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Double photoionization of rotating linear molecules

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Abstract. This communication presents a theoretical study of the angular distribution of one or both of the two electrons emitted in one-photon, one-step double ionization of a linear molecule. Experiments which do or do not detect spin of the photoelectrons have been considered. Effects of molecular rotation on double photoionization have been studied in both Hund's coupling schemes (a) and (b) by using parity-adapted states. Selection rules obtained in this paper are very different from those derived earlier for single photoionization and for Auger decay following the absorption of a photon in a rotating linear molecule. It is shown that complete specification of the spin-unresolved and of spin-resolved angular distributions of both photoelectrons require, respectively, three and seven parameters which depend, among other things, on their energies as well as directions of emission. The approach developed in this paper has been used to analyze spin-unresolved double photoionization in the $3\sigma_g^2$ shell of the N_2 molecule. The angular distribution is quite different depending on whether or not molecular rotation has been taken into account. Also, it is found to change significantly for different rotational transitions. Effects of electron-electron correlation are clearly manifested even in non-coincident, both rotationally resolved—as well as unresolved—double photoionization.

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1 Introduction

Recently developed high-resolution, angle-resolving electron spectrometers are successfully being used [1] to measure photocurrents arising from the production of diatomic ions in different rotational states of H_2^+, N_2^+, NO^+, O_2^+, etc., which have relatively large rotational constants. These spectrometers have been combined with Mott detectors [2] to study experimentally [3,4], and also theoretically [5], the effects of nuclear rotation on spin polarization of photoelectrons emitted from as heavy a molecule as HI.

Ejection of two electrons following the absorption of a single photon in an atom or molecule is the most direct manifestation of electron-electron correlation. The two photoelectrons ejected simultaneously in a single step (*i.e.*, in double photoionization) share between themselves not only the energy of the absorbed photon in excess to the ionization potential, but also the spin-orbit interaction (SOI) present in the continuum of each of the ejected electrons [6]. Since the pioneering work of Byron and Jochain [7], there have been several studies [8] of double photoionization (DPI) in atomic targets. The investigations on DPI of gaseous molecules, on the other hand, are beginning to emerge [9–11]. But none of those [9–11] communications either takes rotation of the molecular nuclei into account or analyzes spin of the ejected electrons.

Motivated by the increasing emphasis on high-resolution molecular spectroscopy with photoelectrons [1] and the importance of studying electron-electron correlation in both atoms [8] as well as in molecules [9–11], we present in this paper probably the first theoretical study of rotational state-to-state transition in DPI of linear molecules in electric dipole ($E1$) approximation. The molecular rotation has been considered in each of Hund's coupling schemes [12,13] (a) and (b) by us. Also, in order to take the symmetry properties of the target properly into account, we have represented the neutral molecular target as well as its doubly charged residual photoion by wave functions of definite parities [13,14]. The use of such parity-adapted states [13,14] determines selection rules for rotationally resolved DPI in $E1$ approximation in linear molecules. Although the formal structure of the expressions developed by us separately for Hund's schemes (a) and (b) is identical, they however have different dynamical terms and, of course, obey different selection rules. In the next Section 2, we derive an angular correlation function for spin-unresolved photocurrent produced in the DPI of a rotating linear molecule.

In order to perform a "complete" [15] DPI experiment, it is necessary that the initial reactants (in the present case, molecule AB plus the radiation field) should be in

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a selected state and the internal properties of the reaction products (*i.e.*, AB^{++} and the two photoelectrons) be analyzed. Thus a proper study of electron-electron correlation in DPI requires that the spin polarization of the two photoelectrons should also be observed, in addition to analysing their energies and angular distributions. Such spin-resolved investigations will constitute also one step forward in the direction of making a "complete" [15] experiment on DPI. But, unfortunately, it is extremely difficult to measure spin polarization of electrons. The main reason for this difficulty is that there is a significant loss (approximately by a factor of 1000 (Ref. [2])) of intensity in a Mott detector used to observe the direction of quantization of the spin of a photoelectron. Consequently, it is probably beyond the reach of the presently existing experimental facilities to measure spin polarization of electrons ejected in DPI. However, probable non-feasibility of angle- and spin-resolved DPI experiments in the near future should not deter one from studying such processes, at least theoretically, even at present. This observation is significant for several reasons.

Firstly, rotationally resolved spin polarization of electrons ejected in an $E1$ process from a gas phase diatomic molecule has already been measured successfully in several experiments [3,4] on single photoionization. Secondly, recent investigations have shown that the fragmentation patterns characterized by the energy partitioning, angular distribution, and spin polarization of photoelectrons and of Auger electrons ejected in double ionization of atoms [16,17] and of molecules [17–19] are much more complicated than those in which spins of the two outgoing electrons are not detected. Similarly, a recent theoretical study [6] of spin-resolved DPI of Yb has shown that the two ejected electrons share not only the energy of the absorbed photon in excess to the ionization potential, but also the SOI present in the continuum of each of the two photoelectrons, in addition to experiencing mutual Coulomb repulsion. Moreover, such angle- and spin-resolved studies of photoelectron-Auger electron coincidence and of DPI spectroscopy of both atomic as well as molecular targets should provide natural experimental tests for Bell's theorem [20,21] and a basis for its proposed practical application [22] in quantum cryptography. Thus, those DPI studies in both atoms and molecules which include an analysis of the spin polarization of two ejected electrons are not only a richer source of information on structure and dynamics of the target as well as on its electron-electron correlation, but also provide natural test for some of the fundamental aspects [20,21] of quantum mechanics and potential applications in a new and emerging field of quantum computation [23].

In Section 3 of this paper, we therefore derive an expression for studying correlation between angle- and spin-resolved photoelectrons ejected in DPI of a rotating linear molecule AB. The molecular rotation, even in Section 3, has been represented by parity-adapted states in Hund's coupling scheme (a) as well as (b). The correlation functions obtained in Sections 2 and 3 are, of course, quite different from each other.

The theories developed in this paper are used to study in Section 4 the angular distribution of spin-unresolved electrons ejected from $3\sigma_g^2$ shell of N_2 in its DPI in Hund's case (b). This application brings out most of the aspects of our theoretical formulation. It clearly demonstrates as to how the simultaneous ejection of a second electron changes, due to correlation effects, the angular distribution of the observed electron even in a non-coincident DPI experiment and the strong dependence of this distribution on the rotational states of N_2, N_2^{++} involved in a transition. The conclusions of this paper are contained in the last Section 5.

2 Angular correlation between spin-unresolved photoelectrons ejected in DPI

Let us consider the following process:

$$h\nu_r(|\mathbf{l}_r|=1, m_r) + AB(J_0M_0p_0) \rightarrow AB^{++}(J_fM_fp_f) + e_1(\mu_1\hat{u}_1\mathbf{k}_1) + e_2(\mu_2\hat{u}_2\mathbf{k}_2) \quad (1)$$

in a rotating linear molecule AB which belongs to one of the two point groups [13] $C_{\infty v}$ or $D_{\infty h}$. Here $|\mathbf{l}_r| = 1$ and $E_r = h\nu_r$ are, respectively, the angular momentum in $E1$ approximation and energy of the absorbed photon. The parameter m_r in equation (1) and elsewhere in this paper specifies the state of polarization of the electromagnetic radiation: $m_r = 0$ for linear polarization (LP), $m_r = +1$ for right circular polarization (RCP), and $m_r = -1$ for left circular polarization (LCP). An even mixture of RCP and LCP beams of photons is considered to be unpolarized (UP). The electromagnetic wave also defines the so-called space (or photon) frame of reference OXYZ with its origin O at the center of mass of the target molecule. The polar OZ-axis of this frame is the space quantization direction and is taken to be along the electric vector of the LP light. A RCP, LCP or UP beam, on the other hand, is incident in the direction of the OZ-axis.

Further in (1), $|J_0M_0p_0\rangle$ and $|J_fM_fp_f\rangle$ are the bound electronic states of AB with energy E_0 and of the doubly charged residual photoion AB^{++} possessing energy E_f, respectively. M_0 and M_f are the respective projections along the space quantization axis of the total angular momentum $\mathbf{J}_0$ of AB and $\mathbf{J}_f$ of AB^{++}; $|J_0M_0p_0\rangle$ state has parity p_0 [14], while p_f is that of state $|J_fM_fp_f\rangle$.

Further in equation (1), $\mathbf{k}_1[k_1, \hat{k}_1(\theta_1,\phi_1)]$ and $\mathbf{k}_2[k_2, \hat{k}_2(\theta_2,\phi_2)]$ are the propagation vectors of the photoelectrons e_1 and e_2, respectively. These two electrons are ejected simultaneously with respective energies $\varepsilon_1 = \hbar^2k_1^2/2m$ and $\varepsilon_2 = \hbar^2k_2^2/2m$. We, therefore, have $\varepsilon_1+\varepsilon_2 = h\nu_r - (E_f - E_0)$ from energy conservation. Projections μ_1 and μ_2 (with μ_1, $\mu_2 = \pm\frac{1}{2}$) of the spin angular momenta of e_1 and e_2 ejected in the DPI (1) are taken to be in the directions $\hat{u}_1(\theta_1', \phi_1')$ and $\hat{u}_2(\theta_2', \phi_2')$, respectively. Each of the two vectors $(\mathbf{k}_1, \hat{u}_1)$ for e_1 and $(\mathbf{k}_2, \hat{u}_2)$ for e_2, used in this paper, have been defined with respect to the space frame OXYZ.

The angular distribution of two spin-unresolved photoelectrons e_1 and e_2 ejected simultaneously in the process (1), is given by

$$\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1 d\hat{k}_1 d\hat{k}_2} = \frac{\mathcal{K}}{2J_0+1} \times \sum_{\substack{M_0 M_f \\ \mu_1\mu_2}} |\langle J_f M_f p_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2 | F_p | J_0 M_0 p_0; 1 m_r\rangle|^2. \quad (2)$$

Here, $\mathcal{K} = 3\pi(e^2/\alpha_0 E_r)^2$ with α_0 the dimensionless fine-structure constant. Expression (2) has been averaged over M_0 and summed over M_f. The two additional sums over μ_1 and μ_2 mean that the expression (2) is for that DPI process (1) in which spins of the photoelectrons e_1 and e_2 are not observed. Further in (2), $F_p = (m/\hbar^2)F$, where F is the photoionization operator taken from equations (7) and (8) in reference [24] in $E1$ length and velocity approximations, respectively. The definitions of the operator F and of the constant $\mathcal{K}$ used in equation (2) are in accord with Bethe and Salpeter [25] such that the expression (2), after the angular integration over $\hat{k}_1$ and $\hat{k}_2$, gives the integrated cross-section for DPI (1) in cm^2.

For further use in this paper, we need to expand the space frame photon state $|1m_r\rangle$, present in (2), in terms of the molecule frame states $|1\lambda_r\rangle$ by the relation [26]

$$|1m_r\rangle = \sum_{\lambda_r} \mathcal{D}^1_{\lambda_r m_r}(\omega)|1\lambda_r\rangle\,. \quad (3)$$

Here, $\mathcal{D}$'s are the rotational harmonics [26] with their argument $\omega(\equiv \alpha\beta\gamma)$ containing three Euler angles. The successive rotations by the angles γ, β, and α bring [26] the space frame in coincidence with the molecule frame. The latter, although concentric with the OXYZ coordinate system, has its polar axis along the molecular axis which, in the case of a linear molecule, is the line joining all the nuclei of AB.

2.1 Hund's coupling scheme (a)

2.1.1 Photoionization matrix elements

In this case, the spin-orbit coupling is strong enough so that the spin angular momentum is quantized along the molecular axis. The parity-adapted state for the molecule AB in the case (a) is given by [13,14].

$$|J_0 M_0 p_0\rangle = \frac{1}{\sqrt{2}}\big(|n_0\Lambda_0\rangle|J_0\Omega_0 M_0\rangle|S_0\Sigma_0\rangle + (-1)^{p_0}|n_0 - \Lambda_0\rangle|J_0 - \Omega_0 M_0\rangle|S_0 - \Sigma_0\rangle\big). \quad (4)$$

In this expression, Λ_0 and Σ_0 are the respective projections of the electronic orbital and spin ($\mathbf{S}_0$) angular momenta along the molecular axis. Their sum $\Omega_0 = \Lambda_0 + \Sigma_0$ is also a good quantum number in the case (a) of Hund's coupling. The letter n_0 stands for all those additional quantum numbers needed to specify the electronic state $|n_0\Lambda_0\rangle$ of AB. $|S_0\Sigma_0\rangle$ is the spin state and

$$\langle\omega|J_0\Omega_0 M_0\rangle = \sqrt{\frac{2J_0+1}{8\pi^2}}\mathcal{D}^{J_0}_{\Omega_0 M_0}(\omega) \quad (5)$$

is the normalized rotational state of the molecular target in the process (1). Replacement of the subscript "0" by "f" will render the states (4) and (5) for the residual photoion AB^{++}.

The spin-orbital for the photoelectron e_1 ejected in the DPI (1) is given by [19,27]

$$|\mu_1\hat{u}_1\mathbf{k}_1\rangle = \sqrt{\frac{\hbar^2}{m}} \sum_{\substack{l_1 m_1 n_1 \\ \lambda_1 \nu_1}} i^{l_1} e^{-i\sigma_{l_1\nu_1}} \mathcal{D}^{l_1}_{m_1 n_1}(\omega) Y^{n_1 *}_{l_1}(\hat{k}_1) \times \mathcal{D}^{\frac{1}{2}*}_{\mu_1\lambda_1}(\omega_1)\mathcal{D}^{\frac{1}{2}}_{\nu_1\lambda_1}(\omega) F^-_{l_1 m_1 \nu_1}. \quad (6)$$

Here, the space part $F^-_{l_1 m_1 \nu_1}$ satisfies the appropriate incoming wave boundary conditions [28] and also depends upon the spin variable ν_1 to take the SOI in the continuum properly into account. A rotation by the Euler angles $\omega_1(\equiv \phi_1', \theta_1', 0)$ brings the photon frame in coincidence with the direction $\hat{u}_1$ along which the spin of the photoelectron e_1 is quantized in space. A spin-orbital $|\mu_2\hat{u}_2\mathbf{k}_2\rangle$, similar to (6), can be written also for the photoelectron e_2. The total system of $(AB^{++} + e_1 + e_2)$ is now described by

$$|J_f M_f p_f; \mu_1\hat{u}_1\mathbf{k}_1; \mu_2\hat{u}_2\mathbf{k}_2\rangle \equiv |J_f M_f p_f\rangle|\mu_1\hat{u}_1\mathbf{k}_1\rangle|\mu_2\hat{u}_2\mathbf{k}_2\rangle. \quad (7)$$

This and all other molecular states used in the present communication are properly antisymmetrized.

We now substitute kets (3), (4), and (7) in the $E1$ photonization matrix element

$$\langle J_f M_f p_f; \mu_1\hat{u}_1\mathbf{k}_1; \mu_2\hat{u}_2\mathbf{k}_2|F_p|J_0 M_0 p_0; 1m_r\rangle\,.$$

It then becomes an algebraic sum of four terms each of which contains, among other things, an integral over the product of seven rotational harmonics of the type $\mathcal{D}^{J_f *}$ $\mathcal{D}^{l_1 *}$ $\mathcal{D}^{l_2 *}$ $\mathcal{D}^{\frac{1}{2}*}$ $\mathcal{D}^{\frac{1}{2}*}$ $\mathcal{D}^{J_0}$ $\mathcal{D}^1$ with Euler angles ω as their arguments. This integral can be evaluated in many ways. We will, however, like to solve it in this section of the present communication in a manner so that we are able to introduce the angular momentum $\mathbf{l}_t$ transferred between the absorbed photon and two photoelectrons observed without their spins. Our procedure is an adaptation to DPI of the coupling scheme originally proposed by Dill and Fano [29] for spin-unresolved single photoionization. The total angular momentum in the present case is

$$\mathbf{J}_T = \mathbf{l}_r + \mathbf{J}_0 = \mathbf{J}_f + (\mathbf{l}_1 + \mathbf{s}_1) + (\mathbf{l}_2 + \mathbf{s}_2)\,. \quad (8)$$

Here, $\mathbf{l}_1$ and $\mathbf{s}_1$ are the respective orbital and spin angular momenta of the photoelectron e_1, while $\mathbf{l}_2$ and $\mathbf{s}_2$ are those of the photoelectron e_2. Consequently, the angular momentum transferred is now given by

$$\mathbf{l}_t = \mathbf{l}_r - \mathbf{l}_p = \mathbf{J}_p - \mathbf{J}_0\,, \quad (9a)$$

where

$$\mathbf{J}_p = \mathbf{J}_f + \mathbf{s}_p\,, \tag{9b}$$

with the respective

$$\mathbf{l}_p = \mathbf{l}_1 + \mathbf{l}_2 \tag{9c}$$

and

$$\mathbf{s}_p = \mathbf{s}_1\left(=\frac{\mathbf{1}}{2}\right) + \mathbf{s}_2\left(=\frac{\mathbf{1}}{2}\right) \tag{9d}$$

the total orbital and spin augular momenta of the two electrons emitted in DPI (1).

In order to introduce $\mathbf{l}_t$ of equation (9a) in the present context, we first combine $\mathcal{D}^{\frac{1}{2}*}$ $\mathcal{D}^{\frac{1}{2}*}$ using the Clebsch-Gordan series [26] in 3-j symbols. The resulting expression is then coupled with $\mathcal{D}^{J_f*}$. The outcome of these two operations is then combined with $\mathcal{D}^{J_0}$. Among the three remaining rotational harmonics, the combination of $\mathcal{D}^{l_1*}$ $\mathcal{D}^{l_2*}$ is coupled with $\mathcal{D}^1$. This procedure will eventually reduce the original product of seven $\mathcal{D}$-functions into a sum of products of ten 3-j symbols and two rotational harmonics. The integral over ω is now readily performed using the orthogonality [26] of $\mathcal{D}$-functions.

