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Molecule effect in inner shell sequential double ionization

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We present a theoretical framework for the angular distribution of the two emitted photoelectrons in sequential inner shell two-photon double ionization (TPDI) of uniformly distributed molecules. As an example, we numerically calculated the sequential double ionization of the 4d shells of the iodine atom in CH_3I with a length and velocity gauge and obtained the corresponding angular anisotropy parameters. For comparison, we also compute the anisotropy parameters for atomic Xenon. The anisotropy parameter for the second ionization of CH_3I , is strongly influenced by the molecular structure, providing a sensitive probe for photoionization dynamics in polyatomic systems. This study provides a computational code for simulating sequential TPDI processes enabling one to computationally study the molecular effects in the angular distribution for sequential inner-shell double ionization.

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I. INTRODUCTION

Intense table-top lasers and free electron lasers have become key tools for modern molecular physics research, enabling experimental access to a broad spectrum of photon energies^{1–3}. In particular, synchrotron and free-electron laser sources in the extreme ultraviolet (XUV) and x-ray regime have greatly advanced studies of the inner-shell electronic structure of atoms and molecules^{4–7}. These high-energy photons can remove electrons from well-defined inner-shell orbitals, and the resultant photoelectron's angular emission pattern encodes information on the underlying electronic structure and potential landscape of the ion core.

We focus here on two-photon double ionization (TPDI) phenomena, which can be categorized into two general mechanisms: non-sequential and sequential^{5–7}. In non-sequential (direct) TPDI, two electrons are removed by two photons in a single, concerted step, occurring when a single photon is insufficient to ionize a singly charged ion. By contrast, once the photon energy exceeds the ionization threshold of the singly charged ion, sequential ionization tends to dominate^{8–10}.

Determining molecular-frame photoelectron angular distributions is often challenging due to difficulties in aligning the molecular axis¹¹ or identifying the molecular frame via ion coincidence measurements¹². In the absence of any preferred orientation, the angular distribution in the laboratory frame depends solely on the emission angle relative to the polarization axis. For one-photon processes, the anisotropy of the resulting photoelectron angular distribution is commonly characterized by the β parameter.

For the two-photon double ionization, the photoelectron angular dependence is less well established. For atoms, earlier work has addressed the photoelectron angular dependence in two-photon ionization processes^{13–17}. The angular distributions of the second photoelectron have been measured in non-coincidence experiments for noble gas atoms.^{17–20} In these type of measurements the emission probability of the second photoelectron was averaged over the emission angles of the first photoelectron, and was thus independent of the angular direction of the first photoelectron. Because the first photoionization aligns the atomic or molecular ion relative to the polarization vector of the incoming light, it is evident that the angular distribution of the second photoelectron can substantially differ from the angular distribution of the first photoelectron.

In a previous work, Fritzsche et al.¹³ established a theory for the sequential two-photon ionization of atoms. They derived the angular distribution of ionization using density-matrix and statistical-tensor formalism, provided the correlation measurement function of the angular distri-

bution for the double ionization, and examined the angular distribution of the second photoelectron. However, there are yet only few studies on the sequential two-photon double ionization of molecules, which are lower in symmetry than atoms, and thus TPDI processes require somewhat different procedures for ab-initio simulations. The angular distribution for single ionization has been calculated and confirmed by experiments^{12,21–23}. In contrast, existing studies on double ionization predominantly focus on processes such as Auger decay following the initial core-hole creation²⁴, hole migration dynamics^{25,26}, and other correlated electronic phenomena²⁷. To the best of our knowledge, no experimental data currently exist for the angular anisotropy of the second photoelectron emitted from the 4d orbital of the iodine atom in CH₃I following a sequential TPDI process.

We also emphasize that although Auger decay constitutes a secondary ionization channel following the creation of a 4d core hole, the kinetic energy of Auger electrons differs in general from that of photoelectrons generated by TPDI. Also, photoelectrons released after Auger decay, have a substantial lower kinetic energy due to the higher charge acquired in the autoionization process.

Computationally, the ePolyScat package^{28–30} calculates the photoelectron angular distribution and asymmetric parameters³¹. The calculation of asymmetry parameters for the second ionization of molecular TPDI has yet to be implemented.

In the present work, we address this gap by formulating and implementing a theoretical approach to calculate orientationally averaged photoelectron angular distributions in sequential two-photon double ionization of molecules, which can also be applied for atoms. We derive analytical expressions for the second-photoelectron angular distribution (β_2 and β_4 parameters) in the laboratory frame and combine these with scattering matrix elements obtained from ePolyScat^{28–30}. Our protocol uses electronic structure information from Molpro^{32,33}, followed by continuum orbital calculations via ePolyScat. We then perform orientational averaging to obtain orientational-averaged angular distributions for the first and second photoelectrons, extending strategies previously used for single-photon ionization^{29,30}.

As a specific example, we apply our methodology to the sequential double ionization of the 4d orbitals in CH₃I and Xe by XUV photons. We compare these molecular results to analogous calculations for Xe, aiming to highlight the role of the molecular structure in shaping the two-electron emission pattern. Section II lays out the derivation of relevant transition amplitudes and cross sections for one- and two-photon ionization steps, while Section III discusses the computational procedure. In Section IV, we illustrate the resulting cross sections and asymmetry parameters,

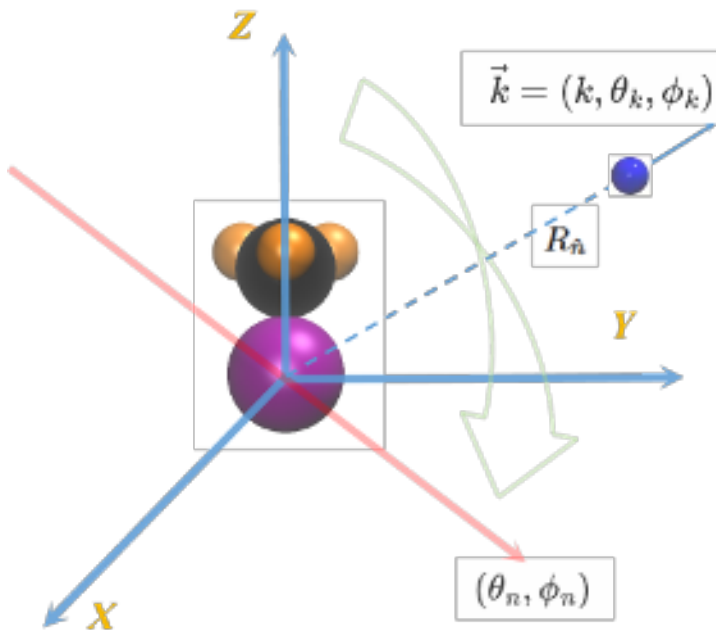


FIG. 1. Schematic of the photoionization process and geometric parameters in the molecule frame. The blue sphere represents an emitted photoelectron. $\vec{k}$ is momentum of the emitted electron. The red arrow represents the incident light polarization vector direction. The solid angle (θ_n, ϕ_n) describes the direction of the polarization vector in the molecule frame. The operator R_n defines a rotation from the lab frame to the molecular frame, with the three Euler angles $(\phi_n, \theta_n, \chi_n)$.

providing insights into the molecular effect on the electron emission distribution. Finally, we conclude in Section V.

