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# Entanglement in double photoionization of rotating linear molecules

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This paper investigates the relationship, if any, which may exist between the electron-electron correlation and spin entanglement of two electrons ejected simultaneously from a linear molecule following the absorption of a single photon. In order to properly learn about the influence of the molecular dynamics on this relationship and also to take into account the parity of the molecular states, double photoionization has been studied by including rotational degrees of freedom in the Hund's coupling schemes (a) and (b). Entanglement properties of the ejected pair of electrons with respect to their spins have been investigated in each of these coupling schemes without or with taking spin dependent interactions into account. The existence, or otherwise, of the entanglement is predicted on the basis of the negativity of the partial transpose of the density matrix calculated for each case considered in this paper.

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## I. INTRODUCTION

Electron-electron correlation is an important physical entity which plays a significant role in determining the properties and behavior of systems containing more than one electron. It has been known to play a crucial role in deciding various electronic and magnetic properties of strongly interacting solids. For example, kinematic correlation among electrons with parallel spins, introduced by the antisymmetry of their wave function, is known to reduce the Coulomb repulsion energy as electrons with parallel spins are seldom very near to each other [1]. Traditionally, correlation energy has come to imply the difference between the exact eigenvalue and the expectation value in the Hartree-Fock approximation of the Hamiltonian of a system in a given state [2].

Recent studies of double photoionization (also called photodouble ionization) of atoms and molecules have shown yet one more process which takes place due to electron-electron correlation. In this process, absorption of a single photon in the electric dipole ($E1$) approximation simultaneously ejects two electrons from an atom [3] or a molecule [4]. These two electrons, which were an integral part of the same system before they became free but now moving in the field of the photo-dication (i.e., residual, doubly charged positive ion), not only share between themselves the energy of the absorbed photon in excess to the potential for double ionization and affect each other's angular distributions, but also have an important influence on the mutual orientation of their spins [5–7]. These two electrons, in the context of double photoionization (DPI), are said to be correlated (with respect to, e.g., their energies, directions of emission and of spin quantization, etc.) in the sense that their simultaneous ejection, following the absorption of a single photon, cannot be understood within the frame-work of an effective one-particle model. Thus DPI is a direct manifestation of electron-electron correlation. Had the independent particle model of an atom or molecule been valid, the simultaneous ejection of two electrons, resulting from the absorption of only a single photon (which will be represented by a one-particle operator), would not have taken place. Moreover, the DPI of an atom or a molecule can be said to be analogous to the parametric down conversion (PDC) [8–12], wherein a single photon in a nonlinear medium decays in two new photons in a single step.

One more phenomenon has recently been ascribed to the word "correlation." Both theoretical as well as experimental studies of this new phenomenon have continued to be the subject of intense activities for the last several years. It was originally proposed by Einstein, Podolsky, and Rosen [13], and later interpreted for two spin-1/2 particles by Bohm [14]. According to the Einstein-Podolsky-Rosen-Bohm [13,14] interpretation, two particles, say electrons, are said to be correlated if their combined state cannot be expressed as a product of the states of two electrons. Such particles in a pair have been called correlated, entangled, nonseparable, or simply an EPR [13] pair of particles. Until about 10–12 years ago, studies of entanglement were confined to purely philosophical implications related to the incompleteness, or otherwise, of quantum theory [13,14]. However, recent suggestions that entangled particles can be used technologically to encrypt [15] and teleport [16] information as well as to build computers [17,18] which can perform certain operations much faster than the presently available "classical" computers, have opened the new field of quantum information theory [19]. These new developments have given rise to activities for the production of pairs of entangled particles, on the one hand, and for suggesting stringent quantitative methods which can be used to determine whether two given particles are entangled or not, on the other hand.

Two particles in which neither [8–12,20–23], both [24–28], or one of the two [29,30] possesses a rest mass different from zero have been used in experimental [8–12,20–26,29] as well as theoretical [27,28,30] studies of entanglement. For example, two photons produced in two-step (cascade) transitions in atoms from a suitable excited state to the ground state [20,21], or simultaneously emitted from a metastable atomic state in a true second-order decay process [22], or ejected in a single step in the PDC [8–12,23] are the entangled particles with no rest mass; photodissociation of dimers of the $^{199}\mathrm{Hg}_2$ isotopomore using a spectroscopy selective stimulated Raman process [25], the interaction of two-level Rydberg atoms with a resonant field [26,27] or atomic DPI [28] are some of the processes which have been suggested to produce particles which are entangled with a nonzero rest mass; Kurtsiefer *et al.* [29] and Chan *et al.* [30], on the other hand, have entangled an spontaneously emitted photon with its recoiling atom.

It is, in principle, believed that if the two particles are not prepared independently and in total isolation of each other then a decomposition of their combined state into a product (i.e., a separable or unentangled) state is, in general, impossible and the particles are necessarily entangled. Probably, a very simple, and the best possible, example of this procedure is provided by the DPI of atoms and molecules. Accordingly, two photoelectrons, whose simultaneous ejection following the absorption of a single photon by the target is due completely to the electron-electron correlation, must always be in a nonseparable state. But, in a recent analysis of the entanglement properties of two electrons produced in DPI of an atomic target, both without and with spin-orbit interaction (SOI), Chandra and Chakraborty [28] found that electron-electron correlation, whose presence is necessary for DPI to take place in an atomic target, is not always sufficient for entangling two simultaneously ejected electrons with respect to their spins. Thus, the word correlation in the context of the atomic DPI has come to mean [28] only those effects in an interacting, quantum, many-body system that are not present in an independent particle model [3–7,31], but are essential for two electrons to come out simultaneously. In view of this meaning of the word correlation for atoms, the two photoelectrons in DPI may or may not be entangled [28] with respect to their spins, but are certainly correlated [31].

Recently, several [4,6,7,32] studies, both theoretical and experimental, have also been performed on DPI of linear molecules. In these targets, in addition to the electron-electron correlation, the nuclear rotation has also been found to influence the DPI [6,7]. Moreover, the spin-dependent interactions in molecules include [33–35], unlike in atomic systems, not only the SOI but also the spin-rotation interaction (SRI). It will be quite interesting to see how and to what extent these two additional physically important interactions, plus other typically molecular effects (e.g., the noncentral nature of the molecular potential, nuclear rotation, etc.) influence the entanglement of the spin of two electrons ejected together in the DPI of a molecule. In this paper, we therefore analyze the spin entanglement properties of a pair of electrons ejected in the DPI of a linear molecule. Rotationally resolved experimental studies of DPI of molecules like $H_2$, $N_2$, NO, $O_2$, etc. are feasible in not too distant a future because integrated and/or angular photocurrents arising from the production of singly charged ions of these and other similar diatomics in their different rotational states have already been measured [36,37].

Molecular systems which have all their nuclei in a straight line belong to either of the $D_{\infty h}$ or $C_{\infty v}$ point group. In addition to taking into account the group theoretical properties of these molecules, it is necessary that their other symmetry properties also be included in a proper theoretical description of their rotational motion and of spin-dependent interactions. In this paper we, therefore, represent the molecular states, both before and after DPI, by the first two [i.e., (a) and (b)] of the four Hund's schemes [33–35] for coupling angular momenta present in a rotating linear molecule.

Each wave function associated with an energy level of an atom or molecule may be classified as having even or odd parity according to whether it remains unchanged or changes sign on inversion of the spatial coordinates of all its particles (i.e., both electrons and nuclei in the case of molecules) through origin. Parity adapted states [e.g., Eqs. (4), (7), and (8)], both for $D_{\infty h}$ and $C_{\infty v}$ molecules, can be prepared [37,38], for example, by multiphoton absorption. It is, however, not at all necessary to use parity adapted states for studying entanglement properties of the electrons ejected in a pair in the DPI of a linear molecule. But there are several advantages of using such states: Their application directly gives [6,7] the parity selection rules for transitions which lead to DPI and are allowed in the $E1$ approximation; use of these states makes it very easy to separately study the influences of SOIs and of SRIs on DPI, in general, and on entanglement, in particular, etc. Parity adapted states [34,35,38] have, therefore, been used for each of the Hund's coupling schemes (a) and (b) considered in the present communication.

Furthermore, the two electrons in DPI are emitted with all possible kinetic energies (subject to the conservation of the total energy) in all possible directions. Also, their spins can be quantized in any direction as well. Moreover, the residual, doubly charged, positive ion (i.e., dication) of the target molecule may be left in any of its energetically accessible rotational-vibrational-electronic (i.e., rovibronic) states. Hence, the two photoelectrons and the dication are in a mixed state after DPI.

A pure separable (i.e., unentangled) state of two particles is always known to satisfy Bell's celebrated inequalities [39]. It has, however, been shown [40–43] that if the two particles are not in a pure state then a nonviolation of Bell's inequalities does not necessarily mean that they are not entangled. Thus, a violation of Bell's inequalities is a necessary and sufficient condition for the entanglement of two particles if they are in a pure state. But, for two particles in a mixed state, this violation does not provide a complete characterization of entanglement. A mixed state can be nonseparable (i.e., entangled) even without violating Bell's inequalities [40–43].

Peres [44], on the other hand, developed a more stringent condition for determining the entanglement of two particles. This condition is equally applicable to both pure as well as mixed states. It was later shown by Horodecki *et al.* [45] to be a sufficient as well as necessary condition for a pure/mixed state of two particles to be nonseparable. According to this Peres-Horodecki [44,45] requirement, the density matrix (DM) of a separable mixed state remains positive when subjected to partial transposition.

In Sec. II, we first establish some relevant conventions and briefly describe density operators and states needed in the present study. The DM for DPI of a rotating linear molecule without taking any spin-dependent interactions (SDIs) into account is developed in Sec. III. This DM is then analyzed for all possibilities in which the DPI of a linear molecule can take place in the absence of SOIs and SRIs according to the stringent Peres-Horodecki [44,45] condition to determine whether electrons ejected in a pair are entangled with respect to their spin angular momenta. Therein, we also study the pure or mixed nature of all the density matrices calculated in Sec. III, and the degree of spin entanglement present in those cases wherein the two photoelectrons are in a non-separable state.

Section IV contains a study of our problem in the presence of spin-dependent interactions. Here we distinguish two different cases arising by the inclusion of only the SRI and of the SRI plus the SOI. Such a study demands that one should develop expressions for two different density matrices, one each obtained in the Hund's coupling schemes (b) and (a), respectively. Although the dynamical terms in the two cases are, of course, very different from each other, the formal structure of the DM for case (a) is found to be identical to that for case (b). Also, the DMs calculated including SDIs in Sec. IV are quite dissimilar in every respect from that obtained in Sec. III when no SDIs are taken into account. The DMs in Sec. IV are then analyzed in terms of the Peres-Horodecki [44,45] condition in order to determine the non-separability of the state of two photoelectrons when they experience either the SRI or both the SOI plus the SRI. Section V presents the conclusions of the investigations performed in this paper.

## II. PRELIMINARIES

Let us represent by $e_1$ and $e_2$ the two freely moving electrons whose entanglement properties we want to investigate. The propagation vector of the $i(=1,2)$-th electron is $\vec{k}_i=(k_i,\theta_i,\phi_i)$ such that its kinetic energy is given by $\epsilon_i=\hbar^2k_i^2/2m$. Also, $\mu_i(=\pm 1/2)$ represents the projection of the spin angular momentum of the $i$-th electron along its spin quantization direction $\hat{u}_i=(\vartheta_i,\varphi_i)$. These two electrons, along with others, form an integral part of a linear molecule, say, $AB$ and are assumed to be simultaneously ejected from it following the absorption of a single photon. If $AB^{2+}$ denotes the residual dication, then our process can schematically be represented by

$$h\nu_r(|\vec{\ell}_r|=1,m_r)+AB|0\rangle\rightarrow AB^{2+}|f\rangle+e_1(\mu_1\hat{u}_1\vec{k}_1)+e_2(\mu_2\hat{u}_2\vec{k}_2). \tag{1}$$

Here, $E_r=h\nu_r$ is the energy of the absorbed photon with $|\ell_r|=1$ its angular momentum in the $E1$ approximation; $|0\rangle$ and $|f\rangle$ represent, respectively, parity adapted [34,35,38] products of the rotational and antisymmetrized electronic states of $AB$ and of $AB^{2+}$. If $E_0$ and $E_f$ are the respective energies of $AB$ in the state $|0\rangle$ and of $AB^{2+}$ in the state $|f\rangle$, we then have $\epsilon_1+\epsilon_2=h\nu_r-(E_f-E_0)$ from energy conservation.

It is well known that only two polarization directions of a photon are linearly independent. (These directions, in addition to being orthogonal to each other, are perpendicular to the photon's direction of propagation as well.) Nevertheless, many workers (see, e.g., Refs. [46], [47]) have represented, for convenience, states of polarization of a photon by the kets $|1m_r\rangle$ (with $m_r=0$ and $\pm 1$) in the $E_1$ approximation. Here [46,47], while $m_r=-1$ and $+1$ correspond, respectively, to left circular polarization (LCP) and right circular polarization (RCP) of the photon, its state with $m_r=0$ is with respect to the electric field vector of the electromagnetic wave. That is, a linearly polarized (LP) photon is represented [46,47] by the state $|10\rangle$ in the present notation. [An unpolarized (UP) electromagnetic wave is taken to be an even mixture of RCP and LCP waves.] According to this specification of the polarization of the incident radiation, the polar axis of our coordinate system, called the photon- (or space-) fixed frame of reference, is taken to be along the electric vector of the LP ionizing radiation; whereas, RCP, LCP, or UP electromagnetic beams are incident in the direction of the $OZ$ axis of our photon frame (PF). This coordinate system and some of the vectors used in this communication are shown in Fig. 1. Unless stated otherwise, all the vectors (e.g., $\vec{k}_i$, $\hat{u}_i$, etc.) used herein refer to the PF.

A molecule can be prepared in a specific rovibronic $|0\rangle$ state in several ways: for example, by its rotational cooling [36], by the electrostatic hexapole method [48], or by multiphoton absorption [37,38]. Let us take the molecule $AB$ to be unpolarized before its DPI. Its density operator is then given by $|0\rangle\langle 0|$. Further, $\rho_r=|1m_r\rangle\langle 1m_r|$ is the density operator of the ionizing radiation. The incident photon and the molecule are uncorrelated before the interaction between the two takes place. This, in other words, means that the density operator of the combined ($AB+$photon) system in Eq. (1) is simply given by the direct product

$$\rho_i=\rho_0\otimes\rho_r. \tag{2}$$

In order to write the density operator for the process represented by Eq. (1), we need to introduce the photoionization operator $F_p=\sqrt{m/\hbar^2}F$, where the operator $F$ in the $E1$ approximation is defined, for example, in Ref. [49]. Then the desired density operator for the present case can readily be written in analogy to that [28] used for the DPI of atomic targets. It is, therefore, given by

$$\rho_f=\mathcal{K}_pF_p\rho_iF_p^{\dagger}. \tag{3}$$

Here [49], $\mathcal{K}_p=3\pi(e^2/\alpha_0E_r)^2$ which contains the dimensionless fine structure constant $\alpha_0$.