A similar procedure is used to evaluate the integrals over the $\mathcal{D}$-functions contained in the three remaining terms present in the photoionization matrix element. Further simplifications yield

see equation (10) next page

Here

see equation (11a) next page

is the reduced matrix element with

see equation (11b) next page

Here we have defined

see equation (12) next page

which includes the definitions

$$|n_0\Lambda_0\rangle|J_0\Omega_0M_0\rangle|S_0\Sigma_0\rangle|1\lambda_r\rangle \equiv$$
$$|n_0\Lambda_0\Sigma_0\Omega_0p_0;1\lambda_r\rangle|J_0\Omega_0M_0\rangle$$

and

$$|n_f\Lambda_f\rangle|J_f\Omega_fM_f\rangle|S_f\Sigma_f\rangle F^-_{l_1m_1\nu_1}F^-_{l_2m_2\nu_2} \equiv$$
$$|n_f\Lambda_f\Sigma_f\Omega_f;l_1m_1\nu_1;l_2m_2\nu_2\rangle|J_f\Omega_fM_f\rangle.$$

The form (10) of the photoionization matrix element has been arrived at by using the property

$$\langle n_f,-\Lambda_f,S_f,-\Sigma_f,-\Omega_f;l_1,-m_1,-\nu_1;l_2,-m_2,\ -\nu_2$$
$$|F|n_0,-\Lambda_0,S_0,-\Sigma_0,-\Omega_0;1,-\lambda_r\rangle =$$
$$\langle n_f\Lambda_fS_f\Sigma_f\Omega_f;l_1,m_1,\nu_1;l_2m_2\nu_2|F|n_0\Lambda_0S_0\Sigma_0\Omega_0;1\lambda_r\rangle$$

applicable to linear molecules in Hund's case (a). The bracket expressions on the right-hand side of (12) are the matrix elements of the $E1$ operator. Their evaluation requires integration over the space and spin variables of all electrons involved in DPI.

2.1.2 Selection rules

In order to obtain selection rules for the DPI process (1) in the present case (a), let us analyse expressions (10) and (11) in terms of the allowed angular momenta and their projections. The 3-j symbols present in (11b) and (12) will vanish unless

$$\Omega_f \pm \Omega_0 = \lambda_r - (m_1+\nu_1) - (m_2+\nu_2)\,. \tag{13a}$$

That is, the sum or the difference of the projections of the total angular momenta of AB and of AB^{++} along the molecular axis should be equal to the difference of the projections of the angular momentum of photon and of the orbital as well as spin angular momenta of e_1 and e_2. This, in fact, is the well-known selection rule applicable to bound-bound transitions in the spectroscopy of linear molecules [12,13]. The possible rotational states of the doubly charged photoion AB^{++} which can be accessed in the DPI process (1) in an E1 approximation are given by the rule

$$|J_0-1| \le J_T \le J_0+1\,. \tag{13b}$$

Here, J_T has been defined by the equation (8).

The following important selection rule

$$l_1+l_2+J_0-J_f+p_0+p_f = \text{even} \tag{13c}$$

is obtained from the expression enclosed in the curly brackets in (12). This rule is very different from those obtained earlier for rotationally resolved state-to-state transitions in single photoionization [5,14,19,27,30] or in Auger spectroscopy [19,27] of linear molecules. According to (13c) for fixed parities p_0 of AB and p_f of AB^{++} as well as for their rotational states J_0 and J_f, respectively, the pair of electrons escaping in DPI (1) too possesses a definite parity $(-1)^{l_1+l_2}$. But neither of the photoelectrons can itself be assumed to have a definite parity. On the other hand, many pairs of l_1+l_2 may contribute to the two-electron continuum state such that l_1+l_2 is always either even or odd (*i.e.*, l_1 and l_2 have the same or opposite parities) for a given $(J_0,p_0)\to(J_f,p_f)$ transition in (1). This property is similar to that which exists [6] in DPI of atomic targets where both the initial target and the final photoion are usually in a parity eigenstate.

$$\langle J_f M_f p_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2 | F_p | J_0 M_0 p_0; 1 m_r \rangle^{(a)} = (-1)^{\Omega - \Omega_0 - M_0 - M} \sqrt{2J_0+1} \sum_{\substack{l_1 l_2 l_p \\ n_1 n_2 n_p}} \sum_{\substack{\lambda_1 \lambda_2 \\ s_p \lambda_p}} \sum_{\substack{J_p N_p \\ l_t n_t}} (-1)^{1+J_p-2\lambda_p}$$
$$\times (2l_t+1)\sqrt{(2s_p+1)(2J_p+1)}[(2l_1+1)(2l_2+1)]^{-\frac{1}{2}} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & s_p \\ -\lambda_1 & -\lambda_2 & \lambda_p \end{pmatrix} \begin{pmatrix} J_f & s_p & J_p \\ -M_f & -\lambda_p & -N_p \end{pmatrix} \begin{pmatrix} J_p & J_0 & l_t \\ N_p & -M_0 & -n_t \end{pmatrix}$$
$$\times \begin{pmatrix} l_1 & l_2 & l_p \\ -n_1 & -n_2 & n_p \end{pmatrix} \begin{pmatrix} 1 & l_p & l_t \\ m_r & -n_p & n_t \end{pmatrix} Y_{l_1}^{n_1}(\hat{k}_1) Y_{l_2}^{n_2}(\hat{k}_2) \mathcal{D}^{\frac{1}{2}}_{\mu_1,\lambda_1}(\omega_1) \mathcal{D}^{\frac{1}{2}}_{\mu_2,\lambda_2}(\omega_2) \langle J_f p_f; (l_1 l_2) l_p; s_p; J_p | F(l_t) | J_0 p_0; 1 \rangle^{(a)}. \quad (10)$$

$$\langle J_f p_f; (l_1 l_2) l_p; s_p; J_p | F(l_t) | J_0 p_0; 1 \rangle^{(a)} = (-i)^{l_1+l_2} e^{i(\sigma_{l_1 \nu_1} + \sigma_{l_2 \nu_2})}$$
$$\times (2l_p+1)\sqrt{(2l_1+1)(2l_2+1)(2s_p+1)(2J_f+1)(2J_p+1)} \sum_{J_T} (2J_T+1) \begin{Bmatrix} 1 & J_0 & J_T \\ J_p & l_p & l_t \end{Bmatrix}$$
$$\times \langle n_f \varLambda_f \varSigma_f \varOmega_f p_f; (l_1 l_2) l_p; (J_f s_p) J_p | F(J_T) | n_0 \varLambda_0 \varSigma_0 \varOmega_0 p_0; 1 \rangle \quad (11a)$$

$$\langle n_f \varLambda_f \varSigma_f \varOmega_f p_f; (l_1 l_2) l_p; (J_f s_p) J_p | F(J_T) | n_0 \varLambda_0 \varSigma_0 \varOmega_0 p_o; 1 \rangle =$$
$$\sum_{\substack{m_1 m_2 m_p \\ \nu_1 \nu_2 \nu_p M_p}} (-1)^{M_p} \begin{pmatrix} l_1 & l_2 & l_p \\ -m_1 & -m_2 & m_p \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & s_p \\ -\nu_1 & -\nu_2 & \nu_p \end{pmatrix} \begin{pmatrix} J_f & s_p & J_p \\ -\varOmega_f & -\nu_p & M_p \end{pmatrix} \begin{pmatrix} l_p & J_p & J_T \\ m_p & M_p & M_T \end{pmatrix}$$
$$\times \langle n_f \varLambda_f \varSigma_f \varOmega_f p_f; l_1 m_1 \nu_1; l_2 m_2 \nu_2 | \overline{F}(J_T) | n_0 \varLambda_0 \varSigma_0 \varOmega_0 p_0; 1 \rangle \,. \quad (11b)$$

$$\langle n_f \varLambda_f \varSigma_f \varOmega_f p_f; l_1 m_1 \nu_1; l_2 m_2 \nu_2 | \overline{F}(J_T) | n_0 \varLambda_0 \varSigma_0 \varOmega_0 p_0; 1 \rangle \equiv \frac{1}{2}\{1 + (-1)^{l_1+l_2+J_0-J_f+p_0+p_f}\} \sum_{\lambda_r} (-1)^{\lambda_r}$$
$$\times \Bigg[\begin{pmatrix} J_0 & 1 & J_T \\ \varOmega_0 & \lambda_r & M_T \end{pmatrix} \langle n_f \varLambda_f \varSigma_f \varOmega_f p_f; l_1 m_1 \nu_1; l_2 m_2 \nu_2 | F | n_0 \varLambda_0 \varSigma_0 \varOmega_0 p_0; 1 \lambda_r \rangle + (-1)^{p_0+2\varOmega_0}$$
$$\times \begin{pmatrix} J_0 & 1 & J_T \\ -\varOmega_0 & \lambda_r & M_T \end{pmatrix} \langle n_f \varLambda_f \varSigma_f \varOmega_f p_f; l_1 m_1 \nu_1; l_2 m_2 \nu_2 | F | n_0 - \varLambda_0 - \varSigma_0 - \varOmega_0; 1 \lambda_r \rangle \Bigg] , \quad (12)$$

2.1.3 Differential cross-section

We next substitute the photoionization matrix element (10) in the expression (2) for angular distribution. Sums over (μ_1, μ_2) and (M_0, M_f) can be analytically performed by using unitarity [26] of rotational harmonics and of 3-j symbols, respectively. After some additional simplifications, the final expression for rotationally resolved angular distribution of spin-unresolved photoelectrons ejected in the DPI (1) of a linear molecule in Hund's coupling scheme (a) can be written as

$$\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1 \mathrm{d}\hat{k}_1 \mathrm{d}\hat{k}_2} = \sum_{\substack{l_1 l_2 l_p \\ l'_1 l'_2 l'_p}} \sum_{s_p J_p l_t} G(1m_r; (l_1 l_2) l_p; (l'_1 l'_2) l'_p; l_t; \hat{k}_1; \hat{k}_2)$$
$$\times \langle J_f p_f; (l_1 l_2) l_p; s_p; J_p | F(l_t) | J_0 p_0; 1 \rangle^{(a)}$$
$$\times \langle J_f p_f; (l'_1 l'_2) l'_p; s_p; J_p | F(l_t) | J_0 p_0; 1 \rangle^{(a)^*}. \quad (14)$$

Here

$$G(1m_r; (l_1 l_2) l_p; (l'_1 l'_2) l'_p; l_t; \hat{k}_1, \hat{k}_2) =$$
$$(-1)^{l_1+l_2+l'_p+l_t+m_r} \frac{\mathcal{K}}{4\pi}(2l_t+1) \begin{pmatrix} 1 & 1 & L_r \\ m_r & -m_r & 0 \end{pmatrix}$$
$$\times \begin{Bmatrix} 1 & 1 & L_r \\ l_p & l'_p & l_t \end{Bmatrix} \sum_{\substack{L_1 L_2 \\ L_r}} (-1)^{L_r} \sqrt{(2L_1+1)(2L_2+1)(2L_r+1)}$$
$$\times \begin{pmatrix} l_1 & l'_1 & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l'_1 & L_1 \\ l_2 & l'_2 & L_2 \\ l_p & l'_p & L_r \end{Bmatrix} \mathcal{Y}^{L_1 L_2}_{L_r 0}(\hat{k}_1; \hat{k}_2) \quad (15)$$

is the geometrical factor containing the bipolar harmonics [31]

$$\mathcal{Y}^{A_1 A_2}_{Bb}(\hat{r}_1, \hat{r}_2) = (-1)^{A_1 - A_2 - b}\sqrt{2B+1}$$
$$\times \sum_{a_1 a_2} \begin{pmatrix} A_1 & A_2 & B \\ a_1 & a_2 & -b \end{pmatrix} Y^{a_1}_{A_1}(\hat{r}_1) Y^{a_2}_{A_2}(\hat{r}_2). \quad (16)$$

Thus in our final expression (14) for the triply differential cross-section for DPI in Hund's coupling scheme (a), the dynamical and geometrical factors are completely separated. The former are obtained from equations (11), whereas the latter is given by equation (15).

2.2 Hund's coupling scheme (b)

2.2.1 Photoionisation matrix elements

Let us consider the case when the spin-orbit coupling is weak. In this so called Hund's scheme (b) [12,13], the spin angular momentum of a molecule is quantized along the polar axis of the space frame. The parity-adapted Hund's case (b) state for AB is given by [13,14]

$$\begin{aligned}|J_0M_0p_0\rangle &= (-1)^{-N_0+S_0-M_0}\sqrt{(2J_0+1)/2}\\ &\times\sum_{M_{N_0}M_{S_0}}\begin{pmatrix}N_0 & S_0 & J_0\\ M_{N_0} & M_{S_0} & -M_0\end{pmatrix}\\ &\times[|n_0\Lambda_0\rangle|N_0\Lambda_0M_{N_0}\rangle+(-1)^{p_0}|n_0-\Lambda_0\rangle\\ &\times|N_0-\Lambda_0M_{N_0}\rangle]|S_0M_{S_0}\rangle\,. \qquad (17)\end{aligned}$$

In this expression, N_0 is the sum of the electron's orbital and nuclear rotational angular momenta with projections Λ_0 and M_{N_0} along the polar axes of the molecule and of the space frame, respectively. In the present case, $|N_0\Lambda_0M_{N_0}\rangle$ represents the nuclear rotational state (5). In Hund's scheme (b), $|S_0M_{S_0}\rangle$ is the spin state of AB with M_{S_0} the projection of S_0 along the space-fixed quantization axis. It is obvious that the state (17) includes spin-rotation interaction. An expression similar to (17) can be written also for the state $|J_fM_fp_f\rangle$ of AB^{++} by replacing the subscript "0" with "f".

In the present coupling scheme of Hund, there will not be any SOI in the continuum as well. Consequently, the spin-orbital of the photoelectron e_1 ejected in the DPI process (1) is given by [19,27]

$$\begin{aligned}|\mu_1\hat{u}_1\mathbf{k}_1\rangle &= \sqrt{\frac{\hbar^2}{m}}\sum_{\substack{l_1m_1\\ n_1\lambda_1}} i^{l_1}e^{-i\sigma_{l_1}}\\ &\times\mathcal{D}^{l_1}_{m_1n_1}(\omega)\mathcal{D}^{\frac{1}{2}*}_{\mu_1\lambda_1}(\omega_1)Y^{n_1*}_{l_1}(\hat{k}_1)|\tfrac{1}{2}\lambda_1\rangle F^{-}_{l_1m_1}\,. \qquad (18)\end{aligned}$$

Thus, unlike in the spin-orbital (6) for the photoelectron in Hund's case (a), neither the Coulomb phase σ_{l_1} nor the space part $F^{-}_{l_1m_1}$ in (18) depend upon the spin variable. Further in (18), $|\frac{1}{2}\lambda_1\rangle$ is the spin state of the photoelectron e_1 quantized along the polar axis of the space frame. One can similarly write the spin-orbital for the second electron e_2 ejected in the DPI in Hund's case (b).

The state which represents the total $(AB^{++}+e_1+e_2)$ system in the scheme (b) of Hund can be written in the following form:

see equation (19) next page

It is obtained by coupling the vector sum $\mathbf{s}_p=\mathbf{s}_1+\mathbf{s}_2$ of the spin angular momenta of e_1 and e_2 to that of AB^{++}. Here, we have defined $|n_f\Lambda_f\rangle F^{-}_{l_1m_1}F^{-}_{l_2m_2}\equiv|n_f\Lambda_f;l_1m_1;l_2m_2\rangle$, and so on.

The photoionization matrix element needed in (2) is calculated using the states (17) and (19) along with the function (5) for the nuclear states in case (b). The $E1$ matrix element then becomes an algebraic sum of four terms. Each of these terms contains, among other things, an integral over ω involving the product $\mathcal{D}^{N_f^*}$ $\mathcal{D}^{l_1^*}$ $\mathcal{D}^{l_2^*}$ $\mathcal{D}^1$ $\mathcal{D}^{N_0}$ of five rotational harmonics. In order to introduce the angular momentum transfer l_t defined by equations (9) in the present coupling scheme, we couple, using the standard methods [26], $\mathcal{D}^1$ $(\mathcal{D}^{l_1^*}$ $\mathcal{D}^{l_2^*})$ and $\mathcal{D}^{N_f^*}$ $\mathcal{D}^{N_0}$. The integrand of the product of five rotational harmonics is thus converted into sums of the products of six 3-j symbols and two rotational harmonics. After some more simplifications, performed using the identities from Racah algebra [26,31], one finds

see equation (20) next page

Here we have defined

see equation (21) next page

with

see equation (22) next page

The form (20) of the photoionization matrix element has been arrived at by using the property

$$\langle n_f,-\Lambda_f;l_1,-m_1;l_2,-m_2|F|n_0,-\Lambda_0;1,-\lambda_r\rangle =$$

$$\langle n_f\Lambda_f;l_1m_1;l_2m_2|F|n_0\Lambda_0;1,\lambda_r\rangle$$

applicable to linear molecules in the scheme (b) of Hund. The bracketed expressions on the right-hand side of (22) are the matrix elements of the $E1$ operator. Their evaluation requires integration only over the space variables of all electrons involved in the DPI (1).