II. THEORETICAL FORMULATION

A. Cross section and angular distributions

To express the angular distribution of the photoelectron in the molecular frame, we use the dipole approximation which is used to describe the interaction between a photon and a molecule, the direction of the electromagnetic field is characterized by the polarization of the photon, while the direction of propagation is just perpendicular to its polarization. One has to consider two solid angles for the final state: the direction into which the photoelectron is emitted, specified by the angles θ_k and ϕ_k , and the direction along which the light is polarized, specified by the angles θ_n and ϕ_n . The definition of these angles is summarized in Fig. 1.

Employing these coordinates and making use of the dipole approximation, the differential cross section for photoionization in the molecular frame assuming linearly polarized light is^{22,23}

$$\frac{d\sigma}{d\Omega_k d\Omega_n}(\theta_k, \phi_k, \theta_n, \phi_n) = \frac{4\pi^2 E}{c} \left| \sum_i T^{(0 \rightarrow i)}(\theta_k, \phi_k, \theta_n, \phi_n) \right|^2, \quad (1)$$

where the summation runs over final states i of the ion with a electron missing in 4d orbital of iodine, $E = k^2/2$ is the kinetic energy of the photoelectron, c is the speed of light, and the molecular-frame transition amplitude for a transition from the ground states 0 to the ionized state i is given by

$$T^{(0 \rightarrow i)}(\theta_k, \phi_k, \theta_n, \phi_n) = \sum_l \sum_{m=-l}^l \sum_{\mu=-1}^1 I_{l,m,\mu}^{(0 \rightarrow i)}(E) Y_{lm}^*(\theta_k, \phi_k) D_{\mu,0}^1(R_n), \quad (2)$$

where the photon is linearly polarized in the lab frame, and the sum of l, m runs over partial wave components for the spherical harmonics $Y_{lm}(\theta_k, \phi_k)$. In Eq. (2), the sum over μ involves the Wigner rotation matrix $D_{\mu,0}^1(R_n)$ that rotates the linear polarization vector to the molecular frame, where the rotation R_n is given by the three Euler angles $(\phi_n, \theta_n, \chi_n)$. Notably, because the polarization just defines a direction, χ_n is ambiguous and can be chosen 0 here. The transition dipole moment in the molecular frame is

$$I_{l,m,\mu}^{(0 \rightarrow i)}(E) = \langle \Psi_0 | \hat{d}_\mu | \Psi_i \phi_{klm} \rangle. \quad (3)$$

In Eq. (3), $|\Psi_0\rangle$ is the initial molecular wave function, $\hat{d}_\mu$ is the μ -th component of the dipole operator, and $|\Psi_i \phi_{klm}\rangle$ is the product wave function involving the wave function of the left-behind molecular ion $|\Psi_i\rangle$ in state i and the partial wave component $|\phi_{klm}\rangle$ of the flying away electron with asymptotic angular momentum quantum numbers l and m .

Employing expressions for the Wigner rotation matrices, the molecular-frame photoelectron angular distribution in Eq. (1) can be expanded into a series of spherical harmonics components.

$$\frac{d\sigma}{d\Omega_k d\Omega_n}(\theta_k, \phi_k, \theta_n, \phi_n) = \frac{4\pi^2 E}{c} \sum_L \sum_{M=-L}^L \sum_{i,i'} b_{L,M}^{(i,i')}(E, R_n) Y_{L,M}(\theta_k, \phi_k), \quad (4)$$

with

$$b_{L,M}^{(0 \rightarrow i, 0 \rightarrow i')}(E, R_n) = \sum_{\mu, \mu'=-1}^1 \sum_{P=0,2} g^{(0 \rightarrow i, 0 \rightarrow i')}(E, L, M, \mu, \mu', P) D_{\mu-\mu',0}^P(R_n). \quad (5)$$

and

$$g^{(0 \rightarrow i, 0 \rightarrow i')}(E, L, M, \mu, \mu', P) = \sum_{\substack{l, m \\ l', m'}} I_{l, m, \mu}^{(0 \rightarrow i)}(E) \left[I_{l', m', \mu'}^{(0 \rightarrow i')}(E) \right]^* \\ (-1)^{M+m-\mu} \sqrt{\frac{(2l+1)(2l'+1)(2L+1)}{4\pi}} (2P+1) \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} l & l' & L \\ -m & m' & -M \end{pmatrix} \begin{pmatrix} 1 & 1 & P \\ \mu & -\mu' & \mu' - \mu \end{pmatrix} \begin{pmatrix} 1 & 1 & P \\ 0 & 0 & 0 \end{pmatrix}, \quad (6)$$

where $\begin{pmatrix} l & l' & L \\ m & m' & M \end{pmatrix}$ is the Wigner 3- j symbol.

From this expression, the orientationally averaged differential cross section in the lab frame is obtained by rotating the spherical harmonics expansion from the molecular frame into the lab frame using the rotation R_n^{-1} and integrating over the three Euler angles that specify the polarization direction,

$$8\pi^2 \frac{d\sigma}{d\Omega_{\text{lab}}}(\theta, \phi) = \frac{4\pi^2 E}{c} \int dR_n \sum_{L, M} \sum_{i, i'} b_{L, M}^{(0 \rightarrow i, 0 \rightarrow i')}(E, R_n) \\ \sum_{M'} \left(D_{M, M'}^L(R_n) \right)^* Y_{L, M'}(\theta, \phi), \quad (7)$$

where the integral $\int dR_n$ means

$$\int_0^{2\pi} d\phi_n \int_0^\pi d\theta_n \sin \theta_n \int_0^{2\pi} d\chi_n. \quad (8)$$

Carrying out the integrations, and employing the orthogonality constraints for Wigner rotation matrices yields the well-know result¹²

$$\frac{d\sigma}{d\Omega_{\text{lab}}}(\theta, \phi) = \frac{\sigma}{4\pi} [1 + \beta_2 P_2(\cos \theta)], \quad (9)$$

with

$$\sigma = \frac{4\pi^2 E}{3c} \sum_{l, m, \mu} \sum_{i, i'} I_{l, m, \mu}^{(0 \rightarrow i)}(E) \left(I_{l, m, \mu}^{(0 \rightarrow i')}(E) \right)^* \quad (10)$$

and

$$\beta_2 = \sqrt{5} \frac{\sum_{\mu, \mu'=-1}^1 \sum_{i, i'} g^{(0 \rightarrow i, 0 \rightarrow i')}(E, 2, \mu - \mu', \mu, \mu', 2)}{\sum_{\mu=-1}^1 \sum_{i, i'} g^{(0 \rightarrow i, 0 \rightarrow i')}(E, 0, 0, \mu, \mu, 0)}. \quad (11)$$

We now generalize the procedure to two emitted electrons, assuming independent and sequential photoionization steps.

For our discussion of TPDI, we assume that the photon energy is above the threshold to ionize a singly ionized ion, and the sequential ionization of the second photoelectron becomes dominant^{9,10}.

