)^2(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma)^2 + (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma)^2(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*)^2, \tag{25f}$$

$$f_4 = -\{(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi)\}(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*)^2 - (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*)^2\{(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi)\}, \tag{25g}$$

$$f_5 = -(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*)^2\{(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma) \cdot (\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi)\} - \{(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma) \cdot (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi)\}(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*)^2, \tag{25h}$$

$$f_6 = |\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma|^2\{(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi)\} + \{(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi)\}|\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma|^2, \tag{25i}$$

$$f_7 = -2\{(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi)\}\{(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi)\}, \tag{25j}$$

$$f_8 = \{(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi)\}\{(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma) \cdot (\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi)\} + \{(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma) \cdot (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi)\}\{(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi)\}, \tag{25k}$$

$$f_9 = -(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*)^2|\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi|^2 - |\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi|^2(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*)^2, \tag{25l}$$

$$f_{10} = \{(\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi)\}|\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi|^2 + |\hat{\boldsymbol{r}}_c \times \hat{\boldsymbol{p}}_\phi|^2\{(\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\gamma^*) \cdot (\hat{\boldsymbol{r}}_d \times \hat{\boldsymbol{p}}_\phi)\}, \tag{25m}$$

where the unit position vectors $\hat{\boldsymbol{r}}_c$ and $\hat{\boldsymbol{r}}_d$ express the detector angular coordinate (Θ_c, Φ_c) and (Θ_d, Φ_d), respectively, as seen in Fig. 1(b), but are not dependent on the other angular coordinate (θ, ϕ) specifying the molecular xyz frame. Here, $\boldsymbol{p}_\gamma$, $\boldsymbol{p}_\phi$, and $\boldsymbol{p}_\rho$ are transition electric dipole moments defined as

$$\boldsymbol{p}_\gamma = \langle 1s|(-e\boldsymbol{r})|2p_{m=1}\rangle, \tag{26a}$$

$$\boldsymbol{p}_\phi = \langle 1s|(-e\boldsymbol{r})|2p_{m=0}\rangle, \tag{26b}$$

$$\boldsymbol{p}_\rho = \langle 1s|(-e\boldsymbol{r})|2p_{m=-1}\rangle, \tag{26c}$$

which have been introduced in Sec. II D: e is the elementary charge ($e > 0$), $|2p_m\rangle$ ($|1s\rangle$) is a $2p$ state ($1s$ state) at the origin O in Fig. 1(a) with the projection of the electron orbital angular momentum on the z axis being m (for the $|1s\rangle$ state, $m = 0$), and $\boldsymbol{r}$ is the position of the electron in reference to the nucleus at the origin O. The transition electric dipole moment is not altered under the translation of the nucleus along the z axis. The unit vector $\hat{\boldsymbol{p}}_\gamma$, for example, is defined as $\hat{\boldsymbol{p}}_\gamma = \boldsymbol{p}_\gamma/p$. Those unit vectors are dependent on MF(θ, ϕ) with respect to the space-fixed XYZ frame since the projection of the electron orbital angular momentum m is associated with the z axis. However, they are not dependent on $(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d) = (\Theta_c, \Phi_c, \Theta_d, \Phi_d)$. The unit vectors $\hat{\boldsymbol{p}}_\gamma$, $\hat{\boldsymbol{p}}_\phi$, and $\hat{\boldsymbol{p}}_\rho$ are explicitly written as a function of (θ, ϕ) as follows:

$$\hat{\boldsymbol{p}}_\gamma = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\ i\\ 0\end{pmatrix}_{xyz} = \frac{1}{\sqrt{2}}\begin{pmatrix}\cos\phi\cos\theta - i\sin\phi\\ \sin\phi\cos\theta + i\cos\phi\\ -\sin\theta\end{pmatrix}_{XYZ}, \tag{27a}$$

$$\hat{\boldsymbol{p}}_\phi = -\begin{pmatrix}0\\ 0\\ 1\end{pmatrix}_{xyz} = -\begin{pmatrix}\cos\phi\sin\theta\\ \sin\phi\sin\theta\\ \cos\theta\end{pmatrix}_{XYZ}, \tag{27b}$$

$$\hat{\boldsymbol{p}}_\rho = \frac{1}{\sqrt{2}}\begin{pmatrix}-1\\ i\\ 0\end{pmatrix}_{xyz} = \frac{1}{\sqrt{2}}\begin{pmatrix}-\cos\phi\cos\theta - i\sin\phi\\ -\sin\phi\cos\theta + i\cos\phi\\ \sin\theta\end{pmatrix}_{XYZ}, \tag{27c}$$

where the x, y, and z components (the X, Y, and Z components) are arranged from the top to the bottom in the column vectors. Because of the relation $\hat{\boldsymbol{p}}_\rho = -\hat{\boldsymbol{p}}_\gamma{}^*$, $\hat{\boldsymbol{p}}_\rho$ does not appear in Eqs. (25). In calculating the matrix elements in Eqs. (25), the following terms appear:

$$e^{\pm i(\frac{\omega}{c})(r_{ca} - r_{cb} + r_{db} - r_{da})}, \tag{28}$$

where r_{ca}, for example, is the distance between the detector c and the nucleus a. The width of the range of $(\frac{\omega}{c})(r_{ca} - r_{cb} + r_{db} - r_{da})$ seems much larger than 2π as $\hat{\boldsymbol{r}}_c$ and $\hat{\boldsymbol{r}}_d$ are changed because the typical distance between the nuclei a and b is 93 μm when a pair of Lyman-α photons is emitted [16] and $\frac{\omega}{c}$ is (19 nm)$^{-1}$ [11]. The terms in Eq. (28) hence oscillate rapidly while the detector positions are changed. Considering that measured is the ACF averaged over the observation volume and the solid angles subtended by the detectors in the experiment [13–16], we may set the terms equal to zero as a result. Although we use the approximation mentioned above as well as some other ones, the matrix in Eq. (24) is held Hermitian: the diagonal elements f_{D1}–f_{D3} are real numbers and the off-diagonal elements f_3 and f_8 are real numbers, too. Interestingly, integrating the matrix elements $f_\ell(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d; \theta, \phi)$ ($\ell = D1, D2, D3, 1-10$) over the entire range of the solid angles for the detectors c and d results in

$$\int f_\ell(\Theta_c, \Phi_c, \Theta_d, \Phi_d; \theta, \phi)d\Omega_c d\Omega_d = \begin{cases}\frac{8}{9}(4\pi)^2 & \text{for } \ell = D1, D2, D3, \quad (29a)\\ 0 & \text{for } \ell = 1-10, \quad (29b)\end{cases}$$

irrespective of (θ, ϕ).