2.2.2 Selection rules

The selection rules applicable to rotationally resolved DPI of a linear molecule in the present Hund's scheme are somewhat different from those obtained in the Section 2.1.2 for the case (a). For example, for the right-hand side of (22) not to vanish identically, the projection of the various angular momenta along the molecular axis now have to satisfy either of the following conditions:

$$\Lambda_f\pm\Lambda_0=\lambda_r-m_1-m_2\,. \qquad (23a)$$

$$
\begin{aligned}
|J_f M_f p_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2\rangle \; &= \frac{\hbar^2}{m} \sum_{\substack{M_{N_f} M_{S_f} \\ s_p \lambda_p \\ S_T M_{S_T}}} \; \sum_{\substack{l_1 m_1 n_1 \lambda_1 \\ l_2 m_2 n_2 \lambda_2}} i^{l_1+l_2} e^{-i(\sigma_{l_1}+\sigma_{l_2})} (-1)^{N_f+s_p-M_{N_f}-2M_{S_T}} \\
&\times \sqrt{(2s_p+1)(2S_T+1)(2J_f+1)/2} \begin{pmatrix} N_f & S_f & J_f \\ M_{N_f} & M_{S_f} & -M_f \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & s_p \\ \lambda_1 & \lambda_2 & -\lambda_p \end{pmatrix} \begin{pmatrix} S_f & s_p & S_T \\ M_{S_f} & \lambda_p & -M_{S_T} \end{pmatrix} \\
&\times \mathcal{D}^{l_1}_{m_1 n_1}(\omega) \mathcal{D}^{l_2}_{m_2 n_2}(\omega) \mathcal{D}^{\frac{1}{2}*}_{\mu_1 \lambda_1}(\omega_1) \mathcal{D}^{\frac{1}{2}*}_{\mu_2 \lambda_2}(\omega_2) Y^{n_1 *}_{l_1}(\hat{k}_1) Y^{n_2 *}_{l_2}(\hat{k}_2) |S_T M_{S_T}\rangle \\
&\times [|n_f \Lambda_f; l_1 m_1; l_2 m_2\rangle |N_f \Lambda_f M_{N_f}\rangle + (-1)^{p_f} |n_f - \Lambda_f; l_1 m_1; l_2 m_2\rangle |N_f - \Lambda_f M_{N_f}\rangle] \, . \qquad (19)
\end{aligned}
$$

$$
\begin{aligned}
\langle J_f M_f k_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2 | F_p | J_0 M_0 p_0; 1 m_r\rangle &= (-1)^{N_f - S_0 - S_f - M_0 + \Lambda_0} \sqrt{2J_0+1} \\
&\times \sum_{\substack{l_1 n_1 \lambda_1 \\ l_2 n_2 \lambda_2}} \sum_{\substack{l_p n_p \\ s_p \lambda_p}} \sum_{\substack{l_t m_t \\ J_p N_p}} (-1)^{\lambda_p + N_p - J_p} (2l_t+1) \sqrt{(2s_p+1)(2J_p+1)} [(2l_1+1)(2l_2+1)]^{-\frac{1}{2}} \\
&\times \begin{pmatrix} l_1 & l_2 & l_p \\ -n_1 & -n_2 & n_p \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & s_p \\ \lambda_1 & \lambda_2 & -\lambda_p \end{pmatrix} \begin{pmatrix} 1 & l_p & l_t \\ m_r & -n_p & m_t \end{pmatrix} \begin{pmatrix} J_f & s_p & J_p \\ M_f & \lambda_p & N_p \end{pmatrix} \begin{pmatrix} J_f & J_0 & l_t \\ N_p & M_0 & -m_t \end{pmatrix} \\
&\times \mathcal{D}^{\frac{1}{2}}_{\mu_1, \lambda_1}(\omega_1) \mathcal{D}^{\frac{1}{2}}_{\mu_2, \lambda_2}(\omega_2) Y^{n_1}_{l_1}(\hat{k}_1) Y^{n_2}_{l_2}(\hat{k}_2) \langle J_f p_f; (l_1 l_2) l_p; s_p; J_p | R(l_t) | J_0 p_0; 1\rangle^{(b)} \, . \qquad (20)
\end{aligned}
$$

$$
\begin{aligned}
&\langle J_f p_f; (l_1 l_2) l_p; s_p; J_p \mid F(l_t) \mid J_0 p_0; 1\rangle^{(b)} = \\
&\qquad (-i)^{l_1+l_2} e^{i(\sigma_{l_1}+\sigma_{l_2})} (2l_p+1) \\
&\qquad \times \sqrt{(2l_1+1)(2l_2+1)(2J_p+1)(2N_0+1)(2S_0+1)(2N_f+1)(2J_f+1)} \\
&\qquad \times \begin{Bmatrix} J_f & s_p & J_p \\ S_0 & N_f & S_f \end{Bmatrix} \begin{Bmatrix} J_p & J_0 & l_t \\ N_0 & N_f & S_0 \end{Bmatrix} \langle n_f N_f \Lambda_f p_f; (l_1 l_2) l_p | F(l_t) | n_0 N_0 \Lambda_0 p_0; 1\rangle^{(b)} \qquad (21)
\end{aligned}
$$

$$
\begin{aligned}
&\langle n_f N_f \Lambda_f p_f; (l_1 l_2) l_p | F(l_t) | n_0 N_0 \Lambda_0 p_0; 1\rangle^{(b)} = \frac{1}{2} \{1 - (-1)^{l_1+l_2+N_0+N_f+p_0+p_f}\} \\
&\times \sum_{\substack{m_1 m_2 m_p \\ \lambda_r m_t}} \begin{pmatrix} l_1 & l_2 & l_p \\ -m_1 & -m_2 & m_p \end{pmatrix} \begin{pmatrix} 1 & l_p & l_t \\ \lambda_r & -m_p & m_t \end{pmatrix} \left[\begin{pmatrix} N_f & N_0 & l_t \\ \Lambda_f & -\Lambda_0 & m_t \end{pmatrix} \langle n_f \Lambda_f; l_1 m_1; l_2 m_2 | F | n_0 \Lambda_0; 1 \lambda_r\rangle + (-1)^{p_0} \right. \\
&\left. \times \begin{pmatrix} N_f & N_0 & l_t \\ \Lambda_f & \Lambda_0 & m_t \end{pmatrix} \langle n_f \Lambda_f; l_1 m_1; l_2 m_2 | F | n_0 - \Lambda_0; 1 \lambda_r\rangle \right] \, . \qquad (22)
\end{aligned}
$$

The rotational states in which AB^{++} can be found after DPI (1) in $E1$ approximation, are given by

$$|N_0 - l_t| \le N_f \le N_0 + l_t \, , \qquad (23b)$$

where l_t is defined by equation (9a).

Yet another important selection rule

$$l_1 + l_2 + N_0 + N_f + p_0 + p_f = \text{ odd} \qquad (23c)$$

is the condition so that the matrix element (22) does not trivially vanish. This selection rule is naturally different from those obtained earlier for single photoionization [19, 27,30] and for photon-induced Auger decay [19,27] of a linear molecule rotating according to Hund's scheme (b). However, similar to Hund's case (a) selection rule (13c), we again find from (23c) that neither of the electrons e_1 and e_2 escaping in DPI can be assumed to possess a definite parity. Instead, their combined parity $(-1)^{l_1+l_2}$ is fixed for a given set of the quantum numbers (N_0, N_f, p_0, p_f). Many pairs of $l_1 + l_2$ with the same parity may contribute to DPI.

2.2.3 Differential cross-section

One can now readily obtain an expression for the triply differential cross-section for DPI in Hund's case (b) by substituting the matrix element (20) in (2) and analytically performing the sums over (μ_1, μ_2) and (M_0, M_f) using Racah algebra. The final result can be written in the following form:

$$\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1 \mathrm{d}\hat{k}_1 \mathrm{d}\hat{k}_2} = \sum_{\substack{l_1 l_2 l_p \\ l'_1 l'_2 l'_p}} \sum_{\substack{s_p J_p \\ l_t}} G(1m_r; (l_1 l_2) l_p; (l'_1 l'_2) l'_p; l_t; \hat{k}_1; \hat{k}_2) \times \langle J_f p_f; (l_1 l_2) l_p; s_p; J_p | F(l_t) | J_0 p_0; 1 \rangle^{(b)} \times \langle J_f p_f; (l'_1 l'_2) l_p; s_p, J_p | F(l_t) J_0 p_0; 1 \rangle^{(b)^*}. \quad (24)$$

Here the geometrical factor is given by equation (15). Thus we have again been able to separate the geometrical and dynamical terms. Moreover the form of the angular distribution (24) is exactly the same as derived in equation (14) in Hund's scheme (a). But the dynamical amplitudes present in (24) are, of course, different from those used in (14). While the latter are given by equation (11), the former are obtained from (21).

2.3 Analysis of the angular distribution

Two differential cross-sections (14) and (24) obtained in Hund's cases (a) and (b), respectively, can be described by a single following expression:

$$\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1 \mathrm{d}\hat{k}_1 \mathrm{d}\hat{k}_2} = \sum_{\substack{l_1 l_2 l_p \\ l'_1 l'_2 l'_p}} \sum_{\substack{s_p J_p \\ l_t}} G(1m_r; (l_1 l_2) l_p; (l'_1 l'_2) l'_p; l_t; \hat{k}_1; \hat{k}_2) \times d_{(l_1 l_2) l_p}(s_p; J_p; l_t) d^*_{(l'_1 l'_2) l'_p}(s_p; J_p; l_t). \quad (25)$$

Here, the dynamical amplitude

$$d_{(l_1 l_2) l_p}(s_p; J_p; l_t) \equiv \langle J_f p_f; (l_1 l_2) l_p; s_p; J_p | F(l_t) | J_0 p_0; 1 \rangle \quad (26)$$

is obtained from the relations (11) for the scheme (a) and from (21) for the scheme (b) of Hund. This unification of DPI in two of the four Hund's coupling schemes means that in cases (a) and (b) it can be treated on the same footing. The following analysis is therefore applicable to the DPI of a linear molecule rotating in either of these two coupling schemes.

It is obvious from the respective equations (9c) and (9d) that each of both l_p and s_p is always integer; the last of these two can be 0 and 1. For an $E1$ transition $|\mathbf{l}_r| = 1$ in equation (9a). These things, in turn, mean that the quantum numbers J_0 and J_f in equations (8) and (9a) are simultaneously either integers or half-integers. That is $|J_f - J_0| =$ integer. Hence in a rotationally resolved DPI experiment in a linear molecule only those transitions are allowed in which J_0 of AB changes by an integral amount.

Furthermore, each of the rotational quantum numbers J_0 and J_f has a finite value. This means, J_p in (9b) is also finite with values J_f, $J_f \pm 1$. That is, the angular momentum transfer l_t in (9a) too is finite, implying that l_p in that equation can take only a finite set of integral values as well. But l_1 and l_2 in (9c) can have only integral values satisfying the inequality $|l_1 - l_2| \le l_p \le l_1 + l_2$ and the requirement imposed by the selection rule either (13c) or (23c) for Hund's case (a) or (b), respectively. This means that, although for each pair of (l_1, l_2) up to three bipolar harmonics $L_r = 0$–2 may only contribute to the geometrical factor (15), both l_1 and l_2 can have a large number of values of same or different parities subject to the condition that $l_1 + l_2$ is always either even or odd.

Expression (25) for the triply differential cross-section contains an incoherent sum over the angular momentum transfer l_t defined in equation (9a). It can therefore be analyzed according to the parity-favoured and -unfavoured transitions [29]. In the present case of DPI, these transitions are respectively characterized by $+1$ and -1 values of $(-1)^{1+l_t-l_p}$. From equation (9a), $l_t = l_p$, $l_p \pm 1$. Therefore $l_t = l_p \pm 1$ correspond to parity-favoured transitions; whereas $l_t = l_p$ are parity-unfavoured transitions. For each pair of $(l_1 + l_2)$, there are $2\min(l_1, l_2) + 1$ unfavoured transitions, whereas the total number of favoured transitions is one if l_1 and l_2 are both zero, two if either l_1 or l_2 is zero, more than two if neither l_1 nor l_2 is zero. In the case of single photoionization, on the other hand, there will only be one $(l_t = l)$ parity-unfavoured and two $(l_t = l \pm 1$ if $l \neq 0)$ parity-favoured transitions, respectively, if the ejected electron is represented by the l-th partial wave. Thus, the presence of two, rather than of one, photoelectrons in continuum in DPI may considerably increase the number of both parity-favoured as well as of -unfavoured transitions. The parity-unfavoured transitions are known to reflect the influence of electron-photoion final-state interaction and have already been observed by Langer *et al.* [32] in the non-resonant single photoionization of the argon atom.

The triply differential cross-section (25) for DPI of a rotating linear molecule has a complicated structure. Several attempts [33] have been made to characterize an equivalent expression for the angular photocurrent ejected in atomic DPI by a finite number of parameters. In this paper we show that the distribution (25) can be completely determined just by three parameters in the following form:

$$\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1 \mathrm{d}\hat{k}_1 \mathrm{d}\hat{k}_2} = A_0(J_0 p_0; J_f p_f; \mathbf{k}_1; \mathbf{k}_2) + \frac{1}{2} m_r A_1(J_0 p_0; J_f p_f; \mathbf{k}_1; \mathbf{k}_2) + \frac{1}{2}(2 - 3m_r^2) A_2(J_0 p_0; J_f p_f; \mathbf{k}_1; \mathbf{k}_2) \quad (27)$$

with

$$A_0(J_0 p_0; J_f p_f; \mathbf{k}_1; \mathbf{k}_2) = \frac{\mathcal{K}}{3(4\pi)^2} \sum_{\substack{l_1 l'_1 \\ l_2 l'_2}} \sum_{\substack{l_p L \\ s_p J_p l_t}} (-1)^{l_p + L_1} (2l_t + 1) \times (2L+1)(2l_p+1)^{-1} \begin{pmatrix} l_1 & l'_1 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l'_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} l_1 & l'_1 & L \\ l'_2 & l_2 & L \end{Bmatrix} \times P_L(\hat{k}_1 \cdot \hat{k}_2) d_{(l_1 l_2) l_p}(s_p; J_p; l_t) d^*_{(l'_1 l'_2) l_p}(s_p; J_p; l_t), \quad (28a)$$

$$A_1(J_0p_0;J_fp_f;\mathbf{k}_1;\mathbf{k}_2)=\frac{\mathcal{K}}{2\pi\sqrt{2}}$$

$$\times\sum_{\substack{l_1l'_1\\l_2l'_2}}\sum_{\substack{l_pl'_p\\s_pl_t}}\sum_{\substack{L_1L_2\\J_p}}(-1)^{l_1+l_2+l_t+l'_p}(2l_t+1)\sqrt{(2L_1+1)(2L_2+1)}$$

$$\times\begin{pmatrix}l_1 & l'_1 & L_1\\0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2 & l'_2 & L_2\\0 & 0 & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & 1\\l_p & l'_p & l_t\end{Bmatrix}\begin{Bmatrix}l_1 & l'_1 & L_1\\l_2 & l'_2 & L_2\\l_p & l'_p & 1\end{Bmatrix}$$

$$\times\mathcal{Y}^{L_1L_2}_{10}(\hat{k}_1,\hat{k}_2)d_{(l_1l_2)l_p}(s_p;J_p;l_t)d^*_{(l'_1l'_2)l'_p}(s_p;J_p;l_t),\quad(28\text{b})$$

and

$$A_2(J_0p_0;J_fp_f;\mathbf{k}_1;\mathbf{k}_2)=\frac{\mathcal{K}}{2\pi\sqrt{6}}$$

$$\times\sum_{\substack{l_1l'_1\\l_2l'_2}}\sum_{\substack{l_pl'_p\\s_pl_t}}\sum_{\substack{L_1L_2\\J_p}}(-1)^{l_1+l_2+l_t+l'_p}(2l_t+1)\sqrt{(2L_1+1)(2L_2+1)}$$

$$\times\begin{pmatrix}l_1 & l'_1 & L_1\\0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_2 & l'_2 & L_2\\0 & 0 & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & 2\\l_p & l'_p & l_t\end{Bmatrix}\begin{Bmatrix}l_1 & l'_1 & L_1\\l_2 & l'_2 & L_2\\l_p & l'_p & 2\end{Bmatrix}$$

$$\times\mathcal{Y}^{L_1L_2}_{20}(\hat{k}_1,\hat{k}_2)d_{(l_1l_2)l_p}(s_p;J_p;l_t)d^*_{(l'_1l'_2)l'_p}(s_p;J_p;l_t)\,.\quad(28\text{c})$$

Thus, the price one has to pay to reduce an otherwise large number of parameters which are usually present [33] in the angular distribution of electrons ejected in DPI, to just to three is that each of (28) contains the propagation vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ of e_1 and e_2, respectively. That is the parameters now depend upon the experimental geometry. However, this dependence can be simplified and readily adapted to any configuration used in an actual experiment on DPI. Some of the geometries for which expressions (28) take particularly simpler forms are discussed hereunder:

(a) Let us observe one of the two photoelectrons, say e_2, along the polar axis of the photon frame, *i.e.*, $\hat{k}_2(0,\phi_2)$. Then each of the three coefficient A_0, A_1, and A_2 becomes independent of the azimuthal angles ϕ_1 and ϕ_2. They now contain only the Legendre polynomials [26] with their argument as cos θ_1. In this geometry, θ_1 is obviously the angle between the directions of two outgoing photoelectrons.

(b) The other experimental arrangement which not only simplifies the geometry dependence of the coefficients A_0, A_1, and A_2 present in (28), but also separates each of these into a geometrical and dynamical part is the one in which two photoelectrons are observed in a collinear configuration in opposite directions. For example, if we take $\hat{k}_1(\theta_1,\phi_1)\equiv(\theta,\phi)$, then $\hat{k}_2\|-\hat{k}_1$, *i.e.*, $\hat{k}_2(\theta_2,\phi_2)\equiv(\pi-\theta,\pi+\phi)$. The triply differential cross-section (25) in this collinear configuration becomes

$$\frac{\mathrm{d}^2\sigma(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\theta}\equiv\left.\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}\right|_{\hat{k}_2\|-\hat{k}_1}=$$

$$A_{12}(J_0p_0;J_fp_f;k_1;k_2)[1+\tfrac{1}{2}m_r\alpha_{12}P_1(\cos\theta)+\tfrac{1}{2}(2-3m_r^2)\beta_{12}P_2(\cos\theta)]\,,\quad(29)$$

where expressions for $A_{12}(J_0p_0;J_fp_f;k_1;k_2),\alpha_{12}$, and β_{12} are readily obtained from equations (27) and (28). None of the three coefficients in (29) depends upon experimental geometry. Here θ is the angle which the line joining two photoelectrons makes with the polar axis of the OXYZ coordinate system. The form (29) of the angular distribution (27) will be obtained even if e_1 and e_2 are observed in the same (*i.e.*, $\hat{k}_2\|\hat{k}_1$), rather than in opposite, direction with, of course, slightly different expressions for A_{12}, α_{12}, and β_{12}.

Thus, in a collinear experimental geometry, the angular correlation between e_1 and e_2 emitted in the process (1) is completely characterized by merely three geometry-independent parameters. Each of the parameters can readily be extracted from experimental measurements. For example, if the ionizing radiation is LP or UP, (29) reduces to

$$\frac{\mathrm{d}^2\sigma(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\sigma_1}=A_{12}(J_0P_0;J_fp_f;k_1;k_2)[1+a\beta_{12}P_2(\cos\theta_1)],\quad(30)$$

with $a=1$ for LP and $a=-1/2$ for UP radiation. This is the well-known form [34] of the angular distribution of photoelectrons ejected in single photoionization of an atom or molecule. A measurement of (30) in the magic angle direction (*i.e.*, $\theta=\theta_m=54.7°$) will immediately yield the coefficient A_{12}; whereas, a subsequent determination of (30) for a single value of θ other than θ_m will determine the angular asymmetry parameter β_{12} for DPI. The remaining parameter α_{12} can now readily be extracted by measuring (29) in the direction θ_m for RCP or LCP radiation.