The first photoelectron is generated in the ionization from the ground state 0 to an ionized state i with a photoelectron energy $E_{0 \rightarrow i}$; the second photoelectron is generated in a successive photoionization from ionized state i to a doubly ionized state j with a photoelectron energy $E_{i \rightarrow j}$. In such a sequential scenario, the differential cross section is given by

$$\begin{aligned} & \frac{d\sigma_{0 \rightarrow j}}{d\Omega_{k_1} d\Omega_{k_2} d\Omega_n} (\theta_{k_1}, \phi_{k_1}, \theta_{k_2}, \phi_{k_2}, \theta_n, \phi_n) \\ &= \sum_i \frac{d\sigma_{0 \rightarrow i}}{d\Omega_{k_1} d\Omega_n} (\theta_{k_1}, \phi_{k_1}, \theta_n, \phi_n) \frac{d\sigma_{i \rightarrow j}}{d\Omega_{k_2} d\Omega_n} (\theta_{k_2}, \phi_{k_2}, \theta_n, \phi_n), \end{aligned} \quad (12)$$

where $\frac{d\sigma_{0 \rightarrow i}}{d\Omega_{k_1}} (\theta_{k_1}, \phi_{k_1}, \theta_n, \phi_n)$ and $\frac{d\sigma_{i \rightarrow j}}{d\Omega_{k_2}} (\theta_{k_2}, \phi_{k_2}, \theta_n, \phi_n)$ are the differential cross sections for the first and second ionization step, respectively.

We focus on the emission direction of the second photoelectron, when it is measured in a non-coincident manner, i.e., independent of the angular distribution of the first photoelectron emission. For this case we obtain

$$\begin{aligned} & \frac{d\sigma_{0 \rightarrow j}}{d\Omega_{k_2} d\Omega_n} (\theta_{k_2}, \phi_{k_2}, \theta_n, \phi_n) \\ &= \int d\Omega_{k_1} \frac{d\sigma_{0 \rightarrow j}}{d\Omega_{k_1} d\Omega_{k_2} d\Omega_n} (\theta_{k_1}, \phi_{k_1}, \theta_{k_2}, \phi_{k_2}, \theta_n, \phi_n) \\ &= \frac{4\pi^2 E_{0 \rightarrow i}}{c} \sqrt{4\pi} \sum_i b_{0,0}^{(0 \rightarrow i, 0 \rightarrow i)} (E_{0 \rightarrow i}, R_n) \frac{d\sigma_{i \rightarrow j}}{d\Omega_{k_2} d\Omega_n} (\theta_{k_2}, \phi_{k_2}, \theta_n, \phi_n), \end{aligned} \quad (13)$$

In the lab frame the second photoelectron is emitted into the direction given by the solid angle $\Omega_2 = (\theta_2, \phi_2)$, the corresponding lab-frame angular distribution (disregarding the direction of the first photoelectron) is given by

$$\begin{aligned} & 8\pi^2 \frac{d\sigma_{0 \rightarrow j}}{d\Omega_{2 \text{ lab}}} (\theta_2, \phi_2) \\ &= \sum_i \frac{\sqrt{4\pi} (4\pi^2)^2 E_{i \rightarrow j} E_{0 \rightarrow i}}{c^2} \int dR_n b_{0,0}^{(0 \rightarrow i, 0 \rightarrow i)} (E_{0 \rightarrow i}, R_n) \\ & \quad \times \sum_{L,M} b_{L,M}^{(i \rightarrow j, i \rightarrow j)} (E_{i \rightarrow j}, R_n) \sum_{M'} \left(D_{M,M'}^L(R_n) \right)^* Y_{L,M'}(\theta_2, \phi_2). \end{aligned} \quad (14)$$

For notation simplicity, we denote $\Delta\mu_i = \mu_i - \mu'_i$, Using the identity

$$\begin{aligned} & \int dR_n D_{\Delta\mu_1,0}^{P_1}(R_n) D_{\Delta\mu_2,0}^{P_2}(R_n) \left(D_{M,M'}^L(R_n) \right)^* \\ &= 8\pi^2 (-1)^M \begin{pmatrix} P_1 & P_2 & L \\ \Delta\mu_1 & \Delta\mu_2 & -M \end{pmatrix} \begin{pmatrix} P_1 & P_2 & L \\ 0 & 0 & 0 \end{pmatrix} \delta_{M',0}, \end{aligned} \quad (15)$$

and carrying out the integration in Eq. (14) yields Eq. (16).

$$\begin{aligned} & \frac{d\sigma_{0 \rightarrow j}}{d\Omega_2 \text{ lab}}(\theta_2, \phi_2) \\ &= \sum_L Y_{L,0}(\theta_2, \phi_2) \sum_i \left\{ \frac{\sqrt{4\pi}(4\pi^2)^2 E_{i \rightarrow j} E_{0 \rightarrow i}}{c^2} \times \sum_{M=-L}^L \sum_{P_1, P_2} \sum_{\substack{\mu_1, \mu'_1 \\ \mu_2, \mu'_2}} \sum_i \right. \\ & \quad g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, 0, 0, \mu_1, \mu'_1, P_1) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, L, M, \mu_2, \mu'_2, P_2) \\ & \quad \left. \times (-1)^M \begin{pmatrix} P_1 & P_2 & L \\ \Delta\mu_1 & \Delta\mu_2 & -M \end{pmatrix} \begin{pmatrix} P_1 & P_2 & L \\ 0 & 0 & 0 \end{pmatrix} \right\}. \end{aligned} \quad (16)$$

Because P_1 and P_2 can only be 0 or 2, respectively, L can only take values of 0, 2, or 4, otherwise the Wigner 3- j terms give 0. This consideration allows us to write the differential cross section as Eq. (17)

$$\begin{aligned} \frac{d\sigma_{0 \rightarrow j}}{d\Omega_2 \text{ lab}}(\theta_2, \phi_2) &= \sum_i \left[\frac{\sqrt{4\pi}(4\pi^2)^2 E_{i \rightarrow j} E_{0 \rightarrow i}}{c^2} \left(Y_{0,0}(\theta_2, \phi_2) A_0^{(i,j)} \right. \right. \\ & \quad \left. \left. + Y_{2,0}(\theta_2, \phi_2) A_2^{(i,j)} + Y_{4,0}(\theta_2, \phi_2) A_4^{(i,j)} \right) \right], \end{aligned} \quad (17)$$

using the definitions

$$A_0^{(i,j)} = \sum_{\mu_1, \mu_2} g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, 0, 0, \mu_1, \mu_1, 0) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, 0, 0, \mu_2, \mu_2, 0) \\ + \frac{1}{5} \sum_{\mu_1, \mu'_1, \mu_2, \mu'_2} g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, 0, 0, \mu_1, \mu'_1, 2) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, 0, 0, \mu_2, \mu'_2, 2) \\ \times \delta_{\Delta\mu_1, \Delta\mu_2} (-1)^{\Delta\mu_1} \quad (18)$$