Following Eq. (21), we have calculated the matrix $[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d)$ as well. Substituting Eq. (23) into Eq. (21), we obtain

$$[\tilde{E}^{(2)}]^b_{(i',j')(i'',j'')}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d) = g(t_c, t_d) \int \sin\theta \, d\theta \, d\phi \, w_{\rm ex}(\theta, \phi) f_{(i',j')(i'',j'')}(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d; \theta, \phi) = g(t_c, t_d)[f]^b_{(i',j')(i'',j'')}(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d). \quad (30)$$

The distribution function of MF(θ, ϕ), $w_{\rm ex}(\theta, \phi)$, is expressed with the dipolar form

$$w_{\rm ex}(\theta, \phi) = \frac{1}{4\pi}[1 + bP_2(\cos\theta)], \quad (31)$$

where the asymmetry parameter b, determined by the doubly excited state "ex," ranges from -1 to 2 and $P_2(x)$ is the Legendre polynomial of degree 2. The $w_{\rm ex}(\theta, \phi)$-averaged $f_{(i',j')(i'',j'')}(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d; \theta, \phi)$ is thus characterized by the parameter b as explicitly shown in Eq. (30). The dipolar form was derived as the angular distribution of photofragments in photoexcitation of a diatomic molecule [20] and is applicable to the distribution of MF(θ, ϕ). The dimensionless functions $[f]^b_{(i',j')(i'',j'')}(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d)$ are arranged in the same matrix form as in Eq. (24),

$$\begin{array}{c} \\ \langle\gamma\gamma| \\ \langle\rho\rho| \\ \langle\gamma\rho| \\ \langle\rho\gamma| \\ \langle\gamma\phi| \\ \langle\phi\gamma| \\ \langle\rho\phi| \\ \langle\phi\rho| \\ \langle\phi\phi| \end{array} \begin{array}{c} \begin{array}{cccc|cccc|c} |\gamma\gamma\rangle & |\rho\rho\rangle & |\gamma\rho\rangle & |\rho\gamma\rangle & |\gamma\phi\rangle & |\phi\gamma\rangle & |\rho\phi\rangle & |\phi\rho\rangle & |\phi\phi\rangle \end{array} \\ \left(\begin{array}{cccc|cccc|c} [f]^b_{D1} & [f]^b_2 & [f]^b_1 & [f]^b_1 & & & & & -[f]^b_7 \\ [f]^b_2 & [f]^b_{D1} & [f]^b_1 & [f]^b_1 & & & 0 & & -[f]^b_7 \\ [f]^b_1 & [f]^b_1 & [f]^b_{D1} & [f]^b_3 & & & & & -[f]^b_8 \\ [f]^b_1 & [f]^b_1 & [f]^b_3 & [f]^b_{D1} & & & & & -[f]^b_8 \\ \hline & & & & [f]^b_{D2} & [f]^b_8 & [f]^b_9 & [f]^b_7 & \\ & 0 & & & [f]^b_8 & [f]^b_{D2} & [f]^b_7 & [f]^b_9 & 0 \\ & & & & [f]^b_9 & [f]^b_7 & [f]^b_{D2} & [f]^b_8 & \\ & & & & [f]^b_7 & [f]^b_9 & [f]^b_8 & [f]^b_{D2} & \\ \hline -[f]^b_7 & -[f]^b_7 & -[f]^b_8 & -[f]^b_8 & & & 0 & & [f]^b_{D3} \end{array}\right) \end{array}, \quad (32)$$

and the matrix is denoted by $[\tilde{f}]^b(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d)$. We thus obtain from Eq. (30)

$$[\tilde{E}^{(2)}]^b(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d) = g(t_c, t_d)[\tilde{f}]^b(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d). \quad (33)$$

The matrix $[\tilde{f}]^b(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d)$ is a Hermitian matrix since the matrix in Eq. (24) is Hermitian and the value of the distribution function $w_{\rm ex}(\theta, \phi)$ is a real number. All the dimensionless elements in Eq. (32), $[f]^b_\ell$ ($\ell = D1, D2, D3, 1{-}10$), are expressed as the same function of $(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d) = (\Theta_c, \Phi_c, \Theta_d, \Phi_d)$ with five coefficients $k^b_{\ell,1}$–$k^b_{\ell,5}$ as shown below,

$$\begin{aligned}[f]^b_\ell(\Theta_c, \Phi_c, \Theta_d, \Phi_d) = {} & k^b_{\ell,1} + k^b_{\ell,2}(\cos2\Theta_c + \cos2\Theta_d) + k^b_{\ell,3}[\cos2(\Theta_c - \Theta_d) + \cos2(\Theta_c + \Theta_d)] \\ & + 2k^b_{\ell,4}\cos(\Phi_c - \Phi_d)[\cos2(\Theta_c - \Theta_d) - \cos2(\Theta_c + \Theta_d)] + 2k^b_{\ell,5}\cos 2(\Phi_c - \Phi_d) \\ & \times [2 - 2\cos2\Theta_c - 2\cos2\Theta_d + \cos2(\Theta_c - \Theta_d) + \cos2(\Theta_c + \Theta_d)]. \end{aligned} \quad (34)$$

Those coefficients $k^b_{\ell,1}$–$k^b_{\ell,5}$, which are dimensionless, are summarized in Table I for $b = 2$ [$w_{\rm ex}(\theta, \phi) = (\frac{3}{4\pi})\cos^2\theta$] in (a) and $b = -1$ [$w_{\rm ex}(\theta, \phi) = (\frac{3}{8\pi})\sin^2\theta$] in (b). We can obtain the coefficients $k^b_{\ell,1}$–$k^b_{\ell,5}$ ($\ell = D1, D2, D3, 1{-}10$) for any value of b from those for $b = 2$ and $b = -1$, following

$$k^b_{\ell,i} = \frac{1+b}{3}k^{b=2}_{\ell,i} + \frac{2-b}{3}k^{b=-1}_{\ell,i} \quad (i = 1{-}5). \quad (35)$$

The matrix $[\tilde{f}]^b(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d)$ is thereby obtained for any value of b and the matrix elements turn out to be real numbers. It is interesting that integrating the matrix elements $[f]^b_\ell(\Theta_c, \Phi_c, \Theta_d, \Phi_d)$ over the entire range of the solid angles for the detectors c and d results in

$$\int [f]^b_\ell(\Theta_c, \Phi_c, \Theta_d, \Phi_d) d\Omega_c d\Omega_d = \begin{cases} \frac{8}{9}(4\pi)^2 & \text{for } \ell = D1, D2, D3, \quad (36a) \\ 0 & \text{for } \ell = 1{-}10 \quad (36b) \end{cases}$$

for any value of $b(-1 \leqslant b \leqslant 2)$. Equations (36) originate from Eqs. (29), and Eqs. (36) in fact hold even for any distribution function $w_{\rm ex}(\theta, \phi)$. Substituting Eq. (33) into Eq. (22), we eventually obtain a useful equation,

$$G^{(2)}_{\rm ex}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d) = g(t_c, t_d){\rm Tr}\big[\tilde{\rho}^{\rm ph}_{\rm ex}\,[\tilde{f}]^b(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d)\big], \quad (37)$$

with the matrix $[\tilde{f}]^b(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d)$ now being known. Using Eq. (37), we can derive the two-photon correlation function of a pair of Lyman-α photons in process 1 for the single-state case. The properties of the doubly excited state "ex" involved in process 1 are copied to the reduced density matrix $\tilde{\rho}^{\rm ph}_{\rm ex}$ for the photonic partial system and the value of b characterizing the distribution function of MF(θ, ϕ).