(c) Let us now consider the non-coincident, angle-resolved photoelectron spectroscopy of, say, e_1 ejected in DPI. The corresponding cross-section is given by

$$\frac{\mathrm{d}^2\sigma(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\theta_1}\equiv\int\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}\mathrm{d}\hat{k}_2=(-1)^{m_r}\frac{\mathcal{K}}{4\pi}$$

$$\times\sum_{\substack{l_1l'_1l_2\\l_pl'_pL_r}}\sum_{\substack{s_pl_t\\J_p}}(-1)^{l_2+l_t}(2l_t+1)(2L_r+1)(2l_2+1)^{-1}$$

$$\times\begin{pmatrix}l_1 & l'_1 & L_r\\0 & 0 & 0\end{pmatrix}\begin{pmatrix}1 & 1 & L_r\\m_r & -m_r & 0\end{pmatrix}\begin{Bmatrix}1 & 1 & L_r\\l_p & l'_p & l_t\end{Bmatrix}\begin{Bmatrix}l_1 & l'_1 & L_r\\l'_p & l_p & l_2\end{Bmatrix}$$

$$\times d_{(l_1l_2)l_p}(s_p;J_p;l_t)d^*_{(l'_1l_2)l'_p}(s_p;J_p;l_t)P_{L_r}(\cos\theta_1)\,.\quad(31)$$

The last expression is obtained by integrating the triply differential cross-section (25) over the propagation direction $\hat{k}_2$ of the photoelectron e_2 unobserved in a non-coincident experiment on DPI.

According to the parity considerations already explained elsewhere in this article, l_1+l_2 and l'_1+l_2 must possess the same parity. This implies that both l_1 and l'_1 in a non-coincident DPI should simultaneously be either even or odd. Then, for the first 3-j symbol in (31) not to vanish identically, L_r must be even. This means that out of the three allowed values, $L_r=0$ and 2 need only be considered. Expression (31) can, consequently, be written as

$$\frac{\mathrm{d}^2\sigma_1(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\theta_1}=\frac{1}{4\pi}\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}\left[1+\frac{1}{2}(2-3m_r^2)\beta_1 P_2(\cos\theta_1)\right]. \tag{32a}$$

Here

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1} = \frac{1}{3}\mathcal{K}\sum_{\substack{l_1 l_2\\ l_p s_p}}\sum_{l_t J_p}(2l_t+1)[(2l_1+1)(2l_2+1)(2l_p+1)]^{-1} \times|d_{(l_1 l_2)l_p}(s_p;J_p;l_t)|^2 \tag{32b}$$

is the integrated photocurrent ejected in DPI and

$$\beta_1 = \left(\frac{d\sigma}{d\varepsilon_1}\right)^{-1}\mathcal{K}\sqrt{\frac{10}{3}}\sum_{\substack{l_1 l_1' l_2\\ l_p l_p' l_t}}\sum_{s_p J_p}(-1)^{l_2+l_t}(2l_t+1) \times(2l_2+1)^{-1}\begin{pmatrix} l_1 & l_1' & 2\\ 0 & 0 & 0\end{pmatrix}\begin{Bmatrix} 1 & 1 & 2\\ l_p' & l_p & l_t\end{Bmatrix}\begin{Bmatrix} l_1 & l_1' & 2\\ l_p' & l_p & l_2\end{Bmatrix} \times d_{(l_1 l_2)l_p}(s_p;J_p;l_t)d^*_{(l_1' l_2)l_p'}(s_p;J_p;l_t) \tag{32c}$$

is the angular asymmetry parameter for the photoelectron e_1 observed in a non-coincident DPI experiment.

Both of the expression (31) and (32) are formally identical to the previously [19] derived angular distribution of electrons ejected in single photoionization of linear molecules rotating in Hund's scheme (a) or (b). Moreover, the form (32a) is identical to that derived by Yang [34] for single photoionization. Furthermore, calculation of the expressions (31), (32b), and (32c) is in the angular momentum transfer scheme described in references [29] with, of course, appropriate modifications introduced in our equation (9) for DPI. This means that the non-coincident angular distribution too can be analysed in terms of parity-favoured and -unfavoured transitions [29] as well.

Thus, similar to the angle-resolved electron spectroscopy of single photoionization, the angular photocurrent in a non-coincident experiment, detecting only one of the two electrons ejected in DPI, is completely characterized by two parameters, $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$ and β_1. These can readily be extracted by measuring $\frac{\mathrm{d}^2\sigma(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\theta_1}$ first along the magic angle θ_m and then in any other direction. $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$ will depend very sensitively on the energy shared between two photoelectrons. The explicit expressions for these two parameters are given in equations (32b) and (32c) for the future as well as present study in Section 4. With the help of expression (32a–32c), one can analyze the angular distribution of electron e_1 emitted in DPI according to the procedures already used very widely for angular distribution of electron ejected in single photoionization.

3 Angular and spin correlation between electrons ejected in DPI

In the following treatment we remove the constraint imposed in the last section and assume that the two electrons freed in the DPI process (1) are detected along with a measurement of their spins. The corresponding differential cross-section

$$\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}=\frac{\mathcal{K}}{2J_0+1} \times\sum_{M_0 M_f}|\langle J_f M_f p_f;\mu_1\hat{u}_1\mathbf{k}_1;\mu_2\hat{u}_2\mathbf{k}_2|F_p|J_0 M_0 p_0;1m_r\rangle|^2 \tag{33}$$

is obtained by removing the sums over μ_1 and μ_2 present in the spin-unresolved angular correlation (2). The triply differential cross-section (33) depends also on the directions $\hat{u}_1$ and $\hat{u}_2$ in which spins of e_1 and e_2 are, respectively, quantized in the photon frame. Hence, (33) is effectively quintuple differential.

3.1 Hund's coupling scheme (a)

3.1.1 Photoionization matrix element

The states to be used to represent AB and $(AB^{++}+e_1+e_2)$ system in Hund's coupling scheme (a) have already been discussed in detail in Section 2.1.1. Those states properly take into account spin-orbit interaction in the bound electrons of AB, and of AB^{++}, as well as in the two continuum electrons e_1 and e_2. Kets (4) and (7) are, therefore, suitable to study even spin-resolved DPI in Hund's case (a).

It has also been discussed in Section 2.1.1 that the use of the kets (4) and (7) renders the photoionization matrix element $\langle J_f M_f p_f;\mu_1\hat{u}_1\mathbf{k}_1;\mu_2\hat{u}_2\mathbf{k}_2|F_p|J_0 M_0 p_0;1m_r\rangle$ into an algebraic sum of four terms each of which contains, among other things, an integral over the product $\mathcal{D}^{J_f *}$ $\mathcal{D}^{l_1 *}$ $\mathcal{D}^{l_2 *}$ $\mathcal{D}^{\frac{1}{2}*}$ $\mathcal{D}^{\frac{1}{2}*}$ $\mathcal{D}^{J_0}$ $\mathcal{D}^{1}$. Remembering that the two photoelectrons are now being observed along with their spins, the correct definition of the angular momentum transferred between unobserved reactants is now [6]

$$\mathbf{j}_t=\mathbf{l}_r-\mathbf{j}=\mathbf{J}_f-\mathbf{J}_0\,. \tag{34a}$$

Here

$$\mathbf{j}=\mathbf{j}_1+\mathbf{j}_2\,, \tag{34b}$$

with

$$\mathbf{j}_1=\mathbf{l}_1+\mathbf{s}_1 \tag{34c}$$

and

$$\mathbf{j}_2=\mathbf{l}_2+\mathbf{s}_2\,. \tag{34d}$$

The definition (34) is an adaptation to DPI of that originally introduced by one [35] of us in the context of angle- and spin-resolved studies of single photoionization of atoms and of molecules. While the total angular momentum for the process (1) is still given by equation (8), $\mathbf{j}$ in (34) is the sum of the angular momenta $\mathbf{j}_1$ and $\mathbf{j}_2$ of e_1 and e_2, respectively.

We now try to evaluate the above-mentioned integral over ω involving seven rotational harmonics according to the angular momentum coupling scheme (34b) which, probably, is most suitable for the present study of spin-resolved DPI. With this aim, we couple each one of the two $\mathcal{D}^{\frac{1}{2}*}$ to $\mathcal{D}^{l_1*}$ and $\mathcal{D}^{l_1*}$ using the Clebsch-Gordan series [26] in 3-j symbols. The results of these two couplings are combined together. The resultant so obtained after these three coupling operations is recoupled to $\mathcal{D}^1$. Finally, the remaining two ($\mathcal{D}^{J_f*}$ and $\mathcal{D}^{J_0}$) of the seven $\mathcal{D}$'s are joined together. The effect of these five successive applications of the Clebsch-Gordan series [26] is to convert the integral containing seven rotational harmonics in a sum of the product of ten 3-j symbols and two $\mathcal{D}$-functions. The integral over ω is now readily evaluated using the orthonormality [26] of $\mathcal{D}$'s.

A similar procedure is used to perform integration over ω in the three remaining terms present in the photoionization matrix element explained elsewhere in the current Section. These, and some other simplifying operations give

$$
\begin{aligned}
&\langle J_f M_f p_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2 | F_p | J_0 M_0 p_0; 1 m_r \rangle = \\
&\quad (-1)^{1+J_f+\Omega_f-\Omega_0-M_0} \sqrt{2J_0+1} \\
&\times \sum_{\substack{l_1 n_1 \lambda_1 \\ l_2 n_2 \lambda_2}} \sum_{\substack{j_1 j_2 j \\ n_{j_1} n_{j_2} n_j}} \sum_{j_t n_t} (-1)^{n_j} (2j_t+1)[(2l_1+1)(2l_2+1)]^{-\frac{1}{2}} \\
&\times \begin{pmatrix} l_1 & \frac{1}{2} & j_1 \\ -n_1 & -\lambda_1 & n_{j_1} \end{pmatrix} \begin{pmatrix} l_2 & \frac{1}{2} & j_2 \\ -n_2 & -\lambda_2 & n_{j_2} \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ -n_{j_1} & -n_{j_2} & n_j \end{pmatrix} \\
&\times \begin{pmatrix} 1 & j & j_t \\ m_r & -n_j & n_t \end{pmatrix} \begin{pmatrix} J_{f_t} & J_0 & j_t \\ M_f & -M_0 & n_t \end{pmatrix} \mathcal{D}^{\frac{1}{2}}_{\mu_1 \lambda_1}(\omega_1) \mathcal{D}^{\frac{1}{2}}_{\mu_2 \lambda_2}(\omega_2) \\
&\times Y^{n_1}_{l_1}(\hat{k}_1) Y^{n_2}_{l_2}(\hat{k}_2) \langle J_f p_f; l_1 l_2; (j_1 j_2) j | F(j_t) | J_0 p_0; 1 \rangle^{(a)}. \quad (35)
\end{aligned}
$$

Here

see equation (36a) next page

with

see equation (36b) next page

The matrix element present on the right-hand side of the last expression has already been defined in equation (12).

3.1.2 Selection rules

Physically, neither a change in the definition of the angular momentum transfer from (9) to (34) nor observation of the spins of photoelectrons should affect the selection rules applicable to DPI in Hund's case (a). One readily verify from equation (36) that all of the three selection rules (13) established in Section 2.1.2 for spin-unresolved DPI are applicable even in the present case when spins of the photoelectrons are being analysed.

3.1.3 Differential cross-section

After substituting the photoionization matrix element (35), the sums over M_0 and M_f present in (33) can be analytically performed. One can further simplify the consequent expression using some identities [31] from Racah algebra. The final form of the angular and spin-correlation function for DPI of a linear molecule rotating according to Hund's coupling scheme (a) can be written as

$$
\begin{aligned}
\frac{\mathrm{d}^3\sigma(m_r; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2)}{\mathrm{d}\varepsilon_1 \mathrm{d}\hat{k}_1 \mathrm{d}\hat{k}_1} &= \sum_{\substack{l_1 l_2 \\ l'_1 l'_2}} \sum_{\substack{j_1 j_2 j \\ j'_1 j'_2 j'}} \sum_{j_t} \\
&\times G(1 m_r; l_1 l_2; l'_1 l'_2; (j_1 j_2) j; (j'_1 j'_2) j'; j_t; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2) \\
&\times \langle J_f p_f; l_1 l_2; (j_1 j_2) j | F(j_t) | J_0 p_0; 1 \rangle^{(a)} \\
&\times \langle J_f p_f; l'_1 l'_2; (j'_2 j'_2) j' | F(j_t) | J_0 p_0; 1 \rangle^{(a)^*}. \quad (37)
\end{aligned}
$$

Here we have defined

see equation (38) next page

3.2 Hund's coupling scheme (b)

3.2.1 Photoionization matrix element

The parity-adapted state of AB in this case of Hund is still given by equation (17). But, in order to introduce the angular momentum transfer (34), the state for the $(AB^{++} + e_1 + e_2)$-system is now obtained by adding the spin angular momenta first of AB^{++} and e_1 and than the sum of these two is coupled to the spin angular momentum of e_2. Consequently, one should use the following ket to represent the particles on the right-hand side of the process (1)

see equation (39) next page

In order to obtain the photoionization matrix element needed in the angle- and spin-resolved correlation function (33), we substitute the kets (17) and (39) in $\langle J_f M_f p_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2 | F_p | J_0 p_0; 1 m_r \rangle$. This substitution will split this matrix element into a sum of four terms each of which contains, in addition to other things, an integral over the product of five rotational harmonics of the form $\mathcal{D}^{N_f*}\mathcal{D}^{l_1*}\mathcal{D}^{l_2*}\mathcal{D}^1\mathcal{D}^{N_0}$ each with its argument the set ω of Euler angles. With the aim to introducing the angular momentum transfer j_t defined in equations (34), we first couple $\mathcal{D}^{l_1*}$ and $\mathcal{D}^{l_2*}$ and their resultant to $\mathcal{D}^1$. Similarly, harmonics $\mathcal{D}^{N_f*}$ and $\mathcal{D}^{N_0}$ are combined together. These three coupling operations reduce the integral to a sum of the product of six 3-j symbols and two $\mathcal{D}$-functions. The desired evaluation of the integral over ω is now readily carried out. This procedure is repeated to perform the

$$\begin{aligned}
\langle J_f p_f; l_1 l_2; (j_1 j_2) j | F(j_t) | J_0 p_0; 1\rangle^{(a)} &= (-i)^{l_1 l_2} e^{i(\sigma_{l_1 j_1} + \sigma_{l_2 j_2})} \\
&\times (2j_1+1)(2j_2+1)(2j+1)\sqrt{(2l_1+1)(2l_2+1)(2J_f+1)} \\
&\times \sum_{J_T} (2J_T+1) \begin{Bmatrix} 1 & J_0 & J_T \\ J_f & j & j_t \end{Bmatrix} \langle n_f \Lambda_f \Sigma_f \Omega_f p_f; l_1 l_2; (j_1 j_2) j | F(J_T) | n_0 \Lambda_0 \Sigma_0 \Omega_0 p_0; 1\rangle \qquad \text{(36a)}
\end{aligned}$$

$$\begin{aligned}
\langle n_f \Lambda_f \Sigma_f \Omega_f p_f; l_1 l_2; (j_1 j_2) j | F(J_T) | n_0 \Lambda_0 \Sigma_0 \Omega_0 p_0; 1\rangle &= \sum_{\substack{m_1 \nu_1 \\ m_2 \nu_2}} \sum_{\substack{m_{j_1} m_{j_2} \\ m_j}} (-1)^{m_j} \\
&\times \begin{pmatrix} l_1 & \frac{1}{2} & j_1 \\ -m_1 & -\nu_1 & m_{j_1} \end{pmatrix} \begin{pmatrix} l_2 & \frac{1}{2} & j_2 \\ -m_2 & -\nu_2 & m_{j_2} \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ -m_{j_1} & -m_{j_2} & m_j \end{pmatrix} \begin{pmatrix} j & J_f & J_T \\ m_j & \Omega_f & M_T \end{pmatrix} \\
&\times \langle n_f \Lambda_f \Sigma_f \Omega_f p_f; l_1 m_1 \nu_1; l_2 m_2 \nu_2; | \bar{F}(J_T) | n_0 \Lambda_0 \Sigma_0 \Omega_0 p_0; 1\rangle \,. \qquad \text{(36b)}
\end{aligned}$$

$$\begin{aligned}
G(1m_r; l_1 l_2; l_1' l_2'; (j_1 j_2) j; (j_1' j_2') j'; j_t; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2) &= (-1)^{1+m_r+\mu_1+\mu_2+j+j_t}(2j_t+1) \\
&\times \mathcal{K} \sum_{\substack{L_1 M_{L_1} \\ L_2 M_{L_2}}} \sum_{\substack{S_1 M_{S_1} \\ S_2 M_{S_2}}} \sum_{\substack{J_1 J_2 \\ M_{12} L_r}} (-1)^{l_1'+l_2'+S_1+S_2} \\
&\times (2J_1+1)(2J_2+1)(2L_r+1)\sqrt{(2L_1+1)(2L_2+1)(2S_1+1)(2S_2+1)} \\
&\times \begin{pmatrix} 1 & 1 & L_r \\ m_r & -m_r & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_1' & L_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2' & L_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S_1 \\ \mu_1 & -\mu_1 & 0 \end{pmatrix} \\
&\times \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & S_2 \\ \mu_2 & -\mu_2 & 0 \end{pmatrix} \begin{pmatrix} L_1 & S_1 & J_1 \\ M_{L_1} & M_{S_1} & M_{12} \end{pmatrix} \begin{pmatrix} L_2 & S_2 & J_2 \\ M_{L_2} & M_{S_2} & -M_{12} \end{pmatrix} \begin{pmatrix} J_1 & J_2 & L_r \\ M_{12} & -M_{12} & 0 \end{pmatrix} \\
&\times \begin{Bmatrix} 1 & 1 & L_r \\ j & j' & j_t \end{Bmatrix} \begin{Bmatrix} l_1 & l_1' & L_1 \\ \frac{1}{2} & \frac{1}{2} & S_1 \\ j_1 & j_1' & J_1 \end{Bmatrix} \begin{Bmatrix} l_2 & l_2' & L_2 \\ \frac{1}{2} & \frac{1}{2} & S_2 \\ j_2 & j_2' & J_2 \end{Bmatrix} \begin{Bmatrix} j_1 & j_2 & j \\ j_1' & j_2' & j' \\ J_1 & J_2 & L_r \end{Bmatrix} \\
&\times Y_{L_1}^{M_{L_1}}(\hat{k}_1) Y_{L_2}^{M_{L_2}}(\hat{k}_2) Y_{S_1}^{M_{S_1}}(\hat{u}_1) Y_{S_2}^{M_{S_2}}(\hat{u}_2) \,. \qquad \text{(38)}
\end{aligned}$$