It has already been discussed in Sec. I that we will investigate herein the entanglement between $e_1$ and $e_2$ both in the absence and in the presence of SDIs. It is well known that the best description of the dynamics of a linear molecule is achieved in the Hund's coupling scheme (b) when SDIs are not taken into account [33–35]. For a proper representation of a molecular state in this, and indeed even in other, schemes, one also needs to include the rotational motion of the constituent nuclei. (Inclusion of the nuclear vibration, on the other hand, merely requires that product of a matrix element with the appropriate initial and final vibrational states be integrated over the internuclear separation. This is readily achieved in all four of the Hund's coupling schemes merely by calculating the desired matrix elements as a function of

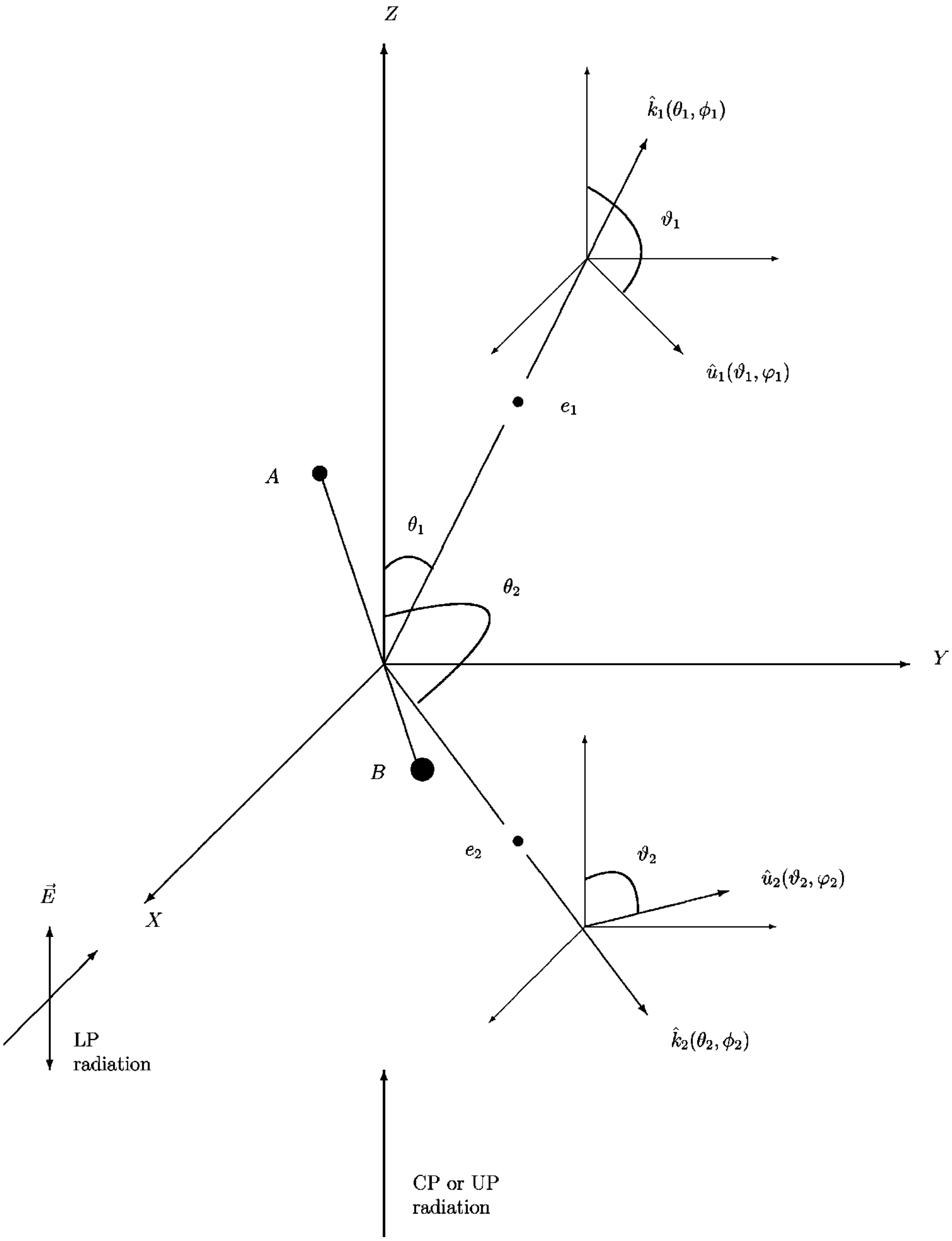

FIG. 1. Coordinate system showing the photon-fixed frame of reference *XYZ* and the propagation directions $(\hat{k}_1,\hat{k}_2)$ as well as the spin quantization directions $(\hat{u}_1,\hat{u}_2)$ of the two photoelectrons $(e_1,e_2)$ simultaneously ejected from the rotating, linear molecule *AB* following the absorption of a single photon. Each electron enters its own Mott detector [58], oriented along $\hat{u}_1(\vartheta_1,\varphi_1)$ for $e_1$ and $\hat{u}_2(\vartheta_2,\varphi_2)$ for $e_2$. These detectors record whether the a photoelectron's spin is up or down with respect to its own quantization direction.

the internuclear separation. Consequently, we no longer mention the vibrational dynamics of a molecule in this paper.)

A parity adapted state of the linear rotating molecule *AB* in Hund's case (b) is given by [34,35,38]

$$|0\rangle=\frac{1}{\sqrt{2}}[|n_0\Lambda_0\rangle|N_0\Lambda_0M_{N_0}\rangle + (-1)^{p_0}|n_0-\Lambda_0\rangle|N_0-\Lambda_0M_{N_0}\rangle]|S_0M_{S_0}\rangle. \qquad (4)$$

In this state, $\Lambda_0(=\vec{N}_0\cdot\hat{R})$ is the projection of the angular momentum $\vec{N}_0=\vec{L}_0+\vec{R}_0$ along the internuclear axis. Here, $\vec{L}_0$ and $\vec{R}_0$ are, respectively, the electronic orbital and nuclear rotational angular momenta of *AB*, whereas $\hat{R}$ is the instantaneous direction of the axis (taken to be along the line joining all the constituent nuclei) of the rotating molecule. $M_{N_0}(=\vec{N}_0\cdot\widehat{OZ})$, on the other hand, is the projection of $\vec{N}_0$ along the polar axis of our PF. Ket $|n_0\Lambda_0\rangle$ in Eq. (4) is the spatial part of the electronic state of *AB*. (Here, $n_0$ represents the additional quantum numbers needed to completely specify $|n_0\Lambda_0\rangle$, but have not explicitly been shown for brevity.) $|S_0M_{S_0}\rangle$, on the other hand, is the spin state of the molecular electrons with total spin angular momentum $\vec{S}_0$ and its projection along the *OZ* axis of Fig. 1 given by $M_{S_0}(=\vec{S}_0\cdot\widehat{OZ})$. The rotation of *AB* in Eq. (1) is described by the normalized function [50]

$$\langle\omega|N_0\Lambda_0M_{N_0}\rangle=\left(\frac{2N_0+1}{8\pi^2}\right)^{1/2}\mathcal{D}^{N_0}_{\Lambda_0M_{N_0}}(\omega) \qquad (5)$$

present in the state $|0\rangle$ defined by Eq. (4). Here, $\omega(\equiv\alpha,\ \beta,\ \gamma)$ represents three Euler angles [50] which specify the instantaneous orientation of the rotating molecule with respect to the PF. $\mathcal{D}$'s in Eq. (5), and elsewhere in this paper, are the rotational harmonics [50]. Furthermore, state (4) always has the parity [34,35,38] $(-1)^{N_0+p_0+s}$ with $p_0=0$ or 1. But, for $\Lambda_0=0$ (i.e., for $\Sigma^{\pm}$)-states, $p_0=0$ [34,35,38] and then Eq. (4) reduces to

$$|0\rangle=|n_0\Lambda_0\rangle|N_0\Lambda_0M_{N_0}\rangle|S_0M_{S_0}\rangle, \tag{6}$$

with parity $(-1)^{N_0+s}$. In addition, the parameter $s=0$ always, except for $\Sigma^-$ states wherein $s=1$. Thus, when Eq. (6) corresponds to a $\Sigma^+$-state, its parity is simply $(-1)^{N_0}$, whereas, if Eq. (6) is to represent a $\Sigma^-$-state, then its parity becomes $(-1)^{N_0+1}$.

The forces which depends on the electronic spin of a rotating molecule can arise due to the interaction of the spin magnetic moment with the magnetic moment produced by nuclear rotation and with that generated by the electronic orbital angular momentum [33]. The former is usually called spin-rotation interaction, whereas, the latter is the well known spin-orbit interaction. It is obvious that SRI can only be present in molecular systems; but both atoms as well as molecules can possess SOI.

In this paper, we want to study the entanglement properties of the twin electrons $(e_1,e_2)$ ejected in process (1) in all the three possibilities, i.e., the target molecule possessing no SDIs, possessing only SRI, or both SRI and SOI. It has already been mentioned elsewhere in this paper that state (4) represents a rotating molecule with neither SRI nor SOI. The state [34]

$$\begin{aligned}|0\rangle={}&(-1)^{S_0-N_0-M_0}\left(\frac{2J_0+1}{2}\right)^{1/2}\\&\times\sum_{M_{N_0}M_{S_0}}\begin{pmatrix}N_0 & S_0 & J_0\\ M_{N_0} & M_{S_0} & -M_0\end{pmatrix}[|n_0\Lambda_0\rangle|N_0\Lambda_0M_{N_0}\rangle\\&+(-1)^{p_0}|n_0-\Lambda_0\rangle|N_0-\Lambda_0M_{N_0}\rangle]|S_0M_{S_0}\rangle,\end{aligned} \tag{7}$$

on the other hand, describes *AB* with only SRI, but SOI has not been taken into account. It is obvious that state (7) also belongs to the Hund's case (b) [34].

In order to properly describe *AB* by including the total SDIs (i.e., both SRI plus SOI), one needs to use Hund's coupling scheme (a). The molecular state in this case is given by [34,35,38]

$$\begin{aligned}|0\rangle={}&\frac{1}{\sqrt{2}}[|n_0\Lambda_0\rangle|J_0\Omega_0M_0\rangle|S_0\Sigma_0\rangle\\&+(-1)^{p_0}|n_0-\Lambda_0\rangle|J_0-\Omega_0M_0\rangle|S_0-\Sigma_0\rangle].\end{aligned} \tag{8}$$

Here, $\vec{J}_0=\vec{N}_0(=\vec{L}_0+\vec{R}_0)+\vec{S}_0$ is the total angular momentum of the molecule. Its projections along the molecular axis and along the polar axis of the PF are given by $\Omega_0=\vec{J}_0\cdot\hat{R}$ and $M_0=\vec{J}_0\cdot\hat{O}Z$, respectively. $\Sigma_0(=\vec{S}_0\cdot\hat{R})$ is the component of the total spin angular momentum of all the electrons of *AB* along its axis. It is obvious from the above discussion that the spin electronic states $[|S_0\Sigma_0\rangle,|S_0-\Sigma_0\rangle]$ in Eq. (8), unlike $|S_0M_{S_0}\rangle$ occurring in Eqs. (4), (6), and (7) and each quantized in the PF, have been referred to the axis of the rotating molecule. The rotational wavefunction $\langle\omega|J_0\Omega_0M_0\rangle$ of the molecule *AB* in the Hund's case (a) state (8) is written analogous to that given in Eq. (5) for case (b).

It is probably needless to write that the appropriate states of the dication $AB^{2+}$ corresponding to Eqs. (4)–(8) for *AB* are readily obtained on replacing the subscript "0" present therein by the subscript "*f*."

Before proceeding further, we need to specify the wave functions for the twin electrons $(e_1,e_2)$ needed to calculate a matrix for the density operator $\rho_f$, defined in Eq. (3), for the DPI process (1). In order to be able to study the entanglement between $e_1$ and $e_2$ for any arbitrary directions of their propagation and energies of motion, the most general form of the spin-orbital for the *i*th electron in Hund's coupling scheme (b) is already discussed in detail in the respective references [51] and [6] in the context of angle- and spin-resolved Auger spectroscopy and of DPI of rotating linear molecules. The required spin orbital in the PF is given by [6,51]

$$\begin{aligned}|\mu_i\hat{u}_i\vec{k}_i\rangle={}&\left(\frac{\hbar^2}{m}\right)^{1/2}\sum_{\substack{\ell_i\lambda_i\\ m_i\nu_i}}i^{\ell_i}e^{-i\sigma_{\ell_i}}\mathcal{D}^{\ell_i}_{\lambda_im_i}(\omega)[\mathcal{D}^{1/2}_{\mu_i\nu_i}(\omega_i)]^*\\&\times[Y^{m_i}_{\ell_i}(\hat{k}_i)]^*\left|\frac{1}{2}\,\nu_i\right\rangle|F^-_{\ell_i\lambda_i}(k_i)\rangle.\end{aligned} \tag{9}$$

Here, $\sigma_{\ell_i}$ is the Coulomb phase [49] for the $\ell_i$th partial wave of the photoelectron; $\lambda_i$ and $m_i$ are the projections of $\ell_i$ along the molecular axis and along $\widehat{OZ}$, respectively. Both the Coulomb phase $\sigma_{\ell_i}$ and the space part $F^-_{\ell_i\lambda_i}(k_i;\vec{r}_i)\equiv\langle\vec{r}_i|F^-_{\ell_i\lambda_i}(k_i)\rangle$ of the spin orbital (9) depend upon energy $\epsilon_i$ (i.e., the magnitude $k_i$ of the propagation vector $\vec{k}_i$) of the photoelectron $e_i$. The superscript "$-$" indicates that $|F^-_{\ell_i\lambda_i}(k_i)\rangle$, in addition, satisfies the incoming wave boundary conditions [52] appropriate for photoionization. $|\tfrac{1}{2}\nu_i\rangle$ is the spin state of the $i$-th photoelectron quantized along the polar axis of the PF, i.e., $\nu_i$ is the projection of this electron's spin angular momentum along the *OZ* axis shown in Fig. 1. A rotation by the Euler angles [50] $\omega_i(\varphi_i,\vartheta_i,0)$ brings the polar axis of the PF in coincidence with the direction $\hat{u}_i(\vartheta_i,\varphi_i)$ along which the spin quantization of the $e_i$th photoelectron is observed in our experiment being performed in the PF. ($\mu_i$ is the projection of the spin of photoelectron $e_i$ along $\hat{u}_i$.) Also, note that in Hund's scheme (b) neither the Coulomb phase $\sigma_{\ell_i}$ nor the space part $|F^-_{\ell_i\lambda_i}(k_i)\rangle$ in Eq. (9) depends upon the spin variable.

A spin-orbital for the *i*th photoelectron in Hund's case (a), on the other hand, is given by [6,51]

$$\begin{aligned}|\mu_i\hat{u}_i,\vec{k}_i\rangle={}&\left(\frac{\hbar^2}{m}\right)^{1/2}\sum_{\substack{\ell_i\lambda_im_i\\ \nu_i\sigma_i}}i^{\ell_i}e^{-i\sigma_{\ell_i\sigma_i}}\mathcal{D}^{\ell_i}_{\lambda_im_i}(\omega)[Y^{m_i}_{\ell_i}(\hat{k}_i)]^*\\&\times[\mathcal{D}^{1/2}_{\mu_i\nu_i}(\omega_i)]^*\mathcal{D}^{1/2}_{\sigma_i\nu_i}(\omega)|F^-_{\ell_i\lambda_i\sigma_i}(k_i)\rangle\end{aligned} \tag{10}$$

Unlike in Eq. (9), both the Coulomb phase $\sigma_{\ell_i \sigma_i}$ and the space part $F^{-}_{\ell_i \lambda_i \sigma_i}(k_i;\vec{r}_i) \equiv \langle \vec{r}_i | F^{-}_{\ell_i \lambda_i \sigma_i}(k_i) \rangle$ in the spin orbital (10) depend upon the spin variable $\sigma_i$ (the projection of the spin angular momentum of the photoelectron $e_i$ along the molecular axis) to take the SOI in the continuum properly into account. But, similar to the orbital (9), these two quantities depend upon the energy $k_i$ of the photoelectron $e_i$ as well.

A state of the (photon+molecule)-system, present on the left hand side of the process (1), can now be written as

$$|0;1m_r\rangle = |0\rangle |1m_r\rangle. \tag{11a}$$

Here, $|0\rangle$ represents one of the states [Eqs. (4) and (6)–(8)] of the molecule *AB* before its DPI. The total $(AB^{2+}+e_1+e_2)$ system on the right hand side of Eq. (1) is, on the other hand, described by

$$|f;\mu_1 \hat{u}_1 \vec{k}_1;\mu_2 \hat{u}_2 \vec{k}_2\rangle = |f\rangle |\mu_1 \hat{u}_1,\vec{k}_1\rangle |\mu_2 \hat{u}_2 \vec{k}_2\rangle. \tag{11b}$$

One merely needs to substitute appropriate kets into (11b), both for the photodication $AB^{2+}$ and the $i$th photoelectron, in Hund's coupling scheme (a) or (b) according to the description already given elsewhere in this paper. Each of the molecular electronic states used herein is properly antisymmetrized.

## III. ENTANGLEMENT IN DPI IN THE ABSENCE OF SPIN DEPENDENT INTERACTIONS

### A. Density matrix

In this section, we will investigate the circumstances in which two electrons simultaneously ejected from a rotating linear molecule, following the absorption of a single photon, can form an EPR pair of particles with respect to their spins. This study is performed disregarding all forces which may arise due to the spins of all electrons participating in process (1) [i.e., electrons in *AB*, in $AB^{2+}$, and the two photoelectrons $(e_1,e_2)$]. Thus, neither the SRI nor SOI is taken into account.

In order to carry out the desired investigations, we first need to obtain a matrix for the density operator $\rho_f$ defined in Eq. (3). It is obvious from the discussion presented in Sec. II that this density matrix should now be calculated in Hund's coupling scheme (b). In the absence of SDIs and due to the spin-independent nature [53] of the $E1$ interaction represented by the operator $F_p$ in Eq. (3), the total spin of the system before and after the DPI process (1) is conserved, i.e., Eq. (A1) in Appendix A of this paper must be satisfied.