$$A_2^{(i,j)} = \frac{1}{5} \sum_{\mu_1, \mu_2, \mu'_2} g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, 0, 0, \mu_1, \mu_1, 0) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, 2, \Delta\mu_2, \mu_2, \mu'_2, 2) \\ + \frac{1}{5} \sum_{\mu_1, \mu'_1, \mu_2} g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, 0, 0, \mu_1, \mu'_1, 2) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, 2, \Delta\mu_1, \mu_2, \mu_2, 0) \\ - \sqrt{\frac{2}{35}} \sum_{\substack{\mu_1, \mu'_1 \\ \mu_2, \mu'_2}} g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, 0, 0, \mu_1, \mu'_1, 2) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, 2, \Delta\mu_1 + \Delta\mu_2, \mu_2, \mu'_2, 2) \\ \times (-1)^{\Delta\mu_1 + \Delta\mu_2} \begin{pmatrix} 2 & 2 & 2 \\ \Delta\mu_1 & \Delta\mu_2 & -(\Delta\mu_1 + \Delta\mu_2) \end{pmatrix} \quad (19)$$

$$A_4^{(i,j)} = \sqrt{\frac{2}{35}} \sum_{\substack{\mu_1, \mu'_1 \\ \mu_2, \mu'_2}} g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, 0, 0, \mu_1, \mu'_1, 2) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, 4, \Delta\mu_1 + \Delta\mu_2, \mu_2, \mu'_2, 2) \\ \times (-1)^{\Delta\mu_1 + \Delta\mu_2} \begin{pmatrix} 2 & 2 & 4 \\ \Delta\mu_1 & \Delta\mu_2 & -(\Delta\mu_1 + \Delta\mu_2) \end{pmatrix}, \quad (20)$$

where the g function is defined as [Eq. \(6\)](#).

In a more compact form, the differential cross section in the lab frame can be written as

$$\frac{d\sigma_{0 \rightarrow j}}{d\Omega_2}_{\text{lab}}(\theta_2, \phi_2) = \frac{\sigma_{0 \rightarrow j}^{(2)}}{4\pi} \left[1 + \beta_2^{(2)} P_2(\cos \theta_2) + \beta_4^{(2)} P_4(\cos \theta_2) \right], \quad (21)$$

with

$$\sigma_{0 \rightarrow j}^{(2)} = \sum_i \frac{(4\pi^2)^2 E_{i \rightarrow j} E_{0 \rightarrow i}}{c^2} A_0^{(i,j)}, \\ \beta_2^{(2)} = \sqrt{5} \frac{\sum_i E_{i \rightarrow j} E_{0 \rightarrow i} A_2^{(i,j)}}{\sum_i E_{i \rightarrow j} E_{0 \rightarrow i} A_0^{(i,j)}}, \\ \beta_4^{(2)} = \sqrt{9} \frac{\sum_i E_{i \rightarrow j} E_{0 \rightarrow i} A_4^{(i,j)}}{\sum_i E_{i \rightarrow j} E_{0 \rightarrow i} A_0^{(i,j)}}. \quad (22)$$

One can proceed from here and consider the more general case in which the emission angles of both photoelectrons are measured, which would require in-coincidence detection of the photo-

electrons. The corresponding double differential cross section reads

$$\begin{aligned}
 & 8\pi^2 \frac{d\sigma_{0 \rightarrow j}}{d\Omega_1 d\Omega_{2 \text{ lab}}} (\theta_1, \phi_1, \theta_2, \phi_2) \\
 &= \sum_i \frac{\sqrt{4\pi}(4\pi^2)^2 E_{i \rightarrow j} E_{0 \rightarrow i}}{c^2} \\
 & \times \int dR_n \left\{ \sum_{L_1, M_1} b_{L_1, M_1}^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, R_n) \sum_{M'_1} \left(D_{M_1, M'_1}^{L_1}(R_n) \right)^* Y_{L_1, M'_1}(\theta_1, \phi_1) \right. \\
 & \times \left. \sum_{L_2, M_2} b_{L_2, M_2}^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, R_n) \sum_{M'_2} \left(D_{M_2, M'_2}^{L_2}(R_n) \right)^* Y_{L_2, M'_2}(\theta_2, \phi_2) \right\} \\
 &= \sum_i \frac{\sqrt{4\pi}(4\pi^2)^2 E_{i \rightarrow j} E_{0 \rightarrow i}}{c^2} \times \left\{ \sum_{\substack{L_1, M_1, M'_1 \\ L_2, M_2, M'_2}} \sum_{\mu_1, \mu'_1} \sum_{P_1, P_2} Y_{L_1, M'_1}(\theta_1, \phi_1) Y_{L_2, M'_2}(\theta_2, \phi_2) \right. \\
 & \times g^{(0 \rightarrow i, 0 \rightarrow i)}(E_{0 \rightarrow i}, L_1, M_1, \mu_1, \mu'_1, P_1) g^{(i \rightarrow j, i \rightarrow j)}(E_{i \rightarrow j}, L_2, M_2, \mu_2, \mu'_2, P_2) \\
 & \times \left. \int dR_n \left[D_{\Delta\mu_1, 0}^{P_1}(R_n) D_{\Delta\mu_2, 0}^{P_2}(R_n) \left(D_{M_1, M'_1}^{L_1}(R_n) \right)^* \left(D_{M_2, M'_2}^{L_2}(R_n) \right)^* \right] \right\}. \quad (23)
 \end{aligned}$$

Because

$$\begin{aligned}
 & \int dR_n D_{\Delta\mu_1, 0}^{P_1}(R_n) D_{\Delta\mu_2, 0}^{P_2}(R_n) \left(D_{M_1, M'_1}^{L_1}(R_n) \right)^* \left(D_{M_2, M'_2}^{L_2}(R_n) \right)^* \\
 &= 8\pi^2 \sum_{L=|L_1-L_2|}^{L_1+L_2} (2L+1) \begin{pmatrix} L_1 & L_2 & L \\ -M_1 & -M_2 & M_1+M_2 \end{pmatrix} \\
 & \begin{pmatrix} L_1 & L_2 & L \\ -M'_1 & -M'_2 & M'_1+M'_2 \end{pmatrix} \begin{pmatrix} P_1 & P_2 & L \\ 0 & 0 & -(M'_1+M'_2) \end{pmatrix} \\
 & \begin{pmatrix} P_1 & P_2 & L \\ \Delta\mu_1 & \Delta\mu_2 & -(M_1+M_2) \end{pmatrix}, \quad (24)
 \end{aligned}$$

one can see that for the azimuthal angular momentum, it must hold $M'_1 = -M'_2$. Moreover, because P_1 and P_2 are 0 or 2, the joint distribution is restricted to values for $L = 0, 2, 4$, which means L_1, L_2 can take any values satisfying the triangular inequality $|L_1 - L_2| \leq L \leq L_1 + L_2$.

B. Dipole matrix elements

We use the package ePolyScat by R. Lucchese et al. to calculate the dipole matrix elements mentioned in Eq. (3).