$$\begin{aligned}
|J_f M_f p_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2\rangle &= (-1)^{1-N_f-M_f} \frac{\hbar^2}{m} \sqrt{\frac{2J_f+1}{2}} \\
&\times \sum_{\substack{l_1 m_1 n_1 \lambda_1 \\ l_2 m_2 n_2 \lambda_2}} \sum_{\substack{M_{N_f} M_{S_f} \\ S_1 M_{S_1} \\ S_2 M_{S_2}}} i^{l_1+l_2} e^{-i(\sigma_{l_1}+\sigma_{l_2})} (-1)^{-S_2-M_{S_1}-M_{S_2}} \sqrt{(2S_1+1)(2S_2+1)} \\
&\times \begin{pmatrix} N_f & S_f & J_f \\ M_{N_f} & M_{S_f} & -M_f \end{pmatrix} \begin{pmatrix} S_f & \frac{1}{2} & S_1 \\ M_{S_f} & \lambda_1 & -M_{S_1} \end{pmatrix} \begin{pmatrix} S_1 & \frac{1}{2} & S_2 \\ M_{S_1} & \lambda_2 & -M_{S_2} \end{pmatrix} \\
&\times \mathcal{D}^{l_1}_{m_1 n_1}(\omega) \mathcal{D}^{l_2}_{m_2 n_2}(\omega) \mathcal{D}^{\frac{1}{2}*}_{\mu_1 \lambda_1}(\omega_1) \mathcal{D}^{\frac{1}{2}*}_{\mu_2 \lambda_2}(\omega_2) Y_{l_1}^{n_1 *}(\hat{k}_1) Y_{l_2}^{n_2 *}(\hat{k}_2) \\
&\times [|n_f \Lambda_f; l_1 m_1; l_2 m_2\rangle |N_f \Lambda_f M_{N_f}\rangle + (-1)^{p_f} |n_f - \Lambda_f; l_1 m_1; l_2 m_2\rangle |N_f - \Lambda_f M_{N_f}\rangle] |S_2 M_{S_2}\rangle \,. \qquad \text{(39)}
\end{aligned}$$

integration over ω present in three other terms of the photoionization matrix element mentioned earlier in this Section. After some additional simplifications, the $E1$ matrix element in the present case can be written as

$$\begin{aligned}
&\langle J_f M_f p_f; \mu_1 \hat{u}_1 \mathbf{k}_1; \mu_2 \hat{u}_2 \mathbf{k}_2 | F_p | J_0 p_0; 1 m_r \rangle = \\
&\quad (-1)^{m_r+N_f+M_f+2S_0+J_0+\Lambda_0} \sqrt{2J_0+1} \\
&\quad \times \sum_{\substack{l_1 n_1 \lambda_1 \\ l_2 n_2 \lambda_2}} \sum_{\substack{j_1 n_{j_1} \\ j_2 n_{j_2} j n_j}} \sum_{j_t n_t} (2j_t+1)[(2l_1+1)(2l_2+1)]^{-1/2} \\
&\quad \times \begin{pmatrix} l_1 & \frac{1}{2} & j_1 \\ -n_1 & -\lambda_1 & n_{j_1} \end{pmatrix} \begin{pmatrix} l_2 & \frac{1}{2} & j_2 \\ -n_2 & -\lambda_2 & n_{j_2} \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ n_{j_1} & n_{j_2} & n_j \end{pmatrix} \\
&\quad \times \begin{pmatrix} J_f & J_0 & j_t \\ -M_f & M_0 & n_t \end{pmatrix} \begin{pmatrix} j_t & 1 & j \\ -n_t & m_r & n_j \end{pmatrix} Y_{l_1}^{n_1}(\hat{k}_1) Y_{l_2}^{n_2}(\hat{k}_2) \\
&\quad \times \langle J_f p_f; l_1 l_2; (j_1 j_2 j) | F(j_t) | J_0 p_0; 1 \rangle^{(b)} \\
&\quad \times \mathcal{D}^{\frac{1}{2}}_{\mu_1 \lambda_1}(\omega_1) \mathcal{D}^{\frac{1}{2}}_{\mu_2 \lambda_2}(\omega_2) \,.
\end{aligned} \tag{40}$$

Here we have defined

$$\begin{aligned}
&\langle J_f p_f; l_1 l_2; (j_1 j_2) j | F(j_t) | J_0 p_0; 1 \rangle^{(b)} = \\
&(-i)^{l_2+l_1} e^{i(\sigma_{l_1}+\sigma_{l_2})} (2j_1+1)(2j_2+1)(2j+1) \\
&\times \sqrt{(2l_1+1)(2l_2+1)(2N_0+1)(2S_0+1)(2N_f+1)(2J_f+1)} \\
&\times \sum_{\substack{l_p s_p \\ l_t S_T}} (2l_p+1)(2l_t+1)(2s_p+1)\sqrt{2S_T+1} \\
&\times \begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & s_p \\ S_f & S_0 & S_T \end{Bmatrix} \begin{Bmatrix} 1 & l_p & l_t \\ s_p & j_t & j \end{Bmatrix} \begin{Bmatrix} N_f & N_0 & l_t \\ S_f & S_0 & s_p \\ J_f & J_0 & j_t \end{Bmatrix} \\
&\times \begin{Bmatrix} l_1 & l_2 & l_p \\ \frac{1}{2} & \frac{1}{2} & s_p \\ j_1 & j_2 & j \end{Bmatrix} \langle n_f N_f \Lambda_f; (l_1 l_2) l_p | F(l_t) | n_0 N_0 \Lambda_0 p_0; 1 \rangle^{(b)},
\end{aligned} \tag{41}$$

with the right-hand side of the last expression containing the matrix element (22)

3.2.2 Selection rules

On comparing the matrix elements (21) and (41), both calculated in Hund's scheme (b) but for two different definitions of the angular momentum transfer, one readily finds that the selection rules (23) derived earlier for DPI of a rotating linear molecule in Hund's scheme (b) are naturally applicable even in the present case.

3.2.3 Differential cross-section

We next substitute the matrix element (40) in the differential cross-section (33). After performing necessary simplifications with the help of Racah algebra, one finds that the final expression for the quintuple differential angle- and spin-correlation between two photoelectrons ejected simultaneously from a linear molecule rotating according to Hund's case (b) can be written in a form identical to (37) already derived by us for rotation of the target according to the scheme (a) of Hund. But the photoionization matrix element to be used in (37) for studying DPI in the case (b) is now given by (41). This unification shows that, similar to the spin-unresolved angular correlation already discussed elsewhere in this paper, angle- and spin-resolved DPI of a rotating linear molecule can be treated on the same footing both for Hund's case (a) or (b). The remaining discussion in the present Section 3 is therefore applicable to both of these coupling schemes.

3.3 Analysis of the spin-resolved angular distribution

Let us write, for brevity, the quintuple differential cross-section (37) in the following form:

see equation (42) next page

Here we have defined

$$\begin{aligned}
&d_{l_1 l_2}(J_f; (j_1 j_2) j; J_0; j_t) \equiv \\
&\qquad \langle J_f p_f; l_1 l_2; (j_1 j_2) j | F(j_t) | J_0 p_0; 1 \rangle
\end{aligned} \tag{43}$$

which is to be taken from equation (36) for Hund's case (a) and from equation (41) for Hund's case (b). Expression (42) has several interesting properties. Firstly, the geometrical and dynamical factors are completely separated. The former is given by equation (38), whereas the latter is obtained from (43). The geometrical factor can be written also in terms of bipolar harmonics [31] in two different manners by combining either $Y_{L_1}^{M_{L_1}}(\hat{k}_1)$ with $Y_{S_1}^{M_{S_1}}(\hat{u}_1)$ and $Y_{L_2}^{M_{L_2}}(\hat{k}_2)$ with $Y_{S_2}^{M_{S_2}}(\hat{u}_2)$ or $Y_{L_1}^{M_{L_1}}(\hat{k}_1)$ with $Y_{L_2}^{M_{L_2}}(\hat{k}_2)$ and $Y_{S_1}^{M_{S_1}}(\hat{u}_1)$ with $Y_{S_2}^{M_{S_2}}(\hat{u}_2)$.

Secondly, the correlation function (42) contains an incoherent sum over the angular momentum $\mathbf{j}_t$ defined in equation (34). Similar to the purely angular correlation (25), expression (42) for the angular- and spin-correlation too can be analysed according to the parity-favoured and -unfavoured transitions. These, in the present case, are characterized by the respective even and odd values of $1 + j_t - j$. In view of (34a), $j_t = j \pm 1$ are the favoured and $j_t = j$ are the unfavoured values of the angular momentum transfer. Then according to equation (34b), $2\min(j_1, j_2) + 1$ is the number of parity-unfavoured transitions for given j_1 and j_2; whereas, the total number of parity-favoured transitions is $2j_1 + 2$ for $j_1 = j_2 \neq 0$, etc. In the case of single photoionization, on the other hand, there will be only one (with $j_t = j$) and two (with $j_t = j \pm 1$) such transitions [35], respectively, for each j. Thus

$$\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1\mathbf{k}_1;\mu_2\hat{u}_2\mathbf{k}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}=\sum_{\substack{l_1l_2\\ l_1'l_2'}}\sum_{\substack{j_1j_2j\\ j_1'j_2'j'}}\sum_{j_t}G(1m_r;l_1l_2;l_1'l_2';(j_1j_2)j;(j_1'j_2')j';j_t;\mu_1\hat{u}_1\mathbf{k}_1;\mu_2\hat{u}_2\mathbf{k}_2)$$
$$\times d_{l_1l_2}(J_f;(j_1j_2)j;J_0;j_t)d^*_{l_1'l_2'}(J_f;(j_1'j_2')j';J_0;j_t)\,. \qquad (42)$$

the presence of two, rather than of one, photoelectrons has considerably increased the number of both parity-favoured as well as -unfavoured transitions contributing to DPI (1).

Another interesting point about (42) is that its form is identical to that already derived by one of us [6] for angle- and spin-resolved DPI in atomic targets. The geometrical factor (38) exactly coincides with equation (9b) of reference [6]. The dynamical factors are, of course, different for atomic and molecular targets. This unification of DPI in rotating linear molecules with that of atoms could be possible because we have represented both AB and AB^{++} in the present paper by parity-adapted states [13,14]. The rest of the discussion in this section on spin-resolved DPI of rotating linear molecules is similar to the treatment presented in reference [6] for the same process in atomic targets.

It is obvious from equation (34c, 34d) that each of j_1 and j_2 is half-integer, implying that j in (34b) is an integer. Consequently, j_t in (34a) is also an integer. This, in turn, means that each of J_0 and J_f, in addition to being finite, is simultaneously either integer or half-integer. Hence, similar to the case of spin-unresolved DPI discussed in Section 2 in this paper, the total angular momentum J_0 of AB can change only by an integral amount. Also, j_t too can take only a finite number (given by $2\min(J_0,J_f)+1$) of integral values. Consequently, on account of the triangular condition $\Delta(|\mathbf{l}_r|=1,j,j_t)$, j is both integer as well as finite. Hence j_1 and j_2 can take only half-integral values compatible with the inequalities (34c) and (34d), $l_1=j_1\pm\frac{1}{2}$ and $l_2=j_1\pm\frac{1}{2}$, respectively. Thus once j_1 and j_2 are known, the partial waves l_1 and l_2 of the photoelectron e_1 and e_2 are automatically known. In conclusion, (38) has $Y_{S_1}^{M_{S_1}}(\hat{u}_1)$ and $Y_{S_2}^{M_{S_2}}(\hat{u}_2)$ for S_1, $S_2=(0,1)$ but a large number of both $Y_{L_1}^{M_{L_1}}(\hat{k}_1)$ and $Y_{L_2}^{M_{L_2}}(\hat{k}_2)$, with $|l_1-l_1'|\le L_1\le l_1+l_1'$ and $|l_2-l_2'|\le L_2\le l_2+l_2'$ respectively, will be present in this geometrical factor.

The angular correlation function for spin-unresolved DPI can be determined also by summing (42) over μ_1 and μ_2. The triply differential cross-section so obtained will in principle be the same as derived in equation (25) in this paper. But the two expressions will have different structure for the simple reason that while the former will correspond to the angular momentum transfer (34), the latter is based on the definition (9). It has already been discussed elsewhere in this paper that the definition (9) is more suitable for spin-unresolved DPI.

The quintuple differential cross-section (42) is extremely complicated. Its analysis will become simpler if it can be parameterized. One of the possible methods to achieve this goal is to write (42) in the following form:

$$\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}=(-1)^{\mu_1+\mu_2}$$
$$\times\sum_{\substack{S_1S_2\\ S_TM}}\begin{pmatrix}\frac{1}{2}&\frac{1}{2}&S_1\\ -\mu_1&\mu_2&0\end{pmatrix}\begin{pmatrix}\frac{1}{2}&\frac{1}{2}&S_2\\ -\mu_1&\mu_2&0\end{pmatrix}$$
$$\times A^{S_1S_2}_{S_TM}(m_r;\mathbf{k}_1;\mathbf{k}_2)\mathcal{Y}^{S_1S_2}_{S_TM}(\hat{u}_1,\hat{u}_2)\,. \qquad (44)$$

Here $\mathcal{Y}$'s are the bipolar harmonics [31] obtained by combining $Y_{S_1}^{M_{S_1}}(\hat{u}_1)$ and $Y_{S_2}^{M_{S_2}}(\hat{u}_2)$ in (42). A straightforward comparison between (42) and (44) will immediately give an expression for the coefficients $A^{S_1S_2}_{S_TM}$. Correlation (44) is completely characterised by sixteen independent parameters which depend upon the experimental configuration through the propagation vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. Expressions for all these parameters are readily derived in terms of $A^{S_1S_2}_{S_TM}$ obtained from equation (42). Each of the sixteen parameters can be analysed in terms of parity-favoured and -unfavoured transitions.

In the remaining part of this Section, we briefly consider some of the important and useful geometries in which the complicated expression (42) (or (44)) takes particularly simpler forms.

a) Let us take both e_1 and e_2 polarized longitudinally along their respective direction of propagation, *i.e.*, $\hat{u}_1\|\hat{k}_1$ and $\hat{u}_2\|\hat{k}_2$. This means that one can make in the geometrical factor (38) the replacement

$$Y_{L_1}^{M_{L_1}}(\hat{k}_1)Y_{S_1}^{M_{S_1}}(\hat{u}_1)\to Y_{L_1}^{M_{L_1}}(\hat{k}_1)Y_{S_1}^{M_{S_1}}(\hat{k}_1)=$$
$$\sum_{A_1a_1}\sqrt{\frac{(2L_1+1)(2S_1+1)(2A_1+1)}{4\pi}}$$
$$\times\begin{pmatrix}L_1&S_1&A_1\\ 0&0&0\end{pmatrix}\begin{pmatrix}L_1&S_1&A_1\\ M_{L_1}&S_{S_1}&a_1\end{pmatrix}Y_{A_1}^{a_1}(\hat{k}_1) \qquad (45)$$

for the photoelectron e_1 and a similar one for the product $Y_{L_2}^{M_{L_2}}(\hat{k}_2)Y_{S_2}^{M_{S_2}}(\hat{u}_2)$ for the photoelectron e_2. Then the sums over (M_{L_1},M_{S_1}) and over (M_{L_2},M_{S_2}) present in (38) are readily performed using unitarity [26] of 3-j symbols. The geometrical factor, after these operations reduces to a form which is considerably simpler than that given in equation (38). The new form of the geometrical factor so obtained is particularly suitable for studying angular distribution of longitudinally polarized electrons in DPI in the two following photon-propagation and electron-detection configurations.

i) Let us observe one, say e_2, of the two longitudinally polarised photoelectrons along the polar axis of the photon frame, *i.e.*, $\hat{k}_2(\theta_2 = 0, \phi_2)$. The quintuple differential cross-section now becomes a series

$$\frac{\mathrm{d}^3\sigma(m_r;\mu_1,\mu_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\theta_1} \equiv \left.\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}\right|_{\substack{\hat{u}_1\|\hat{k}_1\\ \hat{u}_2\|\hat{k}_2\\ \hat{k}_2\|\hat{z}}} = \sum_{J_1} A_{J_1}(m_r;\mu_1k_1;\mu_2k_2)P_{J_1}(\cos\theta_1) \qquad (46)$$

in Legendre polynomials. The argument θ_1 of Legendre polynomials is the angle between e_1 and e_2. The photoelectron e_2 in expression (46) is, however, always observed along the polar axis of the photon frame. Expression for the coefficient A_J in terms of the dynamical quantities can readily be obtained and the values of J_1 contributing to (46) can be determined [6] by using the triangular and other conditions needed to be satisfied by various 3-j, 6-j, and 9-j symbols present in (38).

ii) The other convenient experimental geometry for the detection of two longitudinally polarized photoelectrons is to observe them in opposite directions. The correlation function for the spin-resolved DPI in this collinear experimental arrangement is completely characterised by three geometry-independent parameters as

$$\frac{\mathrm{d}^3\sigma^{\|}(m_r;\mu_1,\mu_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\theta} \equiv \left.\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_2\mathrm{d}\hat{k}_2}\right|_{\substack{\hat{u}_1\|\hat{k}_1\\ \hat{u}_2\|\hat{k}_2\\ \hat{k}_1\|\hat{k}\\ \hat{k}_2\|-\hat{k}}} = A - 2m_rB\cos\theta + \frac{1}{2}(2-3m_r^2)CP_2(\cos\theta)\,. \qquad (47)$$

Here, $\hat{k} = (\theta,\phi)$ with θ the angle between the polar axis for the space frame and the line joining two oppositely moving photoelectrons. Detailed expressions for the parameters A, B and C present in (47) can readily be derived, if needed. The correlation between longitudinally polarised e_1 and e_2 in this collinear geometry is completely determined by a single parameter A for all states $|J_0M_0p_0\rangle$ of AB and $|J_fM_fp_f\rangle$ of AB^{++} if the ionizing radiation is LP/UP and the photoelectrons depart from the target in opposite directions at the magic angle $\theta = \theta_m$. The remaining parameters B and C too are extracted by experimentally measuring (47) first for RCP/LCP radiation with $\theta = \theta_m$ and then with LP/UP light with $\theta \neq \theta_m$. Angular correlation between two longitudinally polarised e_1 and e_2 moving in the same direction will also be described by equation (47) but expressions for A, B, and C will naturally be different from those when they are moving in opposite directions.