G. The extension to the many-state case

Equation (37) yields the analytical expression of the two-photon correlation function $G^{(2)}_{\rm ex}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d)$ originating from the doubly excited state "ex" involved in process 1. In this

TABLE I. Coefficients in Eq. (34). (a) Those for $b = 2$, i.e., $w_{\rm ex}(\theta,\phi) = (\frac{3}{4\pi})\cos^2\theta$, (b) those for $b = -1$, i.e., $w_{\rm ex}(\theta,\phi) = (\frac{3}{8\pi})\sin^2\theta$. Note that the coefficients multiplied by 2240 are shown.

(a)	$k_1^{b=2}$	$k_2^{b=2}$	$k_3^{b=2}$	$k_4^{b=2}$	$k_5^{b=2}$
$[f]^b_{D1}$	2200	328	44	24	2
$[f]^b_{D2}$	1872	−208	−88	−48	−4
$[f]^b_{D3}$	1632	−480	176	96	8
$[f]^b_1$	152	232	12	−24	5
$[f]^b_2$	16	48	72	−32	2
$[f]^b_3$	16	48	72	80	44
$[f]^b_4$	0	0	0	0	0
$[f]^b_5$	0	0	0	0	0
$[f]^b_6$	0	0	0	0	0
$[f]^b_7$	−24	−72	−108	20	4
$[f]^b_8$	24	72	108	64	10
$[f]^b_9$	144	208	−24	48	−10
$[f]^b_{10}$	0	0	0	0	0
(b)	$k_1^{b=-1}$	$k_2^{b=-1}$	$k_3^{b=-1}$	$k_4^{b=-1}$	$k_5^{b=-1}$
$[f]^b_{D1}$	1896	−136	20	16	6
$[f]^b_{D2}$	2032	48	−40	−32	−12
$[f]^b_{D3}$	2208	352	80	64	24
$[f]^b_1$	288	416	−48	−16	8
$[f]^b_2$	48	144	216	−96	6
$[f]^b_3$	48	144	216	128	20
$[f]^b_4$	0	0	0	0	0
$[f]^b_5$	0	0	0	0	0
$[f]^b_6$	0	0	0	0	0
$[f]^b_7$	−16	−48	−72	−24	12
$[f]^b_8$	16	48	72	52	16
$[f]^b_9$	320	512	96	32	−16
$[f]^b_{10}$	0	0	0	0	0

subsection, we derive the equation that relates the overall two-photon correlation function $G^{(2)}_{\rm OA}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d)$ for the many-state case to $G^{(2)}_{\rm ex}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d)$.

The overall density operator for the ensemble of the total systems at $t \to \infty$, $\hat{\rho}_{\rm OA}(\theta,\phi)$, is written for the many-state case in terms of $\hat{\rho}_{\rm ex}(\theta,\phi)$ as

$$\hat{\rho}_{\rm OA}(\theta,\phi) = \sum_{\rm ex} \xi_{\rm ex}(\theta,\phi)\hat{\rho}_{\rm ex}(\theta,\phi). \tag{38}$$

Here, the fractional population $\xi_{\rm ex}(\theta,\phi)$ is written as

$$\xi_{\rm ex}(\theta,\phi) = \frac{q^{L_\alpha L_\alpha}_{\rm ex}(\theta,\phi)}{q^{L_\alpha L_\alpha}_{\rm OA}(\theta,\phi)}, \tag{39}$$

$$q^{L_\alpha L_\alpha}_{\rm OA}(\theta,\phi) = \sum_{\rm ex'} q^{L_\alpha L_\alpha}_{\rm ex'}(\theta,\phi), \tag{40}$$

where $q^{L_\alpha L_\alpha}_{\rm ex}(\theta,\phi)$ is the (θ,ϕ)-differential cross section for the emission of Lyman-α photons originating from the doubly excited state "ex." It is noted that $q^{L_\alpha L_\alpha}_{\rm ex}(\theta,\phi)$ is the cross-section integral over all the directions of the emission of the two photons, i.e., integral over all the range of $(\Theta_c, \Phi_c, \Theta_d, \Phi_d)$. It is obvious that the fractional population $\xi_{\rm ex}(\theta,\phi)$ satisfies the normalization condition

$$\sum_{\rm ex} \xi_{\rm ex}(\theta,\phi) = 1. \tag{41}$$

The cross section $q^{L_\alpha L_\alpha}_{\rm ex}(\theta,\phi)$ is related to the cross section $\sigma^{L_\alpha L_\alpha}_{\rm ex}$ in Eq. (14) as

$$\sigma^{L_\alpha L_\alpha}_{\rm ex} = \int q^{L_\alpha L_\alpha}_{\rm ex}(\theta,\phi)\sin\theta\, d\theta\, d\phi. \tag{42}$$

The quantity $\sigma^{L_\alpha L_\alpha}_{\rm ex}$ is the cross section for emitting a pair of Lyman-α photons, and is the cross-section integral over all the directions of the emission of the two photons and over all the directions of the MF(θ,ϕ). We introduce another cross section $\sigma^{L_\alpha L_\alpha}_{\rm OA}$ defined as

$$\sigma^{L_\alpha L_\alpha}_{\rm OA} = \int q^{L_\alpha L_\alpha}_{\rm OA}(\theta,\phi)\sin\theta\, d\theta\, d\phi. \tag{43}$$

It hence follows from Eqs. (40), (42), and (43) that

$$\sigma^{L_\alpha L_\alpha}_{\rm OA} = \sum_{\rm ex} \sigma^{L_\alpha L_\alpha}_{\rm ex}. \tag{44}$$

It turns out from Eq. (38) that $\tilde{\rho}_{\rm OA}(\theta,\phi)$, the representation matrix of $\hat{\rho}_{\rm OA}(\theta,\phi)$ in terms of $E_f(\theta,\phi)$ defined in Eq. (8), is written as

$$\tilde{\rho}_{\rm OA}(\theta,\phi) = \sum_{\rm ex} \xi_{\rm ex}(\theta,\phi)\tilde{\rho}_{\rm ex}. \tag{45}$$