Furthermore, the twin photoelectrons $(e_1,e_2)$ in a pair, whose spin entanglement we want to study, may have same [$\epsilon_1=\epsilon_2$ (i.e., $k_1=k_2$)] or different [$\epsilon_1 \neq \epsilon_2$ (i.e., $k_1 \neq k_2$)] energies (subject to satisfying the conservation condition) and moving in any two directions $\hat{k}_1$ and $\hat{k}_2$. For this, one needs a density matrix which should be diagonal in energies and in the directions of propagation (i.e., diagonal in $\vec{k}_1$ and $\vec{k}_2$). But this density matrix must necessarily be nondiagonal with respect to the components of the spin angular momenta (i.e., $\mu_1$, $\mu_2$) of the two photoelectrons $(e_1,e_2)$.

In order to obtain such a density matrix, the appropriate functions to be used for the target *AB* and the twin photoelectrons $(e_1,e_2)$ are those given by Eqs. (4), (5), and (9), respectively; whereas a wave function appropriate for the dication $AB^{2+}$ is similar to Eqs. (4) and (5). In Appendix A, we have developed a completely general expression, independent of all dynamical models, for the desired density matrix for process (1) in the absence of SDIs in the Hund's coupling scheme (b). It is shown in Eq. (A7) that this density matrix can be expressed as a product of two independent factors in the following form:

$$\langle f;\mu_1 \hat{u}_1 \vec{k}_1;\mu_2 \hat{u}_2 \vec{k}_2 | \rho_f | f;\mu_1' \hat{u}_1 \vec{k}_1;\mu_2' \hat{u}_2 \vec{k}_2\rangle = \frac{d^3\sigma(m_r)}{d\epsilon_1 d\hat{k}_1 d\hat{k}_2}\, \sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}. \tag{12}$$

This represents, in addition to other things, two particles [i.e., photoelectrons $(e_1,e_2)$] which are not prepared independently and in total isolation of each other. These two electrons, before their simultaneous ejection, were an integral part of a system, i.e., the target molecule *AB*. Thus, the density matrix (12) could only be calculated by fully taking electron-electron correlation (without SDIs, but including, of course, exchange) effects into account in an interacting, many particle system.

It is obvious from Eq. (A8) that the first term [i.e., $d^3\sigma(m_r)/d\epsilon_1 d\hat{k}_1 d\hat{k}_2$] on the right hand side of the density matrix (12) depends upon, among other things, the directions of propagation $(\hat{k}_1,\hat{k}_2)$ as well as energies $(\epsilon_1,\epsilon_2)$ of two photoelectrons $(e_1,e_2)$, the state of polarization of the ionizing radiation. This term, in addition, contains also the dynamical amplitudes defined by Eq. (A9). These are shown in Eq. (A9) to be determined by the electronic states of *AB* and $AB^{2+}$, by the rotational states of these two species through their respective angular momenta $N_0$ and $N_f$. The dynamical amplitude (A9) will, consequently, also depend on the energies of the emitted particles, on the phase shifts, etc. Thus, the presence of the Dirac's bracket (A9) in expression (A8) means that the first term on the right-hand side of the density matrix (12) is very much dependent on the dynamics of DPI which includes, among other things, energies (i.e., $\epsilon_1$ and $\epsilon_2$) of two photoelectrons.

It should also be pointed out herein that $d^3\sigma(m_r)/d\epsilon_1 d\hat{k}_1 d\hat{k}_2$ has an implicit dependence on the spins $S_0$ and $S_f$ of the two molecular systems involved in process (1), for energies of the molecular states $|0\rangle$ and $|f\rangle$ depend on their multiplicities $(2S_0+1)$ and $(2S_f+1)$, respectively. This term, however, remains completely unaffected by the spins of the two photoelectrons $(e_1,e_2)$. In conclusion, one can say that the term $d^3\sigma(m_r)/d\epsilon_1 d\hat{k}_1 d\hat{k}_2$, present in the density matrix (12), represents purely angular correlation between the twin photoelectrons $(e_1,e_2)$ and dynamical effects defined by Eqs. (A8) and (A9) for DPI (1) described in Hund's coupling scheme (b) in the absence of SDIs. This angular correlation is always *positive* and it acts purely as a *multiplicative* factor in the density matrix (12).

The second term [i.e., $\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}$], present in the density matrix (12), is defined in Eq. (A10). Unlike angular correlation (A8), Eq. (A10) is a 4×4 matrix which does not depend on any of those physical quantities [e.g., dynamical term (A9), polarization of the ionizing radiation, electronic as well rotational states and angular momenta of *AB* and $AB^{2+}$, directions of propagation of $(e_1,e_2)$, on any energy, etc.] which contributes to $d^3\sigma(m_r)/d\epsilon_1 d\hat{k}_1 d\hat{k}_2$. The four-dimensional $\sigma(S_0 S_f \hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}$ matrix, on the other hand, is seen from Eq. (A10) to be completely determined by the Euler angles $(\omega_1,\omega_2)$ which specify the directions $(\hat{u}_1,\hat{u}_2)$ of spin quantization, and by the projections $[\mu_1(\mu_1'),\mu_2(\mu_2')]$ along these directions of the spin angular momenta, of the twin photoelectrons $(e_1,e_2)$. Hence, the second term $\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}$ in the density matrix (12) represents purely spin correlation between two electrons simultaneously ejected in DPI of *AB*.

Another important point which deserves a discussion here is that the presence of $S_0$ and of $S_f$, as arguments in $\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}$, suggests that the spin correlation between two photoelectrons should be affected by the total spins of *AB* and $AB^{2+}$. But expression (A10) for $\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}$ contains, on the other hand, neither of these two spin quantum numbers. It is obvious both from Eq. (A1) and the 6-*j* symbol present in Eq. (A10) that 0 and 1 are the only values which can contribute to the sum over $s_e$ present in the latter equation. But, at the same time, this variable must also satisfy the triangular requirement $|S_0-S_f|\leqslant s_e\leqslant S_0+S_f$ implied by the spin conservation condition (A1). This, in other words, means that expression (A10) will cease to identically vanish whenever $S_0=S_f$ and/or $|S_0-S_f|=1$. Thus the spin-correlation term $\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}$ in the density matrix (12) has an implicit dependence on the total spins of *AB* and of $AB^{2+}$. The presence of this condition also gives us a spin selection rule for a double-photoionizing transition in the $E1$ approximation from state $|0\rangle$ of molecule *AB* to the state $|f\rangle$ of the dication in the Hund's coupling scheme (b) in the absence of SDIs. That is, the total spins of these two species must be such that $\Delta S\equiv|S_0-S_f|=0,1$. Thus values of $s_e$ to be included in the sum present in expression (A10) for the spin correlation term $\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}$ be determined from the two conditions given by Eq. (A1).

Hence, in the absence of SDIs, the density matrix for the angle- and spin-resolved DPI process (1) in a rotating molecule reduces to the product of a dynamically determined angular correlation function which is always positive and a light polarization as well as dynamics insensitive 4×4 spin-correlation matrix dependent upon the spins of *AB* and $AB^{2+}$, and on the spin quantization of the twin photoelectrons $(e_1,e_2)$.

### B. Nonseparability of the density matrix

One expects that, as the two photoelectrons in process (1) [in addition to being, before their emission, an integral and correlated part of a single system, i.e., the molecule *AB*] were not prepared independently and in total isolation of each other, a decomposition of their density matrix (12) into a product should, in general, be impossible, implying, thereby, that $(e_1,e_2)$ should form an EPR pair. Peres [44] and Horodecki *et al.* [45] have shown that a necessary and sufficient condition for the separability of a mixed state of two particles is that the partial transpose of its density matrix should remain positive. (A Hermitian matrix is said to be positive if each of its eigenvalues is greater than zero. The determinant of a matrix is well known to be the product of all of its eigenvalues. Hence, a value less than zero of a determinant means that its matrix is negative. If this determinant, on the other hand, is greater than zero, then the corresponding matrix can still be negative if it has an even number of eigenvalues less than zero.)

We have, therefore, investigated the separability of the photoelectrons $(e_1,e_2)$ emitted in process (1) in the absence of SDIs by applying the stringent, as well as necessary and sufficient, condition proposed in Refs. [44], [45] to our density matrix given by Eqs. (12) and (A8)–(A10). It has already been discussed elsewhere in this paper that the angular correlation part $d^3\sigma(m_r)/d\epsilon_1 d\hat{k}_1 d\hat{k}_2$ of the density matrix (12) is always positive and acts simply as a multiplicative factor. We, therefore, do not write the angular correlation explicitly and represent, for brevity, the density matrix (12) simply by its second term. That is, unless stated otherwise, in the present section we write

$$\begin{aligned}\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|\rho_f|f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle\\ \rightarrow\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}.\end{aligned}\tag{13}$$

In the remaining part of this subsection, we study the separability of the density matrix (13) using the Peres-Horodecki [44,45] condition. An application of this condition requires [44,45] a partial transpose of the density matrix (13). Following the definition introduced by Peres [44] and Horodecki *et al.* [45], partial transpose of Eq. (13) is given by

$$\gamma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}=\sigma(S_0;S_f;\hat{u}_1;\hat{u}_2)_{\mu_1\mu_2',\mu_1'\mu_2}.\tag{14}$$

It is obvious from the discussion presented in Sec. III A that there are only three possibilities, depending upon the spins $S_0$ of *AB* and $S_f$ of $AB^{2+}$ for which density matrix (13) cannot vanish identically. In the following, we investigate the entanglement between $(e_1,e_2)$ in all these three cases.

(i) Molecule *AB* and its residual dication $AB^{2+}$ are each in their singlet electronic state (i.e., $S_0$, $S_f=0$). In this case, only a single value, i.e., $s_e=0$, will contribute to the sum present in Eq. (A10). The corresponding density matrix has been calculated in Eq. (A12a). Consequently, the density matrix (A10), when both *AB* and its photodication $AB^{2+}$ are in their singlet electronic states, becomes

$$\sigma(0;0;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}=\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1',\mu_2'}\Big|^{(s_e=0)}.\tag{15a}$$

Its partial transpose

$$\gamma(0;0;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1',\mu_2'} = \gamma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2',}\Big|^{(s_e=0)}, \tag{15b}$$

on the other hand, is obtained from Eq. (A12b). These are completely general forms of the two matrices: Independent of all dynamical models and applicable for any kind of polarization of the ionizing radiation and directions of propagation as well as of spin quantization, including all possible allowed energies, of the simultaneously ejected electrons $(e_1,e_2)$.

These matrices can be diagonalized even in their present general as well as analytical forms using, for example, MATHEMATICA [54]. As both Eqs. (15a) and (15b) are Hermitian, their eigenvalues should necessarily be real. In the present case, these, in addition, are found to be totally independent of all four angles $[\hat{u}_1(\vartheta_1,\varphi_1),\hat{u}_2(\vartheta_2,\varphi_2)]$ which specify the spin quantization directions of $(e_1,e_2)$ in Eq. (15). One, thus, obtains eigenvalues to be (0, 0, 0, 1) with $\det(\sigma)=0$ for the density matrix (15a) and (1/2, 1/2, −1/2, 1/2) with $\det(\gamma)=-2^{-4}$ for its partial transpose (15b). In view of the stringent, as well as necessary and sufficient, condition suggested in Refs. [44], [45], we therefore conclude that the density matrix (15a) represents a nonseparable spin state. Thus, two photoelectrons ejected simultaneously in the DPI of a rotating linear molecule are always entangled as long as neither the target nor its residual photodication possesses any electronic spin angular momentum. This result shall not be affected by either the electronic states of *AB* and of $AB^{2+}$ or the rotational states of these two species, or by the DPI dynamics [i.e., photon polarization, energies involved, propagation $(\hat{k}_1,\hat{k}_2)$ as well as spin quantization $(\hat{u}_1,\hat{u}_2)$ directions of $(e_1,e_2)$].

This result is an obvious consequence of spin conservation in the absence of SDIs. In this case, we have $S_0$, $S_f=0$, implying thereby, in view of Eq. (A1), the sum of the spins of $(e_1,e_2)$, i.e., $s_e=0$. Hence, the photoelectrons $(e_1,e_2)$ are in the well known entangled state $[\alpha(1)\beta(2)-\alpha(2)\beta(1)]/\sqrt{2}$, i.e., a singlet spin state, irrespective of all other physical conditions.

Let us further investigate the properties of the density matrix (15a). Among its four eigenvalues (0, 0, 0, 1), only one is nonzero. This suggests [55] that Eq. (15a) represents a pure state. Even an application of the necessary and sufficient condition [55] for a density matrix to represent a pure state shows that for Eq. (15a), $\mathrm{Tr}(\sigma^2)=(\mathrm{Tr}\sigma)^2=1$. Here, Tr means a trace of a given matrix. This too implies [55] that Eq. (15a) describes a pure state. The reduced density matrix [55] for Eq. (15a) is easily calculated to be

$$\mathrm{Red}[\sigma(0;0;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}]=\begin{pmatrix} 1/2 & 0 \\ 0 & 1/2 \end{pmatrix}.$$

This gives a degree of nonseparability (participation ratio or Schmidt number) [56], defined only for a pure state, $K=[(1/2)^2+(1/2)^2]^{-1}=2$. This means [56], that a pure state, represented by the density matrix (15a), is a Bell state. This is in complete agreement with the result arrived at above that the two photoelectrons $(e_1,e_2)$ in the present case are in a singlet spin state.

The simplest possible example of this result is the DPI of $H_2$ in its ground electronic $({}^1\Sigma_g^+)$ state. The two photoelectrons which simultaneously come out in the DPI of this molecule are not only correlated but also form an EPR pair with respect to their spins. Some of the other possible simple examples for the present case can be DPIs

$$h\nu_r+\mathrm{Li}_2(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2\ {}^1\Sigma_g^+)\rightarrow \mathrm{Li}_2^{2+}(1\sigma_g^2 1\sigma_2^2 2\sigma_g^0\ {}^1\Sigma_g^+) + e_1(\mu_1\hat{u}_1\vec{k}_1)+e_2(\mu_2\hat{u}_2\vec{k}_2)$$

and

$$h\nu_r+\mathrm{CO}(1\sigma^2 2\sigma^2 3\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2\ {}^1\Sigma^+) \rightarrow \mathrm{CO}^{2+}(1\sigma^2 2\sigma^2 3\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^0\ {}^1\Sigma^+) + e_1(\mu_1\hat{u}_1\vec{k}_1)+e_2(\mu_2\hat{u}_2\vec{k}_2)$$

in the ground electronic configurations of $\mathrm{Li}_2$ and CO, respectively. Although the SDIs in neither of these two molecules are as insignificant as, for example, in the case of $\mathrm{H}_2$, nevertheless the two photoelectrons $(e_1,e_2)$ which come out in each of the above two processes, in the absence of spin-dependent interactions, are always correlated as well as entangled in a singlet spin state.

(ii) Spin $S_0$ of molecule *AB* and $S_f$ of its photodication $AB^{2+}$ differ by 1 (i.e., $|S_0-S_f|=1$). Let us now consider the DPI of a rotating linear molecule in the absence of SDIs when either both, or at least one, of *AB* and $AB^{2+}$ is in other than a singlet electronic state. That is, we may now have one of the three situations: $S_0=0$, $S_f=1$; $S_0=1$, $S_f=0$; or $S_f=|S_0\pm 1|$, with $S_0\geqslant 1$. It is obvious from Eqs. (A1) and (A10) that, out of the two (0, 1) possible values, only $s_e=1$ now needs to be taken into account. The required density matrix, again calculated from Eq. (A10), is given in Eq. (A13a). Therefore, in the present cases we have

$$\sigma(|S_0-S_f|=1;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'} = \sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}\Big|^{(s_e=1)} \tag{16a}$$

Its partial transpose (A13b) is readily obtained using Eq. (14) and is written as

$$\gamma(|S_0-S_f|=1;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'} = \gamma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}\Big|^{(s_e=1)}. \tag{16b}$$

An element of (16a) is found to be related to the corresponding element of Eq. (15a) by

$$\sigma(|S_0-S_f|=1;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'} = \frac{1}{3}\delta_{\mu_1\mu_1'}\delta_{\mu_2\mu_2'}-\frac{1}{3}\sigma(0;0;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}. \tag{17}$$

An identical relationship exists between the partial transpose matrices (15b) and (16b). Equation (17), in other words, means that, although the diagonal elements of the two matrices (15) (for $S_0, S_f = 0$) and (16) (for $|S_0 - S_f| = 1$) are linearly independent, their nondiagonal elements have a linear dependence.

The eigenvalues and determinant of the density matrix (16a) are (1/3, 1/3, 0, 1/3) and det($\sigma$)=0, respectively; whereas the corresponding respective quantities for the partial transpose (16b) are (1/6, 1/6, 1/6, 1/2) and det($\gamma$) $=2^{-4}3^{-3}$. That is, the partial transpose of the density matrix remains positive. This, according to the stringent condition developed in Refs. [44], [45], means that the density matrix (16a) represents a separable spin state of $(e_1, e_2)$. Hence, the photoelectrons ejected in process (1) in the absence of SDIs do not form an EPR pair with respect to their spin angular momenta when the spins of $AB$ and of $AB^{2+}$ differ by 1. However, $(e_1, e_2)$ are still correlated. This shows that the correlation and spin entanglement of two electrons ejected simultaneously in the single process of DPI are totally independent and unrelated properties. Two correlated electrons are not necessarily spin entangled. This is a totally general result, independent of all dynamical models and of experimental geometries. The only requirement for it to be applicable is that no SDIs are taken into account, and the spins of the target and of its photodication must differ by one.