b) One may also simplify a DPI experiment by analyzing spin correlation between angle resolved, say, electron e_1 but integrated photocurrent of e_2. The correlation function for such an experiment is given by

$$\frac{\mathrm{d}^2\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1} \equiv \int \frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}\mathrm{d}\hat{k}_2 = \frac{1}{2}\frac{\mathrm{d}^2\sigma_1(m_r;\mu_1\hat{u}_1)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1} + f_{12}(m_r;\mu_1\hat{u}_1\mathbf{k}_1;\mu_2\hat{u}_2)\,, \qquad (48)$$

where the last result has been obtained by using (44). Thus non-observation of the direction of ejection of e_2 has split the correlation function (44) into two distinct terms. In (48), $\mathrm{d}^2\sigma_1(m_r;\mu_1\hat{u}_1)/\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1$ is the angle- and spin-resolved photocurrent due to e_1 ejected in DPI (1) but derived without simultaneous detection of the electron e_2. This expression is thus applicable to non-coincident experiments on angle- and spin-resolved DPI. It has been discussed further in detail in equation (52). The function f_{12}, present on the right-hand side of (48) depends upon the propagation vector $\hat{k}_1$ of e_1 as well as on the spin quantization directions $(\hat{u}_1,\hat{u}_2)$ of the two photoelectrons. This function obviously represents the contribution to the DPI due to analysis of the spin of the photoelectron e_2 whose direction of departure from the target molecule is not detected.

c) Complications present in (48) can be further reduced if one does not detect the propagation direction even of e_1. This pure spin correlation function is given by

$$\frac{\mathrm{d}^2\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1} \equiv \int \frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2 \equiv \frac{1}{4}\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}\big\{1 - 2m_r[\mu_1\gamma_1\cos\theta_1' + \mu_2\gamma_2\cos\theta_2'] + 4\mu_1\mu_2[\gamma_{10}P_1(\hat{u}_1\cdot\hat{u}_2) + m_r\gamma_{11}\sin\theta_1'\sin\theta_2'\sin(\phi_1'-\phi_2') + (3m_r^2-2)\gamma_{12}(\sin\theta_1'\sin\theta_2'\cos(\phi_1'-\phi_2') - 2\cos\theta_1'\cos\theta_2')\big\}. \qquad (49)$$

The form of this distribution is exactly identical to that obtained by us to describe purely spin correlation in DPI of atoms [6] or between a photo-Auger electron pair [17–19] from atomic and molecular targets. Thus, in addition to the spin-unresolved integrated cross-section $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$ for DPI, one needs five additional parameters $(\gamma_1,\gamma_2,\gamma_{10},\gamma_{11},\gamma_{12})$ for complete specification of pure spin-correlation between two electrons ejected simultaneously from a linear molecule rotating according to Hund's coupling scheme either (a) or (b). None of these dynamical parameters involve experimental geometry. Expressions for each of these in terms of the photoionization amplitude (43) can readily be obtained. The following properties of the correlation (49) can be studied even without a knowledge of those expressions.

i) The spin-resolved, integrated photocurrents measured in a non-coincident experiment on DPI are respectively given by

$$\frac{\mathrm{d}\sigma_1(m_r;\mu_1\hat{u}_1)}{\mathrm{d}\varepsilon_1}=\sum_{\mu_2}\frac{\mathrm{d}\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1}=$$
$$\frac{1}{2}\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}(1-2m_r\mu_1\gamma_1\cos\theta_1') \tag{50a}$$

and

$$\frac{\mathrm{d}\sigma_2(m_r;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1}=\sum_{\mu_1}\frac{\mathrm{d}\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1}=$$
$$\frac{1}{2}\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}(1-2m_r\mu_2\gamma_2\cos\theta_2')\,, \tag{50b}$$

when either e_1 or e_2 is only detected, respectively. Thus for the complete specification of each of the non-coincident currents (50), one needs only two parameters, one of these $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$ is the spin-unresolved integrated cross-section for DPI. However, when the spin orientations of both of the photoelectrons are measured simultaneously the number of parameters in (49) increases from two to six. The spin of two electrons departing from AB interact with each other affecting their mutual orientations in space. This interference effect between the quantization directions of e_1 and e_2 is represented by three parameters γ_{10}, γ_{11}, and γ_{12} in equation (49). These may therefore be called three spin-interference parameters.

ii) It is obvious from equation (50) that for non-coincident integrated photocurrents measured in DPI to depend upon the spin of the observed electron, the ionizing radiation in (1) should be neither LP nor UP. This result is the same as those obtained for spin-resolved integrated Auger current [18,19] produced in the decay of a vacancy created by the absorption of electromagnetic radiation and for integrated photocurrent [5,35–37] emitted in single photoionization. The spin correlation function (49), on the other hand, does nor become independent of spin even for the absorption of a LP or UP photoionization. Thus, in order to study the correlation between the orientations of the spins of two photoelectrons emitted in DPI, without detecting their directions of propagation, only CP light need not be used. The simultaneously measured integrated current of both photoelectrons emitted by the absorption of LP or UP light may also depend upon the orientations of the spin of e_1 and e_2 due to two $(\gamma_{10},\gamma_{12})$ of the three spin-interference parameters present in equation (49).

In order to extract the six parameter occurring in (49) and for studying the degree of simultaneous spin polarisation of both e_1 and e_2, one can use the procedure already described in detail in reference [18] for photo-Auger electrons coincidence spectroscopy of molecules.

d) We have already discussed in the Introduction to this paper that due to the reduction [2] in the intensity by order of magnitude of an electron beam in a Mott detector, measurements of the spin orientation of two electrons moving in continuum in DPI are difficult to perform. Consequently, an experiment which is much simpler compared to those already discussed by us in a)-c) in this Section will be the one in which one, say e_1, of the two photoelectrons emitted in the DPI (1) is detected with its spin while the other (*i.e.*, e_2) is observed without its spin. The correlation between angle- and spin-resolved e_1 but only angle-resolved e_2 is given by

$$\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}\equiv\sum_{\mu_2}\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}=$$
$$\frac{1}{2}\frac{\mathrm{d}^3\sigma(m_r)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}+g_{12}(m_r;\mu_1\hat{u}_1\hat{k}_1;\hat{k}_2)\,. \tag{51}$$

In this last expression, obtained by analytically summing (42) over μ_2, $\mathrm{d}^3\sigma(m_r)/\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2$ is the angular correlation function (25) between the spin-unresolved e_1 and e_2 emitted in DPI (1). This correlation has already been discussed in detail in Section 2 of the present paper.

Thus the correlation between an angle- and spin-resolved photoelectron and an angle-resolved photoelectron, both of which are ejected simultaneously in DPI (1), is described by pure angular correlation between them plus another function that arises due to the analysis of the spin of one of the two ejected electrons. A study of the correlation (51) is certainly easier than those discussed earlier in this Section. The angular correlation $\mathrm{d}^3\sigma(m_r)/\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2$, the first term on the right-hand side of (51), between two unpolarized photoelectrons has already been calculated theoretically for example by Rouzo [10] for DPI of H_2. The results of such spin-unresolved studies can directly be used in equation (51) as well. A further calculation of g_{12} will be sufficient to describe the correlation (51) theoretically. Alternatively, the difference in the measured values of $\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1)/\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2$ and of $\mathrm{d}^3\sigma(m_r)/\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2$, will immediately give the experimental value of g_{12} which represents the influence of the detection of the spin of e_1 on its angular correlation with spin-unresolved e_2.

e) The next experiment, in the increasing order of simplicity but with further loss of information, will be the non-coincident measurement of the angle- and spin-resolved photocurrent of, say, e_1 while the second electron e_2 remains unobserved. Cross-section for this spectroscopy is given by

$$\frac{\mathrm{d}^2\sigma_1(m_r;\mu_1\hat{u}_1)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1}=\sum_{\mu_2}\int\frac{\mathrm{d}^3\sigma(m_r;\mu_1\hat{u}_1;\mu_2\hat{u}_2)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1\mathrm{d}\hat{k}_2}\mathrm{d}\hat{k}_2\,.$$

After substituting (44) in the above expression, one can analytically perform integration and sum over $\hat{k}_2$ and μ_2, respectively. After some complicated use of Racah algebra, we find

$$
\begin{aligned}
\frac{\mathrm{d}^2\sigma_1(m_r;\mu_1\hat{u}_1)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1} &= (-1)^{\frac{1}{2}+\mu_1+m_r}\\
&\times\mathcal{K}\sum_{\substack{l_1 l'_1 l_2\\ j_1 j'_1 j_2}}\ \sum_{\substack{j j' j_t\\ L_1 S_1}}\ \sum_{J_1 M_1}(-1)^{l'_1+j_1-j_2+j+j'+j_t+S_1+J_1}\\
&\times\quad(2j_t+1)(2J_1+1)\sqrt{(2L_1+1)(2S_1+1)}\\
&\times\quad[(2l_2+1)(2j_2+1)]^{-1}\\
&\times\begin{pmatrix} l_1 & l'_1 & L_1\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}\frac{1}{2} & \frac{1}{2} & S_1\\ \mu_1 & -\mu_1 & 0\end{pmatrix}\begin{pmatrix} L_1 & S_1 & J_1\\ M_1 & -M_1 & 0\end{pmatrix}\\
&\times\begin{pmatrix} 1 & 1 & J_1\\ m_r & -m_r & 0\end{pmatrix}\begin{Bmatrix} 1 & 1 & J_1\\ j & j' & j_t\end{Bmatrix}\begin{Bmatrix} j & j' & j_1\\ j' & j & j_2\end{Bmatrix}\begin{Bmatrix} l_1 & \frac{1}{2} & j_1\\ l'_1 & \frac{1}{2} & j'_1\\ L_1 & S_1 & J_1\end{Bmatrix}\\
&\times d_{l_1 l_2}(J_f;(j_1 j_2)j;J_0;j_t)d^*_{l'_1 l_2}(J_f;(j'_1 j_2)j';J_0;j_t)\\
&\times Y_{L_1}^{M_1}(\hat{k}_1)Y_{S_1}^{-M_1}(\hat{u}_1)\,. \qquad (52a)
\end{aligned}
$$

In (52a), $J_1 = 0$-2; $S_1 = 0, 1$; $L_1 = 0$-3. But, according to the selection rules discussed elsewhere in this paper, $l_1 + l_2$ and $l'_1 + l_2$ must have same parities. This, in turn, means that l_1 and l'_1 must simultaneously be either even or odd. Since, according to the first 3-j symbol occurring in (52a) $l_1 + l'_1 + L_1 =$ even, *i.e.*, L_1 must be even. Hence, the allowed values of L_1 are 0 and 2. The distribution (52a) can now be written as

$$
\begin{aligned}
\frac{\mathrm{d}^2\sigma_1(m_r;\mu_1\hat{u}_1)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1} &= \frac{1}{8\pi}\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}\\
&\Big\{1+\tfrac{1}{2}(2-3m_r^2)\beta_1 P_2(\cos\theta_1) - 2m_r\mu_1\gamma_1\cos\theta'_1 + 2m_r\mu_1\\
&[P_2(\cos\theta_1)\cos\theta'_1 + \tfrac{1}{2}P_1(\cos\theta_1)\sin\theta'_1\cos(\phi_1-\phi'_1)]\delta_1\\
&+\frac{2}{3}(3m_r^2-2)\mu_1\xi_1 P_2^1(\cos\theta_1)\sin\theta'_1\sin(\phi_1-\phi'_1)\Big\}\,. \qquad (52b)
\end{aligned}
$$

Either or both of the expressions (52) are formally identical to those derived earlier [5,35,37] for angle- and spin-resolved single photoionization of atomic and molecular targets and for [6] non-coincident DPI of atoms. This formal equivalence between (52) and those derived elsewhere [5,6,35,37] is, however, an expected result. This means that the analysis of angle- and spin-resolved photoelectron spectroscopy developed in references [5,6,35], and [37] becomes exactly applicable even in the present case.

Expression (52b) means that the spin-resolved angular photocurrent in a non-coincident experiment on DPI of linear molecules rotating according to Hund's coupling scheme either a) or b) is completely characterized by five geometry-independent parameters $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$, β_1, γ_1, δ_1, and ξ_1. The detailed expressions for each of these parameters are not relevant for the discussion presented further in this paper and have, therefore, not been given herein. These are, however, exactly the same as those derived elsewhere [6]. With the help of those [6] expressions and using the procedure of references [5,6,35] and [37] on can readily analyze the spin-resolved non-coincident photocurrent ejected in DPI of a rotating linear molecule.

f) Finally, let us consider the simplest possible experiment which can be performed in DPI involving spin analysis of photoelectrons, namely the measurement of the non-coincident, spin-resolved integrated photocurrent. For electron e_1, it is given by

$$\sigma_1(m_r;\mu_1\hat{u}_1) = \int\frac{\mathrm{d}^2\sigma_1(m_r;\mu_1\hat{u}_1)}{\mathrm{d}\varepsilon_1\mathrm{d}\hat{k}_1}\mathrm{d}\hat{k}_1\,.$$

This yields an expression identical to that given in equation (50a). The parameter γ_1 present therein is the same as that occurring in (52b). Its explicit form is

$$
\begin{aligned}
\gamma_1 &= (-1)^{\frac{1}{2}}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}\right)^{-1}\frac{\mathcal{K}}{4\pi}\sum_{\substack{l_1 l_2\\ j_2 j_t}}\ \sum_{\substack{j_1 j'_1\\ j j'}}(-1)^{l_1+j_2+j+j'+j_t}\\
&\times(2j_t+1)[(2l_1+1)(2l_2+1)(2j_2+1)]^{-1}\\
&\times\begin{Bmatrix} l_1 & \frac{1}{2} & j_1\\ 1 & j'_1 & \frac{1}{2}\end{Bmatrix}\begin{Bmatrix} j_1 & j_2 & j\\ j' & 1 & j'_1\end{Bmatrix}\begin{Bmatrix} 1 & 1 & 1\\ j & j' & j_1\end{Bmatrix}\\
&\times d_{l_1 l_2}(J_f;(j_1 j_2)j;J_0;j_t)d^*_{l_1 l_2}(J_f;(j'_1 j_2)j';J_0;j_t)\,. \qquad (53a)
\end{aligned}
$$

with

$$
\begin{aligned}
\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1} &= \frac{1}{3}\mathcal{K}\sum_{\substack{l_1 l_2 j\\ j_1 j_2 j_t}}(2j_t+1)\\
&\quad\times[(2l_1+1)(2l_2+1)(2j_1+1)(2j_2+1)(2j+1)]^{-1}\\
&\quad\times|d_{l_1 l_2}(J_f;(j_1 j_2)j;J_0 l j_t)|^2\,. \qquad (53b)
\end{aligned}
$$

The degree of spin polarization of the non-coincident integrated current of photoelectron e_1 is

$$
\begin{aligned}
&P_1(m_r;\hat{u}_1) =\\
&\qquad\frac{\sigma_1(m_r;\frac{1}{2}\hat{u}_1)-\sigma_1(m_r;-\frac{1}{2}\hat{u}_1)}{\sigma_1(m_r;\frac{1}{2}\hat{u}_1)+\sigma_1(m_r;-\frac{1}{2}\hat{u}_1)} = -m_r\gamma_1\cos\theta'_1. \qquad (54)
\end{aligned}
$$

Thus, in order to have a non-zero degree of spin polarization in a non-coincident experiment on DPI, it is necessary that the absorbed photon be CP and the detected electron be spin-resolved in other than x-y plane. This degree is then proportional to a single parameter γ_1. These and other similar properties of the spin-resolved, integrated, non-coincident photocurrent ejected in DPI of a rotating linear molecule are identical to those found to exist in single photoionization [5,35–37] of atoms and molecules, non-coincident DPI of atoms [6], as well as in the Auger spectroscopy [18,19,27].

4 Application

Let us consider, as an example for the application of the framework developed in the preceding sections, DPI in the

$3\sigma_g^2$ shell of N_2, that is

$$h\nu_r + \mathrm{N}_2\left(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^{2 1}\,\Sigma_g^+\right) \to$$
$$\mathrm{N}_2^{++}\left(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 3\sigma_g^{0 1}\,\Sigma_g^+\right)$$
$$+e_1(\mu_1\hat{u}_1\mathbf{k}_1) + e_2(\mu_2\hat{u}_2\mathbf{k}_2)\,. \tag{55}$$

There are several reasons for choosing N_2 as a test case in this, probably the first, study of DPI of a rotating linear molecule. Firstly, N_2 is relatively a "light" molecule. It thus possesses a comparatively "large" rotational constant. Its rotationally resolved photoelectron spectrum has been investigated in several $(m+n)$-REMPI studies [1]. Recently, Ohrwall and Baltzer [38] have performed experiments on angular distribution of electrons ejected in single photoionization of $3\sigma_g^2$ shell of N_2, leaving the photoion N_2^+ in different rotational states. In this experiment [38], rotationally resolved both integrated cross-section σ and angular asymmetry parameter β have been measured. Therefore a comparison of the angle- and rotationally resolved photoelectron spectrum recorded in a non-coincident experiment on DPI in the $3\sigma_g^2$ shell of N_2 with that of its single ionization [38] will be a direct measure of the role played by electron-electron correlation on the angular distribution of the detected photoelectron (e_1, say). In particular, $\sigma_1(\equiv \mathrm{d}\sigma_1/\mathrm{d}\varepsilon_1)$ and β_1 specify, according to equation (32a), the angular distribution of a single photoelectron detected in a non-coincident experiment on DPI. Comparison of these (σ_1 and β_1) parameters with σ and β measured by Ohrwall and Baltzer [38] for single photoionization in the $3\sigma_g^2$ shell of N_2 will give the above-mentioned information for any given rotational transition.

Secondly, both N_2 and N_2^{++} are in their ${}^1\Sigma_g^+$ state, each with a closed-shell electronic configuration. Therefore bound electrons neither in N_2 nor in N_2^{++} contribute to the SOI. The spin polarization of both electrons ejected in the DPI process (55) will therefore be caused by the SOI in the continuum of each of the photoelectrons e_1 and e_2. But its contribution to a light molecules like N_2 will be negligibly small. We have therefore not analyzed the spin of electrons ejected in the process (55) in N_2.