As mentioned in Sec. II E, the representation matrix $\tilde{\rho}_{\rm ex}$ is independent of (θ,ϕ) and it is hence not written as $\tilde{\rho}_{\rm ex}(\theta,\phi)$ but as just $\tilde{\rho}_{\rm ex}$ in contrast with that in Eqs. (10) and (11). The overall two-photon correlation function $G^{(2)}_{\rm OA}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d)$ is given by, from Eq. (11),

$$\begin{aligned} &G^{(2)}_{\rm OA}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d) \\ &\quad = \int {\rm Tr}[\tilde{\rho}_{\rm OA}(\theta,\phi)\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d; \theta,\phi)] \\ &\qquad \times w_{\rm OA}(\theta,\phi)\sin\theta\, d\theta\, d\phi, \end{aligned} \tag{46}$$

where $w_{\rm OA}(\theta,\phi)$ is the overall distribution function of MF(θ,ϕ), and the matrices $\tilde{\rho}_{\rm OA}(\theta,\phi)$ and $\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d; \theta,\phi)$ are 72×72 ones. The line used for obtaining Eq. (11) is available for the many-state case as well. It follows, on substituting Eq. (45) into Eq. (46), that

$$\begin{aligned} &G^{(2)}_{\rm OA}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d) \\ &\quad = \sum_{\rm ex} \int {\rm Tr}[\tilde{\rho}_{\rm ex}\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d; \theta,\phi)] \\ &\qquad \times \xi_{\rm ex}(\theta,\phi) w_{\rm OA}(\theta,\phi)\sin\theta\, d\theta\, d\phi. \end{aligned} \tag{47}$$

The distribution functions $w_{\rm OA/ex}(\theta,\phi)$ are related to the cross sections $\sigma^{L_\alpha L_\alpha}_{\rm OA/ex}$ and $q^{L_\alpha L_\alpha}_{\rm OA/ex}(\theta,\phi)$ as

$$w_{\rm OA/ex}(\theta,\phi) = \frac{1}{\sigma^{L_\alpha L_\alpha}_{\rm OA/ex}} q^{L_\alpha L_\alpha}_{\rm OA/ex}(\theta,\phi). \tag{48}$$

Substituting Eqs. (39) and (48) into (47), we obtain

$$\begin{aligned} &G^{(2)}_{\rm OA}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d) \\ &\quad = \sum_{\rm ex} \left(\frac{\sigma^{L_\alpha L_\alpha}_{\rm ex}}{\sigma^{L_\alpha L_\alpha}_{\rm OA}}\right) \int {\rm Tr}[\tilde{\rho}_{\rm ex}\tilde{\mathscr{E}}^{(2)}(\boldsymbol{r}_c, t_c, \boldsymbol{r}_d, t_d; \theta,\phi)] \\ &\qquad \times w_{\rm ex}(\theta,\phi)\sin\theta\, d\theta\, d\phi. \end{aligned} \tag{49}$$

Considering Eq. (11), we eventually derive a reasonable relation,

$$G^{(2)}_{\rm OA}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)=\sum_{\rm ex}\left(\frac{\sigma^{L_\alpha L_\alpha}_{\rm ex}}{\sigma^{L_\alpha L_\alpha}_{\rm OA}}\right)G^{(2)}_{\rm ex}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d). \quad (50)$$

III. RESULTS

Two-photon correlation functions, angular correlation functions, and angle-differential cross sections

We are ready to derive the two-photon correlation function of a pair of Lyman-α photons in process 1 for the single-state case based on Eq. (37). As mentioned in Sec. II F, all the elements of the matrix $[\tilde{f}]^b(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ are expressed as the same function of $(\Theta_c,\Phi_c,\Theta_d,\Phi_d)$ with five coefficients [see Eq. (34)], and the two-photon correlation function for the single-state case $G^{(2)}_{\rm ex}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ is also written with the same function of $(\Theta_c,\Phi_c,\Theta_d,\Phi_d)$ as the elements of $[\tilde{f}]^b(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ as a result,

$$\begin{aligned}
&G^{(2)}_{\rm ex}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\\
&\quad=g(t_c,t_d)\big\{k^{\rm ex}_1+k^{\rm ex}_2(\cos2\Theta_c+\cos2\Theta_d)\\
&\qquad+k^{\rm ex}_3[\cos2(\Theta_c-\Theta_d)+\cos2(\Theta_c+\Theta_d)]\\
&\qquad+2k^{\rm ex}_4\cos(\Phi_c-\Phi_d)[\cos2(\Theta_c-\Theta_d)-\cos2(\Theta_c+\Theta_d)]\\
&\qquad+2k^{\rm ex}_5\cos2(\Phi_c-\Phi_d)\\
&\qquad\times[2-2\cos2\Theta_c-2\cos2\Theta_d\\
&\qquad+\cos2(\Theta_c-\Theta_d)+\cos2(\Theta_c+\Theta_d)]\big\}\\
&\quad=g(t_c,t_d)F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d), \qquad (51)
\end{aligned}$$

where the dimensionless coefficients $k^{\rm ex}_1$–$k^{\rm ex}_5$ are determined by the elements of $\tilde{\rho}^{\rm ph}_{\rm ex}$, the reduced density matrix of the photonic partial system, and the coefficients $k^b_{\ell,1}$–$k^b_{\ell,5}$ ($\ell=D1,D2,D3,1{-}10$). For example, $k^{\rm ex}_2$ is determined by $\tilde{\rho}^{\rm ph}_{\rm ex}$ and $k^b_{\ell,2}$ ($\ell=D1,D2,D3,1{-}10$). It has turned out from the hermiticity of $\tilde{\rho}^{\rm ph}_{\rm ex}$ and $[\tilde{f}]^b(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ in Eq. (37) that the coefficients $k^{\rm ex}_1$–$k^{\rm ex}_5$ are real numbers. The two-photon correlation function $G^{(2)}_{\rm ex}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ is separated into the temporal part and the angular part as seen in Eq. (51), and the latter part is denoted by $F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$. Equation (51) is the analytical expression of the two-photon correlation function of a pair of Lyman-α photons for the case that a single doubly excited state "ex" is involved in process 1 (the single-state case). We then integrate $F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ over the entire range of the solid angles for the detectors c and d based on Eqs. (36) and the fact that $F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)={\rm Tr}[\tilde{\rho}^{\rm ph}_{\rm ex}[\tilde{f}]^b(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)]$[see Eqs. (37) and (51)] to find that

$$\begin{aligned}
\int F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)d\Omega_c d\Omega_d&=(\rho_{11}+\rho_{22}+\cdots+\rho_{99})\frac{8}{9}(4\pi)^2\\
&=\frac{8}{9}(4\pi)^2 \qquad (52)
\end{aligned}$$

irrespective of the doubly excited state "ex," where ρ_{ij} is the (i,j) element of the 9×9 matrix $\tilde{\rho}^{\rm ph}_{\rm ex}$. The reduced density matrix for the photonic partial system $\tilde{\rho}^{\rm ph}_{\rm ex}$ satisfies the normalization condition, ${\rm Tr}(\tilde{\rho}^{\rm ph}_{\rm ex})=1$, which is used for obtaining Eq. (52). As mentioned in Sec. II E, the matrix $\tilde{\rho}^{\rm ph}_{\rm ex}$ is independent of the detector arrangement $(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$.