The principle of the ePolyScat code is to use the Schwinger variational method to calculate the scattered electron wave function, i.e., the photoelectron at a given continuous energy in the environment of the molecular ion²⁸⁻³⁰. Using the many-electron wave function of the molecular ion, the wave function of the photoelectron under the action of the potential of the ion is found. The corresponding Schrödinger equation for the outgoing electron wave function is given (in atomic units) by,

$$\left[-\frac{1}{2}\nabla^2 + V(\vec{r}) - \frac{k^2}{2} \right] \phi_{\vec{k}}(\vec{r}) = 0, \quad (25)$$

where $V(\vec{r})$ is the static-exchange potential of the ion, $\psi_{\vec{k}}$ represents the continuum wave function of the photoelectron, and $\vec{k}$ is the asymptotic momentum of the outgoing electron³⁰. By considering here the static-exchange potential of the molecular ion, correlation effects that are particular relevant for low-energy outgoing electrons are taken into account.³⁴ Finding solution of Eq. (25) employing asymptotic boundary conditions corresponding to spherical waves with angular quantum numbers l, m , the relevant transition dipole operator matrix elements are computed as

$$\begin{aligned} I_{l,m,\vec{n}}^{(L)} &= (k)^{1/2} \langle \phi_i | \vec{r} \cdot \vec{n} | \phi_{klm} \rangle, \\ I_{l,m,\vec{n}}^{(V)} &= \frac{(k)^{1/2}}{E} \langle \phi_i | \nabla \cdot \vec{n} | \phi_{klm} \rangle, \end{aligned} \quad (26)$$

where the superscripts L, V refer to the gauge in the length form and velocity form, respectively. In Eq. (26), ϕ_i is a bound electron orbital, $E = k^2/2$ is the photon energy, $\vec{k}$ is the momentum of the photoelectron, and $\vec{n}$ is a unit vector into the direction of polarization of the light, and ϕ_{klm} is the photoelectron wave function with asymptotic boundary conditions given by l and m .

III. COMPUTATION IMPLEMENTATION

We investigate the sequential two-photon double ionization (TPDI) of the $4d$ electrons in CH_3I , assuming the molecule is in its equilibrium geometry and electronic ground state. The computational workflow comprises the following steps:

Firstly, we perform Hartree-Fock calculations for the neutral CH_3I molecule with a VTZ basis set for C and H atoms and a VTZ-pp basis set for the iodine atom^{35,36}. Configuration interaction (CI) calculations are conducted to obtain accurate ionization energies for the $4d$ -hole states by specifying the active space with inner hole in Molpro.

The results calculated with Molpro are utilized in ePolyScat²⁸⁻³⁰ to compute dipole transition

matrix elements. Partial-wave expansions up to $l = 35$ for bound orbitals and $l = 12$ for photoelectron scattering states ensure numerical convergence.

Finally, we combine the single-photon ionization results to model the sequential TPDI process as outlined in [section II](#). Transition dipole elements from the ground state to singly ionized states and from singly to doubly ionized states are integrated according to Eqs. (11) and (22). Cross sections and asymmetry parameters are then averaged incoherently over all accessible final states, which means

$$\beta_2 = \frac{\sum_i \sigma_{0 \rightarrow i} \beta_{2;0 \rightarrow i}}{\sum_i \sigma_{0 \rightarrow i}}, \quad (27)$$

$$\beta_{2/4}^{(2)} = \frac{\sum_f \sigma_{0 \rightarrow f} \beta_{2/4;0 \rightarrow f}^{(2)}}{\sum_f \sigma_{0 \rightarrow f}}. \quad (28)$$

$$(29)$$

Where i means intermediate state and f means final state.

The post-processing is performed using the Python package ePSproc³⁷, which extracts necessary matrix elements from ePolyScat outputs. We compute orientationally averaged cross sections and angular-distribution parameters (β_2 , $\beta_2^{(2)}$, and $\beta_4^{(2)}$) by implementing the derived formulas numerically. Optimizations with NumPy and Numba were used to enhance computational efficiency.

IV. RESULTS AND DISCUSSION

In this work, we present a theoretical framework for calculating the double ionization process and developed a computational code to implement this method. We observe that, the molecular effect significantly influences the asymmetric parameters when the electron wavelength aligns with the C-I bond length of CH₃I.

We compare our results for CH₃I with the calculation of the first ionization by Powis et al.²¹ and the experimental data of Lindle et al.³⁸, and the result is shown in [Fig. 2](#) and [Fig. 3](#). The calculated cross section reaches a maximum at about 90 eV and decays for higher energy. A similar behavior can be found in the experimental data, though the computed cross section is much smaller than the measured ones at lower photon energies. Also, the decline with higher photon energies is stronger in the calculations compared with the experiment. Overall, there is only a small difference in the results obtained with the length and velocity gauge. Compared to the earlier calculations Ref. 21 that were conducted with the CMS- X_α method^{39–41}, one finds a

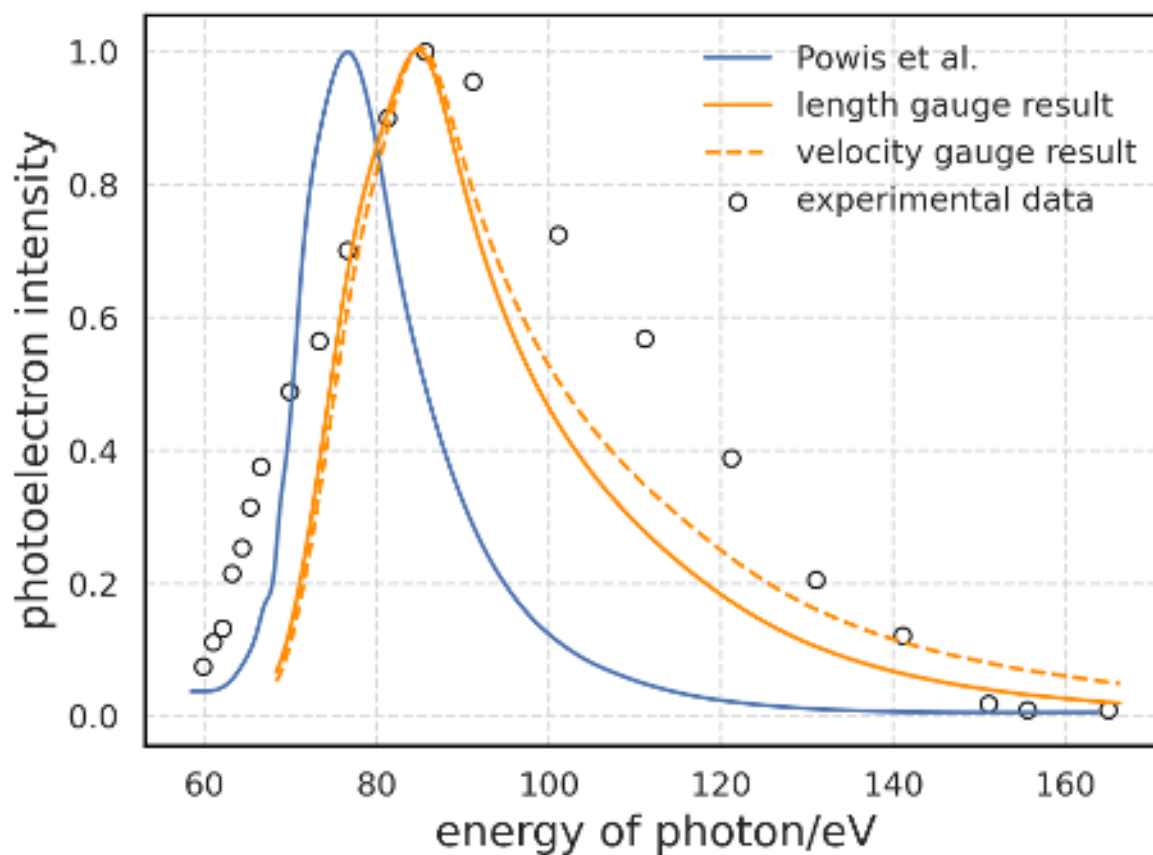


FIG. 2. Comparison of scaled cross-section data ($\sigma/\sigma_{\max}$) for the first photoionization for inner-shell TPDI of the CH_3I molecule. The blue and yellow lines represent results from Powis et al.²¹ and us respectively. The hollow circles mark experimental data of Lindle et al.³⁸.

qualitatively similar behavior, though the peak position is more than 10 eV off and the rise and decline with photon energy is even steeper than in the current calculations. Overall, our current calculation shows a considerable better agreement in cross section with the experimental data than the CMS- X_α calculations extracted from Ref. 21.