In equation (55), both N_2 and N_2^{++} have Λ_0, $\Lambda_f = 0$ with S_0, $S_f = 0$. This means [14] that the parities of these species are p_0, $p_f = 0$. Also, Hund's coupling scheme b) obviously becomes most suitable [13] in the present application. The reduced dipole amplitudes (26) needed for the process (55) are then obtained from equation (21). The triangular conditions to be satisfied by the various angular momenta present in the two 6-j symbols on the right-hand side of equation (21) give $s_p = 0$, $J_0 = N_0$, and J_p, $J_f = N_f$. Equations (26), (21) and (22) now give

$$d_{(l_1 l_2)l_p}(0;N_f;l_t) = \frac{1}{2}\left[1-(-1)^{l_1+l_2+N_0+N_f}\right]$$
$$\times(-i)^{l_1+l_2}e^{i(\sigma_{l_1}+\sigma_{l_2})}(2l_p+1)\sqrt{(2l_1+1)(2l_2+1)(2N_f+1)}$$
$$\times\begin{pmatrix} N_0 & N_f & l_t \\ 0 & 0 & 0 \end{pmatrix}\sum_{\substack{m_1 m_2 \\ \lambda_r}}\begin{pmatrix} l_1 & l_2 & l_p \\ -m_1 & -m_2 & \lambda_r \end{pmatrix}\begin{pmatrix} 1 & l_p & l_t \\ \lambda_r & -\lambda_r & 0 \end{pmatrix}$$
$$\times\langle n_f 0; l_1 m_1; l_2 m_2|F|n_0 0; 1\lambda_r\rangle\,. \tag{56}$$

This provides us with the selection rule $l_1+l_2+N_0+N_f =$ odd, which agrees with that obtained from equation (23c) for an application to the process (55).

In order to proceed further, we need to know the $E1$ amplitudes present on the right-hand side of (56). If one neglects the core relaxation effects by assuming that the one-electron orbitals of N_2 not directly involved in the photoionizing transition (55) remain unchanged, then N_2 can be treated as a two-electron system. Its anti-symmetrized bound electronic state is then given by

$$\langle x_1, x_2|n_0 0\rangle = \frac{1}{\sqrt{2}}3\sigma_g^2(\mathbf{r}_1,\mathbf{r}_2)[\alpha(1)\beta(2)-(1\rightleftharpoons 2)]. \tag{57a}$$

In this expression, x_1 and x_2 represent space and spin coordinates of the two electrons occupying the $3\sigma_g^2$ shell of N_2. The spatial part of the state (57a) is described by the product

$$3\sigma_g^2(r_1;r_2) = \frac{1}{r_1 r_2}\left(\sum_{n_1=0}^{\text{even}} P(3\sigma_g;n_1;r_1)Y_{n_1}^0(\hat{r}_1)\right)$$
$$\times\left(\sum_{n_2=0}^{\text{even}} P(3\sigma_g;n_2;r_2)Y_{n_2}^0(\hat{r}_2)\right) \tag{57b}$$

of two one-electron orbitals. Here, P's are the radial functions of a $3\sigma_g$ orbital of N_2. In the expression (57b), we have used single centre expansion of the molecular bound orbital. These are about the centre of mass of the molecule. On account of the gerade character of the $3\sigma_g$ orbital of N_2 being photoionized in (55), both of the summation indices n_1 and n_2 in (57b) take only even integral values; whereas the angular parts Y_l^m present in (57b) are those which correspond to the projection of the orbital angular momentum of each electron to be zero along the internuclear axis of N_2. Also, in equation (57a), α and β are two spinors.

The anti-symmetrized state of two photoelectrons is

$$\langle x_1, x_2|l_1 m_1, l_2 m_2\rangle = \frac{1}{2}[\langle\mathbf{r}_1|l_1 m_1\rangle\langle\mathbf{r}_2|l_2 m_2\rangle$$
$$+(1\rightleftharpoons 2)][\alpha(1)\beta(2)-(1\rightleftharpoons 2)]\,, \tag{58a}$$

with

$$\langle\mathbf{r}_1|l_1 m_1\rangle \equiv F^-_{l_1 m_1}(\mathbf{r}_1) = \frac{1}{r}P^-(\varepsilon_1 l_1 m_1;r_1)Y_{l_1}^{m_1}(\hat{r}_1) \tag{58b}$$

and a similar expression for $\langle \mathbf{r}_2 | l_2 m_2 \rangle$. In equation (58b), $P^{-}(\varepsilon_1 l_1 m_1; r_1)$ represents the radial part of the spatial function of the photoelectron e_1 in (55). A minus sign on P means that it satisfies the incoming wave boundary conditions [28] appropriate for photoionization. It is normalized on the energy scale such that

$$\int_0^\infty P^{-*}(\varepsilon_1' l_1 m_1; r_1) P^{-}(\varepsilon_1 l_1 m_1; r_1) \mathrm{d}r_1 = \delta(\varepsilon_1 - \varepsilon_1') \,.$$

This normalization is consistent with the definition of the $E1$ operator given in reference [24] and with that of the constant $\mathcal{K}$ used in equation (2) and elsewhere in this paper. Moreover, on account of the cylindrical nature of the nuclear field in a linear molecule, the radial function in (58b) depends upon the projection m_1 of the orbital angular momentum of e_1 along the inter-nuclear axis. Also, we know from equations (6) and (7) in reference [24] that in the dipole length approximation

$$\langle n_f 0; l_1 m_1; l_2 m_2 | F | n_0 0; 1\lambda_r \rangle = A^{(1)} \sqrt{\frac{4\pi}{3}} \left\langle l_1 m_1; l_2 m_2 \left| \sum_{i=1}^{2} r_i Y_1^{\lambda_r}(\hat{r}_i) \right| n_0 0 \right\rangle , \tag{59a}$$

with

$$A^{(1)} = \left(\frac{4\pi}{3} \alpha_0^3 E_r^3 / e^4 \right)^{\frac{1}{2}} \,. \tag{59b}$$

One now substitutes the states (57) and (58) in (59) and simplifies the resulting expression using Racah algebra. The final expression for $\langle n_f 0; l_1 m_1; l_2 m_2 | F | n_0 0; 1\lambda_r \rangle$ so obtained is then used in (56). This procedure gives us the desired expression for the reduced amplitude of DPI in the following form:

$$\begin{aligned} d_{(l_1 l_2) l_p}(0; N_f; l_t) &= \frac{1}{2} [1 - (-1)^{l_0 + l_f + N_0 + N_f}] \\ &\times (2l_p + 1) \sqrt{2N_f + 1} \begin{pmatrix} N_0 & N_f & l_t \\ 0 & 0 & 0 \end{pmatrix} \sum_{\lambda_r} \begin{pmatrix} 1 & l_p & l_t \\ \lambda_r & -\lambda_r & 0 \end{pmatrix} \\ &\times \left[\begin{pmatrix} l_1 & l_2 & l_p \\ -\lambda_r & 0 & \lambda_r \end{pmatrix} I(\varepsilon_2 l_2) I_d(\varepsilon_1 l_1 \lambda_r) \right. \\ &\left. + \begin{pmatrix} l_1 & l_2 & l_p \\ 0 & -\lambda_r & \lambda_r \end{pmatrix} I(\varepsilon_1 l_1) I_d(\varepsilon_2 l_2 \lambda_r) \right] . \end{aligned} \tag{60}$$

Here

$$I(\varepsilon l) = (-i)^l e^{i\sigma_l} \sqrt{2l+1}\, I'(\varepsilon l) \,, \tag{61a}$$

with

$$I'(\varepsilon l) = \int_0^\infty P^{-*}(\varepsilon l 0; r) P(3\sigma_g; l; r) \mathrm{d}r \tag{61b}$$

in the overlap integral between the radial function of bound electron occupying the $3\sigma_g$ shell of N_2 before ionization, and that of a photoelectron. The radial functions present in the integral on the right-hand side of (61b) are defined in equations (58b) and (57b), respectively. On the other hand

$$\begin{aligned} I_d(\varepsilon l \lambda_r) &= (-i)^l e^{i\sigma_l} (-1)^{\lambda_r} (2l+1) A^{(1)} \\ &\times \sum_{n=0}^{\text{even}} \sqrt{2n+1} \begin{pmatrix} l & 1 & n \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & 1 & n \\ \lambda_r & -\lambda_r & 0 \end{pmatrix} I_d'(\varepsilon l \lambda_r; n), \end{aligned} \tag{62a}$$

where

$$I_d'(\varepsilon l \lambda_r; n) = \sqrt{2} A^{(1)} \int P^{-*}(\varepsilon l \lambda_r; r) r P(3\sigma_g; n; r) \mathrm{d}r \tag{62b}$$

is the one-electron radial dipole integral.

In view of the bound-state wave function (57b), l in the overlap integral (61) and n in the dipole integral (62) are always even. However, on account of the first 3-j symbol present in (62a), l in the dipole integral (62b), on the other hand, has to be odd. This, in turn, implies that $l_1 + l_2$ is always odd in the reduced amplitude (60). Consequently, satisfaction of the selection rule $l_1 + l_2 + N_0 + N_f =$ odd, applicable in the present study, requires that $N_0 + N_f$ must always be even. That is, N_0 and N_f are either odd or even simultaneously. Thus, in the DPI process (55), one has a transition from an even rotational state of N_2 to an even rotational state of N_2^{++}, or between odd rotational states of these two species. But transitions connecting even to odd or odd to even rotational states of N_2 and N_2^{++}, respectively, are not allowed in $E1$ approximation. The $E1$ selection rules even → even, odd → odd, even ↛ odd, and odd ↛ even rotational transitions will, in fact, be applicable to DPI in σ_g orbital of all those linear molecules which have a centre of symmetry, *i.e.*, belong to the $D_{\infty h}$ point group.

Let us consider only the first three, *i.e.*, *s*-, *p*-, and *d*-partial waves to represent photoelectrons in the continuum. We then have from (61)

$$\begin{aligned} I(\varepsilon 0) &= e^{i\sigma_0} I'(\varepsilon_0) \,, \\ I(\varepsilon 1) &= 0 \,, \\ I(\varepsilon 2) &= -e^{i\sigma_2} \sqrt{5} I'(\varepsilon 2) \end{aligned} \tag{63a}$$

for the overlap integrals. The dipole integrals (62) for these three partial waves are given by

$$\begin{aligned} I_d(\varepsilon 0 \lambda_r) &= 0 \,, \\ I_d(\varepsilon 2 \lambda_r) &= 0 \,, \\ I_d(\varepsilon 1 \lambda_r) &= -e^{i\sigma_l} (-1)^{\lambda_r} \Big[I_d'(\varepsilon 1 \lambda_r; 0) \\ &\quad + \frac{2}{\sqrt{5}} (2 - 3\lambda_r^2) I_d'(\varepsilon 2 \lambda_r; 2) \Big] \,. \end{aligned} \tag{63b}$$

The permitted combinations of (l_1, l_2) in the present example are $(l_1, l_2) = (0,1)$, $(1,0)$, $(1,2)$, and $(2,1)$. Because $N_0 + N_f$ must always be even, then according to the first 3-j symbol present on the right-hand side of the dipole amplitude (60), one must always have l_t even, otherwise

$d_{(l_1l_2)l_p}(0;N_f;l_t)$ vanishes identically. Therefore, in the present case we have $l_t = 0, 2$, and 4 in expression (60) for the reduced dipole amplitude. For these values of (l_1, l_2), l_p, and of l_t, one needs to consider the following reduced amplitudes out of those given by (60):

$$d_{(01)1}(0;N_f;0) = (-1)^{N_f} g_1(\varepsilon_2) I(\varepsilon_1 0)\delta_{N_0N_f}\,,$$

$$d_{(01)1}(0;N_f;2) = \sqrt{\frac{2(2N_f+1)}{5}} \begin{pmatrix} N_0 & N_f & 2 \\ 0 & 0 & 0 \end{pmatrix} f(\varepsilon_2) I(\varepsilon_1 0),$$

$$d_{(12)1}(0;N_f;0) = (-1)^{N_f} \sqrt{\frac{2}{5}} f(\varepsilon_1) I(\varepsilon_2 2)\delta_{N_0N_f}\,,$$

$$d_{(12)1}(0;N_f;2) = \frac{1}{5}\sqrt{2N_f+1} \begin{pmatrix} N_0 & N_f & 2 \\ 0 & 0 & 0 \end{pmatrix} g_2(\varepsilon_1) I(\varepsilon_2 2)\,,$$

$$d_{(12)3}(0;N_f;2) = \frac{1}{5}\sqrt{2N_f+1} \begin{pmatrix} N_0 & N_f & 2 \\ 0 & 0 & 0 \end{pmatrix} g_3(\varepsilon_1) I(\varepsilon_2 2)\,,$$

$$d_{(12)3}(0;N_f;4) = 2\sqrt{\frac{2N_f+1}{15}} \begin{pmatrix} N_0 & N_f & 4 \\ 0 & 0 & 0 \end{pmatrix} f(\varepsilon_1) I(\varepsilon_2 2). \quad (64)$$

The reduced matrix elements (60) for $(l_1, l_2) = (1, 0)$ and (2,1) are obtained by interchanging ε_1 and ε_2 in the expressions (64) which contain d's for $(l_1, l_2) = (0, 1)$ and (1,2). In relations (64) we have defined

$$\begin{aligned} f(\varepsilon_i) &= I_d(\varepsilon_i 11) - I_d(\varepsilon_i 10)\,, \\ g_1(\varepsilon_i) &= I_d(\varepsilon_i 10) + 2I_d(\varepsilon_i 11)\,, \\ g_2(\varepsilon_i) &= 2I_d(\varepsilon_i 10) + I_d(\varepsilon_i 11)\,, \\ g_3(\varepsilon_i) &= 3I_d(\varepsilon_i 10) + 4I_d(\varepsilon_i 11)\,. \end{aligned} \quad (65)$$

Here I_d's are obtained from equations (63b). For the values of $l_t = 0, 2$, and 4 three possible transitions from the N_0th rotational state of N_2 to the N_fth rotational state of N_2^{++} in the DPI process (55) are $\Delta N \equiv N_f - N_0 = 0, \pm 2$, and ± 4.

With the help of reduced dipole amplitudes (64), one can study angular correlation between photoelectrons emitted simultaneously from the $3\sigma_g^2$ shell of N_2 accompanied with rotational $N_0 \to N_f$ transition $\Delta N = 0, \pm 2$, and ± 4. It can be done in any geometry or experimental arrangement, some of which have been discussed briefly in Section 2.3. Similarly one can take the photon absorbed in equation (55) of any polarization. However, for the reasons mentioned at the beginning of the present Section, we calculate hereafter only the parameters $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$ and β_1, which give, according to equations (32), the angular photocurrent of electron e_1 observed for a $N_0 \to N_f$ transition in non-coincident experiment on DPI (55) of N_2 performed without detecting the photoelectron e_2.

i) $N_0 \to N_f = N_0 \pm 4\,.$

For this transition we have

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1} = (2N_f+1)\frac{4\mathcal{K}}{525}\begin{pmatrix} N_0 & N_f & 4 \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{\substack{i,\,j\,=\,1 \\ i \neq j}}^{2} |f(\varepsilon_i)I(\varepsilon_j 2)|^2, \quad (66a)$$

$$\beta_1 = \frac{1}{35}\,\frac{5+7\rho_4}{1+\rho_4}\,, \quad (66b)$$

with

$$\rho_4 = |d_{(12)3}(0;N_f;4)|^2/|d_{(21)3}(0;N_f;4)|^2 = $$
$$|f(\varepsilon_1)I(\varepsilon_2 2)|^2/|f(\varepsilon_2)I(\varepsilon_1 2)|^2\,. \quad (66c)$$

It is obvious from (66b) and functions (65) that $\beta_1 = \frac{1}{7}$ for $\rho_4 = 0$, *i.e.*, when either the dipole integrals $I_d(\varepsilon_1 10) = I_d(\varepsilon_1 11)$ for the p-wave of the observed photoelectron e_1 or the overlap integral $I(\varepsilon_2 2)$ for the d-wave of the unobserved e_2 vanishes. On the other hand, if the dipole integrals $I_d(\varepsilon_2 10)$ and $I_d(\varepsilon_2 11)$ for the p-wave of the unobserved photoelectron e_2 become equal, or the overlap integral $I(\varepsilon_1 2) = 0$ for the observed e_1, *i.e.*, $\rho_4 = \infty$, the asymmetry parameter β_1 then increases to $\frac{1}{5}$. Thus the angular distribution of photoelectrons observed in non-coincident DPI of $3\sigma_g^2$ shell of N_2 with rotational transition $\Delta N = \pm 4$ does not change much with energy and has asymmetry parameter $\frac{1}{7} \leq \beta_1 \leq \frac{1}{5}$ always.

ii) $N_0 \to N_f = N_0 \pm 2\,.$

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1} = (2N_f+1)\frac{\mathcal{K}}{3}\begin{pmatrix} N_0 & N_f & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{\substack{i,\,j\,=\,1 \\ i \neq j}}^{2} \left\{ \left[\frac{2}{9}|f(\varepsilon_i)I(\varepsilon_j 0)|^2 \right.\right.$$
$$\left. + \frac{1}{15}\left(\frac{1}{3}|g_2(\varepsilon_i)|^2 + \frac{1}{7}|g_3(\varepsilon_i)|^2\right)|I(\varepsilon_j 2)|^2 \right]$$
$$\left. + \frac{2}{175}\begin{pmatrix} N_0 & N_f & 4 \\ 0 & 0 & 0 \end{pmatrix}^2 |f(\varepsilon_i)I(\varepsilon_j 2)|^2 \right\}, \quad (67a)$$

$$\frac{1}{\mathcal{K}}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}\right)\beta_1 = (2N_f+1)\begin{pmatrix} N_0 & N_f & 2 \\ 0 & 0 & 0 \end{pmatrix}^2$$
$$\times \left\{ \frac{2}{135}|f(\varepsilon_1)I(\varepsilon_2 0)|^2 + \frac{1}{1350} \right.$$
$$\times \left(\frac{1}{5}|g_2(\varepsilon_1)I(\varepsilon_2 2)|^2 + |g_2(\varepsilon_2)I(\varepsilon_1 2)|^2\right)$$
$$+ \frac{4}{525}\left(\frac{1}{5}|g_3(\varepsilon_1)I(\varepsilon_2 2)|^2 + 2|g_3(\varepsilon_2)I(\varepsilon_1 2)|^2\right)$$
$$+ \frac{2}{1875}(g_2(\varepsilon_1)g_3^*(\varepsilon_1) + \mathrm{cc})|I(\varepsilon_2 2)|^2$$
$$\left. + \frac{2}{39375}(g_2(\varepsilon_2)g_3^*(\varepsilon_2) + \mathrm{cc})|I(\varepsilon_1 2)|^2 \right\}$$
$$+ \frac{4}{525}(2N_f+1)\begin{pmatrix} N_0 & N_f & 4 \\ 0 & 0 & 0 \end{pmatrix}^2$$
$$\times \left(\frac{1}{5}|f(\varepsilon_1)I(\varepsilon_2 2)|^2 + \frac{2}{7}|f(\varepsilon_2)I(\varepsilon_1 2)|^2\right). \quad (67b)$$

Obviously, the last term on the right-hand side of each of the two expression (67) will contribute if $|N_0 - N_f| \le 4 \le N_0 + N_f$. Thus, in a $N_0 = 0 \to N_f = 2$, or vice versa, transition, three will not be any contributions to (67) from the terms containing $\begin{pmatrix} N_0 & N_f & 4 \\ 0 & 0 & 0 \end{pmatrix}$. Even otherwise, if one neglects, in some suitable approximation, the presence of these terms both from (67a) and (67b) then β_1 for $\Delta N = \pm 2$ transitions becomes independent of the rotational quantum numbers N_0 and N_f. Therefore, β_1, in general, should have a weak dependence on N_0 and N_f in $\Delta N = \pm 2$ transitions in non-coincident DPI (55). In equation (67b) and elsewhere in this paper, letters cc mean complex conjugate of the immediately preceding expression.