According to Eq. (50), even if many doubly excited states are involved in process 1 at a given energy of the incident photon (the many-state case), the two-photon correlation function $G^{(2)}_{\rm OA}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)$ again turns out to be written in the same form as in Eq. (51),

$$\begin{aligned}
&G^{(2)}_{\rm OA}(\boldsymbol{r}_c,t_c,\boldsymbol{r}_d,t_d)\\
&\quad=g(t_c,t_d)\{k_1+k_2(\cos2\Theta_c+\cos2\Theta_d)\\
&\qquad+k_3[\cos2(\Theta_c-\Theta_d)+\cos2(\Theta_c+\Theta_d)]\\
&\qquad+2k_4\cos(\Phi_c-\Phi_d)[\cos2(\Theta_c-\Theta_d)-\cos2(\Theta_c+\Theta_d)]\\
&\qquad+2k_5\cos2(\Phi_c-\Phi_d)\\
&\qquad\times[2-2\cos2\Theta_c-2\cos2\Theta_d\\
&\qquad+\cos2(\Theta_c-\Theta_d)+\cos2(\Theta_c+\Theta_d)]\}\\
&\quad=g(t_c,t_d)F_{\rm OA}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d). \qquad (53)
\end{aligned}$$

The dimensionless coefficients k_i ($i=1{-}5$) are state-averaged values of $k^{\rm ex}_i$ ($i=1{-}5$) in Eq. (51), respectively,

$$k_i=\sum_{\rm ex}\left(\frac{\sigma^{L_\alpha L_\alpha}_{\rm ex}}{\sigma^{L_\alpha L_\alpha}_{\rm OA}}\right)k^{\rm ex}_i \quad (i=1{-}5), \quad (54)$$

and $F_{\rm OA}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ is likewise a state-averaged function of $F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ in Eq. (51) as

$$F_{\rm OA}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)=\sum_{\rm ex}\left(\frac{\sigma^{L_\alpha L_\alpha}_{\rm ex}}{\sigma^{L_\alpha L_\alpha}_{\rm OA}}\right)F_{\rm ex}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d). \quad (55)$$

As for the analytical form of the two-photon correlation function, there is no difference between the single-state case [Eq. (51)] and the many-state case [Eq. (53)]. Equation (53) results in Eq. (51) in the special case that only one doubly excited state is involved in process 1 [see Eq. (50) as well] and it is hence sufficient to simply discuss the many-state case alone. It follows from Eqs. (52) and (55) that

$$\int F_{\rm OA}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)d\Omega_c d\Omega_d=\frac{8}{9}(4\pi)^2, \quad (56)$$

which is apparently the same as Eq. (52). Substituting $F_{\rm OA}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$ in Eq. (53) into (56), we obtain a useful relation among k_1, k_2, and k_3,

$$k_1-\tfrac{2}{3}k_2+\tfrac{2}{9}k_3=\tfrac{8}{9}. \quad (57)$$

Following the procedure mentioned in the last paragraph of Sec. II D (the procedure is mentioned for the single-state case in Sec. II D, but it refers to the many-state case as well), we obtain two quantities from $F_{\rm OA}(\hat{\boldsymbol{r}}_c,\hat{\boldsymbol{r}}_d)$: one is $\frac{d^2P^{L_\alpha L_\alpha}_{\rm OA}}{d\Omega_c d\Omega_d}$, the ACF of a pair of Lyman-α photons, and the other is $\frac{d^2\sigma^{L_\alpha L_\alpha}_{\rm OA}}{d\Omega_c d\Omega_d}$, the angle-differential cross section for the emission of a pair of Lyman-α photons. The ACF, $\frac{d^2P^{L_\alpha L_\alpha}_{\rm OA}}{d\Omega_c d\Omega_d}$, is explicitly written as

$$\begin{aligned}
&\frac{d^2P^{L_\alpha L_\alpha}_{\rm OA}}{d\Omega_c d\Omega_d}(\Theta_c,\Phi_c,\Theta_d,\Phi_d)\\
&\quad=\frac{9}{8(4\pi)^2}\{k_1+k_2(\cos2\Theta_c+\cos2\Theta_d)\\
&\qquad+k_3[\cos2(\Theta_c-\Theta_d)+\cos2(\Theta_c+\Theta_d)]
\end{aligned}$$

$$+ 2k_4 \cos(\Phi_c - \Phi_d)[\cos2(\Theta_c - \Theta_d) - \cos2(\Theta_c + \Theta_d)]$$
$$+ 2k_5 \cos 2(\Phi_c - \Phi_d)$$
$$\times [2 - 2\cos2\Theta_c - 2\cos2\Theta_d$$
$$+ \cos2(\Theta_c - \Theta_d) + \cos2(\Theta_c + \Theta_d)]\}. \quad (58)$$

The angle-differential cross section, $\frac{d^2\sigma_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}$, is related to $\frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}$ as

$$\frac{d^2\sigma_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d} = \sigma_{\rm OA}^{L_\alpha L_\alpha}\left(\frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}\right), \quad (59)$$

and $\frac{d^2\sigma_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}$ is expressed with a trivial function of $(\Theta_c, \Phi_c, \Theta_d, \Phi_d)$. Equations (58) and (59) give the general analytical expressions of the ACF of a pair of Lyman-α photons and the angle-differential cross section for the emission of a pair of Lyman-α photons, respectively, under the relation of Eq. (57).

IV. DISCUSSION

A. General remarks

The ACF in Eq. (58) should have the following two properties:

(i) $\frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}(\Theta_c, \Phi_c, \Theta_d, \Phi_d)$ is invariant under the exchange of the detectors c and d.

(ii) It is invariant under the rotation around the Z axis by any angle, the axis which points to the direction of $\hat{\boldsymbol{\epsilon}}$ as seen in Fig. 1(a).

Property (i) originates from the fact that the detectors are identical and that either one or the other detector may hence be labeled c (d) [the remaining one is then labeled d (c)]. It is obvious that the ACF in Eq. (58) has property (i). Property (ii) originates from the fact that we take account of randomly oriented $H_2(X\,^1\Sigma_g^+)$ molecules with respect to the space-fixed frame in process 1, as mentioned in Sec. II A, and only $\hat{\boldsymbol{\epsilon}}$(//the Z axis) brings the space anisotropy because the photoexcitation in $H_2(X\,^1\Sigma_g^+)$ molecules in process 1 is dominated by the electric dipole transition [see Fig. 1(a)]. The azimuth angles Φ_c and Φ_d are involved in the ACF in Eq. (58) in the form of $(\Phi_c - \Phi_d)$, and the ACF consequently possesses the rotational invariance around the Z axis [property (ii)]. We note that the ACF in Eq. (58) remains unaltered even if we rotate the direction of the incident light beam around the Z axis because of the rotational invariance of the ACF.