Furthermore, the density matrix (16a) has been shown to have more than one nonzero eigenvalue value; also, one finds that Tr($\sigma^2$)[=1/3] is less than $(\mathrm{Tr}\sigma)^2[=1]$. Each of these two facts simply means [55] that the density matrix (16a) represents a mixed state. The two photoelectrons $(e_1, e_2)$ in the present case have been shown to have a total spin angular momentum $s_e = 1$. There are, consequently, three spin states $\{\alpha(1)\alpha(2); \beta(1)\beta(2); [\alpha(1)\beta(2) + \alpha(2)\beta(1)]/\sqrt{2}\}$ available for each pair of ejected electrons. Hence, the state represented by the density matrix (16a) is probably a mixture of the three triplet spin stats of $(e_1, e_2)$.

Among the lightest possible molecules in which such a DPI can take place without much effects from SDIs are $\mathrm{B}_2(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^2\ {}^3\Sigma_g^-)$ and $\mathrm{CO}(1\sigma^2 2\sigma^2 3\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2\ {}^1\Sigma^+)$. The photodication of the two molecules are $\mathrm{B}_2^{2+}(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^0\ {}^1\Sigma_g^+)$ and $\mathrm{CO}^{2+}(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^2 5\sigma^2\ {}^3\Sigma^-)$, respectively. According to the analysis presented herein, the two photoelectrons ejected in either of these two cases are only correlated but not entangled with respect to their spins. There can be many such examples of DPI of rotating linear molecules in the absence of SDI with $|S_0 - S_f| = 1$ wherein one can produce electrons $(e_1, e_2)$ in a pair which are correlated but in a separable, mixed spin state.

(iii) Spin $S_0$ of the molecule $AB$ and $S_f$ of its photodication $AB^{2+}$ are equal and greater than zero (i.e., $S_0 = S_f \geqslant 1/2$). Finally, let us consider entanglement properties of photoelectrons $(e_1, e_2)$ simultaneously emitted in DPI in the absence of SDIs, when multiplicities of the electronic states $|0\rangle$ and $|f\rangle$ involved in process (1) are equal and greater than one. Unlike the last two cases considered so far in this subsection, now both of the two possible values of $s_e(=0,1)$ will simultaneously contribute to the calculation of the density matrix (A10). The density matrix and its partial transpose, in the present case, are

$$\sigma(S_0 = S_f \geqslant 1/2; \hat{u}_1, \hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'} = \sigma(S_0; S_f; \hat{u}_1, \hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}\Big|^{(s_e=0 \text{ and } 1)} \tag{18a}$$

and

$$\gamma(S_0 = S_f \geqslant 1/2; \hat{u}_1, \hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'} = \gamma(S_0; S_f; \hat{u}_1, \hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}\Big|^{(s_e=0 \text{ and } 1)}, \tag{18b}$$

respectively. The right-hand sides of these two respective equations are given by Eqs. (A14a) and (A14b). An element of the density matrix (18a) can also be obtained from the corresponding element of Eq. (15a) by using

$$\sigma(S_0 = S_f \geqslant 1/2; \hat{u}_1, \hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'} = \tfrac{1}{3}\delta_{\mu_1\mu_1'}\delta_{\mu_2\mu_2'} + \tfrac{2}{3}\sigma(0;0;\hat{u}_1, \hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}. \tag{19}$$

This relation can also be used to obtain the partial transpose (18b) from its counterpart (15b).

Both of matrices (18) can readily be diagonalized with their respective eigenvalues given by (1/3, 1/3, 1/3, 1) and (2/3, 2/3, 0, 2/3) and the determinants by $3^{-3}$ and 0. This data show that both the matrices (18a) and its partial transpose (18b) are positive. Hence, applying the stringent as well as sufficient and necessary Peres-Horodecki [44,45] condition, one concludes that the photoelectrons $(e_1, e_2)$ in process (1) in the absence of SDIs are not entangled with respect to their spins if the multiplicities of the electronic states of $AB$ and of $AB^{2+}$ are equal and greater than 1. This, again, is a completely general result and is independent of all dynamical models. Although the photoelectrons $(e_1, e_2)$ are not prepared independently and in total isolation from each other, in addition to being an integral part of the same system (i.e., a linear rotating molecule in the present case) before their emission, they are simply correlated but not spin entangled. The presence of correlation is necessary, otherwise the two electrons would not have come out simultaneously following the absorption of a single photon. This study also proves, similar to what was discussed in section (ii), electron-electron correlation and spin entanglement are two independent properties. Two correlated electrons may or may not form an EPR pair with respect to their spin angular momenta. That is, electron-electron correlation is responsible for the ejection of two electrons simultaneously in DPI but it does not necessarily provide them with spin entanglement. Moreover, in the absence of SDIs, the entanglement properties of electrons with respect to their spin angular momenta do not depend on the photoionization dynamics.

The relevant examples for the present case can be DPI in

$$\mathrm{CN}(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^1\ {}^2\Sigma^+) \to \mathrm{CN}^{2+}(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 1\pi^4 5\sigma^0\ {}^2\Sigma^+)$$

and

$$\mathrm{NO}(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 2\pi^1\ {}^2\Pi)$$
$$\rightarrow \mathrm{NO}^{2+}(1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^1 5\sigma^1 1\pi^4 2\pi^0\ {}^2\Sigma^+).$$

In both these cases, although SDIs may not be as weak as they are, for example, in the case of a lighter molecule, e.g., $H_2$, nevertheless, the analysis presented in this subsection means that the pair of photoelectrons ejected in either of these two processes, although correlated, will never be spin entangled.

Both eigenvalues as well as $\mathrm{Tr}(\sigma^2)[=4/3]\leqslant(\mathrm{Tr}\sigma)^2$ $[=2]$ suggest that the density matrix (18a) represents a mixed state. This density matrix has been arrived at by summing Eq. (A10) over both the possible values of the total spin angular momentum of photoelectrons $(e_1,e_2)$, i.e., $s_e=0$ and 1. This, in other words, means, that the state represented by the density matrix (18a) is, probably, a mixture of the one singlet and three triplet spin states of photoelectrons $(e_1,e_2)$. This mixture forms a product state such that $(e_1,e_2)$ are not spin entangled.

## IV. ENTANGLEMENT IN DPI IN THE PRESENCE OF SPIN DEPENDENT INTERACTIONS

Let us now investigate the entanglement properties of the photoelectrons $(e_1,e_2)$ ejected in process (1) when spin dependent forces are taken into account. If one discards the effects of nuclear spin then, unlike in atomic targets wherein only SOI is effective, one should consider two forces, rather than one force, arising due to electronic spin in a molecule. That is, SRI, in addition to the SOI. It is, however, not necessary that both SOI and SRI are either simultaneously present or are of equal importance in any given molecule. It will, naturally, be quite interesting to see the roles played by these two SDIs separately as well as jointly in entangling two photoelectrons ejected in DPI of a rotating linear molecule. In the following subsection we, therefore, first calculate the DM for DPI by taking only SRI into account; whereas, in Sec. IV B both the SRI and SOI are considered.

### A. Density matrix for DPI with spin-rotation interaction

Appendix B in the present paper describes in detail the calculation of the density matrix for the angle- and spin-resolved DPI of a rotating linear molecule by including SRI. This spin interaction is assumed to be present in the target $AB$ as well as in its photodication $AB^{2+}$. The present density matrix, given in Eq. (B6), is very different as well as much more complicated than Eq. (12) [i.e., Eq. (A7)] obtained in Appendix A without SRI, although both Eqs. (B6) and (A7) have been calculated in Hund's coupling scheme (b).

First, the former equation [i.e., Eq. (B6)], unlike the latter [i.e., Eq. (A7)], cannot be written as a product of an angular correlation factor and a spin correlation matrix. This, consequently, means that in the present case it is not possible to study spin entanglement properties of $(e_1,e_2)$ without considering the dynamics of DPI. That is, unlike in the previous case of DPI without SRI, there will now be important dynamical effects on the spin entanglement of two photoelectrons ejected in the presence of SRI in Hund's coupling scheme (b). Second, although similar to the first density matrix (A7), the present Eq. (B6) too is a $4\times4$ matrix; each of the 16 elements in the latter can, however, be shown to contain a very large ($\simeq 100$) number of complicated terms compared to the three/four simple terms contributing to Eq. (A10) [see, for example, Eqs. (A12a), (A13a), and/or (A14a)].

### B. Density matrix for DPI with spin-rotation and spin-orbit interactions

Finally, let us consider DPI in a rotating linear molecule by taking the full effects of electrons' spin angular momenta into account. For this, one needs to include, in addition to SRI plus SOI in the bound electronic state $|0\rangle$ of $AB$ and $|f\rangle$ of $AB^{2+}$, SOI in the continua [5,6,51] of two photoelectrons emitted in process (1). This requires that one should work in Hund's coupling scheme (a) [33–35]. Appendix C to this paper describes, in detail, calculation of such a density matrix. This again is, obviously, a $4\times4$ matrix which can not be separated into an angular and a spin correlation parts; its each element consists of, similar to that of case (b) in Eq. (B6), about 100 terms.

Furthermore, it is shown in Appendix C that the form of the density matrix calculated in Hund's case (a) by including both SRI plus SOI, is identical to that obtained in Eq. (B6) for Hund's case (b) on the inclusion of only SRI with, of course, different dynamical amplitudes and normalization factors contributing in two cases. In case (b), density matrix (B6), we use the dynamical amplitudes given in Eq. (B5); whereas, for the case (a), amplitudes (C4) are to be substituted in the density matrix (B6).

### C. Entanglement in DPI in the presence of SRI or (SRI+SOI)

It is, fortunately, possible to represent the two density matrices obtained in the Secs. IV A and IV B by a single form given in Eqs. (D1). It [i.e., Eq. (D1)] is a fairly complex expression for any density matrix. In order to analyze such a complicated expression and draw some physically meaningful conclusions from it about the entanglement of two photoelectrons simultaneously ejected in DPI of a rotating linear molecule in the presence of SDIs, we first simplify Eq. (D1) by specializing it to a collinear experimental geometry in which $(e_1,e_2)$ are moving in opposite directions, i.e., $\hat{k}_2=-\hat{k}_1$. The resulting density matrix will further be simplified by aligning the colliner directions of the two ejected electrons along the polar axis of our PF shown in Fig. 1. This means that we specialize Eq. (D1) to $\hat{k}_1(\theta_1=0,\phi_1)$ and $\hat{k}_2(\theta_2=\pi,\pi+\phi_1)$ [i.e., geometry (D2)] and obtain the density matrix (D3).

A reduction of density matrix (D1) to the form of Eq. (D3) for DPI in a collinear geometry means that its each of the 16 elements can now be completely represented by the six parameters $[A_0^{00}(m_r),A_1^{01}(m_r),A_1^{10}(m_r),$ $A_0^{11}(m_r),A_1^{11}(m_r),A_2^{11}(m_r)]$ defined by Eq. (D3b). It is obvious from Eq. (D3b) that these parameters, although do not contain any angles, very much depend upon the dynamics of DPI [which includes also the energies of $(e_1, e_2)$], the angular momenta involved in process (1), among other things. Consequently, unlike in the previous case discussed in detail in Sec. III for DPI in the absence of SDIs, now the entanglement properties of the two photoelectrons will not be independent of the dynamics of DPI as well as of other physical variables present in the density matrix (D3). In order to obtain a quantitative physical insight on the entanglement of $(e_1, e_2)$ in the present case and to see what kind of influence the dynamics of DPI and other physical variables have on it, we further simplify Eq. (D3) by assuming that both photoelectrons $(e_1, e_2)$ have their spins quantized in the *XY* plane of the PF. That is, Eq. (D3) is now specialized to the geometry given in Eq. (D4). After these simplifications, the density matrix (D3) reduces to the form given in Eq. (D6a) which can be analyzed analytically. The partial transpose of this density matrix, readily obtained using relation (14), is given in Eq. (D6b).

A density matrix is supposed to be Hermitian [55]. This demands that, in Eq. (D6a),

$$\left.\begin{array}{l} A_0^* = A_0, \quad A_{01}^* = A_{01}, \quad A_{10}^* = A_{10}, \\ A_m^* = A_m, \quad (A_p + A_{11})^* = A_p - A_{11}. \end{array}\right\}. \tag{20}$$

That is, while four $(A_0, A_{01}, A_{10}, A_m)$ of six parmeters in Eq. (D5), needed to describe the density matrix (D6a) and its partial transpose (D6b) are purely real, the remaining two (i.e., $A_{11}$, $A_p$) can be either complex or purely imaginary. However, the linear combination $(A_p^2 - A_{11}^2)$ of these last two parameters is also a pure real, as well as a positive, quantity.

Using MATHEMATICA [54], one can readily calculate determinants of both matrices (D6) without substituting numerical values of the parameters present therein. We find that, while each of

$$\det(\rho_f) = [(A_0 + A_m)^2 - (A_{01} + A_{10})^2][(A_0 - A_m)^2 - (A_{01} - A_{10})^2 + 4(A_{11}^2 - A_p^2)] \tag{21a}$$

and

$$\det(\gamma_f) = [(A_0 - A_m)^2 - (A_{01} - A_{10})^2][(A_0 + A_m)^2 - (A_{01} + A_{10})^2 + 4(A_{11}^2 - A_p^2)] \tag{21b}$$

is necessarily real, neither of them is positive definite. For determinant (21a) to be less than zero, one should have either

$$(A_{01} + A_{10})^2 > (A_0 + A_m)^2 \tag{22a}$$

or

$$(A_{01} - A_{10})^2 > [(A_0 - A_m)^2 + 4(A_{11}^2 - A_p^2)]. \tag{22b}$$

Determinant (21a) will, however, be positive if both of the inequalities (22) are simultaneously satisfied. Likewise, if one wants determinant (21b) to be negative, one should then satisfy either (but not both) of the conditions

$$(A_{01} - A_{10})^2 > (A_0 - A_m)^2 \tag{23a}$$

or

$$(A_{01} + A_{10})^2 > [(A_0 + A_m)^2 + 4(A_{11}^2 - A_p^2)]. \tag{23b}$$

With a proper combination of Eqs. (22) and (23), one can arrive at the appropriate conditions which will simultaneously make both the density matrix (D6a) and its partial transpose (D6b) negative. For example, let us first assume that $(A_{11}^2 - A_p^2) \leqslant 0$, then both conditions (22a) and (23b) are simultaneously satisfied if one has

$$(A_{01} + A_{10})^2 > (A_0 + A_m)^2. \tag{24a}$$

However, the presence of

$$(A_{01} - A_{10})^2 > (A_0 - A_m)^2 \tag{24b}$$

will, on the other hand, mean that now both Eqs. (22b) and (23a) are applicable. Alternatively, we may have $(A_{11}^2 - A_p^2) \geqslant 0$. In this case, inequalities (22a) and (23b) will simultaneously hold for

$$(A_{01} + A_{10})^2 > [(A_0 + A_m)^2 + 4(A_{11}^2 - A_p^2)], \tag{25a}$$

while, an applicability of

$$(A_{01} - A_{10})^2 > [(A_0 - A_m)^2 + 4(A_{11}^2 - A_p^2)] \tag{25b}$$

will, otherwise, suggest that simultaneous satisfaction of Eqs. (22b) and (23a) make both determinants (21) negative.

Hence, under appropriate conditions, discussed herein in Eqs. (23)–(25), two photoelectrons ejected in process (1) in two opposite directions along the polar axis of the PF and with their spins quantized in the *XY* plane of this coordinate system, are not only correlated but can also be entangled with respect to their spins. This situation occurs when one takes either only the SRI or both the SRI+SOI into account. It is obvious from the discussion given herein, that conditions derived in Eqs. (23)–(25) very much depend upon the polarization of the ionizing radiation as well as on the photoionization dynamics, in addition to several other physical quantities. Another important thing which this discussion shows is that, unlike in the case investigated in Sec. III for DPI without SDIs, now one cannot determine *a priori*, just by looking at the multiplicities of the electronic states of *AB* and that of the photodication $AB^{2+}$, or any of the other physical variables, whether the twin photoelectrons $(e_1, e_2)$ which are necessarily cocorrelated, will be entangled or not. Thus the presence of SDIs, even in the form of merely SRI, has completely changed the entanglement properties of $(e_1, e_2)$. Now, every physical quantity which may influence, in however small way, DPI of a rotating linear molecule in process (1), will possibly also have an effect on the two photoelectrons $(e_1, e_2)$ forming a nonseparable state with respect to their spin angular momenta.