For the asymmetry parameter, the result in this work using the length gauge and the results from Ref. 21 give a similar trend that agrees with the experimental findings. Both calculations have similar maximum values for β_2 around 122 eV. Compared with the experimental data, the maximum value of the calculation has a certain deviation to lower energies. Specifically, the energy of maximal β_2 is about 38 eV lower than in the experimental data.

The results obtained using the length gauge and the velocity gauge deviate. The velocity gauge

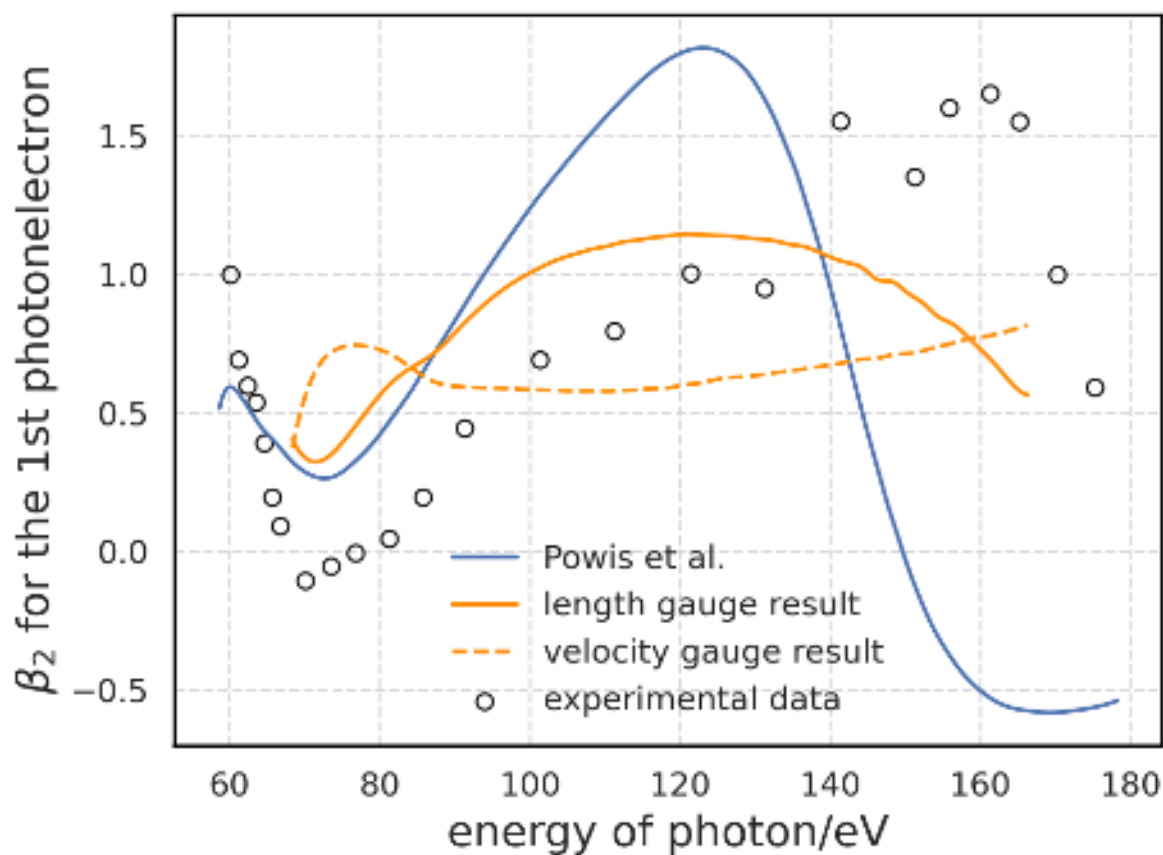


FIG. 3. Comparison of the calculated and measured asymmetry parameters β_2 for the first photoelectron for inner-shell TPD1 of the CH_3I molecule. The blue and yellow lines represent results from Powis et al.²¹ and us respectively. The hollow circles mark experimental data of Lindle et al.³⁸.

shows weaker agreement with the experimental data compared to the length gauge. An overall better agreement is found for the length gauge, indicating its potential superiority in numerical applications for the first photoelectron ionization.

For the second photoelectron, we consider that one does not distinguish different electron configurations of the final ion in the experimental measurements with a given photon energy, so only the average β parameter is meaningful, and we average the β parameters over the final states of the different electron configurations incoherently¹³. The expression is as follows: $\beta_{2/4}^{(2)} = \frac{\sum_j \sigma_{0 \rightarrow j}^2 \beta_{2/4,0 \rightarrow j}^{(2)}}{\sum_j \sigma_{0 \rightarrow j}^2}$. The calculated β parameters for the second photoelectron are plotted in Fig. 4.

We find that for $\beta_2^{(2)}$ the values for velocity and length gauge are very close to each other. It