B. The expansion of the angular correlation function in terms of the spherical harmonics

In this subsection, we expand the ACF in Eq. (58) in terms of the spherical harmonics, i.e., in terms of $\{Y_{\ell_c m_c}(\Theta_c, \Phi_c)Y_{\ell_d m_d}(\Theta_d, \Phi_d)\}$, to find out which terms contribute and to investigate the reason why they do. The result of the expansion is

$$\frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}(\Theta_c, \Phi_c, \Theta_d, \Phi_d)$$
$$= \left(\frac{1}{4\pi}\right)Y_{00}(\Theta_c, \Phi_c)Y_{00}(\Theta_d, \Phi_d)$$
$$+ \frac{9}{8(4\pi)^2}\left\{\left(\frac{16\pi}{\sqrt{45}}\right)\left(k_2 - \frac{2}{3}k_3\right)\right.$$
$$\times [Y_{20}(\Theta_c, \Phi_c)Y_{00}(\Theta_d, \Phi_d) + Y_{00}(\Theta_c, \Phi_c)Y_{20}(\Theta_d, \Phi_d)]$$
$$+ \left(\frac{128\pi}{45}\right)k_3\, Y_{20}(\Theta_c, \Phi_c)Y_{20}(\Theta_d, \Phi_d)$$
$$- \left(\frac{64\pi}{15}\right)k_4[Y_{21}(\Theta_c, \Phi_c)Y_{2,-1}(\Theta_d, \Phi_d)$$
$$+ Y_{2,-1}(\Theta_c, \Phi_c)Y_{21}(\Theta_d, \Phi_d)]$$
$$+ \left(\frac{256\pi}{15}\right)k_5[Y_{22}(\Theta_c, \Phi_c)Y_{2,-2}(\Theta_d, \Phi_d)$$
$$\left. + Y_{2,-2}(\Theta_c, \Phi_c)Y_{22}(\Theta_d, \Phi_d)]\right\}, \quad (60)$$

where (p. 94 in Ref. [19])

$$Y_{00}(\Theta, \Phi) = \frac{1}{(4\pi)^{\frac{1}{2}}}, \quad (61a)$$

$$Y_{20}(\Theta, \Phi) = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}}(3\cos^2\Theta - 1), \quad (61b)$$

$$Y_{2,\pm1}(\Theta, \Phi) = \mp\left(\frac{15}{8\pi}\right)^{\frac{1}{2}}\sin\Theta\cos\Theta\, e^{\pm i\Phi}, \quad (61c)$$

$$Y_{2,\pm2}(\Theta, \Phi) = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}}\sin^2\Theta\, e^{\pm2i\Phi}. \quad (61d)$$

The coefficient k_1 disappears in Eq. (60) because of Eq. (57). It is remarkable that the ACF in Eq. (60) is composed of the term

$$Y_{\ell m}(\Theta_c, \Phi_c)Y_{\ell' m'}(\Theta_d, \Phi_d) + Y_{\ell' m'}(\Theta_c, \Phi_c)Y_{\ell m}(\Theta_d, \Phi_d)$$
$$\text{for } (\ell, m) \neq (\ell', m') \quad (62)$$

and

$$Y_{\ell m}(\Theta_c, \Phi_c)Y_{\ell m}(\Theta_d, \Phi_d). \quad (63)$$

Because of this composition, the ACF in Eq. (60) is invariant under the exchange of the detectors [property (i) mentioned in Sec. IV A]. The manner in Eq. (62) for generating an invariant function under the exchange of the identical detectors is the same as the one used for generating symmetric wave functions of two identical particles under the permutation of those particles. The relation

$$m = -m' \quad (64)$$

should be satisfied in Eq. (62), and the relation

$$m = 0 \quad (65)$$

should be satisfied in Eq. (63) so that the ACF in Eq. (60) comes to possess the rotational invariance around the Z axis [property (ii) mentioned in Sec. IV A]. The ACF in Eq. (60) is in fact composed of the term $[Y_{\ell m}(\Theta_c, \Phi_c)Y_{\ell', -m}(\Theta_d, \Phi_d) + Y_{\ell', -m}(\Theta_c, \Phi_c)Y_{\ell m}(\Theta_d, \Phi_d)](\ell \neq \ell')$ and the term $Y_{\ell 0}(\Theta_c, \Phi_c)Y_{\ell 0}(\Theta_d, \Phi_d)$. No other term is involved in Eq. (60).

It is also remarkable that the spherical harmonics of degree $\ell = 0$ and 2 alone contribute to Eq. (60). The theory of angular correlation of two photons has been well established in cascade emission of two photons from atoms or nuclei in angular momentum eigenstates (pp. 165–176 in Ref. [21], pp. 220–225 in Ref. [22]), and we refer to the theory for discussing the origin of the remarkable point. The ACF of a pair of fluorescence photons in cascade transitions is expressed as a linear combination of $P_\ell(\cos\overline{\Theta})$ ($\ell = 0, 2, 4, \dots$), where $P_\ell(x)$ is the Legendre polynomial of degree ℓ and $\overline{\Theta}$ is the angle between $\hat{\boldsymbol{r}}_c$ and $\hat{\boldsymbol{r}}_d$ (pp. 165–176 in Ref. [21], pp. 220–225 in Ref. [22]). We consider the case in which the fluorescence photons are emitted through electric dipole transitions. An electric dipole photon has the intrinsic angular momentum 1 (pp. 220–225 in Ref. [22]), and the Legendre polynomials of degree $\ell = 2$ and 0 alone are involved in the linear combination of $P_\ell(\cos\overline{\Theta})$ as a result [we consider only the restriction due to the photon field in regard to which $P_\ell(\cos\overline{\Theta})$ contributes (pp. 165–176 in Ref. [21], pp. 220–225 in Ref. [22])]. With the phase convention of the spherical harmonics in Eqs. (61) being considered, the addition theorem of the spherical harmonics (p. 95 in Ref. [22]) is written as

$$P_\ell(\cos\overline{\Theta}) = \frac{4\pi}{2\ell+1}\sum_{m=-\ell}^{\ell}(-1)^m Y_{\ell,-m}(\Theta_c, \Phi_c)Y_{\ell m}(\Theta_d, \Phi_d). \tag{66}$$

The contribution of $Y_{2m}(\Theta, \Phi)$ and $Y_{00}(\Theta, \Phi)$ alone in Eq. (60) hence seems to be attributed to the fact that a pair of electric-dipole photons is emitted in process 1. The difference between Eq. (60) and the ACF of two electric-dipole photons emitted in the cascade transitions shown in pp. 220–225 in Ref. [22] is reasonable because the present process is similar to but not equal to the cascade emission of two electric-dipole photons.