## V. CONCLUSIONS

In the context of DPI word correlation is always used to convey those physical effects which cannot be understood within the framework of an independent particle model and are responsible for simultaneous ejection of two electrons under the action of a one-body operator (i.e., absorption of a single photon in the $E1$ approximation). Had the independent particle model been valid, two electrons would not have simultaneously come out following the absorption of a single photon. Thus, only those two electrons which are correlated by physical effects other than those present in the independent particle model are simultaneously ejected in DPI. Our present analysis shows that these two photoelectrons, which are neither prepared independently nor in isolation from each other and were an integral part of the same system before their ejection, do not necessarily form a state which is entangled with respect to their spin angular momenta. Hence in the context of DPI, correlation and spin entanglement are two independent properties of twin photoelectrons.

Second, the present analysis further shows that the spin entanglement of two correlated electrons ejected in DPI depends upon factors which are different in different physical situations corresponding to the exclusion or inclusion of SDIs. In the absence of SDIs, it is possible to predict *a priori*, by looking at the total spin angular momenta of the target and of its residual photodication, the spin entanglement properties of two simultaneously ejected electrons. For example, the twin photoelectrons are in a nonseparable spin state if and only if both the target molecule and its dication are in their respective singlet electronic states. If either one or both of these species possess a total electronic spin angular momentum which is different from zero, the two ejected electrons, although still correlated, cease to be spin entangled. This result is completely independent of all physical quantities (excluding the multiplicities of the electronic states of $AB$ and $AB^{2+}$) which are needed to characterize the DPI of a rotating linear molecule. On the other hand, if either SRI or both $(\mathrm{SRI}+\mathrm{SOI})$ are taken into account, it is very difficult to say *a priori* any thing about the spin entanglement of the ejected electrons. They may or may not be in a nonseparable state, for the entanglement of their spins now depends on each of those physical entities which matters in the DPI of the targets being considered in this communication.

Recently, Chandra and Chakraborty [28] have analyzed entanglement properties of photoelectrons ejected in the DPI of atoms. Such targets are well known to be completely different from a rotating linear molecule in each and every respects. Moreover, unlike in the latter systems, wherein SRI or $(\mathrm{SRI}+\mathrm{SOI})$ constitutes SDIs, it is only the SOI which needs to be taken into account for those forces which depends on electronic spin in an atom (excluding, of course, nuclear spin in both types of targets). The density matrix obtained in Ref. [28] in the absence of SOI is exactly in the form of the present Eq. (12), i.e., a product of an angular correlation factor and a spin-correlation matrix. Although the angular correlation factors in the two cases naturally involve different sets of angular momenta and dynamical amplitudes, the spin-correlation matrix given in Ref. [28] is, nevertheless, identical to that found in Eq. (A10) herein. In addition to this, density matrices calculated by taking SDIs in the present and the previous [28] papers into account are also identical in their structures while differing in the angular momenta and the dynamical amplitudes involved in the atomic and molecular DPI. Thus, the investigations reported herein and in Ref. [28] have following important ramifications.

(a) Density matrices of identical forms describe the angle- and spin-resolved DPI of atoms and of rotating linear molecules. This is true with or without SDIs. This demonstration puts the DPI of these two entirely different kinds of systems on an equal footing. (b) The spin entanglement properties of two electrons simultaneously ejected from each type of these targets are identical; completely unaffected by the dynamics of DPI in the absence of SDIs, but very dependent on the dynamics of the respective systems in which DPI is taking place in the presence of SDIs. (i) Without SDIs the spin entanglement of two photoelectrons is completely determined by the electronic spin angular momenta of the given target before and after its DPI. Moreover, in this case, the same results are applicable no matter whether the target is an atom or a rotating linear molecule. This, in other words, generalizes the results obtained by Chandra and Chakraborty [28] for spin entanglement without SDIs by restricting the spin angular momenta of each of the two photoelectrons to be in the $XY$ plane of our PF. (ii) In the presence of SDIs, it is possible neither for atomic nor molecular targets to predict *a priori* the existence of entanglement between twin photoelectrons as it is now greatly dependent upon each and every aspects of the complicated dynamics of DPI. (c) Finally, such a kind of formal identity in the behavior of atoms and of rotating linear molecules with respect to the angle- and spin-resolved DPI and the spin entanglement of two photoelectrons could be established because we have taken the rotation of molecular nuclei into account and used parity adapted wave functions, within an appropriate Hund's coupling scheme, to describe rotational and electronic motion of a linear molecule. But the use of parity adapted states is, however, not necessary for studying entanglement properties of rolating linear molecules.

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## APPENDIX A: DENSITY MATRIX FOR DOUBLE PHOTOIONIZATION OF A ROTATING LINEAR MOLECULE WITHOUT SPIN-DEPENDENT INTERACTIONS IN HUND'S COUPLING SCHEME (b)

In this appendix, we briefly describe the derivation of the density matrix used in Sec. III of the present paper. This matrix is obtained for angle- and spin-resolved DPI of a rotating linear molecule in Hund's coupling scheme (b) without taking any interactions which may depend on electronic spin into account. In addition, the photoionization operator [49] $F_p$ in the density operator (3) is also well known [53] to be independent of the spin of the absorbed photon. These things mean that in process (1), the total spin angular momentum before and after DPI should be same. Therefore, in the present case, we have

$$\vec{S}_0=\vec{S}_f+\vec{s}_e\left[=\left(\frac{\vec{1}}{2}\right)_1+\left(\frac{\vec{1}}{2}\right)_2\right] \tag{A1}$$

Here, $(\vec{1}/2)_i$ is the spin angular momentum of the $i$th photoelectron in Eq. (1) quantized along $\hat{u}_i(\vartheta_i,\varphi_i)$.

The most general form of the density operator (2), which represents a non-interacting photon plus an unpolarized molecule *AB* [in Hund's coupling scheme (b)], can now be written as

$$\rho_i=\frac{1}{(2-\delta_{0\Lambda_0})(2N_0+1)(2S_0+1)}\times\sum_{p_0M_{N_0}M_{S_0}}|0;1m_r\rangle\langle 0;1m_r|, \tag{A2}$$

where $|0;1m_r\rangle$ has already been defined in Eq. (11a). In this operator, we have averaged over all degenerate states of *AB* represented by $|0\rangle$ and given in Eq. (4). The density matrix

$$\begin{aligned}&\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|\rho_f|f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle\\&=\mathcal{K}_p\sum_{p_fM_{N_f}M_{S_f}}\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p\rho_i(F_p)^\dagger|\\&\quad\times f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle\end{aligned} \tag{A3}$$

for the angle- and spin-resolved DPI (1) is obtained, on the other hand, by summing over all degenerate states $|f\rangle$ of $AB^{2+}$. [See Eq. (11b) for the definition of $|f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2\rangle$ representing the $(AB^{2+}+e_1+e_2)$ system.] This, on substituting Eq. (A2), becomes

$$\begin{aligned}&\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|\rho_f|f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle\\&=\frac{\mathcal{K}_p}{(2-\delta_{0\Lambda_0})(2N_0+1)(2S_0+1)}\\&\quad\times\sum_{\substack{p_0M_{N_0}M_{S_0}\\p_fM_{N_f}M_{S_f}}}\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle\\&\quad\times\langle f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle^*\end{aligned} \tag{A4}$$

It probably needs to be pointed out here that, according to the declared aim of this appendix, the appropriate states $|0\rangle$ of *AB* and $|\mu_i\hat{u}_i\vec{k}_i\rangle$ of the photoelectron $e_i$ in Hund's case (b) are those given by Eqs. (4) and (9), respectively; whereas, $|f\rangle$ for $AB^{2+}$ is obtained on replacing 0 by $f$ everywhere in its counterpart ket $|0\rangle$ in Eq. (4).

The calculation of the density matrix (A4) requires an evaluation of the matrix elements present on its right hand side. This is done through a lengthy, but straightforward, procedure which requires a rather heavy use of Racah algebra. This matrix element involves an integration over the nuclear angular coordinates [i.e., Euler angles $\omega$ $(=\alpha,\beta,\gamma)$] which represent an orientation in the space of the axis joining all the molecular nuclei, multiplied by integrals over spatial coordinates of all electrons comprising *AB*. All integrals present in Eq. (A4) and elsewhere in this paper involving spatial coordinates of molecular electrons have to be done in the molecule frame (MF) of reference with its polar axis as the line joining all the nuclei and Euler angles $\omega$ specify its orientation with respect to the PF. We, therefore, first transform the photon state $|1m_r\rangle$ from the PF to the MF using rotational harmonics $\mathcal{D}$ [50]:

$$|1m_r\rangle=\sum_{\lambda_r}\mathcal{D}^1_{\lambda_rm_r}(\omega)|1\lambda_r\rangle \tag{A5}$$

Here, $\lambda_r$ represents the component of the absorbed photon's angular momentum (=1 in the $E1$ approximation) along the molecular axis, i.e., the polar axis of the MF. Next, we couple the three spin states $(|1/2\nu_1\rangle$, $|1/2\nu_2\rangle$, and $|S_fM_{S_f}\rangle)$, present in $|f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2\rangle$, according to the vector addition shown on the right hand side of Eq. (A1) obtaining

$$\begin{aligned}&|S_fM_{S_f}\rangle\left[\left(\left|\frac{1}{2}\nu_1\right\rangle\right)_1\left(\left|\frac{1}{2}\nu_2\right\rangle\right)_2\right]\\&=\sum_{s_em_eSM_S}(-1)^{s_e-S_f+m_e+M_S}\sqrt{(2s_e+1)(2S+1)}\\&\quad\times\begin{pmatrix}1/2&1/2&s_e\\\lambda_1&\lambda_2&-m_e\end{pmatrix}\begin{pmatrix}S_f&s_e&S\\M_{S_f}&m_e&-M_S\end{pmatrix}|SM_S\rangle\end{aligned} \tag{A6}$$

We now substitute states (4) of *AB*, Eq. (A5) of the absorbed photon, and Eq. (11b) [along with Eq. (A6)] of $(AB^{2+}+e_1+e_2)$ in the matrix element $\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle$. It then becomes an algebraic sum of four terms each multiplied, among other things, by the inner product of $|SM_S\rangle$ and $|S_0M_{S_0}\rangle$. The orthonormality of these two states imposes the spin conservation condition (A1) on the Dirac's bracket $\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle$ as well as on the density matrix (A4).

Each of the four terms contributing to $\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle$ is multiplied, in addition to other things, by a product of two 3-*j* symbols present in Eq. (A6), two spherical harmonics (SH) of the forms $[Y_{\ell_i}]$, two rotational harmonics (RH) of the forms $[\mathcal{D}^{1/2}(\omega_i)]$, and an integral over a product of five rotational harmonics of the type $[\mathcal{D}^{\ell_1}]^*[\mathcal{D}^{\ell_2}]^*[\mathcal{D}^{N_f}]^*\mathcal{D}^{N_0}\mathcal{D}^1$ with Euler angles $\omega$ as their arguments. This integral over $\omega$ can be evaluated in many ways, but the procedure we have used is as follows: We begin with by combining, with the help of Eq. (4.3.2) from Edmonds [50] which expresses a product of two RH into a triple sum of products of two 3-*j* symbols and one rotational harmonic, the first two as well as the last two of the RH present in the product of five RH each with its argument $\omega$. This procedure reduces $[\mathcal{D}^{\ell_1}]^*[\mathcal{D}^{\ell_2}]^*[\mathcal{D}^{N_f}]^*\mathcal{D}^{N_0}\mathcal{D}^1$ to a six-fold sum of the product of four 3-*j* symbols and three RH. Next we use Eq. (4.6.2) from Ref. [50] which evaluates the integral over $\omega$ of the three remaining RH to another product of two 3-*j* symbols. Finally, each of the four terms present in $\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle$ will, *interalia*, contain two SH and two RH of the types $[Y_{\ell_i}]$ and $[\mathcal{D}^{1/2}(\omega_i)]$, respectively, and a product of eight 3-*j* symbols. A similar expression will be obtained for the second Dirac's bracket, namely, $\langle f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle^*$, present in the density matrix (A4).

Next, we substitute both of these Dirac brackets in Eq. (A4) and simplify the consequent long expression for the density matrix by using unitarity of 3-*j* symbols and combining, for $i=1$ as well as 2, $\mathcal{D}^{1/2}(\omega_i)$ with $[\mathcal{D}^{1/2}(\omega_i)]^*$ and $Y_{\ell_i}(\hat{k}_i)$ with $[Y_{\ell_i'}(\hat{k}_i)]^*$ using Eqs. (4.3.2) and (4.6.5) from Ref. [50], respectively. Next, we consecutively use two times identity (14.42) given by de Shalit and Talmi [57] in order to express a quaternion sum of the product of four 3-*j* symbols into a double sum of the product of two 3-*j* and one 9-*j* symbols; subsequent to this operation, one can twice apply relation (6.2.8) from Ref. [50] for converting a triple sum of the product of three 3-*j* symbols to a product of one 3-*j* and one 6-*j* symbols.

These and some other simplifications can be shown to enable us to write the angle- and spin-resolved density matrix (A4) for the DPI process (1) in the absence of SDIs in the following form:

$$\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|\rho_f|f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle = \frac{d^3\sigma(m_r)}{d\epsilon_1 d\hat{k}_1 d\hat{k}_2}\,\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}. \tag{A7}$$

Here we have defined

$$\begin{aligned}\frac{d^3\sigma(m_r)}{d\epsilon_1 d\hat{k}_1 d\hat{k}_2} ={}& (-1)^{m_r+N_0+N_f}\frac{\mathcal{K}_p}{4\pi(2-\delta_{0\Lambda_0})}(2N_f+1)\sum_{\substack{p_0\ell_1\ell_1'LL'L_1L_T\\ p_f\ell_2\ell_2'NN'L_2M}}(-1)^{\ell_1'+\ell_2'+L'+L_T}(2L_T+1)\sqrt{(2L_1+1)(2L_2+1)}\\ &\times\begin{pmatrix}\ell_1 & \ell_1' & L_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell_2' & L_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}1 & 1 & L_T\\ m_r & -m_r & 0\end{pmatrix}\begin{pmatrix}L_1 & L_2 & L_T\\ M & -M & 0\end{pmatrix}\begin{Bmatrix}L_T & N & N'\\ N_0 & 1 & 1\end{Bmatrix}\begin{Bmatrix}L_T & N & N'\\ N_f & L' & L\end{Bmatrix}\\ &\times\begin{Bmatrix}\ell_1 & \ell_1' & L_1\\ \ell_2 & \ell_2' & L_2\\ L & L' & L_T\end{Bmatrix}[Y_{L_1}^{M}(\hat{k}1)]^*[Y_{L_2}^{-M}(\hat{k}_2)]^*\langle n_fN_f\Lambda_fp_f;[(\ell_1\ell_2)LN_f]N|F|n_0N_0\Lambda_0p_0;(N_01)N\rangle\\ &\times\langle n_fN_f\Lambda_fp_f;[(\ell_1'\ell_2')L'N_f]N'|F|n_0N_0\Lambda_0p_0;(N_01)N'\rangle^*\end{aligned} \tag{A8}$$

with

$$\begin{aligned}&\langle n_fN_f\Lambda_fp_f;[(\ell_1\ell_2)LN_f]N|F|n_0N_0\Lambda_0p_0;(N_01)N\rangle\\ &\quad=(-i)^{\ell_1+\ell_2}e^{i(\sigma_{\ell_1}+\sigma_{\ell_2})}(-1)^N\frac{1}{2}\sqrt{\frac{\hbar^2}{m}}[1-(-1)^{p_0+p_f+\ell_1+\ell_2+N_0+N_f}](2N+1)(2L+1)\sqrt{(2\ell_1+1)(2\ell_2+1)}\\ &\quad\quad\times\sum_{\substack{\lambda_1\lambda_2\lambda_r\\ \Lambda_L\Lambda_N}}(-1)^{\Lambda_L}\begin{pmatrix}\ell_1 & \ell_2 & L\\ \lambda_1 & \lambda_2 & \Lambda_L\end{pmatrix}\begin{pmatrix}N_f & N & L\\ \Lambda_f & \Lambda_N & -\Lambda_L\end{pmatrix}\Bigg[\begin{pmatrix}N_0 & 1 & N\\ \Lambda_0 & \lambda_r & \Lambda_N\end{pmatrix}\langle n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2|F|n_0\Lambda_0;1\lambda_r\rangle\\ &\quad\quad+(-1)^{p_0}\begin{pmatrix}N_0 & 1 & N\\ -\Lambda_0 & \lambda_r & \Lambda_N\end{pmatrix}\langle n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2|F|n_0-\Lambda_0;1\lambda_r\rangle\Bigg].\end{aligned} \tag{A9}$$

The Dirac's brackets, e.g., $\langle n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2|F|n_0\Lambda_0;1\lambda_r\rangle$ in Eq. (A9) is the matrix element of the $E1$ photoionization operator $F$ between states $|n_f\Lambda_f\rangle|F^-_{\ell_{1\lambda_1}}(k_1)\rangle|F^-_{\ell_{2\lambda_2}}(k_2)\rangle\equiv|n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2\rangle$ and $|n_0\Lambda_0\rangle|1\lambda_r\rangle\equiv|n_0\Lambda_0;1\lambda_r\rangle$ [see Eqs. (4), (9), and (11)]. In arriving at Eq. (A8), we have used the definition $F_p=\sqrt{\mathrm{m}/\hbar^2}F$, where the operator $F$ has been explained in Ref. [49] both in the $E1$ length and in $E1$ velocity approximations, and the well known property [6]

$$\langle n_f-\Lambda_f;\ell_1-\lambda_1;\ell_2-\lambda_2|F|n_0-\Lambda_0;1-\lambda_r\rangle=\langle n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2|F|n_0\Lambda_0;1\lambda_r\rangle$$

of the matrix element of an operator between states of a linear molecule.