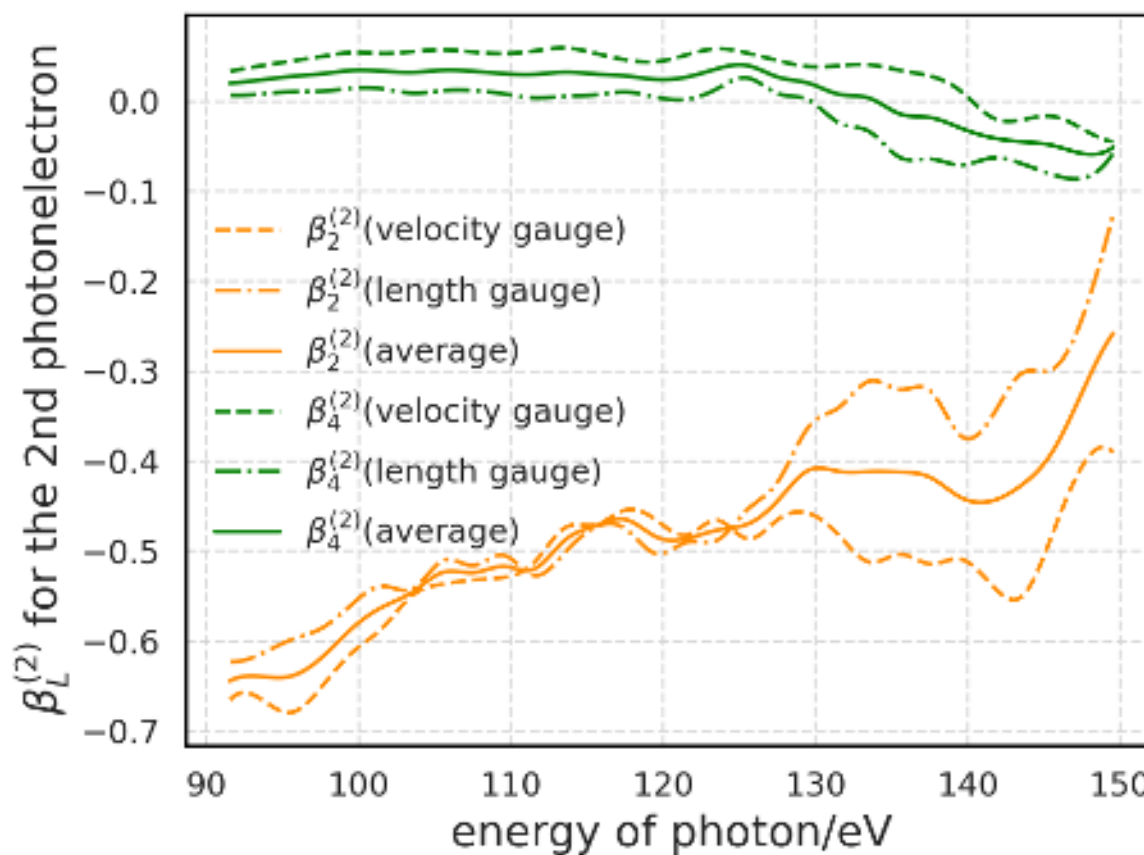


FIG. 4. Calculated $\beta_{(L)}^{(2)}$ β parameters for the 2nd photoelectron for inner-shell TPDI of the CH_3I molecule. The dark orange lines correspond to $L = 2$, the green lines correspond to $L = 4$. The dashed curves use velocity gauge, dash dotted curves use length gauge, and solid curves are average of the two gauges.

can be seen that for photon energies in the 90 eV – 150 eV, $\beta_2^{(2)}$ is negative, ranging from -0.7 to -0.1. For $\beta_4^{(2)}$, the two gauges give results that differ by about 0.03. In order to show the results for $\beta_4^{(2)}$ more clearly, we plot them separately in Fig. 5. As one can see, $\beta_4^{(2)}$ is rather small, it changes from positive to negative values near 130 eV (for the length gauge). The calculated value is mostly around 0.05 for photon energy in the 90 eV – 130 eV. The value of $\beta_4^{(2)}$ becomes negative for photon energies greater than 130 eV.

We also apply our approach for the Xe atom. Xenon ($Z = 54$) has an electronic structure very similar to that of iodine ($Z = 53$) and thus can be seen as a model for an independent atom. The calculation results for the Xe atom are shown in Fig. 6

Figure 6(a) compares the total cross section for CH_3I and for Xe. The resulting cross sections

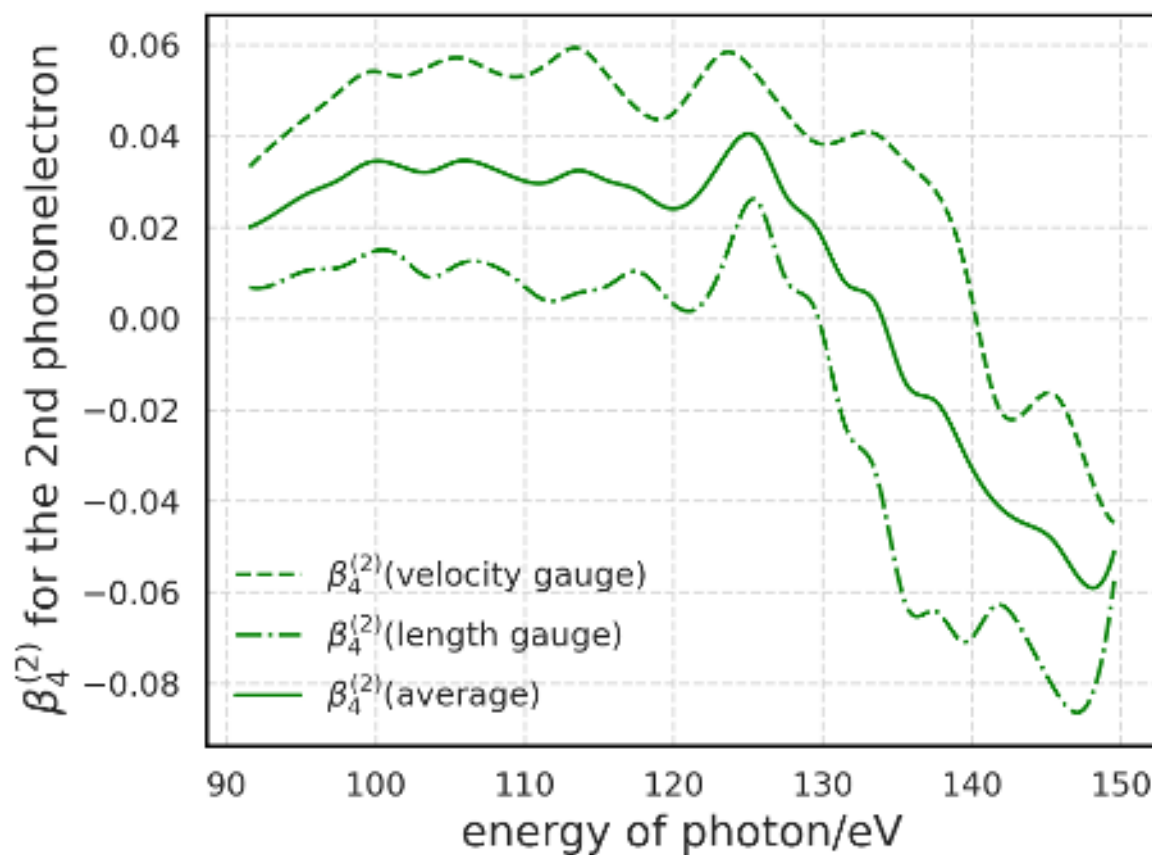
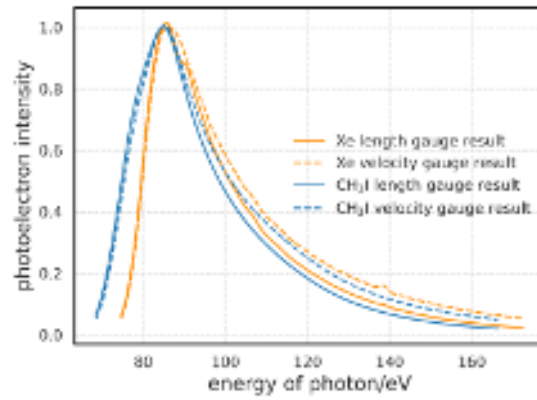


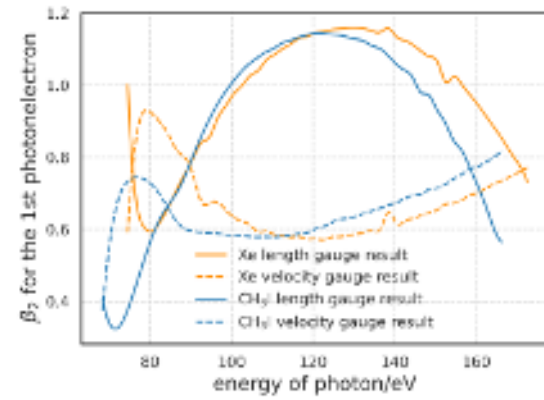
FIG. 5. Calculated $\beta_4^{(2)}$ parameters for the 2nd photoelectron for inner-shell TPDI of the CH_3I molecule. The notations are the same as Fig. 4.

are very similar, in deed. The β parameter for the first photoionization shown in 6(b) turns out to be very similar for photon energies above 80 eV, as well.