It turns out that the relation

$$\begin{aligned}\frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}(\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d) &= \frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}(-\hat{\boldsymbol{r}}_c, \hat{\boldsymbol{r}}_d)\\ &= \frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}(\hat{\boldsymbol{r}}_c, -\hat{\boldsymbol{r}}_d)\\ &= \frac{d^2P_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}(-\hat{\boldsymbol{r}}_c, -\hat{\boldsymbol{r}}_d)\end{aligned} \tag{67}$$

holds because only spherical harmonics of even degree are involved in Eq. (60).

C. Searching for magic pairs of detector arrangements

Suppose that we measure $\sigma_{\rm OA}^{L_\alpha L_\alpha}(=\int(\frac{d^2\sigma_{\rm OA}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d})\,d\Omega_c d\Omega_d)$ in Eq. (59), the angle-integrated cross section for the emission of a pair of Lyman-α photons in process 1, with changing the energy of the incident photon. To this end, we search for a special arrangement of the detectors c and d, $(\Theta_c^M, \Phi_c^M, \Theta_d^M, \Phi_d^M)$, at which arrangement all the angular-dependent terms vanish in the ACF in Eq. (60) and only the first term ($=\frac{1}{(4\pi)^2}$) remains. If such an arrangement exists, we can measure the angle-integrated cross section $\sigma_{\rm OA}^{L_\alpha L_\alpha}$ as a function of the incident-photon energy with the two detectors held fixed there, and we refer to the arrangement as the magic arrangement of the detectors. It is an analogy to the well-known magic angle θ^M in the dipolar form in Eq. (31), in which form only the term $\frac{1}{4\pi}$ remains at $\cos^2\theta^M = \frac{1}{3}$ on the right-hand side. We note that the dipolar form refers to the angular intensity distribution of a fluorescence photon emitted by an excited fragment atom in the photodissociation of a diatomic molecule as well [17].

The definition of the magic arrangement yields the following coupled equations:

$$\begin{aligned}&Y_{20}(\Theta_c^M, \Phi_c^M)Y_{00}(\Theta_d^M, \Phi_d^M)\\ &\quad + Y_{00}(\Theta_c^M, \Phi_c^M)Y_{20}(\Theta_d^M, \Phi_d^M) = 0, &\text{(68a)}\\ &Y_{20}(\Theta_c^M, \Phi_c^M)Y_{20}(\Theta_d^M, \Phi_d^M) = 0, &\text{(68b)}\\ &Y_{21}(\Theta_c^M, \Phi_c^M)Y_{2,-1}(\Theta_d^M, \Phi_d^M)\\ &\quad + Y_{2,-1}(\Theta_c^M, \Phi_c^M)Y_{21}(\Theta_d^M, \Phi_d^M) = 0, &\text{(68c)}\\ &Y_{22}(\Theta_c^M, \Phi_c^M)Y_{2,-2}(\Theta_d^M, \Phi_d^M)\\ &\quad + Y_{2,-2}(\Theta_c^M, \Phi_c^M)Y_{22}(\Theta_d^M, \Phi_d^M) = 0. &\text{(68d)}\end{aligned}$$

Equations (68a) and (68b) result in

$$\cos^2\Theta_c^M = \cos^2\Theta_d^M = \tfrac{1}{3}. \tag{69}$$

Substituting Eq. (69) into Eqs. (68c) and (68d), we obtain

$$\cos(\Phi_c^M - \Phi_d^M) = 0 \text{ and } \cos^2(\Phi_c^M - \Phi_d^M) = \tfrac{1}{2}, \tag{70}$$

respectively. It is obvious that the coupled equations (70) have no solution, and the magic arrangement of the detectors consequently does not exist. The reason is that there are four equations [Eqs. (68)] for three unknown numbers, i.e., $\Theta_c^M, \Theta_d^M, \Phi_c^M - \Phi_d^M$. However, there exists a pseudo-magic-arrangement in a limited case as mentioned below. We set Θ_c and Θ_d so that they satisfy Eq. (69), e.g., they are set as 54.7° or 125.3°. If, for some pair of azimuth angles (Φ_c', Φ_d'), the terms involving $Y_{2m}(54.7°, \Phi')$ ($m \neq 0$) in Eq. (60), i.e., the fourth and fifth terms, are much smaller than $\frac{1}{(4\pi)^2}$ [the first term in Eq. (60)], the arrangement ($\Theta_c = 54.7°$, Φ_c', $\Theta_d = 54.7°$, Φ_d') is practically the magic arrangement and is referred to as the pseudo-magic-arrangement. In brief, the pseudo-magic-arrangement is likely to exist when $k_4, k_5 << k_1, k_2, k_3$ [see Eq. (58) as well].

Considering the reason why the magic arrangement of the detectors does not exist, we then search for a special pair of the detector arrangements, $\{(\Theta_c^M, \Phi_c^M, \Theta_d^M, \Phi_d^M), (\Theta_c^M, \Phi_c^{M'}, \Theta_d^M, \Phi_d^{M'})\}$, at which pair all the angular-dependent terms vanish in the summation of the ACF at $(\Theta_c^M, \Phi_c^M, \Theta_d^M, \Phi_d^M)$ and that at $(\Theta_c^M, \Phi_c^{M'}, \Theta_d^M, \Phi_d^{M'})$ and only the term $\frac{2}{(4\pi)^2}$ remains. The summation is written in terms of

spherical harmonics as

$$\frac{d^2P_{\mathrm{OA}}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}\left(\Theta_c^M, \Phi_c^M, \Theta_d^M, \Phi_d^M\right) + \frac{d^2P_{\mathrm{OA}}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}\left(\Theta_c^M, \Phi_c^{M'}, \Theta_d^M, \Phi_d^{M'}\right)$$
$$= \frac{2}{(4\pi)^2} + \frac{9}{8(4\pi)^2}\left\{\left(\frac{16\pi}{\sqrt{45}}\right)\left(k_2 - \frac{2}{3}k_3\right)\left[Y_{20}\left(\Theta_c^M, \Phi_c^M\right)Y_{00}\left(\Theta_d^M, \Phi_d^M\right) + Y_{00}\left(\Theta_c^M, \Phi_c^M\right)Y_{20}\left(\Theta_d^M, \Phi_d^M\right)\right.\right.$$
$$+ Y_{20}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{00}\left(\Theta_d^M, \Phi_d^{M'}\right) + Y_{00}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{20}\left(\Theta_d^M, \Phi_d^{M'}\right)\left.\right] + \left(\frac{128\pi}{45}\right)k_3\left[Y_{20}\left(\Theta_c^M, \Phi_c^M\right)Y_{20}\left(\Theta_d^M, \Phi_d^M\right)\right.$$
$$\left. + Y_{20}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{20}\left(\Theta_d^M, \Phi_d^{M'}\right)\right] - \left(\frac{64\pi}{15}\right)k_4\left[Y_{21}\left(\Theta_c^M, \Phi_c^M\right)Y_{2,-1}\left(\Theta_d^M, \Phi_d^M\right) + Y_{2,-1}\left(\Theta_c^M, \Phi_c^M\right)Y_{21}\left(\Theta_d^M, \Phi_d^M\right)\right.$$
$$+ Y_{21}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{2,-1}\left(\Theta_d^M, \Phi_d^{M'}\right) + Y_{2,-1}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{21}\left(\Theta_d^M, \Phi_d^{M'}\right)\left.\right] + \left(\frac{256\pi}{15}\right)k_5\left[Y_{22}\left(\Theta_c^M, \Phi_c^M\right)Y_{2,-2}\left(\Theta_d^M, \Phi_d^M\right)\right.$$
$$\left.\left. + Y_{2,-2}\left(\Theta_c^M, \Phi_c^M\right)Y_{22}\left(\Theta_d^M, \Phi_d^M\right) + Y_{22}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{2,-2}\left(\Theta_d^M, \Phi_d^{M'}\right) + Y_{2,-2}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{22}\left(\Theta_d^M, \Phi_d^{M'}\right)\right]\right\}. \tag{71}$$