Let us represent photoelectron by $(l_1, l_2) = (0, 1)$ and (1, 0) partial waves. Then a combination of (67a) and (67b) yields

$$\beta_1 = \frac{1}{5}\frac{1}{1+\rho_2}\,, \tag{68a}$$

where

$$\rho_2 = \left|\frac{f(\varepsilon_2) I(\varepsilon_1 0)}{f(\varepsilon_1) I(\varepsilon_2 0)}\right|^2 . \tag{68b}$$

On taking $\rho_2 = 0$, *i.e.*, p-wave dipole integrals for the unobserved photoelectron e_2, $I_d(\varepsilon_2 11) = I_d(\varepsilon_2 10)$, or the overlap integral $I(\varepsilon_1 0) = 0$ for the observed photoelectron, one finds $\beta_1 = \frac{1}{5}$. This is the well-known value of the angular asymmetry parameter calculated theoretically [39–42] for single photoionization in a σ_g^2 shell of a $D_{\infty h}$ molecule when the photoelectron is represented by a p-partial wave and a $\Delta N = \pm 2$ rotational transition takes place. One further obtains from (68) that $\beta_1 = 0$ for $\rho_2 = \infty$, *i.e.*, the p-wave dipole integrals $I_d(\varepsilon_1 11) = I_d(\varepsilon_1 10)$ for the observed photoelectron e_1, or $I(\varepsilon_2 0) = 0$ for the unobserved photoelectron e_2. Therefore, if one represents the two photoelectrons ejected in DPI of $3\sigma_g^2$ shell of N_2 by $(l_1, l_2) = (0, 1)$ and (1, 0) partial waves, then the asymmetry parameter for observing the photoelectron e_1 in a non-coincident experiment is always given by $0 \le \beta_1 \le \frac{1}{5}$. This result applies to all $N_0 - N_f \equiv \Delta N = \pm 2$ transitions, whatever may be the initial and final rotational quantum numbers N_0 and N_f, respectively. Thus the non-coincident angular distribution in DPI can not be more anisotropic than the corresponding angular photocurrent ejected in single photoionization. The parameter β_1 becoming equal to 1/5, which is the value obtained [39–42] in single photoionization, means that the correlation between the two electrons ejected in DPI completely vanishes when $\rho_2 = 0$. The larger the value of ρ_2, the stronger the correlation between two photoelectrons, the smaller β_1 becomes. Inclusion of partial waves $(l_1, l_2) = (1, 2)$ and (2, 1) (or higher) in the expression (67) may give β_1 greater then 1/5.

In conclusion, one may say, that for $\Delta N = \pm 2$ transitions in DPI of $3\sigma_g^2$ shell of N_2, the angular asymmetry parameter β_1 for a non-coincident experiment will never exceed the value 1/5 (calculated [39–42] in single photoionization) if the two photoelectrons are represented by $(l_1, l_2) = (0, 1)$ and (1,0) partial waves. It (β_1) becomes less then 1/5 due only to the electron-electron correlation. Thus, ρ_2 defined by the relation (68b) is a measure of the correlation effects in this case. On the other hand, $\beta_1 > 1/5$ implies the presence of both higher than s and p partial waves as well as the contribution of electron-electron correlation effects.

iii) $N_0 \to N_f = N_0 (\Delta N = 0)$.

For this rotationally elastic transition, we find

see equation (69a) next page

and

see equation (69b) next page

If one represents each of the two photoelectrons e_1 and e_2 by s and p partial waves (*i.e.*, $(l_1, l_2) = (0, 1)$ and $(1, 0)$) and considers the $N_0 = 0 \to N_f = 0$ rotational transition, relations (69) then give

$$\beta_1 = \frac{2}{1+\rho_0}\,, \tag{70a}$$

with

$$\rho_0 = \frac{|g_1(\varepsilon_2) I(\varepsilon_1 0)|^2}{|g_1(\varepsilon_1) I(\varepsilon_2 0)|^2} = \frac{|[I_d(\varepsilon_2 10) + 2I_d(\varepsilon_2 11)] I(\varepsilon_1 0)|^2}{|[I_d(\varepsilon_1 10) + 2I_d(\varepsilon_1 11)] I(\varepsilon_2 0)|^2} . \tag{70b}$$

It has earlier been shown [39–42] for $0 \to 0$ rotational transition in single photoionization in σ_g shell of a $D_{\infty h}$ molecule that $\beta = 2$ if the photoelectron is represented only by a p-wave. But in the present case we find from equations (70) that $0 \le \beta_1 \le 2$. That is, electron-electron correlation in non-coincident DPI of $3\sigma_g^2$ shell of N_2 tends to reduce the value of the asymmetry parameter β_1 for $0 \to 0$ rotational transition compared to that $(\beta = 2)$ found [39–42] for single photoionization. This happens if the photoelectrons in DPI are represented by s and p partial waves and in single photoionization by p-wave only. In the latter case, the value of β for the $N_0 = 0 \to N_f = 0$ transition has not been found [39–42] to change much from 2 even on the inclusion of higher than p partial waves; even for other $\Delta N = 0$ transitions with $N_0 > 0$, β was shown [39–42] to be about 2 whether the photoelectron is represented by a single p-wave or additional higher partial waves. But in the present case of non-coincident DPI, β_1 has probably a stronger dependence on partial waves higher than p. It is therefore expected that values of β_1 for $\Delta N = 0$ transition in non-coincident DPI should be quite different without and with the inclusion of higher than p partial waves.

iv) If we substitute the $E1$ matrix element (60) in (32b, 32c), we see that both $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$ and β_1 will depend on N_0 and N_f only through $(2N_f + 1)\begin{pmatrix} N_0 & N_f & l_t \\ 0 & 0 & 0 \end{pmatrix}^2$ for allowed values of the pair (l_1, l_2). The sum of this expression over N_f is well known [26] to be unity. Accordingly, we get

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1} = \frac{1}{3}\mathcal{K} \sum_{\substack{i,j=1\\ i\neq j}}^{2} \left\{\frac{1}{9}|g_1(\varepsilon_i)I(\varepsilon_j 0)|^2 + \frac{2}{25}|f(\varepsilon_i)I(\varepsilon_j 2)|^2 + (2N_0+1)\begin{pmatrix} N_0 & N_0 & 2\\ 0 & 0 & 0\end{pmatrix}^2 \right.$$
$$\times \left[\frac{2}{9}|f(\varepsilon_i)I(\varepsilon_j 0)|^2 + \frac{1}{75}\left(\frac{1}{3}|g_2(\varepsilon_i)|^2 + \frac{1}{7}|g_3(\varepsilon_i)|^2\right)|I(\varepsilon_j 2)|^2\right.$$
$$\left.+\frac{12}{315}(2N_0+1)\begin{pmatrix} N_0 & N_0 & 4\\ 0 & 0 & 0\end{pmatrix}^2 |f(\varepsilon_i)I(\varepsilon_j 2)|^2\right\} \tag{69a}$$

$$\frac{1}{\mathcal{K}}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}\right)\beta_1 = \frac{2}{27}\left(|g_1(\varepsilon_1)I(\varepsilon_2 0)|^2 + \frac{1}{125}|f(\varepsilon_1)I(\varepsilon_2 2)|^2 + \frac{1}{25}|f(\varepsilon_2)I(\varepsilon_1 2)|^2\right) + \frac{1}{135}(2N_0+1)\begin{pmatrix} N_0 & N_0 & 2\\ 0 & 0 & 0\end{pmatrix}^2$$
$$\times \left[2|f(\varepsilon_1)I(\varepsilon_2 0)|^2 + \frac{1}{25}\left(\frac{1}{2}|g_2(\varepsilon_1)|^2 + \frac{36}{7}|g_3(\varepsilon_1)|^2 + 18[g_2(\varepsilon_1)g_3^*(\varepsilon_1) + \mathrm{cc}]\right)|I(\varepsilon_2 2)|^2\right.$$
$$\left.+\frac{1}{5}\left(\frac{1}{2}|g_2(\varepsilon_2)|^2 + \frac{72}{49}|g_3(\varepsilon_2)|^2 + \frac{6}{7}[g_2(\varepsilon_2)g_3^*(\varepsilon_2) + \mathrm{cc}]\right)|I(\varepsilon_1 2)|^2\right]$$
$$+\frac{4}{525}(2N_0+1)\begin{pmatrix} N_0 & N_0 & 4\\ 0 & 0 & 0\end{pmatrix}^2\left(\frac{1}{5}|f(\varepsilon_1)I(\varepsilon_2 2)|^2 + \frac{2}{7}|f(\varepsilon_2)I(\varepsilon_1 2)|^2\right). \tag{69b}$$

$$\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}\varepsilon_1} = \sum_{N_f}\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1} = \frac{\mathcal{K}}{3}\left\{\sum_{\substack{i,j=1\\ i\neq j}}^{2}\left[\frac{1}{9}(2|f(\varepsilon_i)|^2 + |g_1(\varepsilon_i)|^2)\right.\right.$$
$$\left.\times\,|(\varepsilon_j 0)|^2 + \frac{1}{225}(2|f(\varepsilon_i)|^2 + |g_2(\varepsilon_i)|^2)|I(\varepsilon_j 2)|^2\right]$$
$$+\frac{1}{5}\left(\frac{4}{35}|f(\varepsilon_2)|^2 + |g_1(\varepsilon_2)|^2\right)|I(\varepsilon_1 2)|^2$$
$$\left.+\frac{1}{525}(12|f(\varepsilon_i)|^2 + |g_3(\varepsilon_i)|^2)|I(\varepsilon_2)|^2\right\} \tag{71a}$$

see equation (71b) next page

Expressions (71) are independent also of the initial rotational level N_0. If we represent the photoelectrons e_1 and e_2 emitted in the process (55) by $(l_1, l_2) = (0,1)$ and $(1,0)$, we find from (71) that

$$\bar{\beta}_1 = \frac{1}{5}\frac{1}{1+\bar{\rho}}, \tag{72a}$$

where

$$\bar{\rho} = \frac{(2|f(\varepsilon_1)|^2 + |g_1(\varepsilon_1)|^2)|I(\varepsilon_2 0)|^2 + |g_1(\varepsilon_2)I(\varepsilon_1 0)|^2}{2|f(\varepsilon_2)I(\varepsilon_2 0)|^2}. \tag{72b}$$

This means that $0 \leq \bar{\beta}_1 \leq \frac{1}{5}$ for rotationally unresolved transition in non-coincident DPI in $3\sigma_g^2$ shell of N_2 when photoelectrons are represented by partial waves not higher than p.

With the help of the relation (28) and (64), one can also obtain expressions for the parameter A_0, A_1, and A_2 needed in (27) to study angular correlation between photoelectrons emitted in the DPI (55) of N_2. Using the procedure described above for non-coincident DPI, one can calculate both rotationally resolved as well as rotationally unresolved angular distributions of the photoelectrons e_1 and e_2 observed simultaneously.

5 Conclusions

This paper presents an angle- and/or spin-resolved theoretical study of DPI in a linear molecule rotating according to either of Hund's coupling schemes (a) or (b). The correlation functions obtained in each of the two Hund's schemes are shown to be formally identical with, of course, different dynamical factors. Use of parity-adapted states both for the molecular target and for th residual doubly charged photoion gives selection rules applicable to DPI. Selection rules obtained for case (a) are naturally different from those applicable in case (b). The present selection rules, in each of the two Hund's coupling schemes considered herein, are different also from the ones derived earlier for single photoionization and for Auger spectroscopy following absorption of a single photon.

Our analysis shows that whereas spin-unresolved angular distribution of the two electrons ejected simultaneously in DPI requires three independent parameters for its complete specification, a different set of sixteen parameters is needed if the spins of the photoelectrons is also analyzed. But each of the parameters in both cases depends upon the experimental geometry through the directions of propagation $\mathbf{k}_1$ and $\mathbf{k}_2$ of the two photoelectrons, in addition to their energies. Various geometrical configurations and experimental arrangements are discussed when it becomes simpler to perform measurements on DPI of a rotating linear molecule.

$$\begin{aligned}\bar{\beta}_1 &= \left(\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}\varepsilon_1}\right)^{-1} \sum_{N_f} \frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_1}\beta_1 = \mathcal{K}\sqrt{\frac{10}{3}} \left(\frac{\mathrm{d}\bar{\sigma}}{\mathrm{d}\varepsilon_1}\right)^{-1} \left\{ \frac{2}{45\sqrt{30}}|f(\varepsilon_2)I(\varepsilon_1 0)|^2 + \frac{1}{9}\sqrt{\frac{2}{15}}|g_1(\varepsilon_1)I(\varepsilon_2 2)|^2 \right.\\ &+\frac{43}{3^2\cdot 5^3\cdot 7\sqrt{30}}|f(\varepsilon_1)I(\varepsilon_2 2)|^2 + \frac{73}{3\cdot 5^2\cdot 7^2\sqrt{30}}|f(\varepsilon_2)I(\varepsilon_1 2)|^2 + \frac{1}{125\sqrt{30}}\left(\frac{1}{18}|g_2(\varepsilon_2)|^2 + \frac{8}{49}|g_3(\varepsilon_2)|^2\right)|I(\varepsilon_1 2)|^2\\ &+\frac{1}{625\sqrt{30}}\left(\frac{1}{9}|g_2(\varepsilon_1)|^2 + \frac{4}{7}|g_3(\varepsilon_1)|^2\right)|I(\varepsilon_2 2)|^2 + \frac{1}{3\cdot 5^3\cdot 7}\sqrt{\frac{2}{15}}(g_2(\varepsilon_2)g_3^*(\varepsilon_2) + \mathrm{cc})|I(\varepsilon_1 2)|^2\\ &+\frac{1}{625}\sqrt{\frac{2}{15}}(g_2(\varepsilon_1)g_3^*(\varepsilon_1) + \mathrm{cc})|I(\varepsilon_2 2)|^2 - \frac{1}{5}\sqrt{\frac{2}{5}}\left[\left(\frac{1}{9\sqrt{7}}g_1(\varepsilon_2)f^*(\varepsilon_2) + \frac{1}{40\sqrt{3}}g_2^*(\varepsilon_2)f(\varepsilon_2) + \frac{1}{15\sqrt{3}}g_3^*(\varepsilon_2)f(\varepsilon_2)\right)\right.\\ &\left.\left.\times I(\varepsilon_1 0)I^*(\varepsilon_1 2) + \mathrm{cc}\right]\right\}. \qquad (71b)\end{aligned}$$

The simplest possible experiment that one can easily perform on DPI is the one in which only one of the two photoelectrons is detected. The angle- and/or spin-resolved photoelectron spectroscopy of such non-coincident experiments on DPI is shown formally to be identical to that of single-photoionization studies performed hitherto very successfully experimentally as well as theoretically. This identity means that, while one of the two electrons emitted in a DPI remains unobserved, the spin-unresolved and spin-resolved angular distributions of the observed electron are completely characterized by, respectively, two and five energy-dependent parameters that are not affected by the geometry of the experiment. It also means that the well-developed theoretical analysis of angle- and/or spin-resolved photoelectron spectroscopy of single photoionization of a rotating linear molecule is applicable to angle- and/or spin-resolved non-coincident experiments on DPI of the same target. Thus, both spin-unresolved as well as spin-resolved, non-coincident experiments on DPI of a rotating linear molecule are, probably, within the reach of the existing experimental facilities, than those in which both of the photoelectrons are simultaneously observed and their properties analyzed.

The theoretical framework developed in this paper is applied to a real physical system. Namely, DPI in the $3\sigma_g$ shell of molecular nitrogen. Both N_2 and its doubly charged residual photoion N_2^{++} formed after DPI are in their ${}^1\Sigma_g^+$ states, each with a closed-shell structure. Hund's coupling scheme (b) is naturally applicable in such cases. Our analysis of the spin-unresolved DPI of N_2 shows that transitions either among even or among odd rotational states are only possible. We have calculated the integrated cross-section $\mathrm{d}\sigma/\mathrm{d}\varepsilon_1$ and the asymmetry parameter β_1 present in the non-coincident angular distributions for rotationally unresolved and for $\Delta N = 0, \pm 2, \pm 4$ rotationally resolved transitions in DPI of N_2. β_1 for $\Delta N = \pm 2$ transitions in found to have a weak dependence on the rotational states N_0 and N_f of N_2 and N_2^{++}, respectively.

On representing the two photoelectrons by s and p partial waves only, we have obtained also the limiting values of β_1 for some of the above-mentioned transitions. A comparison of these values with those calculated for the respective transitions in single photoionization in a σ_g shell of a homonuclear molecule representing the ejected electron by the p partial wave shows a clear manifestation of electron-electron correlation in DPI. We further find that in the present application the rotational effects are included only through the terms $(2N_f+1)\begin{pmatrix} N_0 & N_f & l_t \\ 0 & 0 & 0 \end{pmatrix}^2$ present in the expression for an observable. The sum of this expression over N_f is equal to unity. One can therefore readily study, using the theoretical framework developed in this communication, also the rotationally unresolved DPI in any linear molecule. Such experiments are still easier to perform as they do not require use of high-energy resolving electron spectrometers.

The results obtained in our example of N_2 are general and applicable to DPI in the σ_g shell of any rotating $D_{\infty h}$ molecule which is in its ${}^1\Sigma_g^+$ ground electronic state with a closed-shell electronic configuration. One can also use the methodology developed in our application to perform *ab initio* calculations of rotationally resolved as well as unresolved DPI in such molecules. The model results presented for N_2 will naturally provide a test for sophisticated *ab initio* calculations.

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