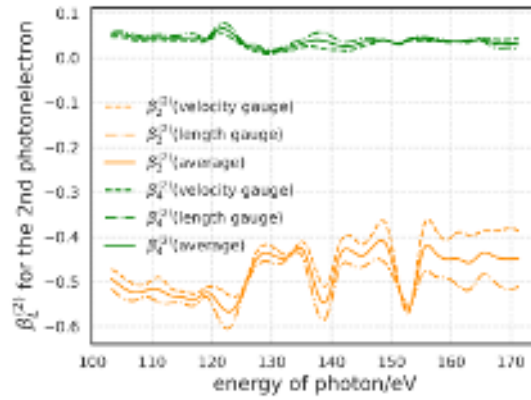
By contrast, the angular distributions observed for the second photoionization of Xenon and CH_3I , as depicted in Fig. 6(c), Fig. 4, and most notably in Fig. 6(d), indicate that the β_4 parameter of CH_3I is significantly influenced by molecular effects, resulting in a sign change within the 130 eV-160 eV range. Furthermore, the behavior of $\beta_4^{(2)}$ in the molecular exhibits a form of oscillation, whereas the $\beta_4^{(2)}$ of an atom is relatively stable. We propose a theoretical explanation for the observed difference between the molecule system CH_3I and atom Xenon. Specifically, when the outgoing electron wavefunction's wavelength matches the bond length of C–I, the interference between the outgoing electron wavefunction and the ion's wavefunction is significantly enhanced. This interference leads to a distinct twist in the angular distribution of the second outgoing elec-



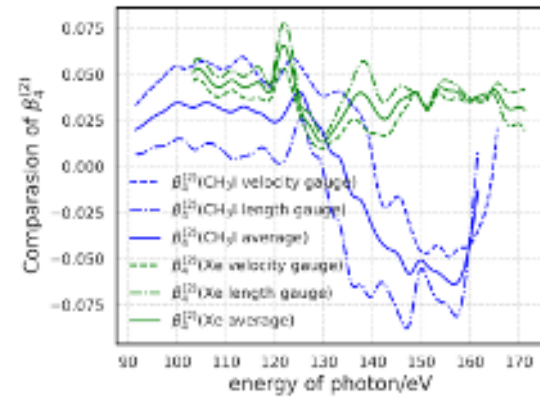
(a) scaled cross section($\sigma/\sigma_{\max}$)



(b) β_2 parameter for the 1st ionization.



(c) $\beta_L^{(2)}$ parameters for the 2nd photoelectron.



(d) $\beta_4^{(2)}$ parameters for the 2nd photoelectron of both CH_3I and Xe.

FIG. 6. Results for Xe atom. In 6(a) and 6(b), we show comparison of data for the scaled cross section and the β_2 parameter of the first photoionization of Xe and CH_3I . The orange lines show theoretical results of Xe and blue for CH_3I . In 6(c) and 6(d), we calculated $\beta_L^{(2)}$ parameters for the 2nd photoelectron of Xe, same line styles are used as in Fig. 4, and comparisons of the $\beta_4^{(2)}$ parameters for the 2nd photoelectron of CH_3I and Xe are explicitly shown in 6(d).

tron, which notably affects the $\beta_4^{(2)}$ parameter. As a verification for the explanation, we perform a simple calculation to find the interference energy of electron.

The C–I bond length of CH_3I is $2.198\text{\AA}$ ⁴². When the de Broglie wavelength λ of the photoelectron is equal to the C–I bond length, the kinetic energy E_k of photoelectron is

$$E_k = \frac{p^2}{2m_e} = \frac{2\pi^2\hbar^2}{m_e\lambda^2} = 31.133 \text{ eV}, \quad (30)$$

and the corresponding photon energy is $E_\nu \approx 125$ eV. From Figure 5, where the $\beta_4^{(2)}$ parameter of CH3I molecule exhibits obvious change beginning from $E_\nu \approx 125$ eV, which is significantly different from that of Xe atom as shown in Fig. 6(d).

We note that, although the resonance with the bond length is significant in the second photoelectron, it does not occur for the first photoelectron. We think that this result is due to the fact that the molecular structure has less influence on the photoelectron electron when emitted from a singly ionized molecule than when it is emitted from a dictation.

V. CONCLUSION

In summary, this work introduces a robust theoretical framework for calculating single and double ionization processes, supported by a computational code that is now available for future research applications. Our results demonstrate the validity of the theory and molecular effect in the sequential two-photon double ionization (TPDI) processes.

The observed divergence in $\beta_4^{(2)}$ can be attributed to enhanced interference between the outgoing electron wavefunction and the ion's wavefunction when the electron wavelength corresponds to the C-I bond length. This interference leads to a distinct twist in the angular distribution of the second outgoing electron, providing a sensitive probe for investigating the underlying mechanisms of complex ionization phenomena across diverse systems.

By accounting for molecular effects in theoretical models, this work contributes to a more accurate description of TPDI processes in non-atomic systems, paving the way for future studies into complex ionization phenomena across a wide range of molecular structures.

SUPPLEMENTARY MATERIAL

See the supplementary material for more details about the computational code, input files, output results, and visualizations. This includes the necessary files for reproducing the results and additional data and figures referenced in the paper.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

* S.T.Z and M.Z. contributed equally to this work.

Shutao Zhang: Conceptualization (equal); Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal); **Ming Zhang:** Conceptualization (equal); Investigation (equal); Writing - original draft (supporting); Writing - review & editing (supporting); **Kiyoshi Ueda:** Conceptualization (equal); Investigation (supporting); Writing - original draft (supporting); Writing - review & editing (supporting); **Robert Lucchese:** Conceptualization (equal); Investigation (supporting); Writing - original draft (supporting); Writing - review & editing (supporting); **Leshi Zhao:** Conceptualization (supporting); Investigation (supporting); Writing - original draft (supporting); Writing - review & editing (supporting); **Shuqiao Zhang:** Conceptualization (supporting); Investigation (equal); Writing - original draft (supporting); Writing - review & editing (supporting); **Bowen Dong:** Conceptualization (supporting); Investigation (supporting); Writing - original draft (supporting); Writing - review & editing (supporting); **Yajiang Hao:** Conceptualization (supporting); Investigation (supporting); Writing - original draft (supporting); Writing - review & editing (supporting); **Ludger Inhester:** Conceptualization (equal); Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal); **Zheng Li:** Conceptualization (equal); Investigation (equal); Writing - original draft (equal); Writing - review & editing (equal);

DATA AVAILABILITY

The source code and datasets used in this study are provided as **Electronic Supplementary Material (ESM)** alongside this article in the Journal of Chemical Physics. Readers can access

them via the journal's online platform.

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