If such a special pair of the detector arrangements exists, we can measure the angle-integrated cross section $\sigma_{\mathrm{OA}}^{L_\alpha L_\alpha}$ as a function of the incident-photon energy with only two coincidence measurements at $(\Theta_c^M, \Phi_c^M, \Theta_d^M, \Phi_d^M)$ and at $(\Theta_c^M, \Phi_c^{M'}, \Theta_d^M, \Phi_d^{M'})$. We refer to the special pair of the detector arrangements as the magic pair of them.

The definition of the magic pair of the detector arrangements yields the following coupled equations:

$$Y_{20}\left(\Theta_c^M, \Phi_c^M\right)Y_{00}\left(\Theta_d^M, \Phi_d^M\right) + Y_{00}\left(\Theta_c^M, \Phi_c^M\right)Y_{20}\left(\Theta_d^M, \Phi_d^M\right) + \left(\Phi_c^M \to \Phi_c^{M'} \text{ and } \Phi_d^M \to \Phi_d^{M'}\right) = 0, \tag{72a}$$
$$Y_{20}\left(\Theta_c^M, \Phi_c^M\right)Y_{20}\left(\Theta_d^M, \Phi_d^M\right) + Y_{20}\left(\Theta_c^M, \Phi_c^{M'}\right)Y_{20}\left(\Theta_d^M, \Phi_d^{M'}\right) = 0, \tag{72b}$$
$$Y_{21}\left(\Theta_c^M, \Phi_c^M\right)Y_{2,-1}\left(\Theta_d^M, \Phi_d^M\right) + Y_{2,-1}\left(\Theta_c^M, \Phi_c^M\right)Y_{21}\left(\Theta_d^M, \Phi_d^M\right) + \left(\Phi_c^M \to \Phi_c^{M'} \text{ and } \Phi_d^M \to \Phi_d^{M'}\right) = 0, \tag{72c}$$
$$Y_{22}\left(\Theta_c^M, \Phi_c^M\right)Y_{2,-2}\left(\Theta_d^M, \Phi_d^M\right) + Y_{2,-2}\left(\Theta_c^M, \Phi_c^M\right)Y_{22}\left(\Theta_d^M, \Phi_d^M\right) + \left(\Phi_c^M \to \Phi_c^{M'} \text{ and } \Phi_d^M \to \Phi_d^{M'}\right) = 0. \tag{72d}$$

Equations (72a) and (72b) result in

$$\cos^2\Theta_c^M = \cos^2\Theta_d^M = \tfrac{1}{3}, \tag{73}$$

which is the same as Eq. (69). Substituting Eq. (73) into Eqs. (72c) and (72d), we obtain

$$\cos\left(\Phi_c^M - \Phi_d^M\right) + \cos\left(\Phi_c^{M'} - \Phi_d^{M'}\right) = 0, \tag{74a}$$
$$\cos^2\left(\Phi_c^M - \Phi_d^M\right) + \cos^2\left(\Phi_c^{M'} - \Phi_d^{M'}\right) = 1, \tag{74b}$$

respectively, which correspond with Eq. (70). In contrast with Eq. (70), however, the coupled equations (74) have the following solutions:

$$\cos\left(\Phi_c^M - \Phi_d^M\right) = \pm\frac{1}{\sqrt{2}} \text{ and } \cos\left(\Phi_c^{M'} - \Phi_d^{M'}\right) = \mp\frac{1}{\sqrt{2}}$$
$$\text{(double-sign corresponds)}. \tag{75}$$

We have thereby substantiated that there exist magic pairs of the detector arrangements. One possible pair from an experimental point of view is, for example, $\{(\Theta_c^M = 54.7^\circ, \Phi_c^M = 0^\circ, \Theta_d^M = 125.3^\circ, \Phi_d^M = 45^\circ), (\Theta_c^M = 54.7^\circ, \Phi_c^{M'} = 0^\circ, \Theta_d^M = 125.3^\circ, \Phi_d^{M'} = 135^\circ)\}$. Lastly, we note that there may be other kinds of magic pairs of detector arrangements because those pairs have not been searched for within the general range $\{(\Theta_c^M, \Phi_c^M, \Theta_d^M, \Phi_d^M), (\Theta_c^{M'}, \Phi_c^{M'}, \Theta_d^{M'}, \Phi_d^{M'})\}$ but they have been searched for within the limited range $\{(\Theta_c^M, \Phi_c^M, \Theta_d^M, \Phi_d^M), (\Theta_c^M, \Phi_c^{M'}, \Theta_d^M, \Phi_d^{M'})\}$ alone.

V. CONCLUSION

We have theoretically obtained a general analytical expression of the two-photon correlation function for a pair of Lyman-α photons in the photodissociation of hydrogen molecules in process 1 with a manner based on both atomic and molecular physics and quantum optics. We have derived from this function the angular correlation function of the photon pair and the angle-differential cross section for the emission of the photon pair. The angular correlation function, depending on four angular variables specifying a detector arrangement, has turned out to be expressed in terms of cosine (sine) functions with five coefficients. The angular correlation function has been expanded in terms of the spherical harmonics so that we investigate which terms are involved and the reason why they are involved. Some interesting features have been revealed in the expansion. We have discovered magic pairs of detector arrangements in the angular correlation function, while it has turned out that there exists no magic arrangement in contrast with the well-known magic arrangement of a single detector in the single-photon-emission process. By virtue of the magic pair of detector arrangements, we can measure the angle-integrated cross section for emit-

ting two Lyman-α photons $\sigma_{\mathrm{OA}}^{L_\alpha L_\alpha}$ against the incident-photon energy without measuring angle-differential cross sections for emitting those photons $\frac{d^2\sigma_{\mathrm{OA}}^{L_\alpha L_\alpha}}{d\Omega_c d\Omega_d}$ on the spherical surface at each photon energy.

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