It is obvious that each of the matrix elements present in Eqs. (A8) and (A9) depends upon energies $[\epsilon_1,\ \epsilon_2$ (i.e., $k_1,\ k_2)]$ of both photoelectrons. For brevity, however, this dependence of the matrix elements on the magnitudes of $\vec{k}_1$ and $\vec{k}_2$ has not explicitly been shown in Eqs. (A8) and (A9) and elsewhere in this paper.

The density matrix (A7) further contains

$$\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}=(-1)^{\mu_1'+\mu_2'}\sum_{s_e}\sum_{\substack{s\zeta\\ \eta_1\eta_2}}(-1)^{s_e-\zeta}(2s+1)\begin{pmatrix}1/2 & 1/2 & s\\ \mu_1 & -\mu_1' & \eta_1\end{pmatrix}\begin{pmatrix}1/2 & 1/2 & s\\ \mu_2 & -\mu_2' & \eta_2\end{pmatrix}\begin{Bmatrix}1/2 & 1/2 & s\\ 1/2 & 1/2 & s_e\end{Bmatrix}$$
$$\times[\mathcal{D}^s_{\eta_1,\zeta}(\omega_1)]^*[\mathcal{D}^s_{\eta_2,-\zeta}(\omega_2)]^*. \tag{A10}$$

It is obvious from Eq. (A1) and from the 6-$j$ symbol present in Eq. (A10) that $s_e=0$ and 1 are the only two values allowed for it. The circumstances which will decide as to how many and which of these values $s_e$ can take in Eq. (A10) were discussed in detail in Sec. III B of the present paper. In the following, we explicitly evaluate Eq. (A10) for all the three possibilities. In order to write the corresponding density matrices in a concise form, let us introduce the following notations:

$$\begin{array}{c} i\equiv\sqrt{(-1)},\quad s_1\equiv\sin\vartheta_1,\quad s_2\equiv\sin\vartheta_2,\quad s\equiv\sin(\varphi_2-\varphi_1),\\ c_1\equiv\cos\vartheta_1,\quad c_2\equiv\cos\vartheta_2,\quad c\equiv\cos(\varphi_2-\varphi_1).\end{array} \tag{A11}$$

(i) The matrix (A10), when the sum over $s_e$ present in it is performed only with $s_e=0$, becomes

$$4\gamma(S_0;S_f;\widehat{u_1},\widehat{u_2})_{\mu_1\mu_2,\mu_1'\mu_2'}|^{(s_e=0)}$$
$$=\begin{array}{c|cccc}
\mu_1\mu_2/\mu_1'\mu_2' & \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2}\\
\hline
\frac{1}{2}\frac{1}{2} & 1-\widehat{u_1}\cdot\widehat{u_2} & \begin{array}{c}c_1s_2-s_1c_2c\\ -s_1s\end{array} & \begin{array}{c}s_1c_2-c_1s_2c\\ +is_2s\end{array} & \begin{array}{c}-s_1s_2-(1+c_1c_2)c\\ -i(c_1-c_2)s\end{array}\\
\frac{1}{2}-\frac{1}{2} & \begin{array}{c}c_1s_2-s_1c_2c\\ +is_1s\end{array} & 1+\widehat{u_1}\cdot\widehat{u_2} & \begin{array}{c}-s_1s_2-(1+c_1c_2)c\\ +i(c_1-c_2)s\end{array} & \begin{array}{c}-s_1c_2+c_1s_2c\\ -is_2s\end{array}\\
-\frac{1}{2}\frac{1}{2} & \begin{array}{c}s_1c_2-c_1s_2c\\ -is_2s\end{array} & \begin{array}{c}-s_1s_2-(1+c_1c_2)c\\ -i(c_1-c_2)s\end{array} & 1+\widehat{u_1}\cdot\widehat{u_2} & \begin{array}{c}-c_1s_2+s_1c_2c\\ +is_1s\end{array}\\
-\frac{1}{2}-\frac{1}{2} & \begin{array}{c}-s_1s_2+(1+c_1c_2)c\\ +i(c_1+c_2)s\end{array} & \begin{array}{c}-s_1c_2+c_1s_2c\\ +is_2s\end{array} & \begin{array}{c}-c_1s_2+s_1c_2c\\ -is_1s\end{array} & 1-\widehat{u_1}\cdot\widehat{u_2}
\end{array}, \tag{A12a}$$

Its partial transpose

$$4\gamma(S_0;S_f;\widehat{u_1},\widehat{u_2})_{\mu_1\mu_2,\mu_1'\mu_2'}|^{(s_e=0)}$$

$$\begin{array}{c|cccc}
\mu_1\mu_2/\mu_1'\mu_2' & \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2} \\
\hline
\frac{1}{2}\frac{1}{2} & 1-\widehat{u_1}\cdot\widehat{u_2} & \begin{array}{c}c_1s_2-s_1c_2c\\+is_1s\end{array} & \begin{array}{c}s_1c_2-c_1s_2c\\+is_2s\end{array} & \begin{array}{c}-s_1s_2-(1+c_1c_2)c\\+i(c_1+c_2)s\end{array} \\
\frac{1}{2}-\frac{1}{2} & \begin{array}{c}c_1s_2-s_1c_2c\\-is_1s\end{array} & 1+\widehat{u_1}\cdot\widehat{u_2} & \begin{array}{c}-s_1s_2+(1-c_1c_2)c\\-i(c_1-c_2)s\end{array} & \begin{array}{c}-s_1c_2+c_1s_2c\\-is_2s\end{array} \\
-\frac{1}{2}\frac{1}{2} & \begin{array}{c}s_1c_2-c_1s_2c\\-is_2s\end{array} & \begin{array}{c}-s_1s_2+(1-c_1c_2)c\\+i(c_1-c_2)s\end{array} & 1+\widehat{u_1}\cdot\widehat{u_2} & \begin{array}{c}-c_1s_2+s_1c_2c\\-is_1s\end{array} \\
-\frac{1}{2}-\frac{1}{2} & \begin{array}{c}-s_1s_2-(1+c_1c_2)c\\-i(c_1+c_2)s\end{array} & \begin{array}{c}-s_1c_2+c_1s_2c\\+is_2s\end{array} & \begin{array}{c}-c_1s_2+s_1c_2c\\+is_1s\end{array} & 1-\widehat{u_1}\cdot\widehat{u_2}
\end{array}, \tag{A12b}$$

on the other hand, is obtained by substituting Eq. (A12a) into Eq. (14).

(ii) On summing over $s_e=1$ only, Eq. (A10) becomes

$$12\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}|^{(s_e=1)}$$

$$\begin{array}{c|cccc}
\mu_1\mu_2/\mu_1'\mu_2' & \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2} \\
\hline
\frac{1}{2}\frac{1}{2} & 3+\hat{u}_1\cdot\hat{u}_2 & \begin{array}{c}-c_1s_2+s_1c_2c\\+is_1s\end{array} & \begin{array}{c}-s_1c_2+c_1s_2c\\-is_2s\end{array} & \begin{array}{c}s_1s_2-(1-c_1c_2)c\\+i(c_1-c_2)s\end{array} \\
\frac{1}{2}-\frac{1}{2} & \begin{array}{c}-c_1s_2+s_1c_2c\\-is_1s\end{array} & 3-\hat{u}_1\cdot\hat{u}_2 & \begin{array}{c}s_1s_2+(1+c_1c_2)c\\-i(c_1+c_2)s\end{array} & \begin{array}{c}s_1c_2-c_1s_2c\\+is_2s\end{array} \\
-\frac{1}{2}\frac{1}{2} & \begin{array}{c}-s_1c_2+c_1s_2c\\+is_2s\end{array} & \begin{array}{c}s_1s_2+(1+c_1c_2)c\\+i(c_1+c_2)s\end{array} & 3-\hat{u}_1\cdot\hat{u}_2 & \begin{array}{c}c_1s_2-s_1c_2c\\-is_1s\end{array} \\
-\frac{1}{2}-\frac{1}{2} & \begin{array}{c}s_1s_2-(1-c_1c_2)c\\-i(c_1-c_2)s\end{array} & \begin{array}{c}s_1c_2-c_1s_2c\\-is_2s\end{array} & \begin{array}{c}c_1s_2-s_1c_2c\\+is_1s\end{array} & 3+\hat{u}_1\cdot\hat{u}_2
\end{array}. \tag{A13a}$$

Its partial transpose is readily obtained, using Eq. (14), to be

$$12\gamma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}\Big|^{(s_e=1)}$$

$$= \begin{array}{cc}
\mu_1\mu_2/\mu_1'\mu_2' & \begin{array}{cccc} \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2} \end{array} \\
\begin{array}{c} \frac{1}{2}\frac{1}{2} \\ \\ \frac{1}{2}-\frac{1}{2} \\ \\ -\frac{1}{2}\frac{1}{2} \\ \\ -\frac{1}{2}-\frac{1}{2} \\ \\ \end{array} &
\begin{pmatrix}
3+\hat{u}_1\cdot\hat{u}_2 & -c_1s_2+s_1c_2c & -s_1c_2+c_1s_2c & s_1s_2+(1+c_1c_2)c \\
 & -is_1s & -is_2s & -i(c_1+c_2)s \\
-c_1s_2+s_1c_2c & 3-\hat{u}_1\cdot\hat{u}_2 & s_1s_2-(1-c_1c_2)c & s_1c_2-c_1s_2c \\
+is_1s & & +i(c_1-c_2)s & +is_2s \\
-s_1c_2+c_1s_2c & s_1s_2-(1-c_1c_2)c & 3-\hat{u}_1\cdot\hat{u}_2 & c_1s_2-s_1c_2c \\
+is_2s & -i(c_1-c_2)s & & +is_1s \\
s_1s_2+(1+c_1c_2)c & s_1c_2-c_1s_2c & c_1s_2-s_1c_2c & 3+\hat{u}_1\cdot\hat{u}_2 \\
+i(c_1+c_2)s & -is_2s & -is_1s &
\end{pmatrix}
\end{array}. \tag{A13b}$$

(iii) Finally, we evaluate Eq. (A10) by summing over $s_e$ for both the values allowed to it, i.e., $s_e=0$ and 1. The matrix (A10) and its partial transpose, in the present case, are

$$6\sigma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}\Big|^{(s_e=0\ \text{and}\ 1)}$$

$$= \begin{array}{cc}
\mu_1\mu_2/\mu_1'\mu_2' & \begin{array}{cccc} \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2} \end{array} \\
\begin{array}{c} \frac{1}{2}\frac{1}{2} \\ \\ \frac{1}{2}-\frac{1}{2} \\ \\ -\frac{1}{2}\frac{1}{2} \\ \\ -\frac{1}{2}-\frac{1}{2} \\ \\ \end{array} &
\begin{pmatrix}
3-\hat{u}_1\cdot\hat{u}_2 & c_1s_2-s_1c_2c & s_1c_2-c_1s_2c & -s_1s_2+(1-c_1c_2)c \\
 & -is_1s & +is_2s & -i(c_1-c_2)s \\
c_1s_2-s_1c_2c & 3+\hat{u}_1\cdot\hat{u}_2 & -s_1s_2-(1+c_1c_2)c & -s_1c_2+c_1s_2c \\
+is_1s & & +i(c_1+c_2)s & -is_2s \\
s_1c_2-c_1s_2c & -s_1s_2-(1+c_1c_2)c & 3+\hat{u}_1\cdot\hat{u}_2 & -c_1s_2+s_1c_2c \\
-is_2s & -i(c_1+c_2)s & & +is_1s \\
-s_1s_2+(1-c_1c_2)c & -s_1c_2+c_1s_2c & -c_1s_2+s_1c_2c & 3-\hat{u}_1\cdot\hat{u}_2 \\
+i(c_1-c_2)s & +is_2s & -is_1s &
\end{pmatrix}
\end{array} \tag{A14a}$$

and

$$6\gamma(S_0;S_f;\hat{u}_1,\hat{u}_2)_{\mu_1\mu_2,\mu_1'\mu_2'}\Big|^{(s_e=0\ \text{and}\ 1)}$$

$$= \begin{array}{c|cccc}
\mu_1\mu_2/\mu_1'\mu_2' & \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2} \\
\hline
\frac{1}{2}\frac{1}{2} & 3-\hat{u}_1\cdot\hat{u}_2 & c_1s_2-s_1c_2c+is_1s & s_1c_2-c_1s_2c+is_2s & -s_1s_2-(1+c_1c_2)c+i(c_1+c_2)s \\
\frac{1}{2}-\frac{1}{2} & c_1s_2-s_1c_2c-is_1s & 3+\hat{u}_1\cdot\hat{u}_2 & -s_1s_2+(1-c_1c_2)c-i(c_1-c_2)s & -s_1c_2+c_1s_2c-is_2s \\
-\frac{1}{2}\frac{1}{2} & s_1c_2-c_1s_2c-is_2s & -s_1s_2+(1-c_1c_2)c+i(c_1-c_2)s & 3+\hat{u}_1\cdot\hat{u}_2 & -c_1s_2+s_1c_2c-is_1s \\
-\frac{1}{2}-\frac{1}{2} & -s_1s_2-(1+c_1c_2)c-i(c_1+c_2)s & -s_1c_2+c_1s_2c+is_2s & -c_1s_2+s_1c_2c+is_1s & 3-\hat{u}_1\cdot\hat{u}_2
\end{array}, \tag{A14b}$$

respectively.

## APPENDIX B: DENSITY MATRIX FOR DOUBLE PHOTOIONIZATION OF A ROTATING LINEAR MOLECULE INCLUDING SPIN-ROTATION INTERACTION IN HUND'S COUPLING SCHEME (b)

This appendix contains a derivation of the density matrix calculated for DPI (1) of a rotating linear molecule taking the interaction of electronic spin and nuclear rotation into account both in the target *AB* and in its residual photodication $AB^{2+}$. As the spin-orbit interaction is not considered at all in this appendix, probably Hund's coupling scheme (b) is again most appropriate [34] to work with. The consequent density matrix has been used in Sec. IV A of the present paper. One now needs to consider Ref. [34] the total angular momentum formed by the vector addition of the total spin angular momentum of electrons and rotational angular momentum of molecular nuclei. These are given by $\vec{J}_0=\vec{N}_0+\vec{S}_0$ and $\vec{J}_f=\vec{N}_f+\vec{S}_f$ for *AB* and $AB^{2+}$, respectively.

The density operator (A2), describing the non-interacting incident photon and the target *AB*, in the present case is given by

$$\rho_i=\frac{1}{(2-\delta_{0\Lambda_0})(2J_0+1)}\sum_{p_0M_0}|0;1m_r\rangle\langle 0;1m_r|, \tag{B1}$$

The ket $|0\rangle$, needed to represent the target *AB* in the product state $|0;1m_r\rangle$ [see Eq. (11a)], is given by Eq. (7) in the present case. Similarly, the ket (11b) which represents $(AB^{2+}+e_1+e_2)$-system, now becomes

$$\begin{aligned}
|f;\mu_1\hat{u}_1\tilde{k}_1;\mu_2\hat{u}_2\tilde{k}_2\rangle={}&(-1)^{1-N_f-M_f}\frac{\hbar^2}{m}\left(\frac{2J_f+1}{2}\right)^{1/2}\sum_{\substack{\ell_1m_1\lambda_1\nu_1S_1M_{S_1}M_{S_f}\\ \ell_2m_2\lambda_2\nu_2S_2M_{S_2}M_{N_f}}}\iota^{\ell_1+\ell_2}e^{-\iota(\sigma_{\ell_1}+\sigma_{\ell_2})}\\
&\times(-1)^{-S_1-M_{S_1}-M_{S_2}}\sqrt{(2S_1+1)(2S_2+1)}\begin{pmatrix} N_f & S_f & J_f\\ M_{N_f} & M_{S_f} & -M_f\end{pmatrix}\begin{pmatrix} S_f & 1/2 & S_1\\ M_{S_f} & \nu_1 & -M_{S_1}\end{pmatrix}\\
&\times\begin{pmatrix} S_1 & 1/2 & S_2\\ M_{S_1} & \nu_2 & -M_{S_2}\end{pmatrix}[\mathcal{D}^{1/2}_{\mu_1\nu_1}(\omega_1)]^*[\mathcal{D}^{1/2}_{\mu_2\nu_2}(\omega_2)]^*\mathcal{D}^{\ell_1}_{\lambda_1m_1}(\omega)\mathcal{D}^{\ell_2}_{\lambda_2m_2}(\omega)\\
&\times[Y^{m_1}_{\ell_1}(\hat{k}_1)]^*[Y^{m_2}_{\ell_2}(\hat{k}_2)]^*[|n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2\rangle|N_f\Lambda_fM_{N_f}\rangle+(-1)^{p_f}|n_f-\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2\rangle|N_f\\
&-\Lambda_fM_{N_f}\rangle]|S_2M_{S_2}\rangle,
\end{aligned}\tag{B2}$$

The required density matrix in the present case is, consequently, given by

$$\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|\rho_f|f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle=\frac{\mathcal{K}_p}{(2-\delta_{0\Lambda_0})(2J_0+1)}\sum_{\substack{p_0M_0\\p_fM_f}}\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle \times\langle f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle^* \tag{B3}$$

In order to proceed further, we now need to calculate each of the two Dirac's bracket present on the right hand side of Eq. (B3). We, therefore, substitute Eqs. (7), (A5), and (B2) into $\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle$. As the photoionization operator $F_p$ is independent of the electronic spin, the orthogonality of the kets $|S_0M_{S_0}\rangle$, in state (7), and of $|S_2M_{S_2}\rangle$, in state (B2), means that total spin is conserved. Hence, Eq. (A1) is valid even in the present case when SRI is taken into account in the DPI (1) of a rotating linear molecule in Hund's coupling scheme (b).

The consequent matrix element, obtained after this simplification, has already been evaluated by Chandra and Sen [6]. The details of its evaluation procedure too are available in Sec. 3.2.1 of Ref. [6]. For the sake of completeness, for its further references in this paper, and for correcting minor mistakes related to the phase factors and normalization constants present in Ref. [6], we write this matrix element as follows:

$$\begin{aligned}&\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle\\&\quad=(-1)^{1+m_r+N_f-M_f+2J_0+\Lambda_0}\sqrt{(2J_0+1)}\sum_{\substack{\ell_1m_1\nu_1j_1n_{j_1}j_tn_t\\\ell_2m_2\nu_2j_2n_{j_2}jn_j}}(2j_t+1)[(2\ell_1+1)(2\ell_2+1)]^{-1/2}\\&\qquad\times\begin{pmatrix}\ell_1&1/2&j_1\\-m_1&-\nu_1&n_{j_1}\end{pmatrix}\begin{pmatrix}\ell_2&1/2&j_2\\-m_2&-\nu_2&n_{j_2}\end{pmatrix}\begin{pmatrix}j_1&j_2&j\\n_{j_1}&n_{j_2}&n_j\end{pmatrix}\begin{pmatrix}J_f&J_0&j_t\\-M_f&M_0&n_t\end{pmatrix}\\&\qquad\times\begin{pmatrix}j_t&1&j\\-n_t&m_r&n_j\end{pmatrix}Y_{\ell_1}^{m_1}(\hat{k}_1)Y_{\ell_2}^{m_2}(\hat{k}_2)\mathcal{D}^{1/2}_{\mu_1\nu_1}(\omega_1)\mathcal{D}^{1/2}_{\mu_2\nu_2}(\omega_2)\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(b)},\end{aligned}\tag{B4}$$

where the reduced matrix amplitude

$$\begin{aligned}\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(b)}=&(-\iota)^{\ell_1+\ell_2}e^{\iota(\sigma_{\ell_1}+\sigma_{\ell_2})}(2j_1+1)(2j_2+1)(2j+1)\\&\times\sqrt{(2\ell_1+1)(2\ell_2+1)(2N_0+1)(2S_0+1)(2N_f+1)(2J_f+1)}\\&\times\sum_{\substack{\ell_ps_p\\\ell_tS_T}}(2\ell_p+1)(2\ell_t+1)(2s_p+1)\sqrt{2S_T+1}\begin{Bmatrix}1&\ell_p&\ell_t\\s_p&j_t&j\end{Bmatrix}\begin{Bmatrix}1/2&1/2&s_p\\S_f&S_0&S_T\end{Bmatrix}\\&\times\begin{Bmatrix}\ell_1&\ell_2&\ell_p\\1/2&1/2&s_p\\j_1&j_2&j\end{Bmatrix}\begin{Bmatrix}N_f&N_0&\ell_t\\S_f&S_0&s_p\\J_f&J_0&j_t\end{Bmatrix}\\&\times\langle n_fN_f\Lambda_fp_f;(\ell_1\ell_2)\ell_p|F(\ell_t)|n_0N_0\Lambda_0p_0;1\rangle^{(b)}\end{aligned}\tag{B5a}$$

is defined in terms of the photoionization amplitude

$$\begin{aligned}\langle n_fN_f\Lambda_fp_f;(\ell_1\ell_2)\ell_p|F(\ell_t)|n_0N_0\Lambda_0p_0;1\rangle^{(b)}=&\frac{1}{2}[1-(-1)^{p_0+p_f+\ell_1+\ell_2+N_0+N_f}]\left(\frac{\hbar^2}{m}\right)^{1/2}\sum_{\substack{\lambda_1\lambda_2\lambda_r\\\lambda_p\lambda_t}}\begin{pmatrix}\ell_1&\ell_2&\ell_p\\-\lambda_1&-\lambda_2&\lambda_p\end{pmatrix}\\&\times\begin{pmatrix}1&\ell_p&\ell_t\\\lambda_r&-\lambda_p&\lambda_t\end{pmatrix}\left[\begin{pmatrix}N_f&N_0&\ell_t\\\Lambda_f&-\Lambda_0&\lambda_t\end{pmatrix}\langle n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2|F|n_0\Lambda_0;1\lambda_r\rangle\right.\\&\left.+(-1)^{p_0}\begin{pmatrix}N_f&N_0&\ell_t\\\Lambda_f&\Lambda_0&\lambda_t\end{pmatrix}\langle n_f\Lambda_f;\ell_1\lambda_1;\ell_2\lambda_2|F|n_0-\Lambda_0;1\lambda_r\rangle\right].\end{aligned}\tag{B5b}$$

Let us now substitute into Eq. (B3) Dirac's bracket (B4) and its complex conjugate. The resulting expression for the density matrix is simplified by using (a) once unitarity of 3-*j* symbols [50]; (b) twice each of the addition theorems (4.3.2) and (4.6.5) for RH and SH, respectively, given in Ref. [50]; (c) thrice the identity (14.42) which converts [57] four sums of a product of four 3-*j* symbols into a double sum of the product of two 3-*j* and one 9-*j* symbols; (d) once Eq. (6.2.8) for reducing [50] a triple sum of the product of three 3-*j* symbols to a product of merely one 3-*j* symbol and one 6-*j* symbol.

With these and some additional simplifications, the density matrix (B3) in the present case of angle- and spin-resolved DPI of a rotating linear molecule on taking SRI into account in Hund's coupling scheme (b) can finally be written in the following convenient form:

$$\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|\rho_f|f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle=(-1)^{\mu_1'+\mu_2'}\sum_{\substack{S_1N_{S_1}M_{S_1}\\ S_2N_{S_2}M_{S_2}}}\begin{pmatrix}1/2 & 1/2 & S_1\\ \mu_1 & -\mu_1' & N_{S_1}\end{pmatrix}$$
$$\times\begin{pmatrix}1/2 & 1/2 & S_2\\ \mu_2 & -\mu_2' & N_{S_2}\end{pmatrix}A^{S_1S_2}_{N_{S_1}M_{S_1};N_{S_2}M_{S_2}}(m_r;\vec{k}_1\vec{k}_2)\mathcal{D}^{S_1}_{-N_{S_1}M_{S_1}}(\omega_1)\mathcal{D}^{S_2}_{-N_{S_2}M_{S_2}}(\omega_2). \tag{B6a}$$

Here, *A*'s are the dynamical amplitudes given by

$$A^{S_1S_2}_{N_{S_1}M_{S_1};N_{S_2}M_{S_2}}=(-1)^{1+m_r+S_1+S_2+N_{S_1}+N_{S_2}}\frac{\mathcal{K}_p}{4\pi(2-\delta_{0\Lambda_0})}(2S_1+1)(2S_2+1)\sum_{\substack{p_0\ell_1\ell_1'j_1j_1'L_1M_{L_1}J_1L_rjj_t\\ p_f\ell_2\ell_2'j_2j_2'L_2M_{L_2}J_2M_Jj'}}(-1)^{\ell_1'+\ell_2'+j+j_t}+L_r$$
$$\times(2J_1+1)(2J_2+1)(2L_r+1)(2j_t+1)\sqrt{(2L_1+1)(2L_2+1)}\begin{pmatrix}\ell_1 & \ell_1' & L_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell_2' & L_2\\ 0 & 0 & 0\end{pmatrix}$$
$$\times\begin{pmatrix}1 & 1 & L_r\\ m_r & -m_r & 0\end{pmatrix}\begin{pmatrix}J_1 & J_2 & L_r\\ M_J & -M_J & 0\end{pmatrix}\begin{pmatrix}L_1 & S_1 & J_1\\ M_{L_1} & M_{S_1} & M_J\end{pmatrix}\begin{pmatrix}L_2 & S_2 & J_2\\ M_{L_2} & M_{S_2} & -M_J\end{pmatrix}\begin{Bmatrix}1 & 1 & L_r\\ j & j' & j_t\end{Bmatrix}$$
$$\times\begin{Bmatrix}\ell_1 & \ell_1' & L_1\\ 1/2 & 1/2 & S_1\\ j_1 & j_1' & J_1\end{Bmatrix}\begin{Bmatrix}\ell_2 & \ell_2' & L_2\\ 1/2 & 1/2 & S_2\\ j_2 & j_2' & J_2\end{Bmatrix}\begin{Bmatrix}j_1 & j_1' & J_1\\ j_2 & j_2' & J_2\\ j & j' & L_r\end{Bmatrix}Y^{M_{L_1}}_{L_1}(\hat{k}_1)Y^{M_{L_2}}_{L_2}(\hat{k}_2)$$
$$\times\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(b)}\langle J_fp_f;\ell_1'\ell_2';(j_1'j_2')j'|F(j_t)|J_0p_0;1\rangle^{(b)*}. \tag{B6b}$$

All of the matrix elements present in relations (B4)–(B6), including the electronic kets in Eq. (B2), depend upon $k_1$ and $k_2$, in addition to other things. This dependence of various matrix elements on the photoelectron energies has not, however, been explicitly shown for brevity.

## APPENDIX C: DENSITY MATRIX FOR DOUBLE PHOTOIONIZATION OF A ROTATING LINEAR MOLECULE INCLUDING SPIN-ORBIT PLUS SPIN-ROTATION INTERACTIONS IN HUND'S COUPLING SCHEME (a)

In the present appendix, we calculate the density matrix for the angle- and spin-resolved DPI of a rotating linear molecule by including, in addition to the spin-rotation, the spin-orbit interaction of all the bound electrons of *AB*, of $AB^{2+}$, and of the two photoelectrons $(e_1,e_2)$ ejected in process (1). The appropriate Hund's coupling scheme to work with now is (a). The appropriate form of the density operator (2) is now given by

$$\rho_i=\frac{1}{(2J_0+1)}\sum_{p_0M_0}|0;1m_r\rangle\langle 0;1m_r|. \tag{C1}$$

Consequently, the density matrix in the present case of angle- and spin-resolved DPI including SDIs (i.e., SOI plus SRI) in Hund's scheme (a) is now calculated from

$$\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|\rho_f|f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2\rangle$$
$$=\frac{\mathcal{K}_p}{(2J_0+1)}\sum_{\substack{p_0M_0\\ p_fM_f}}\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle$$
$$\times\langle f;\mu_1'\hat{u}_1\vec{k}_1;\mu_2'\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle^* \tag{C2}$$

Here, $|0;1m_r\rangle$ is again given by Eq. (11a). The ket $|0\rangle$ [i.e., Eq. (8)] to be used herein is the one which represents *AB* in Hund's coupling scheme (a); whereas $|1m_r\rangle$ is taken from Eq. (A5). In addition to this, one also needs to substitute in Eq. (C2) Eq. (11b) [containing $|f\rangle$ obtained from Eq. (8) after replacing the subscript 0 by the subscript $f$] and product of the photoelectron kets (10) for $i=1$ and 2.

In order to proceed further, next we need to calculate the matrix element $\langle f;\mu_1\hat{u}_1\tilde{k}_1;\mu_2\hat{u}_2\tilde{k}_2|F_p|0;1m_r\rangle$ for the evaluation of the density matrix (C2). This matrix element, for the states of $AB$, of $(AB^{2+}+e_1+e_2)$, and of the absorbed photon (in the $E1$ approximation) to be used herein, has been calculated by Chandra and Sen [6]. That result is directly applicable in the present case as well. For completeness, brevity, and for its further references in the present communication, we write the required matrix element [given by Eqs. (35) and (36) in Ref. [6]] in the following form:

$$\begin{aligned}\langle f;\mu_1\hat{u}_1\vec{k}_1;\mu_2\hat{u}_2\vec{k}_2|F_p|0;1m_r\rangle={}&(-1)^{1+J_f+\Omega_f-\Omega_0-M_0}\sqrt{(2J_0+1)}\sum_{\substack{\ell_1m_1\nu_1j_1n_{j_1}j_tn_t\\ \ell_2m_2\nu_2j_2n_{j_2}jn_j}}(-1)^{n_j}(2j_t+1)[(2\ell_1+1)(2\ell_2+1)]^{-1/2}\\&\times\begin{pmatrix}\ell_1 & 1/2 & j_1\\ -m_1 & -\nu_1 & n_{j_1}\end{pmatrix}\begin{pmatrix}\ell_2 & 1/2 & j_2\\ -m_2 & -\nu_2 & n_{j_2}\end{pmatrix}\begin{pmatrix}j_1 & j_2 & j\\ -n_{j_1} & -n_{j_2} & n_j\end{pmatrix}\begin{pmatrix}1 & j & j_t\\ m_r & -n_j & n_t\end{pmatrix}\\&\times\begin{pmatrix}J_f & J_0 & j_t\\ M_f & -M_0 & n_t\end{pmatrix}Y_{\ell_1}^{m_1}(\vec{k}_1)Y_{\ell_2}^{m_2}(\vec{k}_2)\mathcal{D}^{1/2}_{\mu_1\nu_1}(\omega_1)\mathcal{D}^{1/2}_{\mu_2\nu_2}(\omega_2)\\&\times\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(a)}.\end{aligned}\tag{C3}$$

The reduced matrix element in this case is given by [6]

$$\begin{aligned}\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(a)}={}&(-i)^{\ell_1+\ell_2}e^{\iota(\sigma_{\ell_1j_1}+\sigma_{\ell_2j_2})}(2j_1+1)(2j_2+1)(2j+1)\\&\times\sqrt{(2\ell_1+1)(2\ell_2+1)(2J_f+1)}\sum_{J_T}(2J_T+1)\begin{Bmatrix}1 & J_0 & J_T\\ J_f & j & j_t\end{Bmatrix}\\&\times\langle n_f\Lambda_f\Sigma_f\Omega_fp_f;\ell_1\ell_2;(j_1j_2)j|F(J_T)|n_0\Lambda_0\Sigma_0\Omega_0p_0;1\rangle^{(a)},\end{aligned}\tag{C4a}$$

which contains

$$\begin{aligned}&\langle n_f\Lambda_f\Sigma_f\Omega_fp_f;\ell_1\ell_2;(j_1j_2)j|F(J_T)|n_0\Lambda_0\Sigma_0\Omega_0p_0;1\rangle^{(a)}\\&\quad=\sum_{\substack{\lambda_1\sigma_1m_{j_1}m_j\\ \lambda_2\sigma_2m_{j_2}}}(-)^{m_j}\begin{pmatrix}\ell_1 & 1/2 & j_1\\ -\lambda_1 & -\sigma_1 & m_{j_1}\end{pmatrix}\begin{pmatrix}\ell_2 & 1/2 & j_2\\ -\lambda_2 & -\sigma_2 & m_{j_2}\end{pmatrix}\begin{pmatrix}j_1 & j_2 & j\\ -m_{j_1} & -m_{j_2} & m_j\end{pmatrix}\begin{pmatrix}j & J_f & J_T\\ m_j & \Omega_f & M_T\end{pmatrix}\\&\qquad\times\langle n_f\Lambda_f\Sigma_f\Omega_fp_f;\ell_1\lambda_1\sigma_1;\ell_2\lambda_2\sigma_2|\overline{F}(J_T)|n_0\Lambda_0\Sigma_0\Omega_0p_0;1\rangle^{(a)}\end{aligned}\tag{C4b}$$

and

$$\begin{aligned}&\langle n_f\Lambda_f\Sigma_f\Omega_fp_f;\ell_1\lambda_1\sigma_1;\ell_2\lambda_2\sigma_2|\overline{F}(J_T)|n_0\Lambda_0\Sigma_0\Omega_0p_0;1\rangle^{(a)}\\&\quad=\frac{1}{2}\sqrt{\frac{\hbar^2}{m}}[1+(-1)^{p_0+p_f+\ell_1+\ell_2-J_0+J_f}]\sum_{\lambda_r}(-1)^{\lambda_r}\Bigg[\begin{pmatrix}J_0 & 1 & J_T\\ \Omega_0 & \lambda_r & M_T\end{pmatrix}\\&\qquad\times\langle n_f\Lambda_f\Sigma_f\Omega_fp_f;\ell_1\lambda_1\sigma_1;\ell_2\lambda_2\sigma_2|F_p|n_0\Lambda_0\Sigma_0\Omega_0p_0;1\lambda_r\rangle+(-1)^{p_0+2\Omega_0}\begin{pmatrix}J_0 & 1 & J_T\\ -\Omega_0 & \lambda_r & M_T\end{pmatrix}\\&\qquad\times\langle n_f\Lambda_f\Sigma_f\Omega_fp_f;\ell_1\lambda_1\sigma_1;\ell_2\lambda_2\sigma_2|F_p|n_0-\Lambda_0,-\Sigma_0,-\Omega_0,p_0;1\lambda_r\rangle\Bigg].\end{aligned}\tag{C4c}$$

Each of the matrix elements in Eqs. (C3) and (C4) depends, among other things, on the energies $k_1$ and $k_2$ of the two photoelectrons.

What now remains to be done is the final calculation of the density matrix obtained after substituting photoionization matrix element (C3) and its complex conjugate in Eq. (C2). The resulting expression is simplified by the following successive operations involving (a) double application of the addition theorem (4.3.2) for RH given in Ref. [50]; (b) use of the addition theorem (4.6.5) for SH taken, for example, from Edmonds [50] two times; (c) double use of the identity (14.42) from Ref. [57]

which expresses a quaternion sum of the product of four 3-*j* symbols into a double sum of two 3-*j* and one 9-*j* symbols; (d) unitarity of the 3-*j* symbols; (e) application, once again, of the identity (14.42) from Ref [57]; and finally, (f) conversion of a triple sum of the product of three 3-*j* symbols to a product of one 3-*j* and one 6-*j* symbols using Eq. (6.2.8) from Edmonds [50].

With the help of these and some other simplifications, the density matrix which describes angle- and spin-resolved DPI of a rotating liner molecule in Hund's coupling scheme (a) on the inclusion of SDIs can finally be written in the form of Eqs. (B6a) and (B6b). However, the normalization factor $\mathcal{K}_p/[4\pi(2-\delta_{0\Lambda_0})]$ and the reduced amplitudes $\langle J_f p_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(b)}$ appropriate for Hund's case (b) and present on the right hand side of Eq. (B6b), are now to be replaced by $\mathcal{K}_p/(4\pi)$ and by those given in Eq. (C4a) suitable for using in Hund's coupling case (a).

## APPENDIX D: DENSITY MATRIX FOR DOUBLE PHOTOIONIZATION OF A ROTATING LINEAR MOLECULE INCLUDING SPIN-ORBIT PLUS SPIN-ROTATION INTERACTIONS IN HUND'S COUPLING SCHEME (a) OR SPIN-ROTATION INTERACTION IN HUND'S COUPLING SCHEME (b)

The two density matrices, whose calculations have been described in the last two Appendixes B and C, can conveniently be represented by the following single equation:

$$\langle f;\mu_1\widehat{u_1}\vec{k}_1;\mu_2\widehat{u_2}\vec{k}_2|\rho_f|f;\mu_1'\widehat{u_1}\vec{k}_1;\mu_2'\widehat{u_2}\vec{k}_2\rangle=(-1)^{\mu_1'+\mu_2'+N_{S_1}+N_{S_2}}\sum_{\substack{S_1N_{S_1}M_{S_1}\\ S_2N_{S_2}M_{S_2}}}\begin{pmatrix}1/2 & 1/2 & S_1\\ \mu_1 & -\mu_1' & N_{S_1}\end{pmatrix}$$
$$\times\begin{pmatrix}1/2 & 1/2 & S_2\\ \mu_2 & -\mu_2' & N_{S_2}\end{pmatrix}\mathcal{D}^{S_1}_{-N_{S_1}M_{S_1}}(\omega_1)\mathcal{D}^{S_2}_{-N_{S_2}M_{S_2}}(\omega_2)A^{S_1S_2}_{M_{S_1},M_{S_2}}(m_r;\vec{k}_1;\vec{k}_2),\tag{D1a}$$

with

$$A^{S_1S_2}_{M_{S_1},M_{S_2}}(m_r;\vec{k}_1;\vec{k}_2)=(-1)^{1+m_r+S_1+S_2}(2S_1+1)(2S_2+1)\mathcal{K}^{(\iota)}\sum_{\substack{p_0\ell_1\ell_1'j_1j_1'L_1J_1M_{L_1}L_rjj'\\ p_f\ell_2\ell_2'j_2j_2'L_2J_2M_{L_2}M_Jj_t}}(-1)^{\ell_1'+\ell_2'+j+j_t}(2J_1+1)(2J_2+1)$$
$$\times(2j_t+1)(2L_r+1)\sqrt{(2L_1+1)(2L_2+1)}\begin{pmatrix}\ell_1 & \ell_1' & L_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell_2' & L_2\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L_1 & S_1 & J_1\\ M_{L_1} & M_{S_1} & M_J\end{pmatrix}$$
$$\times\begin{pmatrix}L_2 & S_2 & J_2\\ M_{L_2} & M_{S_2} & -M_J\end{pmatrix}\begin{pmatrix}1 & 1 & L_r\\ m_r & -m_r & 0\end{pmatrix}\begin{pmatrix}J_1 & J_2 & L_r\\ M_J & -M_J & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & L_r\\ j & j' & j_t\end{Bmatrix}\begin{Bmatrix}\ell_1 & 1/2 & j_1\\ \ell_1' & 1/2 & j_1'\\ L_1 & S_1 & J_1\end{Bmatrix}$$
$$\times\begin{Bmatrix}\ell_2 & 1/2 & j_2\\ \ell_2' & 1/2 & j_2'\\ L_2 & S_2 & J_2\end{Bmatrix}\begin{Bmatrix}j_1 & j_2 & j\\ j_1' & j_2' & j'\\ J_1 & J_2 & L_r\end{Bmatrix}Y^{M_{L_1}}_{L_1}(\hat{k}_1)Y^{M_{L_2}}_{L_2}(\hat{k}_2)\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(\iota)}$$
$$\times\langle J_fp_f;\ell_1'\ell_2';(j_1'j_2')j'|F(j_t)|J_0p_0;1\rangle^{(\iota)*}\tag{D1b}$$

Here, the superscript $\iota=1$ or 2, such that the normalization factors $\mathcal{K}^{(1)}\equiv\mathcal{K}_p/[4\pi(2-\delta_{0\Lambda_0})]$, $\mathcal{K}^{(2)}\equiv\mathcal{K}_p/(4\pi)$, with the dynamical amplitudes $\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(1)}\equiv\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(b)}$ given in Eq. (B5) and $\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(2)}\equiv\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(a)}$ obtained from Eq. (C4). Further, similar to Appendixes A, B, and C, the matrix elements on the right hand side of Eq. (D1b) and elsewhere in the current appendix depends also upon the photoelectrons energies $k_1$ and $k_2$.

These definitions mean that in order to obtain a density matrix for the angle- and spin-resolved DPI (1) of a rotating linear molecule in Hund's coupling scheme (b) taking only the SRI into account, one should put $\iota=1$ in Eq. (D1) using the corresponding values of $\mathcal{K}^{(1)}$ and of the dynamical amplitudes $\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(1)}$ given by Eqs. (B5); whereas, $\iota=2$ in Eq. (D1) with appropriate values of $\mathcal{K}^{(2)}$ and of $\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(2)}$ [taken from Eqs. (C4)] will result in a DM for DPI in the presence of both SRI plus SOI in Hund's case (a).

On specializing the density matrix (D1) to the collinear geometry

$$\hat{k}_1(\theta_1=0,\phi_1)\ \text{ and }\ \hat{k}_2(\theta_2=\pi,\pi+\phi_1),\tag{D2}$$

we obtain

$$\begin{aligned}
&\langle f;\mu_1\widehat{u_1},\vec{k}_1;\mu_2\widehat{u_2},\vec{k}_2|\rho_f|f;\mu_1'\widehat{u_1},\vec{k}_1;\mu_2'\widehat{u_2},\vec{k}_2\rangle^{\vec{k}_1\|\widehat{OZ}}_{\vec{k}_2\|-\widehat{OZ}}\\
&\quad\equiv\langle f;\mu_1\widehat{u_1},\phi_1;\mu_2\widehat{u_2},\phi_2|\rho_f|f;\mu_1'\widehat{u_1},\phi_1;\mu_2'\widehat{u_2},\phi_2\rangle\\
&\quad=(-1)^{\mu_1'+\mu_2'+M_1+M_2}\sum_{\substack{SS_1S_2\\MM_1M_2}}\begin{pmatrix}1/2 & 1/2 & S_1\\ \mu_1 & -\mu_1' & M_1\end{pmatrix}\begin{pmatrix}1/2 & 1/2 & S_2\\ \mu_2 & -\mu_2' & M_2\end{pmatrix}\\
&\qquad\times\begin{pmatrix}S_1 & S_2 & S\\ M & -M & 0\end{pmatrix}\mathcal{D}^{S_1}_{-M_1M}(\omega_1)\mathcal{D}^{S_2}_{-M_2-M}(\omega_2)A^{S_1S_2}_S(m_r).
\end{aligned}\tag{D3a}$$

In the above equation, we have defined

$$\begin{aligned}
A^{S_1S_2}_S(m_r)&\equiv A^{S_1S_2}_S(m_r;\vec{k}_1;\vec{k}_2)^{\vec{k}_1\|\widehat{OZ}}_{\vec{k}_2\|-\widehat{OZ}}\\
&=(-1)^{1+m_r}(2S_1+1)(2S_2+1)(2S+1)\frac{\mathcal{K}^{(\iota)}}{4\pi}\sum_{\substack{p_0\ell_1\ell_1'j_1j_1'L_1J_1Ljj_t\\p_f\ell_2\ell_2'j_2j_2'L_2J_2L_rj'}}(-1)^{\ell_1'+\ell_2+j+j_t+J_1+J_2+L_1}\\
&\quad\times(2L_1+1)(2L_2+1)(2L+1)(2J_1+1)(2J_2+1)(2L_r+1)(2j_t+1)\begin{pmatrix}\ell_1 & \ell_1' & L_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\ell_2 & \ell_2' & L_2\\ 0 & 0 & 0\end{pmatrix}\\
&\quad\times\begin{pmatrix}1 & 1 & L_r\\ m_r & -m_r & 0\end{pmatrix}\begin{pmatrix}L_1 & L_2 & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}L & S & L_r\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & L_r\\ j & j' & j_t\end{Bmatrix}\begin{Bmatrix}\ell_1 & 1/2 & j_1\\ \ell_1' & 1/2 & j_1'\\ L_1 & S_1 & J_1\end{Bmatrix}\begin{Bmatrix}\ell_2 & 1/2 & j_2\\ \ell_2' & 1/2 & j_2'\\ L_2 & S_2 & J_2\end{Bmatrix}\\
&\quad\times\begin{Bmatrix}j_1 & j_2 & j\\ j_1' & j_2' & j'\\ J_1 & J_2 & L_r\end{Bmatrix}\begin{Bmatrix}L_1 & S_1 & J_1\\ L_2 & S_2 & J_2\\ L & S & L_r\end{Bmatrix}\langle J_fp_f;\ell_1\ell_2;(j_1j_2)j|F(j_t)|J_0p_0;1\rangle^{(\iota)}\\
&\quad\times\langle J_fp_f;\ell_1'\ell_2';(j_1'j_2')j'|F(j_t)|J_0p_0;1\rangle^{(\iota)*},
\end{aligned}\tag{D3b}$$

where the superscript $\iota$ has its meaning already explained elsewhere in this appendix.

In order to further simplify the above density matrix, we take

$$\omega_1(\varphi_1,\vartheta_1=\pi/2,\gamma_1=0)\ \text{ and }\ \omega_2(\varphi_2,\vartheta_2=\pi/2,\gamma_2=0).\tag{D4}$$

in Eq. (D3a). For writing the consequent simplified density matrix in a concise form, let us introduce the following notations:

$$\begin{aligned}
A_0&=-\frac{1}{2}A^{00}_0(m_r),\ \ A_{01}=\frac{1}{6}A^{01}_1(m_r),\\
A_{10}&=\frac{1}{6}A^{10}_1(m_r),\ \ A_{11}=\frac{1}{6\sqrt{6}}A^{11}_1(m_r),\\
A_p&=\frac{1}{6\sqrt{3}}\left[A^{11}_0(m_r)+\frac{1}{\sqrt{10}}A^{11}_2(m_r)\right],\\
A_m&=\frac{1}{6\sqrt{3}}\left[A^{11}_0(m_r)-\sqrt{\frac{2}{5}}A^{11}_2(m_r)\right]
\end{aligned}\tag{D5}$$

For the geometries [Eqs. (D2) and (D4)], density matrix (D1), finally becomes

$$\langle f;\mu_1\widehat{u_1}\vec{k}_1;\mu_2\widehat{u_2}\vec{k}_2|\rho_f|f;\mu_1'\widehat{u_1}\vec{k}_1;\mu_2'\widehat{u_2}\vec{k}_2\rangle^{\hat{u}_1(\vartheta_1=\pi/2,\varphi_1),\vec{k}_1\|\widehat{OZ}}_{\hat{u}_2(\vartheta_2=\pi/2,\varphi_2),\vec{k}_2\|-\widehat{OZ}}$$

$$\equiv\rho_f(\varphi_1;\varphi_2)=\begin{array}{c|cccc} \mu_1\mu_2/\mu_1'\mu_2' & \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2} \\ \hline \frac{1}{2}\frac{1}{2} & A_0+cA_p-isA_{11} & -A_{01}-cA_{11}+isA_p & -A_{10}+cA_{11}-isA_p & A_m-cA_p+isA_{11} \\ \frac{1}{2}-\frac{1}{2} & -A_{01}+cA_{11}-isA_p & A_0-cA_p+isA_{11} & A_m+cA_p-isA_{11} & -A_{10}-cA_{11}+isA_p \\ -\frac{1}{2}\frac{1}{2} & -A_{10}-cA_{11}+isA_p & A_m+cA_p-isA_{11} & A_0-cA_p+isA_{11} & -A_{01}+cA_{11}-isA_p \\ -\frac{1}{2}-\frac{1}{2} & A_m-cA_p+isA_{11} & -A_{10}+cA_{11}-isA_p & -A_{01}-cA_{11}+isA_p & A_0+cA_p-isA_{11} \end{array}. \tag{D6a}$$

The partial transpose of this density matrix is readily obtained, using relation (14), to be

$$\gamma_f(\phi_1;\phi_2)=\begin{array}{c|cccc} \mu_1\mu_2/\mu_1'\mu_2' & \frac{1}{2}\frac{1}{2} & \frac{1}{2}-\frac{1}{2} & -\frac{1}{2}\frac{1}{2} & -\frac{1}{2}-\frac{1}{2} \\ \hline \frac{1}{2}\frac{1}{2} & A_0+cA_p-isA_{11} & -A_{01}+cA_{11}-isA_p & -A_{10}+cA_{11}-isA_p & A_m+cA_p-isA_{11} \\ \frac{1}{2}-\frac{1}{2} & -A_{01}-cA_{11}+isA_p & A_0-cA_p+isA_{11} & A_m-cA_p+isA_{11} & -A_{10}-cA_{11}+isA_p \\ -\frac{1}{2}\frac{1}{2} & -A_{10}-cA_{11}+isA_p & A_m-cA_p+isA_{11} & A_0-cA_p+isA_{11} & -A_{01}-cA_{11}+isA_p \\ -\frac{1}{2}-\frac{1}{2} & A_m+cA_p-isA_{11} & -A_{10}+cA_{11}-isA_p & -A_{01}+cA_{11}-isA_p & A_0+cA_p-isA_{11} \end{array}. \tag{D6b}$$

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